Welcome to the 67th OSU International Symposium on Molecular Spectroscopy

On behalf of the Executive Committee, Frank DeLucia, Anne B. McCoy, and myself, I extend a heartfelt welcome to all the attendees to the 67th Symposium and welcome you to The Ohio State University and Columbus.

The Symposium presents research in fundamental molecular spectroscopy and a wide variety of related fields and applications. The continued vitality and significance of spectroscopy is annually re-affirmed by the number of talks, their variety, and the fact that many are given by students. These presentations are the heart of the meeting and are documented by this Abstract Book. Equally important is the information flowing from informal exchanges and discussions. As organizers, we strive to provide an environment that facilitates both kinds of interactions.

The essence of the meeting lies in the scientific discussions and your personal experiences this week independent of the number of times that you have attended this meeting. It is our sincere hope that you will find this meeting informative and enjoyable both scientifically and personally, whether it is your first or 50th meeting. If we can help to enhance your experience, please do not hesitate to ask the Symposium staff or the Executive Committee.

Terry A. Miller
Symposium Chair

Contents

67th OSU INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY

JUNE 18-22, 2012

International Advisory Committee
Jose Alonso, U. Valladolid
Vincent Boudon, CNRS-U. Bourgogne
Geoffrey Duxbury, U Strathclyde Glasgow
Yasuki Endo, U. Tokyo
Thomas Giesen, U. Cologne
Michael Heaven, Emory U.*
Caroline Jarrold, Indiana U. Bloomington*
Scott Kable, U. Sydney
*steering committee member
e-mail: mss@molspect.chemistry.ohio-state.edu

Executive Committee
Terry A. Miller, Chair
Frank C. DeLucia
Anne B. McCoy
Please send correspondence to:
Terry A. Miller
International Symposium on
Molecular Spectroscopy
Department of Chemistry
100 West 18th Avenue
Columbus, Ohio 43210 USA
http://molspect.chemistry.ohio-state.edu/symposium/

International Advisory Committee
Sang Kuk Lee, Pusan National U.
Nassar Moazzen-Ahmadi, U. Calgary
Leah O'Brien, S. Illinois U. Edwardsville
Scott Reid, Marquette U.*, Chair
Hanna Reisler, U. Southern California*
David Dale Skatrud, ARO
Mary Ann Smith, NASA, Langley Research
John Stanton, U. Texas*
*steering committee member
614-292-2569 (phone),-1948 (FAX)

Special Sessions

For the 67th Symposium, **Caroline Jarrold**, Indiana University, is organizing a mini-symposium entitled, "Ultimate Electronic Transitions - Photodetachment and Photoionization". This mini-symposium will encompass areas from atomic physics to gas-phase biomolecules to liquid jets, where photodetachment and photoionization studies open the door to fundamental physical and chemical phenomena. Invited speakers include **Frederic Merkt**, ETH Zurich, **Daniel Neumark**, UC-Berkeley, and **Lai-Sheng Wang**, Brown University. A second mini-symposium is being organized by **Gary Douberly**, University of Georgia and **David Anderson**, University of Wyoming. This mini-symposium is designed to bring together researchers interested in studying the spectroscopy and chemistry of cold molecular systems in which quantum mechanical effects dominate. Invited talks for this mini-symposium will be given by **Ken Brown**, Georgia Tech; **Marcel Drabbels**, EPFL; **Takamasa Momose**, University of British Columbia and **Pierre-Nicholas Roy**, University of Waterloo. A third mini-symposium is being organized by **Michael Duncan**, University of Georgia entitled "Spectroscopy of Liquid and Cluster Interfaces." The common properties of liquid interfaces and molecular clusters will be explored by bringing together researchers doing spectroscopy on these different systems. Invited speakers include **Heather Allen**, The Ohio State University, and **Richard Saykally**, UC-Berkeley. A session on theory is being organized by **Anne McCoy**, **John Herbert**, and **Russell Pitzer**, Ohio State University, featuring an invited talk by **Henrik Kjaergaard**, University of Copenhagen.

Picnic

The Symposium picnic will be held on Wednesday evening, June 20, at the Fawcett Center. The cost of the picnic is included in your registration (at below cost to students), so that all may attend the event. The **Coblentz Society** is the host for refreshments at 6:30pm before the picnic which is scheduled to commence at 7:30pm at the Fawcett Center.

Sponsorship

We are pleased to announce the sponsorship for the 67th Symposium. Principal funding comes from the **Army Office of Research** (ARO). We are most grateful to ARO for their continued support. We also acknowledge the many efforts and contributions of **The Ohio State University** in hosting the meeting. Our Corporate sponsors are **Elsevier**, **Coherent**, **Journal of Physical Chemistry A**, **Quantel**, and **Virginia Diodes**. Please see the back of this book for their advertisements and the events they support. We are pleased to acknowledge **Andor Technology**, **Bristol Instruments**, **Bruker Optics**, **Continuum**, **CVI Melles Griot**, **Horiba Scientific**, **Lighthouse Photonics**, **Lockheed Martin/Aculight**, **Newport/Spectra-Physics**, **Princeton Instruments**, **MSquared/Scientific Connections**, and **Toptica Photonics** as Contributing sponsors. **IOS Press** has a special insert in your conferee packet. **Bruker Optics** will have a special Tuesday lunch presentation. Look in your packet for fliers about that. Our sponsors will have exhibits at the Symposium and we encourage you to visit their displays.

Rao Prize

The three Rao Prizes for the most outstanding student talks at the 2011 meeting will be presented. The winners are **Adam J. Fleisher**, University of Pittsburgh; **Justin L. Neill**, University of Virginia; and **Thomas J. Preston**, University of Wisconsin. The Rao Prize was created by a group of spectroscopists who, as graduate students, benefited from the emphasis on graduate student participation, which has been a unique characteristic of the Symposium. This year three more Rao Prizes will be awarded. The award is administered by a Prize Committee chaired by Yunjie Xu, University of Alberta and comprised of Kevin Lehmann, University of Virginia; Brooks Pate, University of Virginia; Rebecca Peebles, Eastern Illinois University; Brenda Winnewisser, The Ohio State University and Tim Zwier, Purdue University. Any questions or suggestions about the Prize should be addressed to the Committee. Anyone (especially post-docs) willing to serve on a panel of judges should contact Yunjie Xu (yunjie.xu@ualberta.ca).

Information

ACCOMMODATIONS: The check-in for dormitory accommodations is located in the Lane Avenue Residence Hall (LARH), 328 W. Lane Avenue, opens at 10a.m. Sunday, June 17, and remains open 24 hours a day through the Symposium.

Other hotels close to campus include: The Blackwell, corner of Tuttle Park Place and Woodruff Avenue, 866-247-4003; Red Roof Inn, State Route 315 & Ackerman Rd., 267-9941. **NOTE:** When making reservations with the Blackwell mention that you are with the Molspec Symposium and you will be given the OSU discount, if available.

MAIL: As in recent years, computer facilities for email will be available. Address your regular mail for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210, U.S.A. FAX number - (614) 292-1948, Telephone number - (614) 292-2569.

PARKING: Parking permits, for the week, are available **only** from the check-in desk at the Lane Avenue Residence Hall. These permits allow you to park in any “C” parking space on campus. The permit must be displayed on the front windshield of your car. Please follow all traffic rules to avoid the issuance of tickets. NOTE: The Symposium takes place during Summer Session so parking on campus can be problematic.

REGISTRATION: The Registration Desk will be located in **Room 2017 McPherson Lab**. It will be open between **4:00-6:00 p.m. Sunday**, and **8:15a.m. - 4:30p.m., Monday through Friday**. Those who have prepaid their registration and who are staying in the dorms will receive their registration packet at LARH upon check-in. If you have prepaid your registration but are not staying at the dorms, pick up your packet at the Registration Desk. **NOTE: If the dates of your stay change after Friday, June 8, please call the Symposium Office to find out your options.**

LIABILITY: The Symposium fees DO NOT include provisions for the insurance of participants against personal injuries, sickness, theft or property damage. Participants and companions are advised to take whatever insurance they consider necessary. Neither the Symposium organizing committee, its sponsors, nor individual committee members assume any responsibility for loss, injury, sickness, or damages to persons or belongings, however caused. The statements and opinions stated during oral presentations or in written abstracts are solely the author’s responsibilities and do not necessarily reflect the opinions of the organizers.

AUDIO/VIDEO INFORMATION: Equipment for computer presentations, i.e. Powerpoint, will be available for each session. For computer presentations, you must go to the **Digital Presentation link** on our web site and follow the instructions. Your PowerPoint file and all supporting documents can be uploaded. These files must be submitted to the Symposium by **MIDNIGHT THE DAY BEFORE** your presentation session. All submitted files will be loaded on the presentation computer one half-hour prior to the beginning of the session.

Please make careful note of the username (p#) and password provided in the email confirming receipt of your abstract - this username/password combination will be required when you submit your digital presentation. If you are submitting multiple presentations you will need to log on separately with the appropriate username and password for each presentation.

ACKNOWLEDGEMENTS: The Symposium Chair wishes to acknowledge the hard work of numerous people who make this meeting possible. Key among these people are Becky Gregory, who solves everyone's problems and keeps the meeting running smoothly; and my student assistants, Terrance Codd and Brennan Walder who ensure the sessions go well. We wish to acknowledge the hospitality of the Chemistry Department in tolerating our invasion this year. Sergey Panov originally wrote the script for the electronic aspects of the Symposium; Computer Support in Chemistry and Physics helps us modernize it as well as keep it and other aspects of our services operational. Finally, all the students in my group play vital roles in helping make sure nothing falls through the cracks.

MA. PLENARY SESSION

MONDAY, JUNE 18, 2012 – 8:45 AM

Room: AUDITORIUM, INDEPENDENCE HALL

Chair: FRANK DE LUCIA, The Ohio State University, Columbus, Ohio

Welcome **8:45**
Caroline C. Whitacre, Vice President for Research
The Ohio State University

MA01 **40 min 9:00**

A NEW SPECTROSCOPIC WINDOW ON HYDROXYL RADICALS AND THEIR ASSOCIATION REACTIONS OF SIGNIFICANCE IN THE ATMOSPHERE[a]

MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

---

[a] This research was supported by the National Science Foundation and the Office of Basic Science of the Department of Energy.

MA02 **40 min 9:45**

SPECTROSCOPY OF MOLECULES IN EXTREME ROTATIONAL STATES USING AN OPTICAL CENTRIFUGE

AMY S. MULLIN, CARLOS TORO, GERALDINE ECHIBIRI and QINGNAN LIU, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

Intermission

RAO AWARDS **10:50**
Presentation of Awards by Yunjie Xu, University of Alberta

2011 Rao Award Winners
Adam J. Fleisher, University of Pittsburgh
Justin L. Neill, University of Virginia
Thomas J. Preston, University of Wisconsin

COBLENTZ AWARD **5 min 11:05**
Presentation of Award by Michael L. Myrick, President, Coblentz Society

MA03 ***Coblentz Society Award Lecture*** **40 min 11:10**

IMAGING EXCITED STATE DYNAMICS WITH 2D ELECTRONIC SPECTROSCOPY

GREGORY S. ENGEL, *Department of Chemistry, The University of Chicago, Chicago USA.*

MF. INFRARED/RAMAN

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: MASARU FUKUSHIMA, Hiroshima City University, Hiroshima, Japan

MF01 **10 min 1:30**

TIME RESOLVED FTIR ANALYSIS OF COMBUSTION OF AN ETHANOL/ISOPROPANOL MIXTURE IN A COMMERICIAL INTERNAL COMBUSTION ENGINE

ALLEN R. WHITE, BHARAT YALAMANCHILI, *Department of Mechanical Engineering, Rose-Hulman Institute of Technology, 5500 Wabash Ave., Terre Haute, IN 47803.*

MF02 **15 min 1:42**

SUB-DOPPLER RESOLUTION DIFFERENCE-FREQUENCY-GENERATION INFRARED SPECTROMETER WITH HIGH SENSITIVITY AND WIDE TUNABILITY

S. OKUBO, H. NAKAYAMA,K. IWAKUNI,H. SASADA, *Department of Physics, Faculty of Science and Technology, Keio University, Yokohama, Japan*; H. INABA, *National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.*

MF03 **15 min 1:59**

OPTICAL FREQUENCY COMB REFERNCED SUB-DOPPLER RESOLUTION DIFFERENCE-FREQUENCY-GENERATION INFRARED SPECTROMETER

K. IWAKUNI, S. OKUBO, H. NAKAYAMA, and H. SASADA, *Department of Phisics, Faculty of Science and Technology, Keio University, Yokohama, Japan*; H. INABA, *National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.*

MF04 **15 min 2:16**

DUAL ETALON FREQUENCY COMB (DEFCOM) SPECTROSCOPY

DAVID W. CHANDLER, KEVIN E. STRECKER, *Sandia National Laboratory, Livermore, CA 94550.*

MF05 **15 min 2:33**

A MULTI-WATT SINGLE FREQUENCY CW OPO SYSTEM TUNABLE FROM 600NM TO 4600NM

A. HENDERSON, *LOCKHEED MARTIN ACULIGHT, 22121 20th Avenue SE, Bothell, WA 98021.*

MF06 **15 min 2:50**

DEVELOPMENT OF A HIGHER RESOLUTION TERAHERTZ TIME-DOMAIN SPECTROMETER

DANIEL B. HOLLAND, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125 (email to D.B.H.: holland@caltech.edu)*; GEOFFREY A. BLAKE, *Division of Geological and Planetary Sciences, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.*

MF07 **15 min 3:07**

QCL SPECTROSCOPY AT 9 μM CALIBRATED WITH A HIGH-POWER THULIUM-BASED FREQUENCY COMB

ANDREW A. MILLS, JIE JIANG, INGMAR HARTL, MARTIN FERMANN, *IMRA America, Ann Arbor, MI*; DAVIDE GATTI, MARCO MARANGONI, *Campus Point, Dipartimento di Fisica del Politecnico di Milano, Milano, Italy.*

Intermission

MF08 **15 min 3:40**

DIRECT MEASUREMENTS OF COLLISIONALLY BROADENED (CO_2-CO_2) S-BRANCH RAMAN COHERENCE LIFETIMES OF CO_2

JOSEPH R. GORD, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; SUKESH ROY, PAUL S. HSU, NAIBO JIANG, WARUNA D. KULATILAKA, and HANS U. STAUFFER, *Spectral Energies, LLC, 5100 Springfield Street, Suite 301, Dayton, OH 45431*; JAMES R. GORD, *Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, OH 45433*.

MF09 **10 min 3:57**

ANALYSIS OF AN ^{18}O AND D ENHANCED FT-IBBCEAS WATER SPECTRUM: NEW ASSIGNMENTS FOR $HD^{18}O$, $HD^{16}O$, $D_2{}^{18}O$ AND $D_2{}^{16}O$ IN THE NEAR-INFRARED REGION (6000-7000 cm^{-1}).

MICHAEL J. DOWN, JONATHAN TENNYSON, *Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK*; JOHANNES ORPHAL, *Karlsruher Institut für Technologie, IMK-ASF, Postfach 36 40, 76021 Karlsruhe, Germany*; PASCALE CHELIN, *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université de Paris-Est, CNRS UMR 7583, Créteil, France*; and ALBERT A. RUTH, *Physics Department and Environmental Research Institute, University College Cork, Cork, Ireland*.

MF10 **10 min 4:09**

TOWARDS PERFECT WATER LINE INTENSITIES

L. LODI, J. TENNYSON, *Department of Physics and Astronomy, University College London, London WC1E 6BT, UK*.

MF11 **15 min 4:21**

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF THE $(1,0,1)-(0,0,0)$ BAND OF C_3

S. THORWIRTH, J. KRIEG, I. KEPPELER, V. LUTTER, S. SCHLEMMER, T. F. GIESEN, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; M. E. HARDING, *Karlsruher Institut für Technologie, Institut für Nanotechnologie, 76021 Karlsruhe, Germany*; J. VÁZQUEZ, *Center for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A*.

MF12 **15 min 4:38**

USING PROGRAM ERHAM TO ANALYZE HIGH-RESOLUTION INFRARED SPECTRA OF MOLECULES WITH INTERNAL ROTORS

P. GRONER, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499*; S. ALBERT, M. QUACK, *Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland*.

MF13 **15 min 4:55**

COMPARISON OF COMPUTED CONDON LOCI WITH FRANCK-CONDON FACTORS IN DESLANDRES TABLES OF MOLECULAR BAND SYSTEMS

R. HEFFERLIN and B. CLARK, *Southern Adventist University, Collegedale, TN 37315*; J. TATUM, *University of Victoria, Victoria, BC V8W 2Y2, Canada*.

MF14 **10 min 5:12**

VIBRATIONAL SPECTRA OF THE $MLCl_2$ COMPLEX FROM THEORETICAL CALCULATIONS

BERNA CATIKKAS, *Department of Physics, Mustafa Kemal University, Hatay, Turkey, 31034 (email to B.Ç.: berna@mku.edu.tr)*.

MG. RADICALS AND IONS

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: TIMOTHY SCHMIDT, The University of Sydney, Sydney, Australia

MG01 **15 min 1:30**

RENNER-TELLER COUPLING IN H_2S+: PARTITIONING THE ROVIBRONIC AND SPINORBIT COUPLING HAMILTONIAN

G. DUXBURY, *Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK*; Ch. JUNGEN, *LAC, 1 Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France*; A. ALIJAH, *GSMA, UMR CNRS 6089, Université de Reims Champagne-Ardenne,B.P. 1039, 51687 Reims Cedex 2, France*.

MG02 **15 min 1:47**

RENNER-TELLER COUPLING IN H_2S+: A COMPARISON OF THEORY WITH OPTICAL SPECTRA AND RECENT PFI AND MATI EXPERIMENTAL RESULTS

G. DUXBURY, *Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK*; Ch. JUNGEN, *LAC, 1 Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France*; A. ALIJAH, *GSMA, UMR CNRS 6089, Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France*.

MG03 **15 min 2:04**

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF SILICON-CARBONYL CATIONS: EVIDENCE FOR ASSYMETRIC CARBONYL COORDINATION.

ANTONIO D. BRATHWAITE, MICHAEL A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602-2256*; ,.

MG04 **15 min 2:21**

INITIAL DEVELOPMENT OF HIGH PRECISION, HIGH RESOLUTION ION BEAM SPECTROMETER IN THE NEAR-INFRARED

MICHAEL PORAMBO, BRIAN SILLER, ANDREW MILLS,[a] MANORI PERERA,[b] and HOLGER KRECKEL, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801*.

---

[a] Present Address: IMRA, Ann Arbor, MI 48105

[b] Present Address: Illinois Wesleyan University, Bloomington, IL 61701

MG05 **15 min 2:38**

MID-IR DIRECT ABSORPTION/DISPERSION SPECTROSCOPY OF A FAST ION BEAM

BRIAN SILLER, MICHAEL PORAMBO, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801*.

MG06 **15 min 2:55**

SPONTANEOUS EMISSION BETWEEN ORTHO- AND PARA-LEVELS OF WATER-ION, H_2O^+

KEIICHI TANAKA, *Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 30010, TAIWAN, Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, 812-8581 JAPAN*; KENSUKE HARADA, *Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, 812-8581 JAPAN*; SHINKOH NANBU, *Department of Materials and Life Sciences, Faculty of Science and Engineering, Sophia University, Tokyo 102-8554, JAPAN*; TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, the Enrico Fermi Institute, the University of Chicago, Chicago, Illinois, 60637, USA.*

Intermission

MG07 **15 min 3:30**

INFRARED SPECTROSCOPY OF THE MASS 31 CATION: PROTONATED FORMALDEHYDE VS. THE TRIPLET METHOXY CATION

J. D. MOSLEY, T. C. CHENG, and M. A. DUNCAN, *University of Georgia, Dept. of Chemistry, 1001 Cedar St, Athens, GA 30602.*

MG08 **15 min 3:47**

INFRARED SPECTROSCOPY OF PROTONATED CARBONYLS: PROTONATED GLYOXAL

J. D. MOSLEY, T. C. CHENG, and M. A. DUNCAN, *University of Georgia, Dept. of Chemistry, 1001 Cedar St, Athens, GA 30602.*

MG09 **15 min 4:04**

TIME-RESOLVED FTIR AND MASS SPECTROSCOPY OF LASER-ABLATED MAGNESIUM.

Y. MIYAMOTO, N. IKEDA, J. TANG, K. KAWAGUCHI, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530, Japan*; C. MASAKI, *Faculty of Science, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530, Japan.*

MG10 **15 min 4:21**

METAL ION BINDING TO POLYPEPTIDES CHARACTERIZED BY IRMPD SPECTROSCOPY. METAL-AMIDE NITROGEN BINDING AND THE IMINOL TAUTOMERIZATION.

ROBERT C. DUNBAR, *Chemistry Department, Case Western Reserve Univ., Cleveland, OH 44106*; NICOLAS POLFER, *Chemistry Department, University of Florida, Gainesville, FL*; GIEL BERDEN, *FOM Institute for Plasma Physics, Nieuwegein, Netherlands*; JOS OOMENS, *FOM Institute for Plasma Physics, Nieuwegein, and University of Amsterdam, Netherlands.*

MG11 **15 min 4:38**

INFRARED SPECTROSCOPIC EVIDENCE FOR ISOTOPOLOGS OF THE HOHOH ANION TRAPPED IN SOLID NEON

MARILYN E. JACOX and WARREN E. THOMPSON, *Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

MG12 **15 min 4:55**

INFRARED STUDY OF THE WATER-HYDROXYL RADICAL COMPLEX TRAPPED IN SOLID NEON

MARILYN E. JACOX and WARREN E. THOMPSON, *Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

MG13 **15 min 5:12**

UV/VIS ABSORPTION EXPERIMENTS ON MASS SELECTED CATIONS BY COUNTER-ION INTRODUCTION INTO AN INERT NEON MATRIX

N. P. ROEHR, J. SZCZEPANSKI, N. C. POLFER, *Department of Chemistry, University of Florida, Gainesville, FL 32608.*

MH. MICROWAVE

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: GARRY GRUBBS, Wesleyan University, Middletown, Connecticut

MH01 **15 min 1:30**

BROADBAND ROTATIONAL SPECTRUM AND MOLECULAR GEOMETRY OF OC $\cdots$AgI

N. R. WALKER, S. L. STEPHENS, W. MIZUKAMI, D. P. TEW AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

MH02 **15 min 1:47**

MICROWAVE SPECTRUM AND GEOMETRY OF $H_3P\cdots$AgI

N. R. WALKER, S. L. STEPHENS, W. MIZUKAMI, D. P. TEW AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

MH03 **15 min 2:04**

MICROWAVE SPECTROSCOPY AND INTERNAL DYNAMICS OF THE Ne-NO_2 VAN DER WAALS COMPLEX

BRIAN J. HOWARD, GEORGE ECONOMIDES and LEE DYER, *Department of Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, United Kingdom.*

MH04 **15 min 2:21**

FTMW SPECTROSCOPY AND DETERMINATION OF THE 3-D POTENTIAL ENERGY SURFACE FOR Ar-CS

CHISATO NIIDA, MASAKAZU NAKAJIMA, YASUKI ENDO, *Department of Basic Science, The University of Tokyo, Tokyo 153-8902, Japan*; YOSHIHIRO SUMIYOSHI, *Department of Chemistry and Chemical biology, Gunma University, Maebashi Gunma, 371-8510, Japan*; YASUHIRO OHSHIMA, *Department of Photo-Molecular Science, Institute for Molecular Science, Okazaki, 444-8585, Japan*; HIROSHI KOHGUCHI, *Department of Chemistry, Hiroshima University, Higashi-Hiroshima, 739-8511, Japan.*

MH05 **15 min 2:38**

OBSERVATION OF THE PURE ROTATIONAL SPECTRA OF THE H_2O-$trans$-HOCO COMPLEX

TAKAHIRO OYAMA, MASAKAZU NAKAJIMA, YASUKI ENDO, *Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan*; and YOSHIHIRO SUMIYOSHI, *Department of Chemistry and Chemical Biology, Gunma University, 4-2 Aramaki-machi, Maebashi City, Gunma, 371-8510 Japan.*

MH06 **15 min 2:55**

STRUCTURE AND INVERSION MOTIONS OF THE WEAKLY BOUND $CH_2F_2\cdots CO_2$ DIMER

REBECCA A. PEEBLES, AMELIA J. THOMAS, MICHAL M. SERAFIN and SEAN A. PEEBLES, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920.*

MH07 **10 min 3:12**

ANALYSIS OF MICROWAVE SPECTRUM, INTERNAL ROTATION AND C–H$\cdots$F INTERACTIONS OF THE $CHF_3\cdots C_2H_3F$ WEAKLY BOUND COMPLEX

LENA F. ELMUTI, DANIEL A. OBENCHAIN, REBECCA A. PEEBLES, SEAN A. PEEBLES, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920.*

MH08 **15 min 3:24**

STRUCTURAL STUDIES OF CH_3SiF_2-X (X = NCO, Cl) BY MICROWAVE SPECTROSCOPY

GAMIL A. GUIRGIS, KORREDA K. GAUSE, *Department of Chemistry & Biochemistry, College of Charleston, Charleston, SC 29424 USA*; NATHAN A. SEIFERT, DANIEL P. ZALESKI, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319*; MICHAEL H. PALMER, *School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*; REBECCA A. PEEBLES, SEAN A. PEEBLES, LENA F. ELMUTI, DANIEL A. OBENCHAIN, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL, 61920 USA.*

Intermission

MH09 **15 min 4:00**

MICROWAVE SPECTRA AND GEOMETRIES OF $H_2C_2\cdots AgCl$ AND $H_2C_2\cdots CuCl$

N. R. WALKER, S. L. STEPHENS, W. MIZUKAMI, D. P. TEW AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

MH10 **15 min 4:17**

MICROWAVE SPECTRA, MOLECULAR STRUCTURES AND INTERNAL DYNAMICS OF $H_2S\cdots ICF_3$ and $H_2O\cdots ICF_3$ REVEALED BY BROADBAND ROTATIONAL SPECTROSCOPY

N. R. WALKER, S. L. STEPHENS AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

MH11 **15 min 4:34**

FOURIER TRANSFORM MICROWAVE SPECTRUM OF CO_2 -$(CH_3)_2$ S

YOSHIYUKI KAWASHIMA and TAKAYUKI MORITANI, *Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN*; EIZI HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.*

MH12 **15 min 4:51**

MICROWAVE SPECTROSCOPY AND PROTON TRANSFER DYNAMICS IN THE FORMIC ACID-ACETIC ACID DIMER

B.J. HOWARD, E. STEER, F. PAGE, M. TAYLER, B. OUYANG, *Department of Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, United Kingdom*; H.O. LEUNG, M.D. MARSHALL, *Department of Chemistry, Amherst College, Amherst, MA 01002*; and J.S. MUENTER, *Department of Chemistry, University of Rochester, Rochester, NY 14627.*

MH13 **15 min 5:08**

STRUCTURE OF THE SEVOFLURANE-BENZENE COMPLEX AS DETERMINED BY CHIRPED-PULSE FTMW SPECTROSCOPY

NATHAN A. SEIFERT, DANIEL P. ZALESKI, JUSTIN L. NEILL, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319*; ALBERTO LESARRI, MONTSERRAT VALLEJO, *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; EMILIO J. COCINERO, FERNANDO CASTANO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Campus de Leioa, Ap. 644, E-48080 Bilbao, Spain.*

MH14 **15 min 5:25**

STRUCTURE OF HIGH-ORDER WATER CLUSTERS OF β-PROPIOLACTONE BY BROADBAND MICROWAVE SPECTROSCOPY

JUSTIN L. NEILL, *University of Michigan. Department of Astronomy 830 Dennison Bldg. 500 Church St. Ann Arbor, MI 48109-1042*; CRISTOBAL PEREZ, MATT T. MUCKLE, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904*; ISABEL PENA, JUAN C. LOPEZ, JOSE L. ALONSO, *Grupo de Espectroscopía Molecular (GEM). Edificio Quifima, Laboratorios de Espectroscopía y Bioespectroscopía. Parque Científico Uva Universidad de Valladolid. 47011 Valladolid, Spain.*

MI. MINI-SYMPOSIUM: PHOTODETACHMENT AND PHOTOIONIZATION

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: CAROLINE JARROLD, Indiana University-Bloomington, Bloomington, Indiana

MI01 *INVITED TALK* **30 min 1:30**

SLOW-ELECTRON VELOCITY-MAP IMAGING OF NEGATIVE IONS: APPLICATIONS TO SPECTROSCOPY AND DYNAMICS

DANIEL NEUMARK, *Department of Chemistry, University of California at Berkeley, B64 Hildebrand Hall, Berkeley, CA 94720.*

MI02 **15 min 2:05**

STATE-RESOLVED PREDISSOCIATION DYNAMICS OF THE FORMYLOXYL RADICAL BY DISSOCIATIVE PHOTODETACHMENT OF HCO_2^- / DCO_2^-

AMELIA W. RAY, BEN B. SHEN, BERWYCK L. J. POAD and ROBERT E. CONTINETTI[a], *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093.*

---

[a] This work is supported by the US Department of Energy under Grant Number DE-FG03-98ER14879

MI03 **15 min 2:22**

PHOTOELECTRON-PHOTOFRAGMENT COINCIDENCE SPECTROSCOPY OF TERT-BUTOXIDE AND THE CARBANION ISOMER

BEN B. SHEN, BERWYCK L. J. POAD, AMELIA W. RAY, and ROBERT E. CONTINETTI[a], *Department of Chemistry and Biochemistry, University of California, San Diego, CA 92093.*

---

[a] This work is supported by the United States Department of Energy under grant number DE-FG03-98ER14879

MI04 **15 min 2:39**

VIBRATIONAL AUTODETACHMENT: INTRAMOLECULAR VIBRATIONAL RELAXATION TO ELECTRONIC MOTION

CHRISTOPHER L. ADAMS, BENJAMIN J. KNURR and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

MI05 **15 min 2:56**

PHOTOELECTRON SPECTROSCOPY OF RARE-GAS SOLVATED NUCLEOBASE ANIONS

ANGELA M. BUONAUGURIO, JING CHEN, AND KIT H. BOWEN, *Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218.*

Intermission

MI06 **15 min 3:30**

A STUDY OF NbMo AND $NbMo^-$ BY ANION PHOTOELECTRON SPECTROSCOPY

PRAVEENKUMAR BOOPALACHANDRAN, SRIJAY S. RAJAN, MELISSA A. BAUDHUIN, and DOREEN G. LEOPOLD , *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.*

MI07 **15 min 3:47**

RESONANT TWO-PHOTON DETACHMENT OF WO_2^-

JENNIFER E. MANN, SARAH E. WALLER, DAVID W. ROTHGEB, AND CAROLINE CHICK JARROLD, *Dept. of Chemistry, Indiana University, Bloomington, Indiana, 47405*.

MI08 **15 min 4:04**

ELECTRONIC STRUCTURES OF $MoAlO_y^-$ ($y = 1 - 4$) DETERMINED BY PHOTOELECTRON SPECTROSCOPY AND DFT CALCULATIONS

SARAH E. WALLER, JENNIFER E. MANN, EKRAM HOSSIAN, AND CAROLINE CHICK JARROLD, *Dept. of Chemistry, Indiana University, Bloomington, Indiana, 47405*.

MI09 **15 min 4:21**

ANION PHOTOELECTRON ANGULAR DISTRIBUTIONS: ELECTRON SCATTERING RESONANCES IN PHOTODETACHMENT

RICHARD MABBS, *Washington University in St. Louis, St. Louis, Mo, 63130*.

MI10 **15 min 4:38**

C-O AND O-H BOND ACTIVATION OF METHANOLE BY LANTHANUM

RUCHIRA SILVA, DILRUKSHI HEWAGE AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*.

MI11 **15 min 4:55**

APPLICATION OF EQUATION-OF-MOTION COUPLED-CLUSTER THEORY TO PHOTODETACHMENT CROSS SECTION CALCULATIONS

TAKATOSHI ICHINO and JOHN F. STANTON, *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712*.

MI12 **15 min 5:12**

ELECTRON PROPAGATOR THEORY OF AQUEOUS HALIDE PHOTOELECTRON SPECTRA

J. V. ORTIZ, *Department of Chemistry and Biochemistry*
Auburn University
Auburn, Alabama 36849-5312.

MJ. MATRIX/CONDENSED PHASE

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: MICHAEL HEAVEN, Emory University, Atlanta, Georgia

MJ01 **15 min 1:30**

IDENTIFICATION OF α- AND β-PROTONATED NAPHTHALENE ($C_{10}H_9{}^+$) AND THEIR NEUTRAL COUNTERPARTS ISOLATED IN SOLID PARA-HYDROGEN

MOHAMMED BAHOU, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*; YU-JONG WU, *National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan*; YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

MJ02 **15 min 1:47**

INFRARED SPECTRA OF THE 2-CHLOROPROPYL RADICAL IN SOLID PARA-HYDROGEN

JAY C. AMICANGELO, *School of Science, Penn State Erie, Erie, PA 16563*; BARBARA GOLEC and YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

MJ03 **15 min 2:04**

DIFFUSION OF HYDROGEN FLUORIDE IN SOLID PARAHYDROGEN.

H. OOE, Y. MIYAMOTO, J. TANG, K. KAWAGUCHI, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530,Japan*; S. KUMA, K. NAKAJIMA, N. SASAO, T. TANIGUCHI, *Research Core for Extreme Quantum World, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530,Japan*; I. NAKANO and M. YOSHIMURA, *Faculty of Science, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530,Japan.*

MJ04 **15 min 2:21**

SPECTROSCOPIC AND COMPUTATIONAL STUDIES OF MATRIX ISOLATED ISO-$CXBr_3$ (X=F, Cl, Br)

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233*; BRIAN J. ESSELMAN, ROBERT J. MCMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

MJ05 **15 min 2:38**

SPECTROSCOPY OF AND PHOTOINDUCED ELECTRON TRANSFER IN THE COMPLEXES OF C_2H_4 WITH I AND I_2

LISA GEORGE, AIMABLE KALUME AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

MJ06 **15 min 2:55**

CALCULATION OF RAMAN FREQUENCIES AS FUNCTIONS OF TEMPERATURE AND PRESSURE IN PHASES OF SOLID I, II AND III (III') OF BENZENE

H. YURTSEVEN, *Department of Physics, Middle East Technical University, 06531 Ankara-Turkey*; O. TARI, *Department of Mathematics, Istanbul Arel University, Istanbul, Turkey.*

Intermission

MJ07 **15 min 3:30**

HELIUM NANODROPLET ISOLATION OF IONIC LIQUID VAPOR: INRARED LASER SPECTROSCOPY OF [EMIM][Tf_2N]

STEVEN D. FLYNN, GARY E.DOUBERLY, *Department of Chemistry, University of Georgia, Athens, Georgia, USA 30602*.

MJ08 **15 min 3:47**

C_{60}^{+} AND C_{60}^{-} IN NEON AND ARGON MATRICES

BASTIAN KERN, DMITRY STRELNIKOV, PATRIK WEIS, ARTUR BÖTTCHER and MANFRED M. KAPPES, *KIT Karlsruhe Institute for Technology, Division of Physical Chemistry of Microscopic Systems, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany*.

MJ09 **10 min 4:04**

FTIR OF METHYL PYRUVATE CONFORMERS IN AN ARGON MATRIX

ALLISON B. COMBS, JORDAN L. PRESTON, SARA E. LILLY, COURTNEY D. HATTEN, and LAURA R. MCCUNN, *Department of Chemistry, One John Marshall Drive, Huntington, WV 25755*.

MJ10 **15 min 4:16**

FTIR AND DFT STUDY OF THE VIBRATIONAL SPECTRUM OF SiC_5 TRAPPED IN SOLID Ar

T. H. LE, and W. R. M. GRAHAM, *Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX 76129*.

MJ11 **15 min 4:33**

VIBRATIONAL SHIFT OF ADSORBED CARBON DIOXIDE WITHIN A METAL-ORGANIC FRAMEWORK

S. FITZGERALD, C. PIERCE, J. SCHLOSS, B. THOMPSON, *Department of Physics and Astronomy, Oberlin College, Oberlin, OH 44074*; J. ROWSELL, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*.

MJ12 **5 min 4:50**

SYMMETRY PECULIARITIES OF THE INTRACRYSTALLINE FIELDS LAYERED SEMICONDUCTOR CRYSTALS $(PbI_2)_{(1-x)}$ $(BiI_3)_{(x)}$

IGOR VERTEGEL, EUGENE CHESNOKOV and ALEKSANDR OVCHARENKO, *Institute of Physics National Academy of Sciences of Ukraine 46, Prospect Nauki, 03680 Kiev, Ukraine*.

MJ13 **15 min 4:57**

COMBINED EXPERIMENTAL AND THEORETICAL STUDIES ON THE VIBRATIONAL SPECTRA OF SOME QUINOLINECARBOXALDEHYDE MOLECULES-I

MUSTAFA KUMRU, *Department of Physics, Faculty of Arts and Sciences, Fatih University, 34500 Büyükçekmece, Istanbul, Turkey, mkumru@fatih.edu.tr*.

TA. ATMOSPHERIC SPECIES

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 160 MATH ANNEX

Chair: LINDA BROWN, Jet Propulsion Laboratory, Pasadena, California

TA01 **15 min 8:30**

FREQUENCY COMB-REFERENCED MEASUREMENTS OF SELF- AND NITROGEN-PERTURBED LINE SHAPE PARAMETERS IN THE $\nu_1 + \nu_3$ BAND OF ACETYLENE

MATTHEW J. CICH, GARY V. LOPEZ, TREVOR J. SEARS[a], *Department of Chemistry, Stony Brook University, Stony Brook, New York 11794*; C. P. MCRAVEN, *Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973*; A. W. MANTZ, *Department of Physics, Astronomy, and Astrophysics, Connecticut College, New London, CT 06320*; and DANIEL HURTMANS, *Service de Chimie Quantique et de Photophysique(Atoms, Molecules et Atmospheres), Universite Libre de Bruxelles, Bruxelles, Belgium B-10050.*

---

[a] also: *Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973*

TA02 **15 min 8:47**

HIGH ACCURACY MEASUREMENTS OF NEAR-INFRARED CO_2 AND O_2 TRANSITIONS TO SUPPORT ATMOSPHERIC REMOTE SENSING

DAVID A. LONG, JOSEPH T. HODGES, *Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA*; and CHARLES E. MILLER, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.*

TA03 **15 min 9:04**

TRACE GAS MEASUREMENTS WITH A MULTIPLEXED INTRA-PULSE QUANTUM CASCADE LASER SPECTROMETER

D. WILSON, G. DUXBURY and N. LANGFORD, *Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland,UK.*

TA04 **15 min 9:21**

ISOTOPICALLY INVARIANT DUNHAM FIT FOR THE $X^3\Sigma_g^-$, $a^1\Delta_g$, AND $b^1\Sigma_g^+$ STATES OF OXYGEN

SHANSHAN YU, CHARLES E. MILLER AND BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; HOLGER S.P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.*

TA05 **15 min 9:38**

THE ROTATIONAL SPECTRA OF O-17 SUBSTITUTED OXYGEN SINGLET DELTA

BRIAN J. DROUIN, HARSHAL GUPTA, SHANSHAN YU, CHARLES E. MILLER, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099*; HOLGER S. P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937, Köln, Germany.*

TA06 **10 min 9:55**

LINE MIXING EFFECTS OF O_2 A-BAND WITH PHOTOACOUSTIC SPECTROSCOPY IN SUPPORT OF REMOTE SENSING

THINH Q. BUI[a], DANIEL HOGAN, PRIYANKA M. RUPASINGHE, MITCHIO OKUMURA, *California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125*; DAVID A. LONG and JOSEPH T. HODGES, *NIST, 100 Bureau Drive, Stop 1070, Gaithersburg, MD 20899-1070*; CHARLES E. MILLER, *Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109.*

---

[a] Support from NSF Graduate Fellowship and NASA OCO Funding are gratefully acknowledged

Intermission

TA07 **10 min 10:30**

BROADBAND OZONE ABSORPTION CROSS SECTIONS IN NEAR UV - NEAR IR

ANNA SERDYUCHENKO, VICTOR GORSHELEV, MARK WEBER and JOHN P. BURROWS, *Institute of Environmental Physics, University of Bremen, Germany.*

TA08 **15 min 10:42**

AIR-BROADENED LINE PARAMETERS FOR THE 2←0 BANDS OF $^{13}C^{16}O$ AND $^{12}C^{18}O$ AT 2.3 μm

V. MALATHY DEVI, D. CHRIS BENNER, *The College of William and Mary, Williamsburg, VA 23187*; M. A. H. SMITH, *Science Directorate, NASA Langley Research Center, Hampton, VA 23681*; A. W. MANTZ, *Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320*; K. SUNG and L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.*

TA09 **15 min 10:59**

SPEED DEPENDENT LINE SHAPES IN 1.61 μm AND 2.07 μm CO_2 ATMOSPHERIC RETRIEVALS FOR THE OCO-2 MISSION

DAVID R. THOMPSON, LINDA R. BROWN, DAVID CRISP, YIBO JIANG, FABIANO OYAFUSO, KEEYOON SUNG, CHARLES E. MILLER, VIJAY NATRAJ, DEBRA WUNCH, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr.,Pasadena, CA 91109, U.S.A.*; D. CHRIS BENNER, V. MALATHY DEVI, *The College of William and Mary, Williamsburg, VA 23187, U.S.A..*

TA10 **15 min 11:16**

THE ν_3 AND ν_4 BANDS OF NITRIC ACID (HNO_3) AT 7.6 μm FOR ATMOSPHERIC STUDIES

A.PERRIN, J.M.FLAUD, *Laboratoire Inter Universitaire des Systemes Atmosphériques, CNRS, Université Paris EST-Créteil, 61 Av du General de Gaulle, 94010 Créteil Cedex France*; M.RIDOLFI, M.CARLOTTI, *Dipartimento di Chimica Fisica e Inorganica (DCFI), Universiy of Bologna, Viale del Risorgimento, 4 - 40136 - Bologna, Italy.*

TA11 **15 min 11:33**

FIRST HIGH RESOLUTION ANALYSIS OF THE 5ν_3 BAND OF NITROGEN DIOXIDE NEAR 1.3 μm

D.MONDELAIN, S.KASSI, A.CAMPARGUE, *Laboratoire Interdisciplinaire de Physique (LIPhy), UMR-CNRS 5588, Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France*; A. PERRIN, *Laboratoire Inter Universitaire des Systemes Atmosphériques (LISA), CNRS, Universités Paris Est and Paris 7, 61 Av du Général de Gaulle, 94010 Créteil Cedex France.*

TB. DYNAMICS

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 170 MATH ANNEX

Chair: SCOTT KABLE, University of Sydney, Sydney, Australia

TB01 **15 min 8:30**

LIFETIMES OF THE Ã STATES OF C_3, C_3-NE, AND C_3-AR

YI-JEN WANG, CHIAO-WEI CHEN, LIUZHU ZHOU, ANTHONY J. MERER, YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei 10617, Taiwan, R. O. C..*

TB02 **15 min 8:47**

ACTION SPECTROSCOPY AND DISSOCIATION ENERGY OF AMMONIA TRIMER

CORNELIA G. HEID, AMANDA S. CASE, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*; COLIN M. WESTERN, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.*; F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

TB03 **15 min 9:04**

VIBRATIONAL ENERGY RELAXATION OF CHOLOROIODOMETHANE IN COLD ARGON

A.JAIN and E.L.SIBERT, *Department of Chemistry, University of Wisconsin, Madison, 53706.*

TB04 **15 min 9:21**

ULTRAFAST PHOTOPHYSICS OF SIMPLE AROMATIC CHROMOPHORES

RAUL MONTERO, ALVARO PERALTA CONDE, MARTA FERNÁNDEZ-FERNÁNDEZ, FERNANDO CASTANO and ASIER LONGARTE, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Ap. 644, E-48080 Bilbao, Spain.*

TB05 **15 min 9:38**

FEMTOSECOND TIMESCALE EVOLUTION OF PYRROLE ELECTRONIC EXCITATION

RAUL MONTERO, ALVARO PERALTA CONDE, VIRGINIA OVEJAS, FERNANDO CASTANO and ASIER LONGARTE, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Ap. 644, E-48080 Bilbao, Spain.*

TB06 **15 min 9:55**

DEVELOPMENT OF FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY AS A PROBE OF PHOTOISOMERIZATION DYNAMICS

RYAN D. KIEDA, ADAM D. DUNKELBERGER, JAEYOON SHIN, TRACY OUDENHOVEN, and F. FLEMING CRIM, *Department of Chemistry, Universtiy of Wisconsin-Madison, Madison, WI 53706.*

Intermission

TB07 **15 min 10:30**

PHOTOISOMERIZATION DYNAMICS OF dMe-OMe-NAIP, A MODEL FOR THE RETINAL CHROMOPHORE

ADAM D. DUNKELBERGER, RYAN D. KIEDA, JAEYOON SHIN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*; RICARDO ROSSI PACCANI, STEFANIA FUSI, *UniversitÃČÂă di Siena, Siena, I-53100, Italy*; MASSIMO OLIVUCCI, *UniversitÃČÂă di Siena, Siena, I-53100, Italy and Bowling Green State University, Bowling Green, OH 43403*; and F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

TB08 **15 min 10:47**

ELECTRON TUNNELING PATHWAY AND ROLE OF ADENINE IN REPAIR OF DAMAGED DNA BY PHOTOLYASE

ZHEYUN LIU, CHUANG TAN, XUNMIN GUO, YA-TING KAO, JIANG LI, LIJUAN WANG, and DONGPING ZHONG, *Department of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210..*

TB09 **15 min 11:04**

MOLECULAR UNDERSTANDING OF EFFICIENT DNA REPAIR MACHINERY OF PHOTOLYASE

CHUANG TAN, ZHEYUN LIU, JIANG LI, XUNMIN GUO, LIJUAN WANG and DONGPING ZHONG, *Departments of Physics, Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Biochemistry, The Ohio State University, Columbus, Ohio, 43210.*

TB10 **15 min 11:21**

TRANSITION METAL ASSISTED DECOMPOSITION KINETICS OF ORGANIC MOLECULES: MODELS FOR CATALYSIS

DARRIN BELLERT, IVANNA LABOREN, and OTSMAR VILLARROEL, *Department of Chemistry, Baylor University, Waco, TX 76798.*

TB11 **15 min 11:38**

TRANSIENT ABSORPTION AND TIME-RESOLVED FLUORESCENCE STUDIES OF SOLVATED RUTHENIUM DIBIPYRIDINE PSEUDO-HALIDE COMPLEXES

R. COMPTON, *National Research Council, Postdoctoral Fellow*; D. WEIDINGER, *Schafer Corporation*; J. C. OWRUTSKY, *Chemistry Division, Naval Research Laboratory.*

TC. MICROWAVE

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 1000 MCPHERSON LAB

Chair: PHILLIP SHERIDAN, Canisius College, Buffalo, New York

TC01 **10 min 8:30**

PURE ROTATIONAL SPECTROSCOPY OF PANHs I: 1,10-PHENANTHROLINE. IMPLICATIONS OF PANHs IN ASTROPHYSICAL ENVIRONMENTS AND OBSERVATIONAL SPECTRA

BRETT A. MCGUIRE, IAN A. FINNERAN, P. BRANDON CARROLL, *Department of Chemistry, California Institute of Technology, Pasadena, CA 91125*; and GEOFFREY A. BLAKE, *Divisions of Geological & Planetary Sciences and Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.*

TC02 **10 min 8:42**

PURE ROTATIONAL SPECTROSCOPY OF PANHs II: ACRIDINE. POSSIBLE APPLICATIONS IN THz COHERENT CONTROL SPECTROSCOPY

IAN A. FINNERAN, P. BRANDON CARROLL, BRETT A. MCGUIRE, *Department of Chemistry, California Institute of Technology, Pasadena, CA 91125*; and GEOFFREY A. BLAKE, *Divisions of Geological & Planetary Sciences and Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.*

TC03 **10 min 8:54**

PURE-ROTATIONAL SPECTROSCOPY OF PANHs III: PHENANTHRIDINE. POSSIBLE APPLICATIONS TO THE SPECTROSCOPY OF PROTONATED AROMATIC SPECIES

P. BRANDON CARROLL, BRETT A. MCGUIRE, IAN A. FINNERAN, *Department of Chemistry, California Institute of Technology, Pasadena CA, 91125*; GEOFFREY A. BLAKE, *Divisions of Geological and Planetary Sciences and Chemistry and Chemical Engineering, California Institute of Technology, Pasadena CA, 91125.*

TC04 **15 min 9:06**

A PURE ROTATIONAL STUDY OF TWO NEARLY-EQUIVALENT STRUCTURES OF HEXAFLUOROACETONE IMINE

DANIEL A. OBENCHAIN, DANIEL J. FROHMAN, G. S. GRUBBS II, B. E. LONG, WALLACE C. PRINGLE, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

TC05 **15 min 9:23**

A ROTATIONAL STUDY OF 2H−3H−PERFLUOROPENTANE AND ITS ISOTOPOLOGUES

CHINH H. DUONG, DANIEL A. OBENCHAIN, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

TC06 **15 min 9:40**

CONFORMATIONS AND BARRIERS TO METHYL GROUP INTERNAL ROTATION IN TWO ASYMMETRIC ETHERS: PROPYL METHYL ETHER AND BUTYL METHYL ETHER

B. E. LONG, *Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Ave, Middletown, CT 06459-0180*; F. DeCHIRICO, S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

TC07 **15 min 9:57**

MW SPECTROSCOPY COUPLED WITH ULTRAFAST UV LASER VAPORIZATION: RIBOSE FOUND IN THE GAS PHASE

EMILIO J. COCINERO, PATRICIA ECIJA, FRANCISCO J. BASTERRETXEA, JOSÉ A. FERNÁNDEZ, FERNANDO CASTANO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Ap. 644, E-48080 Bilbao, Spain*; ALBERTO LESARRI, *Departamento de Química-Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Spain*; JENS-UWE GRABOW, *Institut für Physikalische Chemie, Lehrgebiet A, Universität Hannover, Callinstraße. 3A, D-30167 Hannover, Germany*.

TC08 **15 min 10:14**

FOURIER TRANFORM MICROWAVE STUDIES OF BI-MOLECULES OF CARBOXYLIC ACIDS

LUCA EVANGELISTI, GANG FENG, GOU QIAN, ASSIMO MARIS and W. CAMINATI, *Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy*; LAURA B. FAVERO, *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, Via Gobetti 101, I-40129 Bologna, Italy*; EMILIO COCINERO, PATRICIA EJICA, JOSE' A. FERNANDEZ and FERNANDO CASTANO, *Departamento de Quimica Fisica, Facultad de Ciencia y Tecnologia, Universidad del Pais Vasco, E-48080 Bilbao, Spain*; ALBERTO LESARRI, *Departamento de Quimica Fisica y Quimica Inorganica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; ROLF MEYER, *Sonnenbergstrasse 18, CH-5621 Zufikon, Switzerland*.

Intermission

TC09 **15 min 10:45**

THE ROTATIONAL SPECTRA OF PERFLUOROPROPIONIC ACID AND ITS HYDRATES

WEI LIN, AGAPITO SERRATO III, *Department of Chemistry and Environmental Sciences, University of Texas at Brownsville, 80 Fort Brown, Brownsville, TX 78520*; DANIEL A. OBENCHAIN, G. S. GRUBBS II, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577*.

TC10 **10 min 11:02**

THE MILLIMETER WAVE SPECTRUM OF LINALOOL

COREY J EVANS, STEPHANIE M ALLPRESS, *Department of Chemistry, University of Leicester, Leicester, LE17RH, United Kingdom*; PETER D GODFREY, DON MCNAUGHTON, *School of Chemistry, Monash University, 3800, Victoria, Australia*.

TC11 **15 min 11:14**

THE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM AND POTENTIAL ENERGY CALCULATIONS FOR AN AROMATIC CLAISEN REARRANGEMENT MOLECULE, ALLYL PHENYL ETHER

G. S. GRUBBS II, *Department of Chemistry, Wesleyan University, 52 Lawn Ave., Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577*; and STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Ave., Middletown, CT 06459-0180*.

TC12 **15 min 11:31**

ROTATIONAL SPECTRUM AND LARGE AMPLITUDE MOTIONS OF 3,4-, 2,5- and 3,5-DIMETHYL-BENZALDEHYDE

I. KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris Diderot et Paris Est, 61 av. Général de Gaulle, 94010, Créteil, France*; M. TUDORIE, *Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, 50 av. F-D. Roosevelt, 1050 Bruxelles, Belgique*; M. JAHN, J.-U. GRABOW, *Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany*; M. GOUBET, *Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, F-59655 Villeneuve d'Ascq, France*.

TC13 **15 min 11:48**

SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURES FOR THE EQUATORIAL CONFORMERS OF N-METHYLPIPERIDONE AND TROPINONE BY THE MIXED ESTIMATION METHOD

JEAN DEMAISON, *Laboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France*; NORMAN C. CRAIG, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*; EMILIO J. COCINERO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Ap. 644, E-48080 Bilbao, Spain*; JENS-UWE GRABOW, *Institut für Physikalische Chemie and Elektrochemie, Lehrgebiet A, Gottfried-Wilhelm-Leibniz Universität, Callinstrasse 3A, D-30167 Hannover, Germany*; ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; H. D. RUDOLPH, *Department of Chemistry, University of Ulm, D-89069 Ulm, Germany*.

TD. MINI-SYMPOSIUM: PHOTODETACHMENT AND PHOTOIONIZATION

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 1015 MCPHERSON LAB

Chair: RICHARD MABBS, Washington University in St. Louis, St. Louis, Missouri

TD01 *INVITED TALK* **30 min 8:30**

TRANSITION-METAL-DOPED PLANAR BORON CLUSTERS: A NEW CLASS OF AROMATIC COMPOUNDS WITH HIGH COORDINATION

LAI-SHENG WANG, *Department of Chemistry, Brown University, Providence, Rhode Island.*

TD02 **15 min 9:05**

ELECTRON SPIN STATES AND STRUCTURES OF LANTHANIDE (Ce, Pr, and Nd) COMPLEXES OF CYCLOOCTATERAENE

SUDESH KUMARI, YANG LIU, MOURAD ROUDJANE AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

TD03 **15 min 9:22**

CYCLOPOLYMERIZATION OF ACETYLENE TO BENZYNE AND NAPHTHALENE

DILRUKSHI HEWAGE, RUCHIRA SILVA AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

TD04 **15 min 9:39**

ELECTRONIC RELAXATION OF THE PHENYLALANINE RESIDUE IN GAS PHASE PEPTIDES: ROLE OF THE NEIGHBOURING AMIDE GROUPS IN THE PHOTOPHYSICS

Y. LOQUAIS, H.S. BISWAL, B. TARDIVEL, V. BRENNER, M. MONS, *CEA, IRAMIS, SPAM, Lab. Francis Perrin, URA 2453, Gif-sur-Yvette, F-91191, France*; E. GLOAGUEN, *CNRS, INC & INP, Lab. Francis Perrin, URA 2453, Gif-sur-Yvette, F-91191, France*; C. JOUVET, M. BROQUIER, *CNRS, INP, ISMO, CLUPS, UMR 8214, Orsay, F-91405, France*; M. MALIS, I. LJUBIC and N. DOSLIC, *Ruder Bošković Institute, Department of Physical Chemistry, Zagreb, 10000, Croatia.*

TD05 **15 min 9:56**

PROTON TRANSFER IN NEUTRAL PEPTIDES EXAMINED BY CONFORMATIONAL SPECIFIC IR AND UV SPECTROSCOPY

SANDER JAEQX, JOS OOMENS, *FOM institute Rijnhuizen, Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands*; ANOUK M. RIJS, *Radboud University Nijmegen, Institute of Molecules and Materials (molecular & biophysics), Toernooiveld 7, 6525 ED Nijmegen, the Netherlands.*

Intermission

TD06 **15 min 10:30**

SURPRISING COMPLEXITY OF A SMALL MOLECULE: PHOTOFRAGMENTATION DYNAMICS OF ICN, ICN·Ar_n and ICN·$(\mathrm{CO}_2)_n$

ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*; AMANDA S CASE, JOSHUA P. MARTIN, and W. CARL LINEBERGER, *JILA and Department of Chemistry and Biochemistry University of Colorado, Boulder, CO 80309.*

TD07 **15 min 10:47**

NONRADIATIVE DECAY DYNAMICS OF METHYL-4-HYDROXYCINNAMATE AND ITS MONOHYDRATED COMPLEX REVEALED BY PICOSECOND PUMP-PROBE SPECTROSCOPY

T. EBATA, D. SHIMADA, R. KUSAKA, and Y. INOKUCHI, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; M. EHARA, *Institute for Molecular Science, 38 Myodaiji, Okazaki 444-8585, Japan*.

TD08 **15 min 11:04**

DEUTERATION EFFECT STUDY ON THE VIBRATIONAL DYNAMICS OF PHENOL AND PHENOL-WATER COMPLEX BY PICOSECOND TIME-RESOLVED IR-UV PUMP-PROBE SPECTROSCOPY IN A SUPERSONIC MOLECULAR BEAM

YASUNORI MIYAZAKI, YOSHIYA INOKUCHI, and TAKAYUKI EBATA, *Department of Chemistry, Graduate School of Science, Hiroshima University, Japan*.

TD09 **15 min 11:21**

PICOSECOND TIME-RESOLVED IR-UV PUMP-PROBE SPECTROSCOPIC STUDY ON VIBRATIONAL ENERGY RELAXATION OF BENZENE DIMER AND TRIMER IN THE CH STRETCHING REGION

RYOJI KUSAKA, YOSHIYA INOKUCHI, and TAKAYUKI EBATA, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan*.

TD10 **15 min 11:38**

PHOTOELECTRON SPECTROSCOPY OF ALUMINUM DOPED BORON CLUSTERS

WEI-LI LI, CONSTANTIN ROMANESCU, LAI-SHENG WANG, *Brown University, Chemistry Department, 324 Brook Street,Providence, RI 02912, USA*.

TE. MINI-SYMPOSIUM: SPECTROSCOPY OF INTERFACES

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 2015 MCPHERSON LAB

Chair: MICHAEL DUNCAN, University of Georgia, Athens, Georgia

TE01 *INVITED TALK* **30 min 8:30**

SELECTIVE ADSORPTION OF IONS TO AQUEOUS INTERFACES AND ITS EFFECTS ON EVAPORATION RATES

RICHARD J. SAYKALLY, *Department of Chemistry, University of California and Chemical Sciences Division, Lawrence Berkeley National Laboratory Berkeley, CA 94720-1460.*

TE02 **10 min 9:05**

BISULFATE (HSO_4^-) DEHYDRATION AT THE VAPOR/SOLUTION INTERFACE PROBED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

AARON M. JUBB and HEATHER C. ALLEN, *Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

TE03 **10 min 9:17**

INTERFACIAL WATER STRUCTURE AND CATION BINDING WITH THE DPPC PHOSPHATE AT AIR /AQUEOUS INTERFACES STUDIED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

WEI HUA, HEATHER C. ALLEN, *Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

TE04 **15 min 9:29**

THE SPECTROSCOPIC STUDY OF ESTROGEN AND ITS HYDRATED CLUSTERS IN A SUPER SONIC JET

FUMIYA MORISHIMA, YOSHIYA INOKUCHI and TAKAYUKI EBATA, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-hiroshima, 739-8526, Japan.*

Intermission

TE05 **15 min 10:15**

INFRARED SPECTROSCOPY OF LARGE-SIZED NEUTRAL AND PROTONATED METHANOL CLUSTERS

TOMOHIRO KOBAYASHI, RYUNOSUKE SHISHIDO, ASUKA FUJII, *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*; JER-LAI KUO, *Institute of Atomic and Molecular Science, Academia Sinica, Taipei 10617, Taiwan.*

TE06 **10 min 10:32**

INFRARED SPECTROSCOPY OF $(CH_3)_3N\text{-}H^+\text{-}(H_2O)_n$ (n = 1-22)

RYUNOSUKE SHISHIDO, ASUKA FUJII, *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*; and KUO JER-LAI, *Institute of Atomic and Molecular Sciences Academia Sinica, Taipei, Taiwan.*

TE07 **15 min 10:44**

INVESTIGATING ELECTRONIC PROPERTIES OF IONIZED PAH CLUSTERS

C. JOBLIN, D. KOKKIN, A. BONNAMY, D. TOUBLANC, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*; M. RAPACIOLI, A. SIMON, L. DONTOT, A. GAMBOA, F. SPIEGELMAN, *LCPQ, Université de Toulouse, UPS; CNRS; 118 Route de Narbonne, 31062 Toulouse Cedex 09, France*; P. PARNEIX, T. PINO, O. PIRALI, G. FÉRAUD, H. FRIHA, C. FALVO, P. BRÉCHIGNAC, *ISMO; Université Paris-Sud 11; CNRS; Bât. 210, 91405 Orsay Cedex, France*; G. GARCIA, L. NAHON, *Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, B.P. 48, 91192 Gif sur Yvette, France*; G. MULAS, *INAF; Osservatorio Astronomico di Cagliari, Strada n. 54, Loc. Poggio dei Pini, 09012 Capoterra, CA, Italy*.

TE08 **15 min 11:01**

QUANTUM STATE-RESOLVED REACTIVE AND INELASTIC SCATTERING AT GAS-LIQUID AND GAS-SOLID INTERFACES

MONIKA GRÜTTER, DANIEL J. NELSON AND DAVID J. NESBITT, *JILA, University of Colorado and National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, U.S.A.*.

TE09 **15 min 11:18**

PROBING THE STRUCTURE OF IONIC LIQUID SURFACES BY ROTATIONALLY AND ELECTRONICALLY INELASTIC SCATTERING OF NO

M. P. ZIEMKIEWICZ, A. ZUTZ, and D. J. NESBITT , *JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado, USA*.

TE10 **10 min 11:35**

PHOTOELECTRON SPECTROSCOPY OF SOLVATED ELECTRONS IN LIQUID MICROJETS

MADELINE ELKINS, ALEXANDER STREVE, and DANIEL NEUMARK, *Department of Chemistry, University of California - Berkeley, Berkeley, CA 94720*.

TF. INFRARED/RAMAN

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: KEEYOON SUNG, JPL-CalTech, Pasadena, California

TF01 **15 min 1:30**

THE HIGH-RESOLUTION FAR-INFRARED SPECTRA OF SULFUR DI-CYANIDE, $S(CN)_2$ AND THE PURSUIT OF THAT OF CYANOGEN ISO-THIOCYANATE, NCNCS

MANFRED WINNEWISSER, BRENDA P. WINNEWISSER, FRANK C. De LUCIA, *Department of Physics, The Ohio State University, Columbus Ohio, 43210-1106, USA*; DENNIS W. TOKARYK, DAMIEN FORTHOMME, SEPHEN C. ROSS, *Department of Physics and Centre for Laser, Atomic, and Molecular Sciences, University of New Brunswick, P.O. Box 4400, Fredericton NB E3B 5A3, Canada*; BRANT E. BILLINGHURST, *Canadian Light Source, Inc., University of Saskatchewan, Saskatoon, SK, Canada*.

TF02 **15 min 1:47**

COMBINATION BANDS OF THE NONPOLAR OCS DIMER INVOLVING INTERMOLECULAR MODES

M. REZAEI, J. NOROOZ OLIAEE, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada*; A.R.W. MCKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*.

TF03 **15 min 2:04**

PHOTOIONIZATION INDUCED WATER MIGRATION OF 4-AMINOBENZONITRILE-$(H_2O)_1$ CLUSTER

TAKASHI NAKAMURA, *Chemical Resources Laboratory, Tokyo Tech, 4259 Nagatsuta-machi, Midori-ku, Yokohama-shi, Kanagawa, 226-8503, Japan*; MITSUHIKO MIYAZAKI, MASAAKI FUJII, *Chemical Resources Laboratory, Tokyo Tech, 4259 Nagatsuta-machi, Midori-ku, Yokohama-shi, Kanagawa, 226-8503, Japan*; and KOICHI TSUKIYAMA, *Department of Chemistry, Faculty of Science Division I, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan*.

TF04 **15 min 2:21**

ISOLATION OF ION-DRIVEN CONFORMATIONS IN DIPHENYLACETYLENE MOLECULAR SWITCHES USING CRYOGENIC INFRARED SPECTROSCOPY

ARRON B. WOLK, *Yale University, 225 Prospect Street, New Haven, CT 06520*; ETIENNE GARAND, *Yale University, 225 Prospect Street, New Haven, CT 06520*; IAN M. JONES, *Yale University, 225 Prospect Street, New Haven, CT 06520*; MICHAEL Z. KAMRATH, *Yale University, 225 Prospect Street, New Haven, CT 06520*; ANDREW HAMILTON, *University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA*; and MARK A. JOHNSON, *Yale University, 225 Prospect Street, New Haven, CT 06520*.

TF05 **15 min 2:38**

INFRARED SPECTROSCOPY OF COLD, HYDRATED ALKALINE EARTH-HYDROXIDE CLUSTERS

CHRISTOPHER JOHNSON, CHRISTOPHER LEAVITT, JOSEPH FOURNIER, MARK JOHNSON, *Department of Chemistry, Yale University, New Haven, CT 06520*.

TF06 **15 min 2:55**

A HIGH RESOLUTION FAR INFRARED STUDY OF LOW LYING VIBRATIONAL BANDS OF 3-OXETANONE

ZIQIU CHEN AND JENNIFER VAN WIJNGAARDEN, *Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada*.

Intermission

TF07 **15 min 3:30**

GAS-PHASE SPECTROSCOPY OF TYROSINE BY LASER DESORPTION SUPERSONIC JET TECHNIQUE - STABILIZATION MECHANISM OF THE MOST STABLE CONFORMER

YOKO SHIMOZONO, SHUN-ICHI ISHIUCHI, MASAAKI FUJII , *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama 226-8503 Japan*; and KOICHI TSUKIYAMA , *Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601 Japan*.

TF08 **15 min 3:47**

POLARIZED MATRIX INFRARED SPECTRA OF CYCLOPENTADIENONE

THOMAS K. ORMOND, ADAM M. SCHEER, G. BARNEY ELLISON, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215*; MARK R. NIMLOS, *Center for Renewable Chemical, Technologies & Materials, NREL, 1617 Cole Blvd., Golden, CO 80401*; JOHN W. DAILY, *Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309-0427*; JOHN F. STANTON, *Institute for Theoretical Chemistry, Department of Chemistry, University of Texas, Austin, TX 78712*.

TF09 **15 min 4:04**

MIXED HELICES IN THE GAS PHASE: CONFORMATION-SPECIFIC UV AND IR SPECTROSCOPY OF POLYGLYCINE Z-(GLY)$_n$ (n=1,3,5)

JACOB C. DEAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*.

TF10 **15 min 4:21**

UTILIZING FORCE FIELD METHODS TO EXPLORE POTENTIAL ENERGY LANDSCAPES OF FLEXIBLE BIOMOLECULES

ZACHARY S. DAVIS, *Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*; JOANNE M. CARR, IVAN Y. W. TAN, DAVID J. WALES, *Cambridge University Center for Computational Chemistry, Lensfield, Cambridge, United Kingdom CB2 1EW*; TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*.

TF11 **10 min 4:38**

BINDING OF Na$^+$ AND K$^+$ TO THE HEADGROUP OF PALMITIC ACID MONOLAYERS STUDIED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

ZISHUAI HUANG and HEATHER C. ALLEN, *Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210*.

TF12 **15 min 4:50**

CONFORMATIONAL AND STRUCTURAL STUDIES OF ISOPROPYLAMINE FROM TEMPERATURE DEPENDENT RAMAN SPECTRA OF XENON SOLUTIONS AND *AB INITIO* CALCULATIONS

JOSHUA J. KLAASSEN, IKHLAS D. DARKHALIL, JAMES R. DURIG, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110, USA*.

TG. ELECTRONIC

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: JOSH BARABAN, Massachusetts Institute of Technology, Cambridge, Massachusetts

TG01 **10 min 1:30**

IMPROVED EXPERIMENTAL LINE POSITIONS FOR THE (1,1) BAND OF THE $b^1\Sigma^+$ - $X^3\Sigma^-$ TRANSITION OF O_2 BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

LEAH C. O'BRIEN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652*; EMILY C. O'BRIEN, JAMES J. O'BRIEN, *Department of Chemistry & Biochemistry and Center for NanoScience, University of Missouri, St. Louis, MO 63121-4400.*

TG02 **15 min 1:42**

SPECTROSCOPY OF CuN IN THE NEAR INFRARED BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

LEAH C. O'BRIEN, KAITLIN A. WOMACK, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652*; JAMES J. O'BRIEN, *Department of Chemistry & Biochemistry and Center for NanoScience, University of Missouri, St. Louis, MO 63121-4400.*

TG03 **15 min 1:59**

THE SOLUTION TO THE ELECTRONIC SPECTRUM OF THE CHLORINE CATION (Cl_2^+)

MOHAMMED A. GHARAIBEH and DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*; APOSTOLOS KALEMOS, *National and Kapodistrian University of Athens, School of Natural Sciences, Department of Chemistry, Laboratory of Physical Chemistry, P.O. Box 64 004, 157 10 Zografou, Athens, Greece*; ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.*

TG04 **15 min 2:16**

CAVITY RINGDOWN ABSORPTION SPECTRUM OF THE $T_1(n,\pi^*) \leftarrow S_0$ TRANSITION OF ACROLEIN: ANALYSIS OF THE 0_0^0 BAND ROTATIONAL CONTOUR

NIKOLAUS C. HLAVACEK, MICHAEL O. MCANALLY, and STEPHEN DRUCKER, *Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702.*

TG05 **15 min 2:33**

COMPUTATIONAL APPROACHES TO THE DETERMINATION OF THE MOLECULAR GEOMETRY OF ACROLEIN IN ITS $T_1(n,\pi^*)$ STATE

MICHAEL O. MCANALLY, NIKOLAUS C. HLAVACEK, and STEPHEN DRUCKER, *Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702.*

Intermission

TG06 **15 min 3:10**

CONSISTENT ASSIGNMENTS OF THE VIBRATIONS OF SUBSTITUTED BENZENES

ADRIAN M. GARDNER and TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

TG07 **15 min 3:27**

ELECTRONIC AND PHOTOELECTRON SPECTROSCOPY OF TOLUENE

ADRIAN M. GARDNER, ALISTAIR M. GREEN, VICTOR TAMÉ-REYES and TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

TG08 **15 min 3:44**

RESONANCE ENHANCED MULTIPHOTON IONIZATION (REMPI) SPECTROSCOPY OF WEAKLY BOUND COMPLEXES

LLOYD MUZANGWA, SILVER NYAMBO, BRANDON UHLER AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

TG09 **15 min 4:01**

CONFORMATION-SPECIFIC INFRARED AND ULTRAVIOLET SPECTROSCOPY OF α-METHYLBENZYL RADICAL: PROBING THE STATE-DEPENDENT EFFECTS OF METHYL ROCKING AGAINST A RADICAL SITE

NATHANAEL M. KIDWELL, DEEPALI N. MEHTA, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*; NEIL J. REILLY, DAMIAN L. KOKKIN, and MICHAEL C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.*

TG10 **15 min 4:18**

VIBRONIC SPECTROSCOPY OF PHENYLVINYLNITRILE

DEEPALI N. MEHTA, POLINA NAVOTNAYA, ALEX PAROBEK, RACHEL CLAYTON, VANESA VAQUERO VARA, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084 U.S.A.*

TH. MICROWAVE

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: SHANSHAN YU, Jet Propulsion Laborabory, Pasadena, California

TH01 **15 min 1:30**

PROTIC ACID HYDROGEN BONDING IN CHLOROFLUOROETHYLENES: THE HYDROGEN FLUORIDE-VINYL CHLORIDE COMPLEX

HELEN O. LEUNG AND MARK D. MARSHALL, *Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.*

TH02 **15 min 1:47**

BROADBAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND MOLECULAR STRUCTURE OF THE ARGON-*(Z)*-1-CHLORO-2-FLUOROETHYLENE COMPLEX

HELEN O. LEUNG AND MARK D. MARSHALL, *Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.*

TH03 **15 min 2:04**

ROTATIONAL SPECTRUM OF Ar...PROPARGYL ALCOHOL COMPLEX

DEVENDRA MANI, ABHISHEK SHAHI and E. ARUNAN, *Department of Inorganic and Physical Chemistry, Indian Institute of Science Bangalore, India-560012.*

TH04 **15 min 2:21**

ROTATIONALLY-RESOLVED SPECTRA OF 2-METHYLFURAN FROM THE CM-WAVE TO THE FAR INFRARED

STEVEN T. SHIPMAN and IAN A. FINNERAN, *Division of Natural Sciences, New College of Florida, Sarasota, FL 34243*; SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; JENNIFER VAN WIJNGAARDEN, *Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada*.

TH05 **15 min 2:38**

THE FOURIER TRANSFORM MICROWAVE (FTMW) SPECTRA OF CYCLOHEXENE OXIDE AND ITS ARGON COMPLEX

DANIEL J. FROHMAN, STEWART E. NOVICK, and WALLACE C. PRINGLE, *Department of Chemistry, Wesleyan University, 52 Lawn Ave., Middletown, CT 06459-0180.*

TH06 **15 min 2:55**

MICROWAVE SPECTRA OF DEUTERIUM ISOTOPOLOGUES OF *cis*-HEXATRIENE

NORMAN C. CRAIG, HANNAH A. FUSON, HENGFENG TIAN, and HERMAN VAN BESIEN, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*; ANDREW A. CONRAD AND MICHAEL J. TUBERGEN, *Department of Chemistry, Kent State University, Kent, OH 44242*.

TH07 **15 min 3:12**

THE CONFORMATIONS AND STRUCTURES OF 1H-NONAFLUOROBUTANE

JOSEPH A. FOURNIER, ROBERT K. BOHN, *Dept. of Chemistry, Univ. of Connecticut, Storrs, CT 06269-3060*; JOHN A. MONTGOMERY, JR., *Dept. of Physics, Univ. of Connecticut, Storrs, CT 06269-3046*.

TH08 **15 min 3:29**

ROTATIONAL SPECTRA AND STRUCTURES OF THE MONO- AND DI-FLUORINATED PYRIDINES

CODY W. VAN DIJK, MING SUN AND JENNIFER VAN WIJNGAARDEN, *Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada.*

Intermission

TH09 **15 min 4:00**

MILLIMETER AND SUBMILLIMETER-WAVE SPECTRUM OF AMINOACETONITRILE (NH_2CH_2CN)

YUTA MOTOKI, YUKARI TSUNODA, HIROYUKI OZEKI, *Department of Environmental Science, Toho University, 2-2-1 Miyama, Funabashi, 274-8510, Japan*; KAORI KOBAYASHI, *Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555, Japan.*

TH10 **15 min 4:17**

PERTURBATIONS AND VIBRATIONAL ENERGIES IN ACRYLONITRILE FROM GLOBAL ANALYSIS OF ITS MM-WAVE TO THZ ROTATIONAL SPECTRUM

ZBIGNIEW KISIEL, LECH PSZCZÓŁKOWSKI, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; BRIAN J. DROUIN, CAROLYN S. BRAUER, SHANSHAN YU, JOHN C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA*; IVAN R. MEDVEDEV, *Department of Physics, Wright State University, Dayton, OH 45435, USA*; SARAH FORTMAN, CHRISTOPHER NEESE, *Department of Physics, The Ohio State University, Columbus, OH 43210, USA.*

TH11 **15 min 4:34**

STRUCTURE AND ROTATIONAL DYNAMICS OF ISOAMYL ACETATE AND METHYL PROPIONATE STUDIED BY MICROWAVE SPECTROSCOPY

W. STAHL, H. V. L. NGUYEN, L.W. SUTIKDJA, D. JELISAVAC, H. MOUHIB, *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany*; I. KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris Diderot et Paris Est, 61 av. Général de Gaulle, 94010, Créteil, France.*

TH12 **15 min 4:51**

ROTATIONAL ENERGIES IN VARIOUS TORSIONAL LEVELS OF CH_2DOH[a]

L. H. COUDERT, A. EL HILALI, *LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France*; L. MARGULÈS, R. A. MOTIYENKO, *Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; and S. KLEE, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany.*

---

[a] Work supported by the CNES, the INSU program PCMI, and the ANR-08-BLAN-0225 and ANR-08-BLAN-0054 contracts.

TH13 **15 min 5:08**

INTENSITIES IN THE ROTATIONAL-TORSIONAL SPECTRUM OF METHANOL

SARAH M. FORTMAN, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, *Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210, USA.*

TH14 **15 min 5:25**

ROTATIONAL SPECTRUM OF NEOPENTYL ALCOHOL, $(CH_3)_3CCH_2OH$

ZBIGNIEW KISIEL, LECH PSZCZÓŁKOWSKI, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; ZHIFENG XUE, MARTIN A. SUHM, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6, 37077 Göttingen, Germany.*

TI. RADICALS AND IONS

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: JINJUN LIU, University of Louisville, Louisville, Kentucky

TI01 **15 min 1:30**

MODERATE RESOLUTION JET COOLED CAVITY RINGDOWN SPECTRA OF THE $\tilde{A}$ STATE OF NO_3 RADICAL

TERRANCE J. CODD, MING-WEI CHEN[a], MOURAD ROUDJANE and TERRY A. MILLER, *Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.*

---

[a] present address: University of Illinois at Urbana-Champaign, Urbana, IL 61801

TI02 **15 min 1:47**

HIGH RESOLUTION JET COOLED CAVITY RINGDOWN SPECTROSCOPY OF THE $\tilde{A}$ STATE 3_0^1 BAND OF THE NO_3 RADICAL

TERRANCE J. CODD, MOURAD ROUDJANE and TERRY A. MILLER, *Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.*

TI03 **15 min 2:04**

HIGH RESOLUTION CAVITY RING DOWN SPECTROSCOPY OF THE 4_0^3 BAND OF THE $\tilde{A}^2E''$ STATE OF NO_3 RADICAL.

MOURAD. ROUDJANE, TERRANCE J. CODD and TERRY A. MILLER, *Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.*

TI04 **10 min 2:21**

FTIR SPECTROSCOPY OF THE ν_4 BANDS OF $^{14}NO_3$ and $^{15}NO_3$

R. FUJIMORI, N. SHIMIZU, J. TANG, K. KAWAGUCHI, *Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan*; T. ISHIWATA, *Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, Japan,.*

TI05 **15 min 2:33**

FTIR SPECTRUM AND PERTURBATION ANALYSIS OF THE ν_2 BAND OF $^{15}NO_3$

N. SHIMIZU, R. FUJIMORI, J. TANG, K. KAWAGUCHI, *Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan*; T. ISHIWATA, *Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, Japan,.*

TI06 **15 min 2:50**

DISPERSED FLUORESCENCE SPECTROSCOPY OF THE $\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$ TRANSITION OF NO_3

MASARU FUKUSHIMA and TAKASHI ISHIWATA, *Faculty of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.*

TI07 **15 min 3:07**

ENERGY LEVELS OF THE NITRATE RADICAL BELOW 2000 CM^{-1}

J.F. STANTON AND C.S. SIMMONS, *Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.*

Intermission

TI08 **15 min 3:40**

OXYGEN-18 STUDIES OF HOCO AND HONO FORMATION

OSCAR MARTINEZ, JR. and MICHAEL C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138.*

TI09 **15 min 3:57**

A UV+VUV MULTIPHOTON IONIZATION SCHEME FOR OH RADICALS[a]

JOSEPH M. BEAMES, FANG LIU and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

---

[a] This research was supported by the Office of Basic Science of the Department of Energy.

TI10 **15 min 4:14**

CONFIRMED ASSIGNMENTS OF ISOMERIC DIMETHYLBENZYL RADICALS GENERATED BY CORONA DISCHARGE

YOUNG WOOK YOON, SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Korea.*

TI11 **15 min 4:31**

CAVITY-RINGDOWN SPECTROSCOPY OF THE VIBRONICALLY MIXED $\tilde{A}\,^2A_2 - \tilde{B}\,^2B_2$ EXCITED STATES OF THE BENZYL RADICAL AND THE $\tilde{1}\,^2A_2 \leftarrow \tilde{X}\,^2B_1$ TRANSITION OF THE PHENOXY RADICAL IN A SUPERSONIC JET EXPANSION

MICHAEL N. SULLIVAN, KEITH FREEL, J. PARK, M.C. LIN, and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

TI12 **15 min 4:48**

THE CYCLOPENTADIENYL RADICAL REVISITED: THE EFFECTS OF ASYMMETRIC DEUTERATION OF JAHN-TELLER MOLECULES

SAMANTHA STROM, JINJUN LIU, *University of Louisville, Department of Chemistry, Louisville, KY 40292.*

TI13 **15 min 5:05**

THE PHENALENYL FREE RADICAL - A JAHN-TELLER-HERZBERG-TELLER D3H PAH

G. D. O'CONNOR, T. P. TROY, D. A. ROBERTS, N. CHALYAVI, B. FÜCKEL, M. J. CROSSLEY, K. NAUTA, T.W. SCHMIDT, *School of Chemistry, The University of Sydney, NSW 2006, Australia*; and J. F. STANTON, *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165, United States.*

TI14 **15 min 5:22**

LASER INDUCED FLUORESCENCE STUDY OF $\widetilde{B}$ - $\widetilde{A}$ TRANSITION OF ISOPROPOXY RADICAL

RABI CHHANTYAL-PUN, JINJUN LIU[a] and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210*.

---

[a] Present address: Department of Chemistry, University of Louisville, 2320 South Brook Street, Louisville, Kentucky 40292

TI15 **15 min 5:39**

ANALYSIS OF THE ROTATIONALLY-RESOLVED SPECTRA OF ISOPROPOXY RADICAL USING MULTIMODE VIBRONIC CALCULATIONS

DMITRY G. MELNIK, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210*; JINJUN LIU, *Department of Chemistry, University of Louisville, 2320 South Brook Street, Louisville, Kentucky 40292*.

TJ. MINI-SYMPOSIUM:SPECTROSCOPY OF INTERFACES

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: ASUKA FUJII, Tohoku University, Sendai, Japan

TJ01 *INVITED TALK* **30 min 1:30**

ION ORGANIZATION AND REVERSED ELECTRIC FIELD AT AIR/AQUEOUS INTERFACES REVEALED BY HETERODYNE-DETECTED SUM FREQUENCY GENERATION SPECTROSCOPY

WEI HUA, ZISHUAI HUANG, AARON M. JUBB, HEATHER C. ALLEN, *Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

TJ02 **15 min 2:05**

BROADBAND SUM-FREQUENCY GENERATION SPECTROSCOPY OF HIGH-FREQUENCY VIBRATIONS OF WATER MOLECULES AT SILICA SURFACES

OLEKSANDR ISAIENKO, SATOSHI NIHONYANAGI, DEVIKA SIL and ERIC BORGUET, *Temple University, Department of Chemistry, 1901 North 13th Street, Philadelphia, Pennsylvania, 19122 USA.*

TJ03 **15 min 2:22**

STRUCTURE, ENERGETICS AND FINITE TEMPERATURE OH-STRETCH SPECTROSCOPY OF THE WATER HEXAMER

C. J. TAINTER, J. L. SKINNER, *Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, WI 53706.*

TJ04 **15 min 2:39**

INFRARED SPECTROSCOPY OF PROTONATED BENZENE-WATER NANOCLUSTERS: HYDRONIUM, ZUNDEL AND EIGEN AT A HYDROPHOBIC INTERFACE

T. C. CHENG, B. BANDYOPADHYAY, and M. A. DUNCAN, *University of Georgia, Dept. of Chemistry, 1001 Cedar St, Athens, GA 30602.*

TJ05 **15 min 2:56**

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF VANADIUM-CARBON DIOXIDE CATIONS: EVIDENCE FOR AN INTRACLUSTER REACTION.

ANTONIO D. BRATHWAITE, ALLEN M. RICKS, MICHAEL A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602-2256*; ,.

Intermission

TJ06 **15 min 3:30**

UV AND IR SPECTROSCOPIC STUDIES OF COLD ALKALI METAL ION-BENZO CROWN ETHER COMPLEXES IN THE GAS PHASE

YOSHIYA INOKUCHI, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; OLEG V. BOYARKIN, *Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland*; RYOJI KUSAKA, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; TAKEHARU HAINO, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; TAKAYUKI EBATA, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; and THOMAS R. RIZZO, *Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland.*

TJ07 **15 min 3:47**

GAS PHASE HYDRATION OF MODEL PEPTIDE CHAINS: FAR/MID INFRARED SIGNATURE OF WATER INTERMOLECULAR MOTIONS IN THE MONOHYDRATE

M. CIRTOG, Y. LOQUAIS, V. BRENNER, B. TARDIVEL, M. MONS, *CEA, IRAMIS, SPAM, Lab. Francis Perrin, URA 2453, F-91191, Gif-sur-Yvette, France*; E. GLOAGUEN, *CNRS, INC & INP, Lab. Francis Perrin, URA 2453, F-91191, Gif-sur-Yvette, France*; A. M. RIJS, *Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 7, 6525 ED Nijmegen, the Netherlands*.

TJ08 **15 min 4:04**

IR SPECTROSCOPY OF $Au^{-}\cdot(CO_2)_n$ CLUSTERS: STRONG CLUSTER SIZE DEPENDENCE OF METAL-LIGAND INTERACTION

BENJAMIN J. KNURR and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

TJ09 **15 min 4:21**

THE THZ SPECTRUM OF LANTHANIDE AND TRANSITION METAL HALIDES - EFFECTS ON THE WATER SPECTRUM

G. SCHWAAB, VINAY SHARMA AND MARTINA HAVENITH, *Physical Chemistry II, Department of Chemistry and Biochemistry, Ruhr University Bochum, D-44780 Bochum, Germany*.

WA. PLENARY SESSION

WEDNESDAY, JUNE 20, 2012 – 8:30 AM

Room: AUDITORIUM, INDEPENDENCE HALL

Chair: ANNE B. MCCOY, The Ohio State University, Columbus, Ohio

WA01 **40 min 8:30**

THE ATACAMA LARGE MILLIMETER/SUBMILLIMETER ARRAY (ALMA): EARLY RESULTS

ALWYN WOOTTEN, *National Radio Astronomy Obsy, 520 Edgemont Rd, Charlottesville, Va 22903.*

WA02 **40 min 9:15**

TERAHERTZ SPECTROSCOPY OF MOLECULES, RADICALS AND IONS USING EVENSON-TYPE TUNABLE FIR SPECTROMETER

FUSAKAZU MATSUSHIMA, *Department.of Physics, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan.*

Intermission

WA03 **40 min 10:20**

FEMTOSECOND ROTATIONAL RAMAN FOUR-WAVE MIXING SPECTROSCOPY

SAMUEL LEUTWYLER and HANS-MARTIN FREY, *Departement für Chemie und Biochemie, Freiestrasse 3. CH-3012 Bern, Switzerland.*

WA04 **40 min 11:05**

CALCULATING RO-VIBRATIONAL SPECTRA USING AN ECKART FRAME

XIAOGANG WANG and TUCKER CARRINGTON, JR., *Chemistry Department, Queen's University, Kingston, Canada.*

WF. INFRARED/RAMAN

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: ISABELLE KLEINER, CNRS, University Paris 7, Paris Est, Creteil, France

WF01 **15 min 1:30**

HIGH RESOLUTION INFRARED SPECTRA OF AR-WATER AND NE-WATER AT 6 μm

X. LIU and Y. XU, *Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2*.

WF02 **15 min 1:47**

DIODE LASER SPECTROSCOPY OF N2–D2O COMPLEX IN THE V2 BEND REGION OF D2O

SONG LI, RUI ZHENG, YU ZHU, YU YANG, and CHUANXI DUAN, *College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China*.

WF03 **15 min 2:04**

ANALYSIS OF THE HIGH-RESOLUTION MID-INFRARED SPECTRUM OF DEUTERATED WATER CLUSTERS

BRADLEY M. GIBSON and JACOB T. STEWART, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801*.

WF04 **15 min 2:21**

OVERTONE VIBRATIONAL SPECTROSCOPY AND DYNAMICS IN H_2-H_2O COMPLEXES: A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

MICHAEL P. ZIEMKIEWICZ, CHRISTIAN PLUETZER, DAVID J. NESBITT, *JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado*; YOHANN SCRIBANO, *CNRS-Université de Bourgogne, Dijon, France*; ALEXANDRE FAURE, *CNRS, Institut de Planétologie et d'Astrophysique de GrenobleÃŕÂ£Â¡(IPAG), France*; AD VAN DER AVOIRD, *Radboud University, 6525 AJ Nijmegen, The Netherlands*.

WF05 **15 min 2:38**

OVERTONE VIBRATIONAL SPECTROSCOPY AND DYNAMICS IN H_2-H_2O COMPLEXES: A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

MICHAEL P. ZIEMKIEWICZ, CHRISTIAN PLUETZER and DAVID J. NESBITT , *JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado, USA*; YOHANN SCRIBANO, *CNRS-UniversitÃĆÂt'e de Bourgogne, Dijon, France*; ALEXANDRE FAURE, *CNRS, Institut de PlanÃĆÂt'etologie et dÃćÂĂÂŹAstrophysique de Grenoble(IPAG), France*; and AD VAN DER AVOIRD, *Radboud University, Nijmegen, The Netherlands*.

Intermission

WF06 **15 min 3:10**

INFRARED SPECTRA OF He-, Ne-, AND Ar-C_2D_2 COMPLEXES

M. REZAI, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N 1N4, Canada*; A.R.W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*; BERTA FERNÁNDEZ, *Department of Physical Chemistry and Center for Research in Biological Chemistry and Molecular Materials (CIQUS), University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain*; DAVID FARRELLY, *Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300*.

WF07 **15 min 3:27**

COMBINATION BANDS OF THE NONPOLAR N_2O DIMER AND INFRARED SPECTRA OF $(C_2D_4)_2$ AND $(C_2D_4)_3$ USING A QUANTUM CASCADE LASER

M. REZAEI, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada*; A.R.W. MCKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*; K.H. MICHAELIAN, *Natural Resources Canada, CANMET Western Research Center, 1 Oil Patch Drive, Suite A202 Devon Alberta T9G 1A8, Canada..*

WF08 **15 min 3:44**

HIGH RESOLUTION OVERTONE SPECTROSCOPY OF ACETYLENE-WATER VAN DER WAALS COMPLEXES

K. DIDRICHE, T. FOLDES, M. HERMAN, *Service de Chimie quantique et Photophysique CP160/09, Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Av. Roosevelt, 50, B-1050, Bruxelles, Belgium.*

WF09 **10 min 4:01**

HIGH RESOLUTION INFRARED SPECTRA OF JET-COOLED FORMAMIDE AND FORMAMIDE DIMER IN THE C=O STRETCH REGION

FUMIE X. SUNAHORI, YUNJIE XU, *Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.*

WF10 **15 min 4:13**

ANALYSIS OF AB INITIO NORMAL-MODE DISPLACEMENT VECTORS ALONG THE INTERNAL ROTATION PATH FOR THE THREE C-H STRETCHING VIBRATIONS IN METHANOL

LI-HONG XU, RONALD M. LEES, *Centre for Laser, Atomic and Molecular Sciences (CLAMS) Physics Department University of New Brunswick, 100 Tucker Park Road, Saint John, NB, Canada E2L 4L5*; JON T. HOUGEN, *Sensor Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

WF11 **15 min 4:30**

TWO MODEL HAMILTONIANS FOR TORSION-INVERSION TUNNELING IN THE CH-STRETCH VIBRATIONALLY EXCITED STATES OF METHYLAMINE

MAHESH B DAWADI, AND DAVID S PERRY, *Department of Chemistry, The University of Akron, OH 44325-3601.*

WF12 **15 min 4:47**

ELUCIDATING THE COUPLING IN THE CH STRETCH SPECTRAL REGION

EVAN G. BUCHANAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804*; EDWIN L. SIBERT, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706-1322.*

WG. ELECTRONIC

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: J. MATHIAS WEBER, University of Colorado, Boulder, Colorado

WG01 **15 min 1:30**

UNGERADE POLYADS IN THE $45800 - 46500$ CM^{-1} REGION OF THE S_1 STATE OF C_2H_2

J. H. BARABAN, P. B. CHANGALA, R. G. SHAVER, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

WG02 **15 min 1:47**

IDENTIFICATION OF NEW *CIS* VIBRATIONAL LEVELS IN THE S_1 STATE OF C_2H_2

J. H. BARABAN, P. B. CHANGALA, R. G. SHAVER, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

WG03 **15 min 2:04**

UNUSUAL ANHARMONICITIES IN ISOMERIZING SYSTEMS: THE S_1 STATE OF C_2H_2

J. H. BARABAN, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

WG04 **15 min 2:21**

UNKNOWN BANDS OBSERVED IN THE 266 NM PHOTOLYSIS OF IODOMETHANES

JIA-JEN DU, CHIA-HSIN CHEN, and BOR-CHEN CHANG, *Department of Chemistry, National Central University, 300 Jhongda Road, Jhongli 32001, Taiwan.*

WG05 **15 min 2:38**

UV AND 532 NM PHOTODISSOCIATION OF O-NITROTOLUENE: DETECTION OF ELECTRONICALLY EXCITED NITRIC OXIDE IN NITROGEN AND ARGON

HELENA DIEZ-Y-RIEGA and HERGEN EILERS, *Applied Sciences Laboratory, Institute for Shock Physics, Washington State University, Spokane, WA 99210-1495, USA.*

WG06 **15 min 2:55**

FLUORESCENCE EMISSION AND EXCITATION SPECTRA OF PHOTO-FRAGMENTED NITROBENZENE.

CHRISTOPHER J. LUE, CHAKREE TANJAROON, J. BRUCE JOHNSON, SUSAN D. ALLEN, SCOTT W. REEVE, *Arkansas Center for Laser Applications and Science and Department of Chemistry and Physics, P.O. Box 419 State University, AR 72467.*

WG07 **15 min 3:12**

MIMICKING TRIMERIC INTERACTIONS IN THE AROMATIC SIDE CHAINS OF THE PROTEINS: A GAS PHASE STUDY OF INDOLE...(PYRROLE)$_2$ HETEROTRIMER

ALOKE DAS and SUMIT KUMAR, *Indian Institute of Science Education and Research, 900 NCL Innovation Park, Dr. Homi Bhabha Road, Pune-411008, Maharashtra, India.*

Intermission

WG08 **15 min 3:45**

VIBRONIC COUPLING IN A FLEXIBLE BICHROMOPHORE: 1,2-DIPHENOXYETHANE

EVAN G. BUCHANAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804*; DAVID F. PLUSQUELLIC, *National Institute of Standards and Technology, Radiation and Biomolecular Physics Division, Gaithersburg, MD 20899-8443.*

WG09 **15 min 4:02**

COMPREHENSIVE SPECTROSCOPIC CHARACTERIZATION OF MODEL AROMATIC SUBSTITUENTS OF LIGNIN

JACOB C. DEAN, VANESA VAQUERO VARA, KELLY M HOTOPP, BRIAN C. DIAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

WG10 **15 min 4:19**

SPECTROSCOPIC INVESTIGATION OF LIGNIN LINKAGES: UV AND IR SIGNATURES OF PRIMARY DILIGNOLS

JACOB C. DEAN, PATRICK S. WALSH, JOSEPH R. GORD, BIDYUT BISWAS, P. V. RAMACHANDRAN, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

WG11 **15 min 4:36**

SYNERGISTIC TWO-PHOTON ABSORPTION ENHANCEMENT IN PHOTOSYNTHETIC LIGHT HARVESTING

KUO-MEI CHEN, YU-WEI CHEN and TING-FONG GAO, *National Sun Yat-sen University, Kaohsiung, Taiwan, Republic of China.*

WG12 **15 min 4:53**

EMISSION AND fs/ns-TRANSIENT ABSORPTION OF ORGANOMETALLIC COMPLEXES BOUND TO A DINUCLEAR METAL CENTER

CHRISTOPHER B. DURR, SAMANTHA E. BROWN-XU and MALCOLM H. CHISHOLM, *The Ohio State University, Department of Chemistry and Biochemistry, Columbus, Ohio 43210.*

WG13 **15 min 5:10**

TUNING FÖRESTER RESONANCE ENERGY TRANSFER (FRET) IN DNA-FLUOROPHORE CONSTRUCTS

MARVIN POLLUM and CARLOS E. CRESPO HERNÁNDEZ, *Department of Chemistry and Center for Chemical Dynamics, Case Western Reserve University, Cleveland, OH 44106.*

WH. ASTRONOMICAL SPECIES AND PROCESSES

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: ERIC HERBST, University of Virginia, Charlottesville, Virginia

WH01 **15 min 1:30**

A CONFUSION LIMITED SPECTRAL SURVEY OF ORION

J. CERNICHARO, B. TERCERO, N. MARCELINO, T. BELL, *CAB. Dpt Astrophysics. Crta Torrejón Km 4. 28850 Torrejón de Ardoz. Madrid. Spain*; A. PALAU, *ICE, Campus UAB, Torre C5, 08193 Bellaterra. Spain*.

WH02 **15 min 1:47**

HERSCHEL OBSERVATIONS OF EXTRAORDINARY SOURCES (HEXOS).

J. L. NEILL, N. R. CROCKETT, E. A. BERGIN, *Department of Astronomy, University of Michigan, 500 Church St, Ann Arbor, MI 48109, USA*; and THE HEXOS TEAM, *http://www.hexos.org/team.php/*.

WH03 **15 min 2:04**

UNRAVELING THE MYSTERIES OF COMPLEX INTERSTELLAR ORGANIC CHEMISTRY USING HERSCHEL/HIFI SPECTRAL LINE SURVEYS

SHIYA WANG, MARY L. RADHUBER, JACOB C. LAAS, JAY A. KROLL, JAMES L. SANDERS, AND SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; DARIUSZ C. LIS, *Division of Physics, Mathematics, and Astronomy, California Institute of Technology, Pasadena, CA 91125*; ERIC HERBST, *Departments of Chemistry, Physics, and Astronomy, University of Virginia, Charlottesville, VA 22904*.

WH04 **15 min 2:21**

ANALYSIS OF OH^+, H_2O^+, AND H_3^+ IN A DIFFUSE MOLECULAR CLOUD TOWARD W51

NICK INDRIOLO, DAVID A. NEUFELD, *Department of Physics & Astronomy, Johns Hopkins University, Baltimore, MD 21218*; MARYVONNE GERIN, *LERMA, CNRS UMR 8112, 24 rue Lhomond, 75231 Paris Cedex 05, France*; THOMAS R. GEBALLE, *Gemini Observatory, Hilo, HI 96720*.

WH05 **15 min 2:38**

OBSERVATIONS OF OH^+ AND H_2O^+ ACROSS THE GALAXY WITH HERSCHEL

NICK INDRIOLO, DAVID A. NEUFELD, *Department of Physics & Astronomy, Johns Hopkins University, Baltimore, MD 21218*; MARYVONNE GERIN, *LERMA, CNRS UMR 8112, 24 rue Lhomond, 75231 Paris Cedex 05, France*; THE PRISMAS CONSORTIUM,.

WH06 **15 min 2:55**

MORPHOLOGY OF GAS IN THE GALACTIC CENTER FROM SPECTROSCOPY OF H_3^+

TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637*; THOMAS R. GEBALLE, *Gemini Observatory, Hilo, HI 96720*; NICK INDRIOLO, *Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218*; MIWA GOTO, *Universitäts-Sternwarte München, MüÃČÂijnchen Germany 81679*.

Intermission

WH07 **15 min 3:30**

CH$^+$ SPECTRUM AND DIFFUSE INTERSTELLAR BANDS TOWARD HERSCHEL 36 EXCITED BY DUST EMISSION

JULIE DAHLSTROM, *Carthage College*; TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637*; SEAN JOHNSON, DANIEL E. WELTY, LEW M. HOBBS, and DONALD G. YORK, *Department of Astronomy and Astrophysics, University of Chicago, Chicago, IL 60637*.

WH08 **15 min 3:47**

MOLECULAR CONTENT OF THE HELIX NEBULA

L.N. ZACK, N. R. ZEIGLER, and L.M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721*.

WH09 **15 min 4:04**

THE MOLECULAR CONTENT OF PLANETARY NEBULAE: THE DUMBBELL AND THE RED SPIDER

JESSICA L. EDWARDS, LUCY M. ZIURYS, ERIN G. COX, NEVILLE J. WOOLF, *Department of Chemistry and Biochemistry, Department of Astronomy, Steward Observatory, The University of Arizona, Tucson, AZ 85721*.

WH10 **15 min 4:21**

SPECTRAL LINE SURVEYS OF YOUNG STELLAR OBJECTS USING THE CALTECH SUBMILLIMETER OBSERVATORY

JAMES L. SANDERS III, MARY L. RADHUBER, JACOB C. LAAS, JAY A. KROLL and SUSANNA L. WIDICUS WEAVER, *Emory University, Department of Chemistry, Atlanta, Georgia 30322*.

WH11 **15 min 4:38**

IDENTIFYING LOCAL CHEMICAL ENVIRONMENTS IN ORION KL BY BROADBAND DATA CUBE ANALYSIS

BRENT J.HARRIS, CLARE YANG, KEVIN K. LEHMANN, BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904*; ANTHONY J. REMIJAN, CRYSTAL L.BROGAN, *National Radio Astronomy Observatory, Charlottesville, VA 22904*.

WH12 **15 min 4:55**

THE ROTATIONAL SPECTRUM OF HCl$^+$

HARSHAL GUPTA, B. J. DROUIN, J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology*[a], *Pasadena, CA 91109*.

---

[a] A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2012© California Institute of Technology. All rights reserved.

WH13 **15 min 5:12**

HERSCHEL/HIFI IDENTIFICATION OF HCl$^+$ IN THE INTERSTELLAR MEDIUM

M. DE LUCA, M. GERIN, E. FALGARONE, *LERMA-LRA, UMR 8112 du CNRS, Observatoire de Paris, École Normale Supérieure, UPMC & UCP, 24 rue Lhomond, 75231, Paris Cedex 05, France*; HARSHAL GUPTA, B. J. DROUIN, J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology*[a], *Pasadena, CA 91109*; D. A. NEUFELD, *The Johns Hopkins University, Baltimore, MD 21218*; D. C. LIS, R. MONJE, T. G. PHILLIPS, *California Institute of Technology, Pasadena, CA 91125*; D. TEYSSIER, *European Space Astronomy Centre, ESA, Madrid, Spain*; J. R. GOICOECHEA, B. GODARD, T. A. BELL, *Centro de Astrobiología (CSIC/INTA), Madrid, Spain*; A. COUTENS, *Université de Toulouse, UPS-OMP, IRAP, Toulouse, France*.

---

[a] A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2012© California Institute of Technology. All rights reserved.

WH14 **15 min 5:29**

INTEGRAL FIELD SPECTROSCOPY OF THE RED RECTANGLE: UNRAVELING THE CARRIER OF THE RRBs IN 2D

D. L. KOKKIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. Colonel Roche, BP 44346, F-31028 Toulouse Cedex 4, France*; R. G. SHARP, *Research School of Astronomy & Astrophysics, Mount Stromlo Observatory, Cotter Road, Weston Creek, ACT 2611, Australia*; M. NAKAJIMA, *Department of Chemical System Engineering, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*; T. W. SCHMIDT, *School of Chemistry, The University of Sydney, New South Wales, 2006, Australia.*

WI. RADICALS AND IONS

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: KENTAROU KAWAGUCHI, Okayama University, Okayama, Japan

WI01 **15 min 1:30**

THE PREDICTED INFRARED SPECTRUM OF THE HYPERMETALLIC MOLECULE CaOCa IN ITS LOWEST TWO ELECTRONIC STATES $\tilde{X}\ ^1\Sigma_g^+$ AND $\tilde{a}\ ^3\Sigma_u^+$

B. OSTOJIĆ, *Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Studentski trg 14-16, 11 000 Belgrade, Serbia*; P. R. BUNKER, P. SCHWERDTFEGER, *Centre for Theoretical Chemistry and Physics (CTCP), The New Zealand Institute for Advanced Study(NZIAS), Massey University Auckland, Private Bag 102904, North Shore City, 0745 Auckland, New Zealand*; ARTUR GERTYCH, PER JENSEN, *FB C – Physikalische und Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany*.

WI02 **15 min 1:47**

INTERMOLECULAR INTERACTIONS BETWEEN THE SUPEROXIDE RADICAL AND HYDROGEN FLUORIDE

WAFAA M. FAWZY, YUCHENG ZHANG, and MAHMOUD ELSAYED, *Department of Chemistry, Murray State University, Murray, KY 42071*.

WI03 **15 min 2:04**

INTERMOLECULAR INTERACTIONS BETWEEN URACIL AND REACTIVE SPECIES

SIJIN REN and WAFAA M. FAWZY, *Department of Chemistry, Murray State University, Murray, KY 42071*.

WI04 **15 min 2:21**

A NEW APPROACH TO INVESTIGATE PAH DERIVED CATIONS AS DIB CARRIERS

D. L. KOKKIN, C. MARSHALL, A. BONNAMY, and C. JOBLIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*; A. SIMON, *LCPQ, Université de Toulouse, UPS; CNRS; 118 Route de Narbonne, 31062 Toulouse Cedex 09, France*.

WI05 **15 min 2:38**

HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPIC STUDY OF CYCLOPROPENE (c-C_3H_4)

KONSTANTINA VASILATOU, JULIE M. MICHAUD, GUIDO GRASSI, DENITSA BAYKUSHEVA and FREDERIC MERKT, *Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zürich, Switzerland*.

WI06 **15 min 2:55**

SUB-DOPPLER SPECTROSCOPY OF MOLECULAR IONS IN THE MID-INFRARED

JAMES N. HODGES, KYLE N. CRABTREE, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy, and Physics, Univeristy of Illinois, Urbana, IL 61801*.

WI07 **15 min 3:12**

THE INFRARED SPECTRUM OF CH_5^+ REVISITED

KYLE N. CRABTREE, JAMES N. HODGES, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy, and Physics, University of Illinois, Urbana, IL 61801*.

Intermission

WI08 **15 min 3:45**

INFRARED PHOTODISSOCATION SPECTROSCOPY OF ALUMINUM BENZENE CATION COMPLEXES

B. BANDYOPADHYAY, K. N. REISHUS, M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602-2256..*

WI09 **15 min 4:02**

STRUCTURES AND SPECTROSCOPIC PROPERTIES CALCULATED FOR $C_6H_7^+$ AND ITS COMPLEXES WITH Ne, Ar, N_2, OR CO_2

P. BOTSCHWINA and R. OSWALD, *Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*.

WI10 **15 min 4:19**

ROVIBRATIONAL STATES OF $ClHCl^-$ ISOTOPOMERS: A JOINT THEORETICAL AND SPECTROSCOPIC INVESTIGATION

P. BOTSCHWINA, P. SEBALD, and R. OSWALD, *Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*; K. KAWAGUCHI, *Department of Chemistry, Okayama University, Tsushimanaka 3-1-1, Okayama 700-8530, Japan*.

WI11 **15 min 4:36**

VIBRONIC SPECTROSCOPY OF JET-COOLED 2-FLUORO-m-XYLYL AND 2-CHLORO-m-XYLYL RADICALS GENERATED BY CORONA DISCHARGE

YOUNG WOOK YOON, CHANG SOON HUH, SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Korea*.

WI12 **15 min 4:53**

SPECTROSCOPY IDENTIFICATION OF BENZYL-TYPE RADICALS GENERATED BY CORONA DISCHARGE OF PRECURSORS OF MIXED SUBSTITUENTS

YOUNG WOOK YOON, CHANG SOON HUH, SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Korea*.

WI13 **15 min 5:10**

JET-COOLED, BROAD RANGE NEAR-IR SCAN OF REACTIVE INTERMEDIATES USING CAVITY RINGDOWN SPECTROSCOPY

NEAL D. KLINE, TERRANCE J. CODD, MING-WEI CHEN[a], And TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210..*

---

[a] Present Address: Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, 61801

WI14 **15 min 5:27**

SPECTROSCOPIC AND KINETIC MEASUREMENTS OF ORGANIC PEROXY RADICALS BY DUAL-WAEVELENGTH CAVITY RING DOWN SPECTROSCOPY

DMITRY G. MELNIK, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210*.

WJ. MINI-SYMPOSIUM: PHOTODETACHMENT AND PHOTOIONIZATION

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: DONG-SHENG YANG, University of Kentucky, Lexington, Kentucky

WJ01 ***Journal of Molecular Spectroscopy Review Lecture*** **30 min 1:30**

HIGH-RESOLUTION PHOTOELECTRON AND PHOTOIONIZATION SPECTROSCOPY

F. MERKT, *Laboratorium für Physikalische Chemie, ETH Zurich, CH 8093 Zurich, Switzerland.*

WJ02 **15 min 2:05**

THE GAS-PHASE SPECTROSCOPY STUDY OF ThN and ThN^+

I. O. ANTONOV, B. J. BARKER, M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

WJ03 **15 min 2:22**

MASS-ANALYZED THRESHOLD IONIZATION OF M_2O_2 (M = Ce and Pr)

LU WU, BENI DANGI, MOURAD ROUNJANE, and DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

WJ04 **15 min 2:39**

PREFERRED METAL BINDING SITE OF ANILINE

SUDESH KUMARI, BRAD SOHNLEIN AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

Intermission

WJ05 **15 min 3:10**

PHOTOIONIZATION OF ALKALI-DOPED HELIUM NANODROPLETS

MORITZ THEISEN, FLORIAN LACKNER, GÜNTER KROIS, MARKUS KOCH and WOLFGANG E. ERNST, *Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.*

WJ06 **15 min 3:27**

PHOTOIONIZATION SPECTROSCOPY OF ISOLATED Cr ATOMS IN ULTRACOLD HELIUM NANODROPLETS

ANDREAS KAUTSCH, MATTHIAS HASEWEND, MARTIN RATSCHEK, MARKUS KOCH, and WOLFGANG E. ERNST, *Institute of Experimental Physics, TU Graz, Petersgasse 16, 8010 Graz, Austria.*

WJ07 **15 min 3:44**

PHOTOIONIZATION OF HIGHLY CHARGED ARGON IONS AND THEIR DIAGNOSTIC LINES

SULTANA N. NAHAR, *Department of Astronomy, The Ohio State University, Columbus, OH 43210.*

WJ08 **15 min 4:01**

HIGH-RESOLUTION PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF $\mathrm{Cl_2}$: THE GROUND ($\mathrm{X^+\ {}^2\Pi_g}$) AND FIRST EXCITED ($\mathrm{A^+\ {}^2\Pi_u}$) ELECTRONIC STATES OF $\mathrm{Cl_2^+}$

SANDRO MOLLET, and FRÉDÉRIC MERKT, *ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang Pauli-Strasse 10, 8093 Zürich, Switzerland.*

WJ09 **15 min 4:18**

ROTATIONALLY RESOLVED PHOTOELECTRON SPECTROSCOPY OF ArXe AND KrXe

LORENA PITICCO, MARTIN SCHÄFER, and FRÉDÉRIC MERKT, *ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland.*

WJ10 **15 min 4:35**

PROBING THE ADSORPTION OF CARBON MONOXIDE ON TRANSITION METAL CLUSTERS USING IR ACTION SPECTROSCOPY

VIVIKE J. F. LAPOUTRE, JOS OOMENS and JOOST M. BAKKER, *FOM Institute Rijnhuizen, Edisonbaan 14, 3439MN Nieuwegein, The Netherlands.*

RA. ELECTRONIC

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 160 MATH ANNEX

Chair: JOEL TELLINGHUISEN, Vanderbilt University, Nashville, Tennessee

RA01 **15 min 8:30**

ELECTRONIC TRANSITIONS OF PALLADIUM MONOBORIDE AND PLATINUM MONOBORIDE

Y. W. NG, H. F. PANG, Y. S. WONG, YUE QIAN, and A. S-C. CHEUNG , *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.*

RA02 **15 min 8:47**

THE OPTICAL STARK SPECTRUM OF THE $[11.9]\Omega = 3/2 - X^3\Pi_{3/2}$ BAND SYSTEM OF PLATINUM MONOFLUORIDE, PtF

CHENGBING QIN AND TIMOTHY C. STEIMLE , *Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287.*

RA03 **15 min 9:04**

X-RAY RESONANT IRRADIATION AND HIGH-Z RADIOSENSITIZATION IN CANCER THERAPY USING PLATINUM NANO-REAGENTS

SULTANA N. NAHAR, *Department of Astronomy, The Ohio State University, Columbus, OH 43210*; S. LIM, *Biophysics Program, The Ohio State University, Columbus, OH 43210*; M. MONTENEGRO, *Catholic University of Chile*; A.K. PRADHAN, *Department of Astronomy, Biophysics Program, Chemical Physics, The Ohio State University, Columbus, OH 43210*; R. BARTH, *Pathology Department, The Ohio State University, Columbus, OH 43210*; E. BELL, *Radiation Oncology, The Ohio State University, Columbus, OH 43210*; C. TURRO, R. PITZER, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

RA04 **15 min 9:21**

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF SCANDIUM MONOIODIDE

ZHENWU LIAO, MEI YANG, MAN-CHOR CHAN, *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong*; YE XIA, A. S.-C. CHEUNG, *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.*

RA05 **15 min 9:38**

THE SPECTROSCOPY STUDY OF UF AND UF^+

J. H. BARTLETT, I. O. ANTONOV, M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

RA06 **15 min 9:55**

THE OPTICAL STARK SPECTRUM OF the $[17.8]0^+ - X^1\Sigma^+$ BAND OF GOLD MONOFLUORIDE,AuF

RUOHAN ZHANG, CHENGBING QIN, AND TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287*; THOMAS VARBERG, *Department of Chemistry,Macalaster College,1600 Grand Avenue, St. Paul,MN 55105.*

Intermission

RA07 **15 min 10:30**

LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF JET-COOLED NiF: AN INVESTIGATION OF THE Ω-TYPE DOUBLING IN THE Ω=1/2 STATES OF THE $3d^9$ GROUND ELECTRONIC CONFIGURATION

D. L. ARSENAULT, D. W. TOKARYK, C. LINTON, *Department of Physics and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*; A. G. ADAM, *Department of Chemistry and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*.

RA08 **10 min 10:47**

EXOMOL: MOLECULAR LINE LISTS FOR ASTROPHYSICAL APPLICATIONS. A THEORETICAL LINE LIST FOR NICKEL HYDRIDE.

S. N. YURCHENKO, L. LODI, A. KERRIDGE and J. TENNYSON, *University College London, Department of Physics and Astronomy, London WC1E 6BT, UK*.

RA09 **15 min 10:59**

LABORATORY MEASUREMENTS OF THE ZEEMAN EFFECT IN THE F–X SYSTEM OF IRON MONOHYDRIDE

PATRICK CROZET, GUILLAUME TOURASSE, AMANDA J. ROSS, *LASIM, Université Lyon 1 & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France*; D. W. TOKARYK, *Department of Physics and Center for Laser, Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, Canada E3B 5A3*; FRÉDÉRIC PALETOU, *Observatoire Midi-Pyrenées (CNRS) 14 Av Edouard Belin, 31400 Toulouse, France*; ARTURO LÓPEZ ARISTE, *THEMIS Telescope, CNRS UPS 853, C/Via Lactea s/n, 38200 La Laguna, Tenerife, Spain*.

RA10 **15 min 11:16**

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $E^2\Pi$–$X^2\Sigma^+$ TRANSITIONS OF SrH, SrD AND BaH.

R.S. RAM, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA*; K. TERESZCHUK, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; P.F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 USA; Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; and K.A. WALKER, *Department of Physics, University of Toronto, Toronto, Ont., M5S 1A7, Canada.*

RA11 **15 min 11:33**

NEAR INFRARED LASER SPECTROSCOPY OF SCANDIUM MONOBROMIDE

YE XIA, A. S.-C. CHEUNG, *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.*; ZHENWU LIAO, MEI YANG, MAN-CHOR CHAN, *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong*.

RA12 **15 min 11:50**

MEASUREMENT OF HYPERFINE STRUCTURE AND PERMANENT ELECTRIC DIPOLE MOMENTS IN THE ELECTRONIC SPECTRUM OF IRIDIUM MONOHYDRIDE AND DEUTERIDE

C. LINTON, *Physics Department and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*; A. D. GRANGER and A. G. ADAM, *Chemistry Department and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*; S. E. FREY, A. LE and T. C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287, USA..*

RB. ATMOSPHERIC SPECIES

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 170 MATH ANNEX

Chair: V. MALATHY DEVI, College of William and Mary, Williamsburg, Virginia

RB01 **15 min 8:30**

MULTISPECTRUM FITTING OF FTS AND CRDS SPECTRA SIMULTANEOUSLY

D. CHRIS BENNER, V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA*; KEEYOON SUNG, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, U.S.A.*; JOSEPH T. HODGES, *National Institute of Standards and Technology, Gaithersburg, MD 20899.*

RB02 **15 min 8:47**

CAUSAL CORRELATION FUNCTIONS AND FOURIER TRANSFORMS: APPLICATION IN CALCULATING PRESSURE INDUCED SHIFTS

Q. MA, *NASA/Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025, USA*; R. H. TIPPING, *Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487, USA*; N. N. LAVRENTIEVA, *V. E. Zuev Institute of Atmospheric Optics SB RAS, 1, Akademician Zuev square, Tomsk 634021, Russia.*

RB03 **15 min 9:04**

EVALUATION OF THE EXPERIMENTAL AND THEORETICAL INTENSITIES OF WATER-VAPOR LINES IN THE 2 μm REGION USING SOLAR-POINTING FTS SPECTRA

I. E. GORDON, L. S. ROTHMAN, *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA*; L. LODI, J. TENNYSON , *University College London, Department of Physics and Astronomy, London, UK*; G. C. TOON, L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA.*

RB04 **15 min 9:21**

THE COF_2 HOT BANDS IN THE ν_6 REGION AND THE $2\nu_6$ OVERTONE[a]

E. A. COHEN, B. J. DROUIN, and L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

---

[a] This work was done at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.

RB05 **15 min 9:38**

PHOTO-TAUTOMERIZATION OF ACETALDEHYDE TO VINYL ALCOHOL: A NEW MECHANISM FOR ORGANIC ACID FORMATION IN THE TROPOSPHERE

D.U. ANDREWS, B.R. HEAZLEWOOD, A.T. MACCARONE, T. CONROY, R.J. PAYNE, M.J.T. JORDAN and S.H. KABLE , *School of Chemistry, University of Sydney, Sydney, NSW, 2006, Australia.*

RB06 **15 min 9:55**

HIGH RESOLUTION STIMULATED RAMAN SPECTROSCOPY OF CARBON TETRAFLUORIDE CF_4

V. BOUDON, *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne, 9. Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*; D. BERMEJO, R. Z. MARTÍNEZ, *Instituto de Estructura de la Materia, CSIC Serrano 123, E-28006 Madrid, Spain.*

Intermission

RB07 **15 min 10:30**

PRELIMINARY MODELING OF CH_3D FROM 4000 TO 4550 cm^{-1}

A. V. NIKITIN, *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russian Federation*; LINDA R. BROWN, K. SUNG, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; M. REY, Vl. G. TYUTEREV, *Groupe de SpectromÃl'trie MolÃl'culaire et AtmosphÃl'rique, UMR CNRS 6089, UniversitÃl' de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France*; M. A. H. SMITH, *Science Directorate, NASA Langley Research Center, Hampton, VA 23681, USA*; A. W. MANTZ, *Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320, USA*.

RB08 **15 min 10:47**

SUBMILLIMETER SPECTRUM OF METHYL CHLORIDE: ANALYSIS OF THE ν_3=1 EXCITED STATE

ALISSA P. FISHER, *Auburn University*; DANE J. PHILLIPS, *Kratos Defense and Security Solutions Digital Fusion, 4904 Research Dr., Huntsville, Al, 35805*; DENNIS G. WILSON, *Massachusetts Institute of Technology*; ELIZABETH RHODES, *University of Alabama Tuscaloosa*; HENRY O. EVERITT, *Army Aviation and Missile RD&E Center, Weapon Sciences Directorate, Redstone Arsenal, AL, 35898.*

RB09 **15 min 11:04**

IMPROVED LINE PARAMETERS FOR CH4 AROUND 1.6 MICRONS

VICTOR GORSHELEV, ANNA SERDYUCHENKO, M. BUCHWITZ, , J. BURROWS, *University of Bremen, Germany*; N. HUMPAGE, J. REMEDIOS, *University of Leicester, UK*.

RB10 **15 min 11:21**

ANALYTICAL CHEMICAL SENSING IN THE SUBMILLIMETER/TERAHERTZ SPECTRAL RANGE

BENJAMIN L. MORAN, ALYSSA M. FOSNIGHT, IVAN R. MEDVEDEV, *Department of Physics, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA*; CHRISTOPHER F. NEESE, *Department of Physics, Ohio State University, 191 West Woodruff Ave., Columbus, OH 43210, USA*.

RC. ASTRONOMICAL SPECIES AND PROCESSES

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 1000 MCPHERSON LAB

Chair: HARSHAL GUPTA, Jet Propulsion Laboratory, Pasadena, California

RC01 **15 min 8:30**

CDMS AND JPL MOLECULAR SPECTROSCOPY CATALOGUES IN A COMMON INFRASTRUCTURE: VAMDC

S. SCHLEMMER, C. P. ENDRES, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; B.J. DROUIN, S. YU, J.C. PEARSON, *Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109* ; H. S. P. MÜLLER, P. SCHILKE, J. STUTZKI, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*.

RC02 **15 min 8:47**

CDMS 2012: A DATABASE WITHIN THE FRAMEWORK OF THE VIRTUAL ATOMIC AND MOLECULAR DATA CENTRE – RECENT DEVELOPMENTS

HOLGER S. P. MÜLLER, C. P. ENDRES, J. STUTZKI, S. SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*.

RC03 **15 min 9:04**

OBSERVING MOLECULES IN THE INTERSTELLAR MEDIA: THEORETICAL AND EXPERIMENTAL STUDIES OF ENERGY TRANSFER.

LAURENT WIESENFELD, ALEXANDRE FAURE, *UJF-Grenoble 1/CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, France*; FRANÇOIS LIQUE, *LOMC – CNRS, Le Havre University, 76058 Le Havre France*; and NICOLE FEAUTRIER, *LERMA and UMR 8112 of CNRS, Observatoire de Paris-Meudon, 92195 Meudon Cedex, France*.

RC04 **15 min 9:21**

COMPUTATION OF COLLISION-INDUCED ABSORPTION BY SIMPLE MOLECULAR COMPLEXES, FOR ASTROPHYSICAL APPLICATIONS

MARTIN ABEL, LOTHAR FROMMHOLD, *Department of Physics, The University of Texas at Austin, Austin, TX 78712*; XIAOPING LI, KATHARINE L. C. HUNT, *Department of Chemistry, Michigan State University, East Lansing, MI 48824*.

RC05 **15 min 9:38**

METHANOL PHOTODISSOCIATION STUDIES USING MILLIMETER AND SUBMILLIMETER SPECTROSCOPY

JACOB C. LAAS and SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*.

Intermission

RC06 **15 min 10:10**

TIME-SLICE VELOCITY-MAP ION IMAGING STUDIES OF THE PHOTODISSOCIATION OF ASTROPHYSIC IMPORTANT SMALL MOLECULES IN THE VACUUM ULTRAVIOLET REGION BY RESONANT SUM/DIFFERENCE FOUR-WAVE MIXING

HONG GAO, YU SONG, LEI YANG, JINGANG ZHOU, C. Y. NG, WILLIAM M. JACKSON, *Department of Chemistry, University of California, Davis, Davis, CA 95616, USA*; YANG PAN, *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China*.

RC07 **15 min 10:27**

OSCILLATOR STRENGTHS AND PREDISSOCIATION RATES FOR RYDBERG COMPLEXES IN $^{12}C^{16}O$ BETWEEN 92.9 AND 93.4 NM

M. EIDELSBERG, J. L. LEMAIRE, *Observatoire de Paris, Paris, France*; S. R. FEDERMAN, *Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606*; G. STARK, A. N. HEAYS, *Department of Physics, Wellesley College, Wellesley, MA 02481*; L. GAVILAN, *Observatoire de Paris, Paris, France*; J. H. FILLION, *Université PVI UMPC, Paris, France*; F. ROSTAS, *Observatoire de Paris, Paris, France*; J. R. LYONS, *IGPP, University of Califormia, Los Angeles, CA 90095*; P. L. SMITH, *Department of Physics, Wellesley College, Wellesley, MA 02481*; N. DE OLIVEIRA, D. JOYEUX, M. ROUDJANE, L. NAHON, *Synchrotron SOLEIL, Saint Aubin, France*.

RC08 **15 min 10:44**

THE ANALYSIS OF ASTROPHYSICAL ‘WEEDS’ USING 3-D SUBMILLIMETER SPECTROSCOPY

SARAH M. FORTMAN, JAMES P. MCMILLAN, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, *Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210, USA*.

RC09 **15 min 11:01**

COMPUTATIONAL STUDY AND LABORATORY SPECTROSCOPY OF PREBIOTIC MOLECULES PRODUCED BY O(^{1}D) INSERTION REACTIONS

BRIAN M. HAYS, BRIDGET A. DEPRINCE, SUSANNA L. WIDICUS WEAVER, *Emory University, Department of Chemistry, Atlanta, GA 30322*.

RC10 **15 min 11:18**

HIGH RESOLUTION SPECTROSCOPY OF HEXAMETHYLENETETRAMINE (HMT) $C_6N_4H_{12}$

V. BOUDON, *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne, 9. Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*; O. PIRALI[a], *Ligne AILES – Synchrotron SOLEIL, L’Orme des Merisiers, F-91192 Gif-sur-Yvette, France*.

---

[a] Also at: Institut des Sciences Moléculaires d’Orsay, UMR8214 CNRS-Université Paris-Sud, Bat.210, 91405 Orsay cedex, France.

RC11 **15 min 11:35**

NUCLEAR SPIN OF H_3^+ AND H_2 IN DENSE MOLECULAR CLOUDS

KYLE N. CRABTREE, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy, and Physics, University of Illinois, Urbana, IL 61801*.

RC12 **15 min 11:52**

GAS-GRAIN MODELING OF O_2 IN INTERSTELLAR CLOUDS

DONGHUI QUAN, *Department of Chemistry, Eastern Kentucky University, Richmond, KY 40475*; ERIC HERBST, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904*.

RD. MINI-SYMPOSIUM: COLD QUANTUM SYSTEMS

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 1015 MCPHERSON LAB

Chair: GARY DOUBERLY, University of Georgia, Athens, Georgia

RD01 *INVITED TALK* **30 min 8:30**

PROBING MOLECULES WITH LASER-COOLED ATOMIC IONS

KENNETH R. BROWN, *Schools of Chemistry and Biochemistry; Computational Science and Engineering; and Physics*
Georgia Institute of Technology, Atlanta, GA 30332-0400.

RD02 **15 min 9:05**

SPECTROSCOPIC APPLICATIONS OF STATE-SELECTED SYMPATHETICALLY-COOLED MOLECULAR IONS

XIN TONG, MATTHIAS GERMANN and STEFAN WILLITSCH, *Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.*

RD03 **15 min 9:22**

DETECTING HYDROGEN ATOMS IN SOLID PARAHYDROGEN USING FTIR SPECTROSCOPY

DAVID T. ANDERSON and MAHMUT RUZI, *Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.*

RD04 **15 min 9:39**

PHOTOCHEMICAL STUDIES OF CH_3OH ISOLATED IN SOLID PARAHYDROGEN

DAVID T. ANDERSON, KYLIE A. KUFELD, DOMINIQUE SCHOECH, ROBERT B. SLIPP, AND FARAJ M. ALMARRI, *Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.*

RD05 **15 min 9:56**

FTIR STUDIES OF AMMONIA PHOTOCHEMISTRY IN SOLID PARAHYDROGEN

MAHMUT RUZI and DAVID T. ANDERSON, *Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.*

RD06 **15 min 10:13**

DECELERATING MOLECULES WITH MICROWAVE FIELDS

MELANIE SCHNELL, *Center for Free-Electron Laser Science, Hamburg, Germany*; SIMON MERZ, NICOLAS VANHAECKE, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*; WOLFGANG JÄGER, *University of Alberta, Edmonton, Canada*; GERARD MEIJER, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.*

Intermission

RD07 **15 min 10:45**

HOW CHLORINE ATOM REACTS WITH H_2 IN IR-IRRADIATED SOLID PARA-HYDROGEN

JEN-YU WU, MOHAMMED BAHOU, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*; AND YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

RD08 **15 min 11:02**

THEORETICAL SPIN-ORBIT SPECTROSCOPY OF Cl DOPANTS IN SOLID PARAHYDROGEN

ROBERT HINDE, *Department of Chemistry, University of Tennessee, Knoxville, TN 37996 USA.*

RD09 **15 min 11:19**

INFRARED SPECTROSCOPY OF 1-CHOLOROMETHYLALLYL AND 1-METHYLALLYL RADICALS PRODUCED IN A SOLID PARA-HYDROGEN MATRIX.

MOHAMMED BAHOU, JEN-YU WU, KEIICHI TANAKA, *Dept of Applied Chemistry, National Chiao Tung University, Hsinchu, 30010, TAIWAN* ; YUAN-PERN LEE, *Dept of Applied Chemistry, National Chiao Tung University, and Institute of Atomic & Molecular Sciences, Academia Sinica, Taipei 10617, TAIWAN.*

RD10 **15 min 11:36**

IR-IR DOUBLE RESONANCE EXPERIMENT OF CH_3F-$(ortho\text{-}H_2)_n$ CLUSTERS IN SOLID $para$-H_2

Y. MIYAMOTO, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530 JAPAN*; A. MIZOGUCHI, and H. KANAMORI, *Department of Physics, Tokyo Institute of Technology, Tokyo, 152-8551 JAPAN.*

RD11 **15 min 11:53**

LINESHAPE ANALYSIS OF CH_3F-(*ortho*-$H_2)_n$ ABSORPTION SPECTRA IN 3000 cm^{-1} REGION IN SOLID *para*-H_2

Y. MIYAMOTO, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530, Japan*; T. MOMOSE, *Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada*; H. KANAMORI, *Department of Physics, Tokyo Institute of Technology, Ohokayama 2-12-1, Tokyo 152-8551, Japan.*

RE. DYNAMICS

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 2015 MCPHERSON LAB

Chair: GEOFFREY DUXBURY, University of Strathclyde, Glasgow, United Kingdom

RE01 **15 min 8:30**

GAIN AND LASING OF OPTICALLY PUMPED METASTABLE RARE GAS ATOMS

JIANDE HAN and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

RE02 **15 min 8:47**

COOPERATIVE EFFECTS IN A RYDBERG GAS

YAN ZHOU, DAVID GRIMES, ANTHONY COLOMBO, and ROBERT FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02319.*

RE03 **15 min 9:04**

USING A HIGH RESOLUTION MID-IR OPO FOR CHEMICAL DYNAMICS STUDIES OF HIGHLY EXCITED MOLECULES

GERALDINE O. ECHEBIRI, MATTHEW D. SMARTE, WENDELL W. WALTERS and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

RE04 **10 min 9:21**

OPTICAL PROBING OF OCS IN EXTREME ROTATIONAL STATES

QINGNAN LIU, CARLOS TORO and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

RE05 **15 min 9:33**

POLARIZATION DEPENDENT DYNAMICS OF CO_2 TRAPPED IN AN OPTICAL CENTRIFUGE

CARLOS TORO, GERALDINE ECHEBIRI, QINGNAN LIU and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

RE06 **15 min 9:50**

IR/THZ DOUBLE RESONANCE SPECTROSCOPY OF METHYL FLUORIDE AND COLLISION PARTNERS SELF, N_2, Ar, He, CO_2, AND AIR

DANE J. PHILLIPS, *Kratos Defense and Security Solutions Digital Fusion, 4904 Research Dr., Huntsville, Al, 35805*; FRANK C. DE LUCIA, *Department of Physics, 191 Woodruff Ave. Ohio State University, Columbus, OH 43210*; HENRY O. EVERITT, *Army Aviation and Missile RD&E Center, Weapon Sciences Directorate, Redstone Arsenal, AL, 35898.*

Intermission

RE07 **15 min 10:20**

ULTRAVIOLET PHOTODISSOCIATION DYNAMICS OF THE 1-PROPENYL RADICAL

MICHAEL LUCAS, *Department of Chemistry, University of California at Riverside, Riverside, CA 92521*; YU SONG, *Department of Chemistry, University of California at Davis, Davis, CA 95616*; JINGSONG ZHANG [a], *Department of Chemistry, University of California at Riverside, Riverside, CA 92521*; CHRISTOPHER BRAZIER, *Department of Chemistry and Biochemistry, California State University, Long Beach, Long Beach, CA 90840.*

---

[a] Corresponding author.

RE08 **15 min 10:37**

OBSERVATION OF VIBRATIONALLY HOT CH_2CHO IN THE 351NM PHOTODISSOCIATION OF XCH_2CH_2ONO (X=F,Cl,Br,OH)

RABI CHHANTYAL-PUN, MING-WEI CHEN[a] and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

---

[a] Present address: School of Chemical Science, University of Illinois at Urbana Champaign,106 Noyes Lab, 505 S. Mathews, Urbana, IL 61801

RE09 **15 min 10:54**

PRODUCT STATE AND SPEED DISTRIBUTIONS IN PHOTOCHEMICAL TRIPLE FRAGMENTATIONS

M.S. QUINN, G. DE WIT, B.R. HEAZLEWOOD, K. NAUTA, S.H. KABLE, and M.J.T. JORDAN, *School of Chemistry, University of Sydney, Sydney, NSW, 2006, Australia*; S.A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI, 53233, USA*; A.T. MACCARONE, *Department of Chemistry, University of Wollongong, Wollongong, NSW, 2522, Australia.*

RE10 **15 min 11:11**

HYDROGEN ABSTRACTION FROM CH_3D BY CHLORINE RADICALS WITH VARYING KINECTIC ENERGY DISTRIBUTIONS

ANDREW E. BERKE, ETHAN H. VOLPA, F. FLEMING CRIM, *Chemistry Department, University of Wisconsin - Madison, Madison, Wisconsin 53706.*

RE11 **15 min 11:28**

VIBRATIONALLY DRIVEN HYDROGEN ABSTRACTION BY THE BROMINE ATOM FROM CYCLOHEXANE

THOMAS J. PRESTON, MICHAEL A. SHALOSKI, and F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

RE12 **15 min 11:45**

THE MARRIAGE OF SPECTROSCOPY AND DYNAMICS: CHIRPED-PULSE FOURIER-TRANSFORM MM-WAVE (CP-FT-MMW) SPECTROSCOPY IN PULSED UNIFORM SUPERSONIC FLOWS

CHAMARA ABEYSEKERA, JAMES M. OLDHAM, ARTHUR G. SUITS, *Department of Chemsitry, Wayne State University, Detroit, MI 48202*; G. BARRATT PARK, ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.*

RF. ASTRONOMICAL SPECIES AND PROCESSES

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: NICHOLAS INDRIOLO, Johns Hopkins University, Baltimore, Maryland

RF01 **15 min 1:30**

THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

R. D. GEHRZ, *Department of Astronomy, University of Minnesota, 116 Church Street, S. E., Minneapolis, MN 55455*; E. E. BECKLIN, *Universities Space Research Association, NASA Ames Research Center, MS 211-3, Moffett Field, CA 94035.*

RF02 **15 min 1:47**

INFRARED SPECTROSCOPIC STUDIES WITH THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

R. D. GEHRZ, *Minnesota Institute for Astrophysics, University of Minnesota, 116 Church Street, S. E., Minneapolis, MN 55455*; E. E. BECKLIN, *Universities Space Research Association, NASA Ames Research Center, MS 211-3, Moffett Field, CA 94035.*

RF03 **15 min 2:04**

ROTATIONAL SPECTRA OF VIBRATIONALLY EXCITED HCL

BRIAN J. DROUIN, HARSHAL GUPTA, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

RF04 **15 min 2:21**

THE ROTATIONAL SPECTRA OF OH DOUBLET PI ISOTOPOLOGUES

BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

RF05 **15 min 2:38**

MICROWAVE STUDY OF METHYL FORMATE IN THE NEW VIBRATIONAL EXCITED STATES

YUSUKE SAKAI, KAORI KOBAYASHI, *Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan*; MASAHIRO TSUKAMOTO, MASAHARU FUJITAKE, and NOBUKIMI OHASHI, *Kanazawa University, Japan.*

RF06 **15 min 2:55**

LABORATORY STUDY OF THE ROTATIONAL SPECTRUM OF 2-BUTANONE

JAY A. KROLL and SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; STEVEN T. SHIPMAN, *Division of Natural Sciences, New College of Florida, Sarasota, FL 34243..*

Intermission

RF07 **15 min 3:30**

USING HOT EMISSION SPECTRA IN GENERATING LINE LISTS OF MOLECULES (NH_3, CH_4) FOR ASTROPHYSICAL APPLICATIONS

R.J. HARGREAVES, L. MICHAUX, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; G. LI, *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, MS#50, 60 Garden St., Cambridge, MA, 02138,USA*; C. BEALE, *Department of Chemistry & Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, VA, 23529-0126, USA*; M. IRFAN, *School of Physics and Astronomy, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK*; and P.F. BERNATH, *Department of Chemistry & Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, VA, 23529-0126, USA; and University of York, Dept. of Chemistry, Heslington, York, YO10 5DD, UK.*

RF08 **15 min 3:47**

BROADBAND SCREENING FOR INTERSTELLAR SPECIES: ADDITIONAL LABORATORY MEASUREMENTS AND INTERSTELLAR DETECTION OF ETHANIMINE (CH_3CHNH) IN SGR B2(N)

RYAN A. LOOMIS, DANIEL P. ZALESKI, AMANDA L. STEBER, JUSTIN L. NEILL, MATT T. MUCKLE, NATHAN A. SEIFERT, and BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904*; VALERIO LATTANZI, OSCAR MARTINEZ, JR., and MICHAEL C. MCCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138*; ANTHONY J. REMIJAN, *National Radio Astronomy Observatory, 520 Edgemont Rd., Charlottesville, VA 22904.*

RF09 **10 min 4:04**

UNRAVELING THE COMPLEX NEAR-UV SPECTRUM OF Si_2C

N. J. REILLY and M. C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138*; D. L. KOKKIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*; R. C. FORTENBERRY, and T. D. CRAWFORD, *Department of Chemistry, Virginia Tech, Blacksburg, VA 24061.*

RF10 **15 min 4:16**

LABORATORY DETECTIONS OF CYANOTHIOFORMALDEHYDE (HCSCN) AND MERCAPTOACETONITRILE ($HSCH_2CN$) BY CP-FTMW SPECTROSCOPY

DANIEL P. ZALESKI, JUSTIN L. NEILL, MATT T. MUCKLE, NATHAN A. SEIFERT, AMANDA A. STEBER, BRENT J. HARRIS, AND BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904*; VALERIO LATTANZI AND MICHAEL MCCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.*; ANTHONY J. REMIJAN, *National Radio Astronomy Observatory, 520 Edgemont Rd., Charlottesville, VA 22904..*

RF11 **10 min 4:33**

HIGH RESOLUTION SPECTRUM OF THE $^{13}C^{12}C^{12}C$ LOWEST BENDING MODE

C. P. ENDRES, V. LUTTER, J. KÖTTING, J. KRIEG, S. THORWIRTH, S. SCHLEMMER, T. F. GIESEN, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; M. E. HARDING, *Karlsruher Institut für Technologie, Institut für Nanotechnologie, 76021 Karlsruhe, Germany*; J. VÁZQUEZ, *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA.*

RF12 **15 min 4:45**

ASSIGNMENTS, PERTURBATIONS, PATHOLOGIES AND A ROTATIONAL ANALYSIS OF THE SPECTRUM OF CH_2DOH

JOHN C. PEARSON, SHANSHAN YU, BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109.*

RF13 **15 min 5:02**

THZ AND LONG PATH FOURIER TRANSFORM SPECTROSCOPY OF METHANOL; TORSIONALLY COUPLED HIGH-K LEVELS

JOHN C. PEARSON, SHANSHAN YU, BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109*; RONALD M. LEES, LI-HONG XU, *Centre for Laser, Atomic and Molecular Sciences (CLAMS) Physics Department University of New Brunswick, 100 Tucker Park Road, Saint John, NB, Canada E2L 4L5*; BRANT E. BILLINGHURST, *Canadian Light Source Inc, University of Saskatchewan, 100 Perimeter Drive, Saskatchewan, SK, Canada S7N 0X4*.

RF14 **15 min 5:19**

ON THE ELECTRONIC SPECTROSCOPY OF CLOSED SHELL CATIONS DERIVED FROM RESONANCE STABILIZED RADICALS: INSIGHTS FROM THEORY AND FRANCK-CONDON ANALYSIS

TYLER P. TROY, SCOTT H. KABLE, TIMOTHY W. SCHMIDT, *School of Chemistry, The University of Sydney, NSW 2006, Australia*; SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233*.

RG. ELECTRONIC

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: YEN-CHU HSU, Academia Senica, Taipei, Taiwan

RG01 **10 min 1:30**

DIRECT POTENTIAL FITTING FOR THE $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ STATES OF Br_2

TOKIO YUKIYA, NOBUO NISHIMIYA, MASAO SUZUKI, *Department of Electronics and Information Technology, Tokyo Polytechnic University, Iiyama 1583, Atsugi City, Kanagawa 243-0297, Japan*; ROBERT J. LE ROY, *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.*

RG02 **15 min 1:42**

ANALYSIS OF THE VISIBLE ABSORPTION SPECTRUM OF I_2 IN INERT SOLVENTS USING A PHYSICAL MODEL

J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235.*

RG03 **5 min 1:59**

WAVELENGTH ANOMALIES IN UV-Vis SPECTROPHOTOMETRY

J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235.*

RG04 **15 min 2:06**

DEPERTURBATION STUDIES OF AlO : INTERACTIONS IN THE $\mathrm{A}^2\Pi \sim \mathrm{X}^2\Sigma^+$ STATES

K. SUNANDA, M. D.SAKSENA, and B. N. JAGATAP, *Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085,India*; M. N. DEO, *High Pressure Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*; N. MHASKE and S. H. BEHERE, *Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India.*

RG05 **15 min 2:23**

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $\mathrm{A}^2\Pi$–$\mathrm{X}^2\Sigma^+$ (RED) SYSTEM OF $^{13}\mathrm{C}^{14}\mathrm{N}$.

R.S. RAM, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA*; and P.F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 USA; Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.*

RG06 **15 min 2:40**

HYPERFINE-RESOLVED SATURATION SPECTROSCOPY OF METASTABLE N_2 IN THE (1-0) BAND OF THE $\tilde{B}^3\Pi_g - \tilde{A}^3\Sigma_u^+$ ELECTRONIC TRANSITION

D. FORTHOMME, C. MCRAVEN, G. E. HALL, T. J. SEARS, *Chemistry Department, Brookhaven National Laboratory, Bldg. 555A, P.O. Box 5000, Upton, NY 11973, USA.*

RG07 **15 min 2:57**

PRODUCTION OF A BEAM OF HIGHLY VIBRATIONALLY EXCITED CO USING PERTURBATIONS

N. BARTELS, T. SCHÄFER, J. HÜHNERT, A. M. WODTKE, *Georg August Universität Göttingen, Institut für Physikalische Chemie, Tammanstrasse 6, 37075 Göttingen, Germany*; and R. W. FIELD, *Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA.*

Intermission

RG08 **15 min 3:30**

IS THE EQUILIBRIUM STRUCTURE OF BeOH LINEAR OR BENT?

KYLE J. MASCARITOLO, JEREMY M. MERRITT, and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

RG09 **15 min 3:47**

AN EXPERIMENTAL AND QUANTUM CHEMICAL STUDY OF THE ELECTRONIC SPECTRUM OF THE HBCl FREE RADICAL

MOHAMMED A. GHARAIBEH, RAMYA NAGARAJAN and DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*; RICARDO TARRONI, *Dipartimento di Chimica Fisica ed Inorganica, UniversitÃă di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*.

RG10 **15 min 4:04**

GAS PHASE SPECTROSCOPIC INVESTIGATION OF CHROMATE-ESTERS

SYDNEY H. KAUFMAN and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

RG11 **15 min 4:21**

ELECTRONIC SPECTROSCOPY OF THE NO-X (X = RARE GAS, ALKANE) COMPLEXES

ADRIAN M. GARDNER, VICTOR TAMÉ-REYES, JOE HARRIS, JODIE McDANIEL and TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

RG12 **15 min 4:38**

GAS PHASE ELECTRONIC PHOTODISSOCIATION SPECTRA OF COPPER NITRATE CLUSTER IONS

SYDNEY H. KAUFMAN, CASEY R. CHRISTOPHER and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

RG13 **15 min 4:55**

THE OPTICAL SPECTRUM OF THE SILICON TERMINATED CARBON CHAINS SiCnH

D. L. KOKKIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France and Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138*; N. J. REILLY, and M. C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138*; R. C. FORTENBERRY, and T. D. CRAWFORD, *Department of Chemistry, Virginia Tech, Blacksburg, VA 24061.*

RG14 **15 min 5:12**

LASER INDUCED FLUORESCENCE SPECTROSCOPY SiCN : ROTATIONAL ANALYSIS OF THE $\tilde{A}\,^2\Delta - \tilde{X}\,^2\Pi$ TRANSITION

MASARU FUKUSHIMA and TAKASHI ISHIWATA, *Faculty of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.*

RH. MICROWAVE

THURSDAY, JUNE 20, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: JENNIFER VAN WIJNGAARDEN, University of Manitoba, Winnipeg, MB, Canada

RH01 **15 min 1:30**

THE ROTATIONAL SPECTRUM OF $D_2{}^{17}O$: ACCURATE SPECTROSCOPIC AND HYPERFINE PARAMETERS

CRISTINA PUZZARINI, GABRIELE CAZZOLI, *Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy*; JUANA VÁZQUEZ, *Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, USA*; MICHAEL E. HARDING, *Karlsruher Institut für Technologie, Institut für Nanotechnologie, 76021, Karlsruhe, Germany*; JÜRGEN GAUSS, *Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany*.

RH02 **15 min 1:47**

IDENTIFICATION OF THE CAGE, PRISM, AND BOOK ISOMERS OF WATER HEXAMER AND THE PREDICTED LOWEST ENERGY HEPTAMER AND NONAMER CLUSTERS BY BROADBAND ROTATIONAL SPECTROSCOPY

CRISTOBAL PEREZ, MATT T. MUCKLE, DANIEL P. ZALESKI, NATHAN SEIFERT, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904*; ZBIGNIEW KISIEL, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; BERHANE TEMELSO, GEORGE C. SHIELDS, *Dean's Office, College of Arts and Sciences, and Department of Chemistry, Bucknell University, Lewisburg, PA 17837*.

RH03 **15 min 2:04**

WATER CLUSTERS OBSERVED BY CHIRPED-PULSE ROTATIONAL SPECTROSCOPY: STRUCTURES AND HYDROGEN BONDING

ZBIGNIEW KISIEL, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; CRISTOBAL PEREZ, MATT T. MUCKLE, DANIEL P. ZALESKI, NATHAN SEIFERT, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319*; BERHANE TEMELSO, GEORGE C. SHIELDS, *Dean's Office, College of Arts and Sciences, and Department of Chemistry, Bucknell University, Lewisburg, PA 17837*.

RH04 **15 min 2:21**

FTMW SPECTROSCOPY OF SILYL MERCAPTAN, H_3SiSH

S. THORWIRTH, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; V. LATTANZI, OSCAR MARTINEZ, JR., MICHAEL C. MCCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, U.S.A. and School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, U.S.A.*; LI-HONG XU, *Department of Physics, Centre for Laser, Atomic and Molecular Studies (CLAMS) University of New Brunswick, Saint John, New Brunswick, Canada E2L 4L5*.

RH05 **15 min 2:38**

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF SCS ($X^2\Sigma$), YS ($X^2\Sigma$) AND VS ($X^4\Sigma$)

L. M. ZIURYS, G. R. ADANDE, D. T. HALFEN, *Department of Chemistry and Steward Observatory, University of Arizona, Tucson, AZ 85721*.

RH06 **15 min 2:55**

THE CCN ($\tilde{X}^2\Pi_{1/2}$) RADICAL REVISITED: NEW FOURIER TRANSFORM MICROWAVE MEASUREMENTS

J. K. ANDERSON, D. T. HALFEN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

RH07 **15 min 3:12**

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF ALKALI METAL HYDROSULFIDES: DETECTION OF KSH

P. M. SHERIDAN, M. K. L. BINNS, J. P. YOUNG, *Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY 14208*; M. P. BUCCHINO, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

Intermission

RH08 **15 min 3:45**

MICROWAVE SPECTRUM OF HEXAFLUOROISOPROPANOL

ABHISHEK SHAHI, DEVENDRA MANI and E. ARUNAN, *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India.*

RH09 **15 min 4:02**

MILLIMETER-WAVE SPECTROSCOPY OF ETHYLMERCURY HYDRIDE

M. GOUBET, R. A. MOTIYENKO, L. MARGULÈS, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS - ENSCR, 35708 Rennes Cedex 7, France.*

RH10 **15 min 4:19**

CHIRPED-PULSE AND CAVITY BASED FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF THE METHYL LACTATE-AMMONIA ADDUCT

JAVIX THOMAS, OLEKSANDR SUKHORUKOV, WOLFGANG JAEGER and YUNJIE XU, *Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada.*

RH11 **15 min 4:36**

HALOGEN BOND AND INTERNAL MOTIONS: THE LOW-BARRIER CASE OF CF_3Cl-DIMETHYLETHER

LUCA EVANGELISTI, GANG FENG, QIAN GOU and WALTHER CAMINATI, *Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy*; JENS-UWE GRABOW, *Lehrgebiet Physikalische Chemie A, Institut für Physikalische Chemie und Elektrochemie, Universtät Hannover, Callinstr. 3A, D-30167 Hannover, Germany.*

RH12 **15 min 4:53**

THE COMMON CHLORINE NUCLEAR ELECTRIC QUADRUPOLE COUPLING TENSOR FOR ACYL CHLORIDES

R. A. POWOSKI, *Glori Energy, Inc., 4315 South Dr, Houston, Texas 77053*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

RH13 **15 min 5:10**

THE MILLIMETER WAVE SPECTRUM OF ESTRAGOLE AND VERBENONE

COREY J EVANS, STEPHANIE M ALLPRESS, *Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom*; PETER D GODFREY, DON MCNAUGHTON, *School of Chemistry, Monash University, 3800, Victoria, Australia.*

RI. MINI-SYMPOSIUM: COLD QUANTUM SYSTEMS

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: TAKAMASA MOMOSE, The University of British Columbia, Vancouver, BC, Canada

RI01 *INVITED TALK* **30 min 1:30**

SPECTRA OF COLD MOLECULAR IONS FROM HOT HELIUM NANODROPLETS

MARCEL DRABBELS, *Laboratoire de Chimie Physique Moléculaire, Ecole polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.*

RI02 **15 min 2:05**

HOT MOLECULES IN HELIUM NANODROPLETS: A NEW ROUTE TO OPTICAL SPECTRA

BENJAMIN SHEPPERSON, ADRIAN BOATWRIGHT, CHENG FENG, DANIEL SPENCE, SHENGFU YANG, and ANDREW M. ELLIS, *Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK.*

RI03 **15 min 2:22**

HELIUM NANODROPLET ISOLATION SPECTROSCOPY OF NO_2 AND VAN DER WAALS COMPLEXES

ROBERT R. FEHNEL, KEVIN K. LEHMANN, *Department of Chemistry, University of Virginia, Charlottesville VA, 22904-4319.*

RI04 **15 min 2:39**

SATURATION OF THE NO_2 $\nu_1 + \nu_3$ AND THE CH_4 ν_3 TRANSITIONS IN HELIUM NANODROPLETS

ROBERT R. FEHNEL, KEVIN K. LEHMANN, *Department of Chemistry, University of Virginia, Charlottesville VA, 22904-4319.*

RI05 **15 min 2:56**

INFRARED SPECTROSCOPY OF OH AND OH-C_2H_2 EMBEDDED IN HELIUM NANODROPLETS

PAUL RASTON, TAO LIANG, STEVEN D. FLYNN, ALEXANDER M. MORRISON, AND GARY E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, GA 30602-2556.*

Intermission

RI06 *INVITED TALK* **30 min 3:30**

DOPANT ROTATION IN MOLECULAR SUPERFLUID CLUSTERS

PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.*

RI07 **10 min 4:05**

OBSERVATION OF VORTICES IN SUPERFLUID He DROPLETS

LUIS F. GOMEZ, EVGENY LOGINOV, ANDREY F. VILESOV, *Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.*

RI08 **15 min 4:17**

PYRIDINE AGGREGATION IN HELIUM NANODROPLETS

PABLO NIETO, TORSTEN POERSCHKE, DANIEL HABIG, GERHARD SCHWAAB and MARTINA HAVENITH, *Department of Physical Chemistry II, Ruhr-Universität Bochum, Germany*.

RI09 **15 min 4:34**

PROBING TRANS-HOOO/DOOO AND HOOO-$(O_2)_n$ CLUSTERS: A HENDI APPROACH

T. LIANG, P. RASTON, and G. E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556*.

RI10 **15 min 4:51**

ON THE OUTCOME OF THE REACTIONS BETWEEN HYDROCARBON RADICALS AND O_2 IN HELIUM NANODROPLETS

A. M. MORRISON and G. E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556*.

RI11 **15 min 5:08**

INFRARED SPECTROSCOPY OF HOCl EMBEDDED IN HELIUM NANODROPLETS

PAUL RASTON, DONALD KELLOWAY, AND WOLFGANG JÄGER, *Department of Chemistry, University of Alberta, Edmonton, Alberta T6G-2G2, Canada*.

RI12 **15 min 5:25**

ASYMMETRIC TOP ROTORS IN SUPERFLUID *PARA*-HYDROGEN NANO-CLUSTERS

TAO ZENG, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1*; HUI LI, *Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, 2519 Jiefang Road, Changchun 130023, People's Republic of China*; and PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1*.

RI13 **15 min 5:42**

MOLECULAR DYNAMICS SIMULATIONS ON VARIOUS WEAKLY BOUND WATER-PARAHYDROGEN SYSTEMS AT ULTRACOLD TEMPERATURE

MATTHEW SCHMIDT, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1*; CHRISTOPHER ING, *Department of Biochemistry, University of Toronto, 27 King's College Circle, Toronto, Ontario, Canada M5S 1A1*; STEPHEN CONSTABLE, TAO ZENG, JING YANG, MICHAEL NYMAN and PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1*.

RJ. THEORY

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: PETER BOTSCHWINA, University of Goettingen, Goettingen, Germany

RJ01 *INVITED TALK* **30 min 1:30**

INTENSITIES OF FUNDAMENTAL AND OVERTONE VIBRATIONAL TRANSITIONS

HENRIK G. KJAERGAARD, *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark.*

RJ02 **15 min 2:05**

HIGH-ACCURACY POTENTIALS FOR VAN DER WAALS SYSTEMS

RICHARD DAWES, *Missouri University of Science and Technology, Rolla, MO 65409, USA*; XIAO-GANG Wang, JAMES BROWN, TUCKER CARRINGTON, JR., *Queen's University, Kingston, Ontario, K7L 3N6 Canada.*

RJ03 **15 min 2:22**

THE AMMONIA DIMER REVISITED

RICHARD DAWES, *Missouri University of Science and Technology, Rolla, MO 65409-0010*; AD VAN DER AVOIRD, *Radboud University, 6525 AJ Nijmegen, The Netherlands.*

RJ04 **15 min 2:39**

RESONANCE AND REVIVALS I. QUANTUM ROTOR AND INFINITE-WELL DYNAMICS

WILLIAM G. HARTER, *Department of Physics, University of Arkansas, Fayetteville, AR 72701*; ALVASON ZHENHUA LI, *Microelectronics-Photonics, University of Arkansas, Fayetteville, AR 72701.*

RJ05 **15 min 2:56**

RESONANCE AND REVIVALS II. MORSE OSCILLATOR AND DOUBLE MORSE WELL DYNAMICS

ALVASON ZHENHUA LI, *Microelectronics-Photonics Program, University of Arkansas, Fayetteville, AR 72701*; WILLIAM G. HARTER , *Department of Physics, University of Arkansas, Fayetteville, AR 72701.*

Intermission

RJ06 **15 min 3:30**

MULTI-VALUED VERSUS SINGLE-VALUED LARGE-AMPLITUDE BENDING-TORSIONAL-ROTATIONAL COORDINATE SYSTEMS FOR SIMULTANEOUSLY TREATING TRANS-BENT AND CIS-BENT ACETYLENE IN ITS S_1 EXCITED ELECTRONIC STATE

JON T. HOUGEN, *Sensor Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA.*

RJ07 **15 min 3:47**

USING FIXED-NODE DIFFUSION MONTE CARLO TO PROBE ROTATION-VIBRATION COUPLING IN HIGHLY FLUXIONAL ASYMMETRIC TOP MOLECULES

ANDREW S. PETIT, BETHANY A. WELLEN, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

RJ08 **15 min 4:04**

EXTENSIONS OF FIXED-NODE DIFFUSION MONTE CARLO TO THE STUDY OF THE ROTATIONALLY EXCITED STATES OF H_2D^+

BETHANY A. WELLEN, ANDREW S. PETIT, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

RJ09 **15 min 4:21**

EXPLORING ROTATION-VIBRATION COUPLING IN HIGHLY FLUXIONAL MOLECULES USING SURFACE HOPPING DIFFUSION MONTE CARLO

ANDREW S. PETIT, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

RJ10 **10 min 4:38**

BOUND AND SCATTERING STATE SOLUTIONS OF SCHRODINGER EQUATION FOR ASYMMETRIC WOODS SAXON POTENTIAL

N. CANDEMIR, *Physics Department, Science Faculty, Anadolu University, Eskişehir, 26470, Turkey.*

FA. ASTRONOMICAL SPECIES AND PROCESSES

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 160 MATH ANNEX

Chair: JOHN C. PEARSON, Jet Propulsion Laboratory, Pasadena, California

FA01 **15 min 8:30**

THEORETICAL AND EXPERIMENTAL WATER COLLISIONS WITH NORMAL AND PARAHYDROGEN

BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099*; LAURENT WIESENFELD, *UJF-Grenoble 1/CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France*.

FA02 **15 min 8:47**

ROTATIONAL SPECTROSCOPY OF ISOCYANIC MOLECULES: ALLYL ISOCYANIDE AND DIISOCYANOMETHANE

R. A. MOTIYENKO, L. MARGULES, I. HAYKAL, T. R. HUET, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; E. J. COCINERO, P. ECIJA, J. A. FERNANDEZ, F. CASTANO, *Dpto. Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Barrio Sarriena s/n, 48940, Leioa, Spain*; A. LESARRI, *Dpto. Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena s/n, 47005, Valladolid, Spain*; J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS - ENSCR, 35708 Rennes Cedex 7, France*.

FA03 **15 min 9:04**

TERAHERTZ SPECROSCOPY OF METHYLAMINE

R. A. MOTIYENKO, L. MARGULÈS, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; V. V. ILYUSHIN, E. A. ALEKSEEV, *Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine*; B. DROUIN, S. YU, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA*; J. CERNICHARO, B. TERCERO, *Centro de Astrobiología (CSIC-INTA). Laboratory of Molecular Astrophysics. Department of Astrophysics. Ctra de Ajalvir, Km 4, 28850 Torrejòn de Ardoz, Madrid, Spain*.

FA04 **15 min 9:21**

THZ SPECTROSCOPY OF ACETALDEHYDE AND SEARCH OF ^{13}C SPECIES IN ORION

L. MARGULÈS, R. A. MOTIYENKO, *Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; V. V. ILYUSHIN, *Institute of Radio Astronomy of NASU, Chervonopraporna Str., 4, 61002 Kharkov, Ukraine*; B. TERCERO, J. CERNICHARO, *Centro de Astrobiología (CSIC-INTA). Laboratory of Molecular Astrophysics. Department of Astrophysics. Ctra de Ajalvir,Km 4, 28850 Torrejón de Ardoz, Madrid, Spain*; and J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France*.

FA05 **15 min 9:38**

SPECTROSCOPY OF A MAJOR COMPLEX ORGANIC MOLECULE: MONO-DEUTERATED DIMETHYL ETHER

C. RICHARD, L. MARGULÈS, R. A. MOTIYENKO, *Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; P. GRONER, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499*; L. H. COUDERT, *LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France*; J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France*.

Intermission

FA06 **15 min 10:10**

TOWARDS AN ACCURATE INFRARED LINELIST FOR SO_2

XINCHUAN HUANG, *SETI Institute, 189 Bernardo Ave, Suite #100, Mountain View, CA, 94043*; DAVID W. SCHWENKE, *MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035*; TIMOTHY J. LEE, *MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035*.

FA07 **15 min 10:27**

THEORETICAL NH_3 SPECTRA IN 5800-7000 CM^{-1} REGION AND CO_2 IR INTENSITY: UPDATES

XINCHUAN HUANG, *SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, CA, 94043*; DAVID W. SCHWENKE, *MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035*; TIMOTHY J. LEE, *MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035*; KEEYOON SUNG, LINDA R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109*; and SERGEY A. TASHKUN, *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 634055, Tomsk, Russia*.

FA08 **15 min 10:44**

LINE PARAMETERS OF THE PH_3 PENTAD IN THE $4-5\mu$m REGION

V. MALATHY DEVI, D. CHRIS BENNER, *The College of William and Mary, Williamsburg, VA 23187*; I. KLEINER, *Laboratoire Interuniversitaire des Systemes Atmospheriques (LISA), UMR 7583 CNRS/IPSL-Universites Paris-ESt and Diderot, 94010 Creteil Cedex, France*; R. L. SAMS, T. A. BLAKE, *Pacific Northwest National Laboratory, Richland, WA 99352*; LINDA R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; L. N. FLETCHER, *Department of Physics, University of Oxford, Clarendon Laboratory, Oxford, OX1 3PU, UK*.

FA09 **15 min 11:01**

LINE BY LINE SPECTRAL PARAMETERS IN THE $4\nu_3$ SPECTRAL REGION OF METHANE

D. CHRIS BENNER, V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*; J. J. O'BRIEN, S. SHAJI, *Department of Chemistry, University of Missouri - St. Louis, St. Louis, MO 63121-4400*; P. T. SPICKLER, C. P. HOUCK, J. A. COAKLEY, J. DOLPH, K. RANKIN, *Department of Physics, Bridgewater College, Bridgewater, VA 22812*.

FA10 **15 min 11:18**

A GLOBAL FREQUENCY ANALYSIS OF $^{13}CH_3CH_3$ INCLUDING DATA FROM THE LOWEST FOUR VIBATIONAL STATES

N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada*; V.-H. HORNEMAN, *Department of Physical Sciences, University of Oulu, PO Box 3000, Fin-90014, Oulu, Finland*.

FA11 ***Post-deadline Abstract*** **15 min 11:35**

DIRECT FREQUENCY COMB SPECTROSCOPY FOR THE STUDY OF MOLECULAR DYNAMICS IN THE INFRARED FINGERPRINT REGION.[a]

ADAM J. FLEISHER, BRYCE BJORK, KEVIN C. COSSEL, JUN YE, *JILA, National Institute of Standards and Technology and University of Colorado, Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA*; LORA NUGENT-GLANDORF, FLORIAN ADLER, TYLER NEELY, and SCOTT DIDDAMS, *National Institute of Standards and Technology, Boulder, Colorado 80305-3337, USA*.

---

[a] This research is supported by AFOSR, DTRA, NSF, NRC, and NIST

FA12 ***Post-deadline Abstract*** **15 min 11:52**

MILLIMETRE-WAVE SPECTRUM OF ANTI-$^{13}C_1$ AND $^{13}C_2$ ISOTOPOLOGUES OF ETHANOL AND APPLICATIONS TO RADIO ASTRONOMY

AURELIA BOUCHEZ, ADAM WALTERS, SANDRINE BOTTINELLI, *IRAP, Université de Toulouse, UPS-OMP, CNRS; 9 Av. colonel Roche, BP 44346, 31028 Toulouse Cedex 4, France*; HOLGER S. P. MÜLLER, MATTHIAS H. ORDU, FRANK LEWEN, MONICA KOERBER, CHRISTIAN P. ENDRES, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany*.

FA13 ***Post-deadline Abstract*** **10 min 12:09**

INFRARED SPECTRAL STUDIES OF THE THERMALLY-DRIVEN CHEMISTRY PRESENT ON ICY SATELLITES

MARK J. LOEFFLER, REGGIE L. HUDSON, *NASA Goddard Space Flight Center, Astrochemistry Laboratory, Mail Code 691.1, Greenbelt, Md 20771.*

FB. INFRARED/RAMAN

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 170 MATH ANNEX

Chair: SVEN THORWIRTH, University of Cologne, Koeln, Germany

FB01 **15 min 8:30**

HIGH RESOLUTION EMISSION SPECTROSCOPY OF THE VIBRATION-ROTATION BANDS OF HBO AND HBS.

G. LI[a], R.S. RAM, R.J. HARGREAVES, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; P.F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 USA; Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; and H. LI, *State Key Lab of Theoretical and Computational Chemistry, Jilin University, Changchun City, China, 130023*.

---

[a] Current address: Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, MS#50, 60 Garden St., Cambridge, MA, 02138, USA.

FB02 **15 min 8:47**

FIRST INFRARED SPECTRA OF NITROUS OXIDE PENTAMER

M. REZAEI, J. NOROOZ OLIAEE, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N 1N4, Canada*; A.R.W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*.

FB03 **15 min 9:04**

“PROTON SPONGES": A RIGID ORGANIC SCAFFOLD TO REVEAL THE QUANTUM STRUCTURE OF THE INTRAMOLECULAR PROTON BOND

ANDREW F. DEBLASE, MARK A. JOHNSON, *Yale University, P. O. Box 208107, New Haven, CT, 06520*; MICHAEL T. SCERBA, STEVEN BLOOM, AND THOMAS LECTKA, *Johns Hopkins University, 3400 North Charles Street, Baltimore, MD, 21218*; TRAVIS DUDDING, *Brock University, St. Catherines, ON, Canada L2S 3A1*.

FB04 **15 min 9:21**

OBSERVATION OF SINGLE AND DOUBLE IONIC H-BONDS IN PROTONATED DIPEPTIDE IONS USING IR-IR DOUBLE RESONANCE SPECTROSCOPY

CHRISTOPHER M. LEAVITT, ARRON B. WOLK, JOSEPH A. FOURNIER, MICHAEL Z. KAMRATH, ETIENNE GARAND and MARK A. JOHNSON , *Sterling Chemistry Laboratory, Yale University, PO Box 208107, New Haven, CT 06520*; MICHAEL J. VAN STIPDONK, *Department of Chemistry, Wichita State University, 1845 Fairmont Ave, Wichita, KS 67208*.

FB05 **15 min 9:38**

VIBRATIONAL COOLING OF LARGE MOLECULES IN SUPERSONIC EXPANSIONS: THE CASE OF C_{60} AND PYRENE

JACOB T. STEWART, BRIAN E. BRUMFIELD,[a] BRADLEY M. GIBSON, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801*.

---

[a] Present Address: Department of Electrical Engineering, Princeton University, Princeton, NJ 08544

Intermission

FB06 **15 min 10:10**

SUB-TERRAHERTZ SPECTROSCOPY OF E.COLI DNA: EXPERIMENT, STATISTICAL MODEL, AND MD SIMULATIONS

I. SIZOV, T. DOROFEEVA, T. KHROMOVA, B. GELMONT, and T. GLOBUS, *Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, VA 22904*.

FB07 **15 min 10:27**

ISOMER-SPECIFIC INFRARED SPECTROSCOPY AS A DIAGNOSTIC TOOL FOR REACTIVE INTERMEDIATES TOWARDS NAPHTHALENE

NATHANAEL M. KIDWELL, DEEPALI N. MEHTA, JOSEPH A. KORN, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*; JOSHUA A. SEBREE, *NASA Goddard Space Flight Center, Greenbelt, MD 20771*.

FB08 **15 min 10:44**

SINGLE CONFORMATION SPECTROSCOPY OF SUBEROYLANILIDE HYDROXAMIC ACID: A MOLECULE BITES ITS TAIL

DI ZHANG, JACOB DEAN and TIMOTHY S. ZWIER, *Department of chemistry, Purdue University, West Lafayette, IN 47906.*.

FB09 **10 min 11:01**

DFT STUDY OF SOLVENT EFFECTS ON CONFORMATIONAL EQUILIBRIA AND VIBRATIONAL SPECTRA OF 4-(1-PYRROLIDINYL)PIPERAZINE

O. BAGLAYAN, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*; G. KESAN, *Faculty of Science, University of South Bohemia, Czech Republic*; C. PARLAK, *Department of Physics, DumlupÃ¡nar University, Kutahya, 43100, Turkey*; and M. SENYEL, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*.

FB10 **10 min 11:13**

DFT, FT-RAMAN AND FT-IR INVESTIGATIONS OF 1-CYCLOPENTYLPIPERAZINE

O. BAGLAYAN, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*; M. FATIH KAYA, *Department of Physics, DumlupÃ¡nar University, Kutahya, 43100, Turkey*; C. PARLAK, *Department of Physics, DumlupÃ¡nar University, Kutahya, 43100, Turkey*; O. ALVER, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*; M. SENYEL, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*.

FB11 **15 min 11:25**

FEMTOSECOND TIME-RESOLVED INFRARED SPECTRA OF ORGANOMETALLIC COMPLEXES BOUND TO A DINUCLEAR METAL CENTER

SAMANTHA E. BROWN-XU and CHRISTOPHER B. DURR, *The Ohio State University, Department of Chemistry and Biochemistry, Columbus, Ohio 43210*.

FB12 ***Post-deadline Abstract*** **10 min 11:42**

ANALYSIS OF HIGH RESOLUTION INFRARED SPECTRA OF 1,1-DICHLOROETHYLENE IN THE $500-1000\ \mathrm{cm}^{-1}$ RANGE

REBECCA A. PEEBLES, SEAN A. PEEBLES, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920*; DANIEL A. OBENCHAIN, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*.

FC. MICROWAVE

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 1000 MCPHERSON LAB

Chair: SUSANNA WIDICUS WEAVER, Emory University, Atlanta, Georgia

FC01 **15 min 8:30**

A NEW U-BAND (40 - 60 GHz) FOURIER TRANSFORM MICROWAVE SPECTROMETER

D. T. HALFEN, J. MIN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

FC02 **15 min 8:47**

FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE AlC_2 ($\tilde{X}^2A_1$) RADICAL

D. T. HALFEN, J. MIN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

FC03 **15 min 9:04**

THE FOURIER TRANSFORM MICROWAVE SPECTRUM OF YOH AND YOD ($\tilde{X}^1\Sigma^+$)

D. T. HALFEN and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

FC04 **15 min 9:21**

DEVELOPMENT OF A SUBMILLIMETER MULTIPASS SPECTROMETER FOR THE STUDY OF MOLECULAR IONS

A. CARROLL, B. ROCHER, J. C. LAAS, B. A. DePRINCE, B. HAYS, S. L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; S. LANG, *Department of Chemistry, New College of Florida, Sarasota, FL 34243.*

FC05 **15 min 9:38**

THE DEVELOPMENT AND IMPLEMENTATION OF CHIRPED-PULSE FREQUENCY COMBS AT MILLIMETER WAVELENGTHS

AMANDA L. STEBER, BRENT J. HARRIS, JUSTIN L. NEILL, KEVIN K. LEHMANN, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904.*

FC06 **10 min 9:55**

CHIRPED-PULSE FOURIER TRANSFORM MM-WAVE SPECTROSCOPY FROM 260-290 GHz

BRENT J.HARRIS, AMANDA L. STEBER, JUSTIN L. NEILL, KEVIN K. LEHMANN, BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904.*

Intermission

FC07 **15 min 10:30**

BROADBAND MICROWAVE SPECTROSCOPY OF LARGE MOLECULES

V. ALVIN SHUBERT, DAVID SCHMITZ, THOMAS BETZ, and MELANIE SCHNELL, *Max-Planck Advanced Study Group at the Center for Free-Electron Science, Hamburg, Germany and Max-Planck-Institut für Kernphysik, Heidelberg, Germany.*

FC08 **15 min 10:47**

SENSITIVITY LIMITS OF DEEP AVERAGE BROADBAND MICROWAVE AND MM-WAVE SPECTRA

MATT T. MUCKLE, DANIEL P. ZALESKI, AMANDA STEBER, BRENT HARRIS, AND BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319.*

FC09 **10 min 11:04**

PRECISE THZ MEASUREMENTS OF HCO^+, N_2H^+ AND CF^+

CRISTINA PUZZARINI, GABRIELE CAZZOLI, *Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy.*

FC10 **15 min 11:16**

MOLECULAR SUPERFLUIDITY IN SMALL CLUSTERS OF $(p\mathrm{H}_2)_N$-HCN STUDIED WITH ROTATIONAL SPECTROSCOPY

STEVE P. DEMPSTER and WOLFGANG JÄGER, *Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.*

FC11 **15 min 11:33**

PUMP/PROBE MICROWAVE-OPTICAL DOUBLE RESONANCE (PPMODR) STUDY OF TUNGSTEN CARBIDE (WC) AND PLATINUM CARBIDE (PtC)

FANG WANG and TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry Arizona State University Tempe, Arizona 85287-1604 U.S.A.*

FC12 **15 min 11:50**

LABORATORY DETECTION AND MICROWAVE SPECTRUM of ScC_2 RADICAL (X^2A_1)

JIE MIN, DEWAYNE T. HALFEN, LUCY. M. ZIURYS, *Department of Chemistry and Biochemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

FC13 ***Post-deadline Abstract*** **15 min 12:07**

SUB-MILLIMETER/TERAHERTZ SPECTROSCOPY OF FeH AND FeD ($X^4\Delta_i$)

M. P. BUCCHINO and L. M. ZIURYS, *Department of Chemistry and Biochemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, Arizona 85721.*

FD. MINI-SYMPOSIUM: COLD QUANTUM SYSTEMS

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 1015 MCPHERSON LAB

Chair: DAVID ANDERSON, University of Wyoming, Laramie, Wyoming

FD01 *INVITED TALK* **30 min 8:30**

SPECTROSCOPY AND CHEMISTRY OF COLD MOLECULES

TAKAMASA MOMOSE, *Department of Chemistry, The University of British Columbia, Vancouver, CANADA.*

FD02 **15 min 9:05**

COLD ION-MOLECULE CHEMISTRY WITH A STARK DECELERATOR BEAMLINE

JAMES M. OLDHAM, MARTIN T. BELL, LEE D. HARPER, TIMOTHY P. SOFTLEY, *Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, United Kingdom OX1 3TA.*

FD03 **15 min 9:22**

PROGRESS TOWARD SLOWING AND COOLING OF CaF WITH OPTICAL BICHROMATIC FORCES

EDWARD E. EYLER and MICHAEL A. CHIEDA, *Department of Physics, University of Connecticut, Storrs, CT 06269, USA.*

FD04 **15 min 9:39**

SPECTROSCOPIC ANALYSIS OF THE A AND 3 $^1\Sigma^+$ STATES OF ^{39}K^{85}Rb

JIN-TAE KIM, *Department of Photonic Engineering, Chosun University, Gwangju, 501-759, Korea*; YONGHOON LEE, *Department of Chemistry, Mokpo National University, Jeonnam 534-729, Korea*; BONGSOO KIM, *Department of Chemistry, KAIST, Daejeon, 305-701, Korea*; DAJUN WANG, *Department of Physics,The Chinese University of Hong Kong, Shatin, Hong Kong*; PHILLIP L. GOULD, EDWARD E. EYLER, and WILLIAM C. STWALLEY, *Department of Physics, University of Connecticut, Storrs, CT 06269-3046, USA.*

FD05 **15 min 9:56**

OBSERVATION OF BLUE-DETUNED PHOTOASSOCIATION TO THE 2 (0_g^+) STATE OF ^{85}Rb$_2$ VIA REMPI

M. A. BELLOS, R. CAROLLO, D. RAHMLOW, J. BANERJEE, M. BERMUDEZ, E. E. EYLER, P. L. GOULD, and W. C. STWALLEY, *Department of Physics, University of Connecticut, Storrs, CT 06269.*

Intermission

FD06 **15 min 10:30**

DEVELOPING CONTINUOUS-WAVE RAMAN LASERS USING SOLID PARA-HYDROGEN AND BARIUM NITRATE FOR MOLECULAR SPECTROSCOPY APPLICATIONS

WILLIAM R. EVANS, *Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; TAKAMASA MOMOSE, *Department of Chemistry, The University of British Columbia, Vancouver, BC Canada V6T 1Z1*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy and Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

FD07 **15 min 10:47**

IMPROVED ANALYTICAL POTENTIALS FOR THE $a\,{}^3\Sigma_u^+$ and $X\,{}^1\Sigma_g^+$ STATES OF Cs_2

JESSE BALDWIN, ROBERT J. LE ROY, *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.*

FD08 **15 min 11:04**

RUBIDIUM ATOMS ON HELIUM DROPLETS: ANALYSIS OF AN EXOTIC RYDBERG COMPLEX

FLORIAN LACKNER, GÜNTER KROIS, MARKUS KOCH, and WOLFGANG E. ERNST, *Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.*

FD09 **10 min 11:21**

PHOTOABSORPTION OF Ag (N = 6 - 6000) CLUSTERS IN He DROPLETS: A TRANSITION FROM SINGLE- TO MULTI-CENTERED GROWTH

LUIS F. GOMEZ, EVGENY LOGINOV, RUSSELL SLITER, ANDREY F. VILESOV, *Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482*; AVIK HALDER, NAIHAO CHIANG, NICHOLAS GUGGEMOS, VITALY V. KRESIN, *Department of Physics, University of Southern California, Los Angeles, CA 90089-0484.*

FD10 ***Post-deadline Abstract*** **15 min 11:33**

MOLECULAR ION SPECTROSCOPY OF BACL^+

STEVEN J. SCHOWALTER, KUANG CHEN, WADE G. RELLERGERT, SCOTT T. SULLIVAN, AND ERIC R. HUDSON, *Department of Physics and Astronomy, University of California, Los Angeles, California 90095, USA.*

FE. THEORY

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 2015 MCPHERSON LAB

Chair: RUSSELL PITZER, The Ohio State University, Columbus, Ohio

FE01 **10 min 8:30**

OBSERVATION OF SINGLET-TRIPLET TRANSITIONS IN CAPACITIVE PHOTOCURRENT SPECTROSCOPY OF ORGANIC SOLAR CELLS

HUI LIU, JINJUN LIU, *Department of Chemistry, University of Louisville, Louisville, KY 40292*; HEMANT M. SHAH, AND BRUCE W. ALPHENAAR, *Department of Electrical & Computer Engineering, University of Louisville, Louisville, KY 40292.*

FE02 **15 min 8:42**

REMARKS ON THE PHASE CHANGE OF THE ELECTRONIC WAVE FUNCTION UPON GOING ONCE AROUND A JAHN-TELLER CONICAL INTERSECTION IN VIBRATIONAL COORDINATE SPACE

JON T. HOUGEN, *Sensor Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA.*

FE03 **15 min 8:59**

AN AB INITIO MODEL HAMILTONIAN FOR THE $e' \otimes e'$ and $e' \otimes e''$ SINGLET STATES OF Si_3

D. A. MATTHEWS, J. F. STANTON, *Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712.*

FE04 **15 min 9:16**

DIFFUSION MONTE CARLO STUDIES OF THE GROUND-STATE STRUCTURE AND ENERGETICS OF H_5^+ AND ITS ISOTOLOGUES

ZHOU LIN and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

FE05 **15 min 9:33**

MODELING SPIN-ORBIT COUPLING IN THE MONOHALOCARBENES

SILVER NYAMBO AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

FE06 **15 min 9:50**

THEORETICAL INVESTIGATION OF THE M^+-RG_2 (M = ALKALINE EARTH METAL; RG = RARE GAS) COMPLEXES

ADRIAN M. GARDNER, RICHARD J. PLOWRIGHT, JACK GRANEEK, TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*; and W. H. BRECKENRIDGE, *Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112, USA.*

FE07 ***Post-deadline Abstract*** **15 min 10:07**

ELUCIDATION OF PROTON-ASSISTED FLUXIONALITY IN TRANSITION-METAL OXIDE CLUSTERS

RAGHUNATH O. RAMABHADRAN, NICHOLAS J. MAYHALL, EDWIN L. BECHER III, AREFIN CHOWDHURY, KRISHNAN RAGHAVACHARI(S), *Department of chemistry, Indiana University, Bloomington, IN-47405.*

MA. PLENARY SESSION

MONDAY, JUNE 18, 2012 – 8:45 AM

Room: AUDITORIUM, INDEPENDENCE HALL

Chair: FRANK DE LUCIA, The Ohio State University, Columbus, Ohio

Welcome **8:45**
Caroline C. Whitacre, Vice President for Research
The Ohio State University

MA01 **40 min 9:00**

A NEW SPECTROSCOPIC WINDOW ON HYDROXYL RADICALS AND THEIR ASSOCIATION REACTIONS OF SIGNIFICANCE IN THE ATMOSPHERE[a]

MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

The weakly bound hydrogen trioxy radical (HOOO), produced in the association reaction of the hydroxyl radical (OH) with molecular oxygen (O_2), has been postulated to play an important role in atmospherically relevant reactions. Experimental studies in this laboratory have utilized infrared action spectroscopy to probe the structure, vibrational frequencies, and stability of this weakly bound species.[a] Recent experimental and theoretical results on HOOO will be presented, and used in assessing its significance in the atmosphere.[b]
Most studies of the hydroxyl radical and its association products utilize laser-induced fluorescence on the well-characterized OH $A^2\Sigma^+$ - $X^2\Pi$ band system for detection. This laboratory has recently demonstrated a new photoionization scheme combining initial UV excitation on the $A^2\Sigma^+$ - $X^2\Pi$ band system with subsequent fixed-frequency VUV ionization via autoionizing Rydberg states.[c] The photoionization mechanism as well as the applicability of this quantum state-selective photoionization scheme will be presented.

---

[a] This research was supported by the National Science Foundation and the Office of Basic Science of the Department of Energy.

[a] C. Murray, E. L. Derro, T. D. Sechler, and M. I. Lester, Acc. Chem. Res. **42**, 419-427 (2009).

[b] J. M. Beames, M. I. Lester, C. Murray, M. E. Varner, and J. F. Stanton, J. Chem. Phys. **134**, 044304 (2011).

[c] J. M. Beames, F. Liu, M. I. Lester, and C. Murray, J. Chem. Phys. **134**, 241102 (2011).

MA02 **40 min 9:45**

SPECTROSCOPY OF MOLECULES IN EXTREME ROTATIONAL STATES USING AN OPTICAL CENTRIFUGE

AMY S. MULLIN, CARLOS TORO, GERALDINE ECHIBIRI and QINGNAN LIU, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

Our lab has developed a high-power optical centrifuge that is capable of trapping and spinning large number densities of molecules into extreme rotational states. By coupling this device with high resolution transient IR absorption spectroscopy, we measure the time-resolved behavior and energy profiles of individual ro-vibrational states of molecules in very high rotational states. Recent results will be discussed on the spectroscopy of new rotational states, collisional dynamics in the optical centrifuge, spatially-dependent energy profiles and possibilities for new chemistry induced by centrifugal forces.

Intermission

RAO AWARDS **10:50**
Presentation of Awards by Yunjie Xu, University of Alberta

2011 Rao Award Winners
Adam J. Fleisher, University of Pittsburgh
Justin L. Neill, University of Virginia
Thomas J. Preston, University of Wisconsin

COBLENTZ AWARD **5 min 11:05**
Presentation of Award by Michael L. Myrick, President, Coblentz Society

MA03 ***Coblentz Society Award Lecture*** **40 min 11:10**

IMAGING EXCITED STATE DYNAMICS WITH 2D ELECTRONIC SPECTROSCOPY

GREGORY S. ENGEL, *Department of Chemistry, The University of Chicago, Chicago USA.*

Excited states in the condensed phase have extremely high chemical potentials making them highly reactive and difficult to control. Yet in biology, excited state dynamics operate with exquisite precision driving solar light harvesting in photosynthetic complexes though excitonic transport and photochemistry through non-radiative relaxation to photochemical products. Optimized by evolution, these biological systems display manifestly quantum mechanical behaviors including coherent energy transfer, steering wavepacket trajectories through conical intersections and protection of long-lived quantum coherence. To image the underlying excited state dynamics, we have developed a new spectroscopic method allowing us to capture excitonic structure in real time. Through this method and other ultrafast multidimensional spectroscopies, we have captured coherent dynamics within photosynthetic antenna complexes. The data not only reveal how biological systems operate, but these same spectral signatures can be exploited to create new spectroscopic tools to elucidate the underlying Hamiltonian. New data on the role of the protein in photosynthetic systems indicates that the chromophores mix strongly with some bath modes within the system. The implications of this mixing for excitonic transport will be discussed along with prospects for transferring underlying design principles to synthetic systems.

MF. INFRARED/RAMAN

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: MASARU FUKUSHIMA, Hiroshima City University, Hiroshima, Japan

MF01 **10 min 1:30**

TIME RESOLVED FTIR ANALYSIS OF COMBUSTION OF AN ETHANOL/ISOPROPANOL MIXTURE IN A COMMERICIAL INTERNAL COMBUSTION ENGINE

ALLEN R. WHITE, BHARAT YALAMANCHILI, *Department of Mechanical Engineering, Rose-Hulman Institute of Technology, 5500 Wabash Ave., Terre Haute, IN 47803.*

In order to measure infrared (IR) emission from combustion in an internal combustion engine, a small commercial spark ignition engine was modified with a ZnSe optical access window. This modification allows for transmission of IR radiation for time-resolved spectroscopic measurements by a Fourier-Transform IR (FTIR)spectrometer. By using a Step-scan equipped Fourier transform spectrometer, temporally resolved infrared spectral data were acquired and compared for combustion in the modified engine. These measurements provide insight into the energy transfer vectors during the combustion process and also provides an in situ measurement of the progress of combustion (via CO2 production). Measurements were performed using an ethanol and isopropanol mixture to provide additional IR sources to trace during the combustion process.

MF02 **15 min 1:42**

SUB-DOPPLER RESOLUTION DIFFERENCE-FREQUENCY-GENERATION INFRARED SPECTROMETER WITH HIGH SENSITIVITY AND WIDE TUNABILITY

S. OKUBO, H. NAKAYAMA,K. IWAKUNI,H. SASADA, *Department of Physics, Faculty of Science and Technology, Keio University, Yokohama, Japan*; H. INABA, *National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.*

We made a 3.4-μm spectrometer that consists of a 1.06-μm Nd:YAG laser as a pump source, a 1.55-μm extended-cavity laser diode (ECLD) as a signal source, and a waveguide-type periodically-poled lithium niobate (PPLN) with a difference-frequency-generation efficiency of 10 %/W. The linewidth of the ECLD is reduced less than 50 kHz by stabilizing the 3.4-μm frequency to one of the modes of a Fabry-Perot cavity, which is also employed as an absorption cell to increase the effective absorption length and to enhance the optical field strength at the antinodes. The spectrometer conjunction with wavelength modulation spectroscopy allows us to record 300 kHz wide Lamb dips of the ν_3 band of ^{12}CH$_4$ and ^{13}CH$_4$ from 88.2 to 90.5 THz. The tunable range currently limited by the phase matching condition of the PPLN can be extended from 83 to 94 THz.

MF03 **15 min 1:59**

OPTICAL FREQUENCY COMB REFERNCED SUB-DOPPLER RESOLUTION DIFFERENCE-FREQUENCY-GENERATION INFRARED SPECTROMETER

K. IWAKUNI, S. OKUBO, H. NAKAYAMA, and H. SASADA, *Department of Phisics, Faculty of Science and Technology, Keio University, Yokohama, Japan*; H. INABA, *National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.*

We have determined absolute frequencies of 56 transition of the ν_3 band of ^{12}CH$_4$ and ^{13}CH$_4$ with at a typical uncertainty level of 2 kHz. While the frequency of the difference-frequency-generation (DFG) source is stabilized to the Lamb dip of the methane transition, the frequencies of the pump and signal source are measured with a 1.5-μm optical frequency comb (OFC). The determined value is consistent with the International Committee for Weight and Measures recommendation within the uncertainty. We have also developed OFC-referenced frequency sweep, which allow us to accumulate spectral data for long time without any frequency drift and to determine the frequency of the transition which are too weak to use the frequency reference for the frequency stabilization.

MF04 **15 min 2:16**

DUAL ETALON FREQUENCY COMB (DEFCOM) SPECTROSCOPY

DAVID W. CHANDLER, KEVIN E. STRECKER, *Sandia National Laboratory, Livermore, CA 94550.*

A new spectrometer based on an interferogram produced by the output of two separate confocal etalons is described and first experiments will be described. This spectrometer has the resolution of the Free Spectral Range (FSR) of the etalons on a single laser shot over the bandwidth of the light source that that is used to excite the etalons. With signal averaging and scanning of the etalon mirror the resolution can be that of the "ring-down" time of the etalons. By placing the sample of interest within one of the etalons one obtains the sensitivity of cavity ring down spectroscopy while performing Cavity Ring Down (CRD) spectroscopy over the entire bandwidth of the laser source used to excite the etalon. First data on measurements of overtone absorptions of water and weak electronic gamma-band absorption of oxygen will be presented. *Work supported by DOE Basic Energy Sciences.*

MF05 **15 min 2:33**

A MULTI-WATT SINGLE FREQUENCY CW OPO SYSTEM TUNABLE FROM 600NM TO 4600NM

A. HENDERSON, *LOCKHEED MARTIN ACULIGHT, 22121 20th Avenue SE, Bothell, WA 98021.*

The output wavelength range of commercial CW OPOs has been dramatically extended to reach both further into the mid-infrared and into the visible/ near-infrared, providing a tuning range from 600nm to 4600nm. Specific examples of new capabilities are provided below:

(1) Extension of the mid-infrared wavelength coverage to 4630nm by annealing of the PPLN crystal to reduce OH absorption
(2) Generation of 3Watts of orange radiation tunable 604nm to 616nm by intra-cavity sum frequency generation of OPO pump and signal
(3) Generation of over 100mW near-IR radiation tunable 1240nm to 1500nm by extra-cavity second harmonic generation of OPO idler

In each case, the same robust 1064nm fiber laser pump source may be interchanged between these OPO modules to access specific wavelength ranges. In all of the examples above, the wide (100GHz) mode-hop-free tunability of the source is retained, making the output ideal for high resolution spectroscopy. The high power, narrow (sub-MHz) linewidth and excellent beam quality of the OPO output make it an ideal pump source for secondary nonlinear processes to reach further into the visible/UV and mid-infrared / Terahertz while providing spectroscopic measurement capability.

MF06 **15 min 2:50**

DEVELOPMENT OF A HIGHER RESOLUTION TERAHERTZ TIME-DOMAIN SPECTROMETER

DANIEL B. HOLLAND, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125 (email to D.B.H.: holland@caltech.edu)*; GEOFFREY A. BLAKE, *Division of Geological and Planetary Sciences, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.*

We report on our development of a terahertz (THz) time-domain spectrometer employing asynchronous optical sampling (ASOPS) between two commercial Ti:Sapphire lasers operating with a repetition rate of approximately 80 MHz. THz time-domain spectrometers typically achieve control of sampling time delay via the use of mechanical delay lines, yielding a practically feasible resolution limit of several GHz. There are commercially available THz time-domain spectrometers employing ASOPS with GHz repetition rate lasers; they achieve 1 GHz resolution. The use of our lower repetition rate lasers, while introducing technical challenges, offers a theoretical resolution limit of 80 MHz, an important benefit for our primary application of collecting THz spectra in support of astronomy in the far-infrared. Technical data on instrument design and performance as well as initial spectra are to be presented.

MF07 **15 min 3:07**

QCL SPECTROSCOPY AT 9 μM CALIBRATED WITH A HIGH-POWER THULIUM-BASED FREQUENCY COMB

ANDREW A. MILLS, JIE JIANG, INGMAR HARTL, MARTIN FERMANN, *IMRA America, Ann Arbor, MI*; DAVIDE GATTI, MARCO MARANGONI, *Campus Point, Dipartimento di Fisica del Politecnico di Milano, Milano, Italy*.

Optical frequency comb synthesizers (OFCS) comprised of mode-locked femtosecond lasers can be stabilized with Hertz-level accuracy and used in combination with cw lasers for high resolution spectroscopy. As currently established OFCS technologies are confined to the near-IR, mid-IR spectroscopy requires either down-conversion of near-IR combs or up-conversion of the probing laser. Due to the near-IR absorption edge of the nonlinear crystals with extended mid-IR transparency, the conversion efficiency of nonlinear processes increases with the wavelength of the interacting fields. A more straightforward and efficient link between comb and probing laser is thus expected to be obtained by increasing the wavelength of the comb synthesizer. In this work, the use of a novel, powerful Thulium-based OFCS[a] with emission wavelengths near 2 μm is shown to be an excellent candidate to obtain absolute frequency calibration of quantum cascade lasers (QCL) operating at wavelengths as long as 9 μm. Specifically, by combining the frequencies of a 9 μm QCL with the high power 2 μm comb in a $AgGaSe_2$ crystal, SFG light is created near 1.6 μm. A portion of the 2 μm comb is non-linearly shifted to 1.6 μm. As the carrier envelope offset frequency (f_{ceo}) is the same for the SFG radiation and the shifted comb at 1.6 μm, heterodyning the two signals produces a beat signal independent of f_{ceo}, eliminating the need for an octave spanning comb and f-2f interferometer. We report on the development of this instrument, and the absolute line transitions of NH_3 at 9 μm, enabled by rapid scanning of the repetition rate of the comb enabled to increase the signal-to-noise ratio.[b]

---

[a] J. Jiang, C. Mohr, J. Bethge, M. Fermann, and I. Hartl, in *CLEO/Europe and EQEC 2011 Conference Digest, OSA Technical Digest (CD)* **PDB_1**, 2001

[b] D. Gatti, A. Gambetta, A. Castrillo, G. Galzerano, P. Laporta, L. Gainfrani and M. Marangoni *Op. Exp.* **19**, 17520 2011

Intermission

MF08 **15 min 3:40**

DIRECT MEASUREMENTS OF COLLISIONALLY BROADENED (CO_2-CO_2) S-BRANCH RAMAN COHERENCE LIFETIMES OF CO_2

JOSEPH R. GORD, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; SUKESH ROY, PAUL S. HSU, NAIBO JIANG, WARUNA D. KULATILAKA, and HANS U. STAUFFER, *Spectral Energies, LLC, 5100 Springfield Street, Suite 301, Dayton, OH 45431*; JAMES R. GORD, *Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, OH 45433*.

We report direct measurement of S-branch Raman coherence lifetimes of CO_2 due to CO_2-CO_2 collisions by employing picosecond time-resolved coherent anti-Stokes Raman scattering (CARS) spectroscopy. A custom-built, high-peak-power, nearly transform-limited ps laser system offers an ideal combination of frequency and temporal resolution for such measurements. The rotational S-branch transitions of CO_2 ground state [0,0^0,0] with rotational quantum number J= $0 - 52$ were simultaneously excited by using a broadband (∼3-nm) laser pulse with a full-width-half-maximum (FWHM) of ∼100 ps. The coherence lifetimes of self-broadened CO_2 for a pressure range of 0.05-1.5 bar were directly measured by probing the rotational coherence with a nearly transform-limited, 80-ps-long laser pulse. The measured linewidth of J=6 and J=50 transitions are found to be ∼0.106±0.0002 and ∼0.070±0.0002, respectively. As expected, the energy-transfer from high J levels has a significantly longer coherence lifetime because of the inertia associated with higher angular momentum. These measurements are very significant for performing accurate thermometry or CO_2 concentration measurements in gas-phase reacting flows.

MF09 **10 min 3:57**

ANALYSIS OF AN ^{18}O AND D ENHANCED FT-IBBCEAS WATER SPECTRUM: NEW ASSIGNMENTS FOR $HD^{18}O$, $HD^{16}O$, $D_2{}^{18}O$ AND $D_2{}^{16}O$ IN THE NEAR-INFRARED REGION (6000-7000 cm^{-1}).

MICHAEL J. DOWN, JONATHAN TENNYSON, *Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK*; JOHANNES ORPHAL, *Karlsruher Institut für Technologie, IMK-ASF, Postfach 36 40, 76021 Karlsruhe, Germany*; PASCALE CHELIN, *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université de Paris-Est, CNRS UMR 7583, Créteil, France*; and ALBERT A. RUTH, *Physics Department and Environmental Research Institute, University College Cork, Cork, Ireland.*

An experimental infrared spectrum[a] recorded using isotopically enriched water in the 6000-7000 cm^{-1} region with a spectral resolution of 0.02 cm^{-1} is analysed and assigned. The spectrum employs a combination of Fourier-transform (FT) spectroscopy and incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) [b]. Application of FT-IBBCEAS to a sample mixture of 8.0 mbar of D_2O and 12.4 mbar of pure $H_2{}^{18}O$ in the optical cavity resulted in the observation of a large number of new absorption features in the spectrum, notably due to the rare $HD^{18}O$ isotope of water. This was possible due to the superior absorption sensitivity of FT-IBB-CEAS compared to other techniques previously employed in this region combined with the prescence of $D_2{}^{16}O$ in the sample. The assignment procedure is based on the use of known transition frequencies for $H_2{}^{16}O$ and $H_2{}^{18}O$, existing variational line lists for $HD^{16}O$ and $D_2{}^{16}O$ and newly calculated variational line lists for $HD^{18}O$ and $D_2{}^{18}O$, with a uniform intensity threshold applied. The main absorption comes from $HD^{16}O$ and $HD^{18}O$, for which there are few previous assignments in the region. The following new spectral features were identified. $D_2{}^{16}O$: 265 (all labelled); $D_2{}^{18}O$: 194 (all lower levels labelled); $HD^{16}O$: 213 (all labelled); $HD^{18}O$: 743 (all lower and 612 upper levels labelled). In all 3226 of the 4768 lines observed in the spectrum are assigned, resulting in a significant number of newly determined energy levels. The analysis demonstrates both the usefulness of this experimental approach for spectroscopic investigations of isotopic or dangerous samples, and the validity of the new variational line lists.

---

[a] J. Orphal, A. A. Ruth, Opt. Express 16 (2008) 19232-19243.

[b] A. A. Ruth, J. Orphal, S.E. Fiedler, Appl. Opt. 46 (2007) 3611-3616.

MF10 **10 min 4:09**

TOWARDS PERFECT WATER LINE INTENSITIES

L. LODI, J. TENNYSON, *Department of Physics and Astronomy, University College London, London WC1E 6BT, UK.*

Over the last ten years the increased availability of computational resources and the steady refinement of theoretical methods have permitted more and more accurate first principle calculations of water-vapor spectra as exemplified, e.g., by the very successful BT2 line list[a]. There are two requirements for computing accurate line lists from first principles: a high-accuracy potential energy surface (PES), affecting both line positions and intensities, a reliable dipole moment surface (DMS), affecting line intensities. It is also very useful to several application to give reasonable uncertainty bars for computed quantities, an aspect which traditionally has received little attention.

We report here recent progress leading to very accurate room-temperature linelists covering the range 0.05–20 000 cm^{-1}, complete with uncertainty bars, for the $H_2^{18}O$ and $H_2^{17}O$ water isotopologues[b]. Line intensities were produced using a recent DMS produced by our group[c] which is capable of giving line intensites accurate to 1% for most medium and strong transitions. Line positions are based if possible on the experimentally derived energy levels recently produced by a IUPAC task group[d] and have a typical accuracy of 0.0002 cm^{-1}; when experimentally derived energy levels are unavailable calculated line position are provided, with an accuracy of the order of 0.2 cm^{-1}.

An extension to the main isotopologue $H_2^{16}O$ is currently underway.

---

[a] R. J. Barber, J. Tennyson, G. J. Harris and R. N. Tolchenov, Mon. Not. R. Astron. Soc. **368**, 1087-1094 (2006).

[b] L. Lodi and J. Tennyson, J. Quant. Spectrosc. Radiat. Trans. (2012), doi:10.1016/j.jqsrt.2012.02.023

[c] L. Lodi, J. Tennyson and O. L. Polyansky, J. Chem. Phys. **135**, 034113 (2011).

[d] J. Tennyson at al., J. Quant. Spectrosc. Radiat. Trans. **110**, 573-96 (2009).

MF11 **15 min 4:21**

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF THE $(1,0,1)-(0,0,0)$ BAND OF C_3

S. THORWIRTH, J. KRIEG, I. KEPPELER, V. LUTTER, S. SCHLEMMER, T. F. GIESEN, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; M. E. HARDING, *Karlsruher Institut für Technologie, Institut für Nanotechnologie, 76021 Karlsruhe, Germany*; J. VÁZQUEZ, *Center for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.*

Using the carbon cluster experiment at Cologne in combination with a home-made optical parametric oscillator operating at three microns, the $(1,0,1)-(0,0,0)$ combination band of the C_3 cluster has been investigated around $3260\,\mathrm{cm}^{-1}$. In addition, the associated $(1,1,1)-(0,1,0)$ hot band has been observed. Using sample rods enriched in ^{13}C, the $(1,0,1)-(0,0,0)$ band was also studied for the two isotopologs ^{13}CCC and C^{13}CC. The experimental molecular parameters obtained compare very favorably with results from coupled-cluster calculations.

MF12 **15 min 4:38**

USING PROGRAM ERHAM TO ANALYZE HIGH-RESOLUTION INFRARED SPECTRA OF MOLECULES WITH INTERNAL ROTORS

P. GRONER, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499*; S. ALBERT, M. QUACK, *Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland.*

The effective rotational Hamiltonian for molecules with one or two periodic large-amplitude motions [a] implemented in program ERHAM has been adapted to enable prediction and least-squares fits of rotationally resolved lines in vibration-rotation spectra in the infrared region. The modified program is currently applied to assign the band of methyl formate at 925 cm^{-1} that has been measured at ETH in Zurich on the IFS125 Bruker prototype ZP 2001 FTIR spectrometer [b] at a resolution of 0.001 cm^{-1}. An external glass cell with an optical path length of 3 m contained the sample, and 150 interferograms were co-added. Right now it looks as if the splitting into A and E components were a little too small to be resolved sufficiently for positive identification.

---

[a] P. Groner, *J. Chem. Phys.* 107, 4483 (1997).

[b] S. Albert, M. Quack, *ChemPhysChem* 8, 1271 (2007)

MF13 **15 min 4:55**

COMPARISON OF COMPUTED CONDON LOCI WITH FRANCK-CONDON FACTORS IN DESLANDRES TABLES OF MOLECULAR BAND SYSTEMS

R. HEFFERLIN and B. CLARK, *Southern Adventist University, Collegedale, TN 37315*; J. TATUM, *University of Victoria, Victoria, BC V8W 2Y2, Canada.*

The literature often shows a Condon parabola not quite tracking the Franck-Condon factors for the strongest bands in the Deslandres table for a diatomic molecular band system [a]; often the parabola appears to have been hand-drawn [b]. We have calculated Condon loci, assuming originally that the lower and upper electronic potentials are simple harmonic potentials, and assuming now that they are Morse potentials. In the harmonic case the Condon loci are parabolas. These calculations are for small vibrational quantum numbers, where the Morse loci also begin as parabolas. We will present these loci for representative molecular band systems and discuss the extent to which the loci track the strongest Franck-Condon factors. In the event that neither does, calculations for arbitrary potentials are available. The importance of this study is that we have previously calculated the latera recta and the symmetry-axis angles of the harmonic oscillator parabolas in Deslandres tables appropriate to molecules in several isoelectronic sequences. We have found that the angle increases along the sequence until the species one proton-shift away from âĂIJrare-gasâĂİ molecules, such as LiNe, is reached. This phenomenon is a suggestion that diatomic molecules are periodic with respect to each of their two atoms.

---

[a] G. Herzberg, Molecular Spectra and Molecular Structure, 1950, pg. 197

[b] D. J. Flynn, R. J. Spindler; S. Fifer; M. Kelly, J. Quant. Spectr. Radiat. Transfer 4, 271-282, (1964); R. W. Nicholls, J. Quant. Spectr. Radiat. Transfer 28, 481-492, (1982).

MF14 **10 min 5:12**

VIBRATIONAL SPECTRA OF THE $MLCl_2$ COMPLEX FROM THEORETICAL CALCULATIONS

BERNA CATIKKAS, *Department of Physics, Mustafa Kemal University, Hatay, Turkey, 31034 (email to B.Ç.: berna@mku.edu.tr).*

The geometric and vibrational parameters (harmonic and anharmonic frequencies) of the $MLCl_2$ [M= Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg; L= Ethylenediamine (en)] donor-acceptor complexes have been studied by using HF and MPW1PW91+iop(3/76=00572004280)/gen methods. Binding, reorganization, atomization, HOMO-LUMO and ionization potential energies have also been calculated with the same method. SQM calculations have been performed by using anharmonic frequencies and experimental data. The obtained results were found to be in good agreement with the corresponding experimental findings.

MG. RADICALS AND IONS

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: TIMOTHY SCHMIDT, The University of Sydney, Sydney, Australia

MG01 **15 min 1:30**

RENNER-TELLER COUPLING IN H_2S+: PARTITIONING THE ROVIBRONIC AND SPINORBIT COUPLING HAMILTONIAN

G. DUXBURY, *Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK*; Ch. JUNGEN, *LAC, 1 Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France*; A. ALIJAH, *GSMA, UMR CNRS 6089, Université de Reims Champagne-Ardenne,B.P. 1039, 51687 Reims Cedex 2, France*.

The stretch-bender reference-frame[a] was developed to allow the separation of large amplitude bending motion and symmetric stretching. It has been used to calculate vibrational resonances, the effects of spin-orbit coupling, and of overall rotation. Its use allows the block factorisation of the Renner-Teller interaction matrix. We wish to show the utility of this approach when two different approaches by Dixon and Duxbury,[b] and Jungen and Merer[c], are used to minimise the effects of the large amplitude bending upon the Renner-Teller interaction. It also allows the effects of large amplitude motion on the rotational structure to be calculated, including the switchover from bent to linear behaviour.

---

[a] J. Chem. Phys. 108, 2336 (1998) and J. Mol. Spectrosc. 211, 7 (2002)

[b] Molec. Phys. 43, 255 (1981)

[c] Molec. Phys. 40, 1 (1981)

MG02 **15 min 1:47**

RENNER-TELLER COUPLING IN H_2S+: A COMPARISON OF THEORY WITH OPTICAL SPECTRA AND RECENT PFI AND MATI EXPERIMENTAL RESULTS

G. DUXBURY, *Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK*; Ch. JUNGEN, *LAC, 1 Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France*; A. ALIJAH, *GSMA, UMR CNRS 6089, Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France*.

Most of the early studies of H_2S+ focussed on the comparison between the medium resolution photoelectron spectra of hydrogen sulphide with the emission spectrum of the A-X emission spectrum of the ion[a]. Recently, with the advent of improved photoelectron and pulsed field ionisation spectrometers[b], and also a mass-analysed threshold ionisation approach[c], there has been a renewal of interest in the spectroscopy and dynamics of the formation and the fragmentation of the hydrogen sulphide ion. In this contribution we compare the results derived from these new experiments with the analysis of the original emission spectra. The results are also compared with the predictions made using the stretch-bender approach to the calculation of the effects on the Renner-Teller coupling of large amplitude vibrational motion.

---

[a] G. Duxbury, Ch. Jungen, and J. Rostas, Molec. Phys. 48, 719 (1983)

[b] M. Hochlaf, K-M. Weitzel, and C. Y. Ng, J. Chem. Phys. 120, 6994 (2004).

[c] S. Han, T. Y. Kang, and S. K. Kim, J. Chem. Phys. 132, 124304 (2010)

MG03 **15 min 2:04**

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF SILICON-CARBONYL CATIONS: EVIDENCE FOR ASSYMETRIC CARBONYL COORDINATION.

ANTONIO D. BRATHWAITE, MICHAEL A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602-2256*; ,.

Cationic silicon carbonyl clusters, consisting of up to twenty carbonyl ligands, are produced via laser vaporization with a pulsed nozzle source and cooled in a supersonic beam. The cations and their argon tagged analogues are mass selected in a reflectron time-of-flight mass spectrometer and studied with infrared laser photodissociation spectroscopy near the free molecular CO vibration (2143 cm^1). Silicon carbonyl complexes having more than two ligands fragment by loss of CO, whereas the argon tagged complexes fragment by loss of argon. All clusters have resonances near the free molecular CO stretch that provide distinctive patterns from which information on their structure and bonding can be obtained. The number of infrared-active bands, their frequency positions and relative intensities, indicate that species larger than n=2 consist of an asymmetrically coordinated $Si(CO)_2^+$ core with additional CO ligands attached via van der Waals interactions. Density functional theory computations are carried out in support of the experimental spectra.

MG04 **15 min 2:21**

INITIAL DEVELOPMENT OF HIGH PRECISION, HIGH RESOLUTION ION BEAM SPECTROMETER IN THE NEAR-INFRARED

MICHAEL PORAMBO, BRIAN SILLER, ANDREW MILLS,[a] MANORI PERERA,[b] and HOLGER KRECKEL, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

Interest in molecular ions stretches across many fields, from combustion to astrochemistry. These ions can be difficult to study spectroscopically in the laboratory, however. Obstacles include the relatively small density of ions produced in samples compared to neutral molecules and high rotational temperatures of the ions (which lead to dilution of the energy levels). To overcome some of these challenges of molecular ion spectroscopy, we are developing a fast ion beam spectrometer system we call Sensitive, Cooled, Resolved Ion BEam Spectroscopy (SCRIBES). This setup will enable the sensitive study of a supersonically cooled ion beam, taking advantage of narrow linewidths, a mass-dependent Doppler shift for mass identification of each spectral line, and on-line mass spectrometry for beam composition studies. Presently, the spectrometer contains an ion beam source that produces ions at high rotational temperature. We have characterized the spectrometer using the near-infrared rovibronic transitions of N_2^+, optimizing the sensitivity of the instrument. Furthermore, we have used an optical frequency comb for highly accurate frequency calibration, measuring a N_2^+ transition to within an accuracy of 8 MHz. This work in the near-infrared has laid the foundation for mid-infrared and indirect THz ion beam spectroscopy of many interesting molecular ions at a high level of precision, accuracy, and resolution.

---

[a] Present Address: IMRA, Ann Arbor, MI 48105

[b] Present Address: Illinois Wesleyan University, Bloomington, IL 61701

MG05 15 min 2:38

MID-IR DIRECT ABSORPTION/DISPERSION SPECTROSCOPY OF A FAST ION BEAM

BRIAN SILLER, MICHAEL PORAMBO, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

The direct absorption/dispersion ion beam instrument in the near-IR has been extended into the mid-IR using a difference frequency generation (DFG) laser created from combining a Ti:Sapphire laser with a Nd:YAG laser in a periodically poled lithium niobate (PPLN) crystal. The Nd:YAG laser is locked to an iodine hyperfine transition using a dither lock with 3f demodulation, while the Ti:Sapph laser is measured with an optical frequency comb for absolute frequency determination of the mid-IR beam to $<$1 MHz. Detection of ions within the beam is done using NICE-OHMS (noise immune cavity enhanced optical heterodyne molecular spectroscopy) together with velocity modulation of the ion beam for near shot noise limited sensitivity.

Initial studies are being done with a hydrogenic plasma in an uncooled cold cathode discharge source to observe H_3^+ in the ion beam to test the system. Once the instrument is fully characterized in mid-IR operation, we will implement a continuous supersonic expansion discharge source to enable observation of rotationally cold molecules and enable spectroscopy of more complex molecular ion systems.

MG06 15 min 2:55

SPONTANEOUS EMISSION BETWEEN ORTHO- AND PARA-LEVELS OF WATER-ION, H_2O^+

KEIICHI TANAKA, *Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 30010, TAIWAN, Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, 812-8581 JAPAN*; KENSUKE HARADA, *Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, 812-8581 JAPAN*; SHINKOH NANBU, *Department of Materials and Life Sciences, Faculty of Science and Engineering, Sophia University, Tokyo 102-8554, JAPAN*; TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, the Enrico Fermi Institute, the University of Chicago, Chicago, Illinois, 60637, USA.*

Nuclear spin conversion interaction of water ion, H_2O^+, has been studied to derive spontaneous emission lifetime between *ortho-* and *para*-levels. H_2O^+ is a radical ion with the $^2B_1$ electronic ground state. Its off-diagonal electron spin-nuclear spin interaction term, $T_{ab}(S_a\Delta I_b + S_b\Delta I_a)$, connects *para* and *ortho* levels, because $\Delta \boldsymbol{I} = \boldsymbol{I}_1 - \boldsymbol{I}_2$ has nonvanishing matrix elements between $I = 0$ and 1. The mixing by this term with T_{ab} = 72 MHz predicted by $ab\ initio$ theory in the MRD-CI/Bk level,[a] is many orders of magnitude larger than for closed shell molecules because of the large magnetic interaction due to the un-paired electron. Using the molecular constants reported by Mürtz et al. by FIR-LMR[b], we searched for *ortho* and *para* coupling channels below 1000 cm^{-1} with accidental near degeneracy between *para* and *ortho* levels. For example, hyperfine components of the $4_{2,2}(ortho)$ and $3_{3,0}(para)$ levels mix by 1.2×10^{-3} due to their near degeneracy (ΔE = 0.417 cm^{-1}), and give the *ortho-para* spontaneous emission lifetime of about 0.63 year. The most significant low lying $1_{0,1}(para)$ and $1_{1,1}(ortho)$ levels, on the contrary, mix only by 8.7×10^{-5} because of their large separation (ΔE = 16.267 cm^{-1}) and give the spontaneous emission lifetime from $1_{0,1}(para)$ to $0_{0,0}(ortho)$ of about 100 year.These results qualitatively help to understand the observed high *ortho-* to *para-* H_2O^+ ratio of 4.8 ± 0.5[c] toward Sgr B2 but they are too slow to compete with the conversion by collision unless the number density of the region is very low ($n \sim 1$ cm^{-3}) or radiative temperature is very high ($T_r > 100$ K).

---

[a] M. Staikova, B. Engels, M. Perić, and S.D. Peyerimhoff, *Mol. Phys.* **80**, 1485 (1993)
[b] P. Mürtz, L.R. Zink, K.M. Evenson, and J.M. Brown *J. Chem. Phys.* **109**, 9744 (1998).
[c] LP. Schilke, et al., *A&A* **521**, L11 (2010).

Intermission

MG07 **15 min 3:30**

INFRARED SPECTROSCOPY OF THE MASS 31 CATION: PROTONATED FORMALDEHYDE VS. THE TRIPLET METHOXY CATION

J. D. MOSLEY, T. C. CHENG, and M. A. DUNCAN, *University of Georgia, Dept. of Chemistry, 1001 Cedar St, Athens, GA 30602.*

The m/z=31 cation is produced by ionization and fragmentation of methanol, ethanol, dimethyl ether, etc. Two structures have been proposed, protonated formaldehyde ($^1CH_2OH^+$) and the triplet methoxy cation ($^3CH_3O^+$). The infrared spectrum of the mass 31 cation is obtained using infrared photodissociation spectroscopy with Ar tagging. The spectrum reveals the presence of two stable isomers, protonated formaldehyde ($^1CH_2OH^+$) and the triplet methoxy cation ($^3CH_3O^+$). The triplet methoxy cation has been studied extensively and is predicted to interconvert to protonated formaldehyde through an essentially barrierless process on a timescale much faster than our experiment ($> 100\ \mu$s). The presence of two structural isomers is verified by comparison of spectra from different precursors and spectra of different temperature ions from the same precursor.

MG08 **15 min 3:47**

INFRARED SPECTROSCOPY OF PROTONATED CARBONYLS: PROTONATED GLYOXAL

J. D. MOSLEY, T. C. CHENG, and M. A. DUNCAN, *University of Georgia, Dept. of Chemistry, 1001 Cedar St, Athens, GA 30602.*

The protonation site of carbonyls is usually at oxygen, allowing studies of the $O - H^+$ and carbonyl stretch vibrations and their variation with the local chemical environment. We have already studied protonated acetone and its proton-bridged dimer and now extend the study of protonated carbonyls to protonated glyoxal. Glyoxal is the simplest α-oxoaldehyde, which has the chance to form an intramolecular bridging proton structure upon protonation. Computational chemistry predicts the proton-bridged *cis* isomer to be the lowest energy structure. The infrared spectrum of mass-selected protonated glyoxal is obtained using infrared photodissociation spectroscopy with Ar tagging. The spectrum shows the presence of only the higher energy *trans* isomer when compared with purely harmonic calculations. The frequencies of the $O - H^+$ and carbonyl stretch vibrations of protonated glyoxal are compared to other protonated carbonyls.

MG09 **15 min 4:04**

TIME-RESOLVED FTIR AND MASS SPECTROSCOPY OF LASER-ABLATED MAGNESIUM.

Y. MIYAMOTO, N. IKEDA, J. TANG, K. KAWAGUCHI, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530, Japan*; C. MASAKI, *Faculty of Science, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530, Japan.*

Laser-ablated Magnesium (Mg) was subjected to time-resolved Fourier transform emission spectroscopy combined with quadrupole mass spectroscopy. Emission of Mg atoms was observed in 2000 $\sim$ 4000 cm^{-1} region with resolution of 0.03 cm^{-1}. It was found that emission lines consist of two components with different Doppler width. One with wider linewidth appeared just after ablation, while the other appeared after about 10 μs. Doppler width of the narrow one corresponds to estimated velocity of atoms sputtered directly from bulk Mg. Mass spectra suggested major products of the ablation under our experimental conditions are Mg$^+$ and Mg$_2{}^+$. MgO$^+$ was also observed in the mass spectra under thin oxygen condition ($\sim 10^{-4}$ Torr). Considering the linewidth and energy levels of these species, the wide component is attributed to Mg atoms produced by dissociative recombination of MgO$^+$ and electrons. Information about the electronic energy level of MgO$^+$ was also obtained, which is compared with *ab initio* calculations.

MG10 **15 min 4:21**

METAL ION BINDING TO POLYPEPTIDES CHARACTERIZED BY IRMPD SPECTROSCOPY. METAL-AMIDE NITROGEN BINDING AND THE IMINOL TAUTOMERIZATION.

ROBERT C. DUNBAR, *Chemistry Department, Case Western Reserve Univ., Cleveland, OH 44106*; NICOLAS POLFER, *Chemistry Department, University of Florida, Gainesville, FL*; GIEL BERDEN, *FOM Institute for Plasma Physics, Nieuwegein, Netherlands*; JOS OOMENS, *FOM Institute for Plasma Physics, Nieuwegein, and University of Amsterdam, Netherlands*.

We have recently uncovered a new binding mode for the complexation of metal ions with gas-phase peptides. Termed the iminol mode, this binding mode is adopted by strongly binding divalent metal ions including Mg2+ and Ni2+. The metal ion displaces the amide hydrogen, which moves to protonate the amide carbonyl oxygen. A spectroscopic signature of the tautomerization is the disappearance of the characteristic Amide II band normally seen in peptide ion infrared spectra. We find that in peptides up to pentapeptides, multiple iminol binding can take place, such that all amide linkages are tautomerized to the iminol form, and chelate the metal ion. However, the iminol tautomerization depends on the nature of the metal ion, as will be discussed. Spectra of the ions were acquired by irradiating the cell of the Fourier-transform ion cyclotron resonance mass spectrometer with infrared light from the FELIX laser at wavelengths in the approximate range 500 to 1900 cm^{-1}.

MG11 **15 min 4:38**

INFRARED SPECTROSCOPIC EVIDENCE FOR ISOTOPOLOGS OF THE HOHOH ANION TRAPPED IN SOLID NEON

MARILYN E. JACOX and WARREN E. THOMPSON, *Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

Although properties of the HOHOH anion have long been sought, only recently have quantum chemical calculations converged on a centrosymmetric structure for it. One vibrational fundamental, the antisymmetric stretching motion of the central H atom along the OHO axis, has even more recently been identified in the gas phase [a]. In experiments involving the codeposition at 4.3 K of a Ne:O_2 mixture with a Ne:H_2 mixture that has been passed through a microwave discharge, this fundamental absorption appears very close to its gas-phase position. Experiments involving partial and full deuterium enrichment confirm the presence of multiple H atoms in the anion and provide the first observation of the corresponding fundamental of the fully deuterium-substituted species.

---

[a] E. G. Diken, J. M. Headrick, J. R. Roscioli, J. C. Bopp, M. A. Johnson, and A. B. McCoy, J. Phys. Chem. A 109, 1487 (2005).

MG12 **15 min 4:55**

INFRARED STUDY OF THE WATER-HYDROXYL RADICAL COMPLEX TRAPPED IN SOLID NEON

MARILYN E. JACOX and WARREN E. THOMPSON, *Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

The most prominent infrared absorptions which appear when a Ne:O_2 mixture is codeposited at 4.3 K with a Ne:H_2 mixture that has been passed through a microwave discharge are those of H_2O, HO_2, the HOHOH anion, and the $H_2O(HO)$ complex. The absorptions of this complex correspond well with those previously obtained in argon-matrix experiments [a]. Photodetachment of the HOHOH anion leads to extremely great intensification of the absorptions of the $H_2O(HO)$ complex. The infrared spectra of the normal and deuterium- substituted complex and the mechanisms of formation and photodestruction of the HOHOH anion will be considered.

---

[a] A. Engdahl, G. Karlström, and B. Nelander, J. Chem. Phys. 118, 7797 (2003).

MG13 **15 min 5:12**

UV/VIS ABSORPTION EXPERIMENTS ON MASS SELECTED CATIONS BY COUNTER-ION INTRODUCTION INTO AN INERT NEON MATRIX

N. P. ROEHR, J. SZCZEPANSKI, N. C. POLFER, *Department of Chemistry, University of Florida, Gainesville, FL 32608.*

Obtaining UV/Vis absorption spectra of cations is a challenging endeavor due to the low densities that can be achieved in the gas phase. In matrix isolation, ions of interest are accumulated in a cold inert matrix of a rare gas (e.g. Argon, Neon) until sufficient concentrations are attained for direct spectroscopic characterization [a]. Nonetheless, in order to ensure neutralization of the matrix, experimentalists often rely on non-ideal, energetic processes, such as electron emission from metal surfaces upon cation bombardment [b]. A better method for matrix neutralization would involve co-depositing a molecular counter-ion. In this talk, a two-ion source instrument is presented, where cations and anions are deposited into a cold inert matrix. Mass-selected cation beams are generated in an electron ionization source and filtered in a quadrupole mass filter (5-10 nA mass-selected naphthalene radical cations recorded). Anion beams are generated in a chemical ionization source (20 nA SF_6^- recorded). Both ion beams are introduced into an octopole ion guide via a quadrupole deflector. Cations and anions can be deposited simultaneously or separately; in the latter case, alternating layers of each species can be formed. Target cations of interest include open-shell naphthalene and tetracene, for which UV/Vis absorption spectra are recorded after deposition [c,d]. The counter-ion of choice is SF_6^-, due to the high electronegativity of SF_6.

---

[a] J. P. Maier, *et al.*, J. Chem. Phys. 90, 600(1989).

[b] Godbout, *et al.*, J. Phys. Chem. 100 2892-2899(1996).

[c] P. Brechignac, *et al.*, J. Chem. Phys. 22 7337-7347(1999).

[d] M. Vala, *et al.*, Chem. Phys. Lett. 245 539-548(1995).

MH. MICROWAVE

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: GARRY GRUBBS, Wesleyan University, Middletown, Connecticut

MH01 **15 min 1:30**

BROADBAND ROTATIONAL SPECTRUM AND MOLECULAR GEOMETRY OF OC $\cdots$AgI

N. R. WALKER, S. L. STEPHENS, W. MIZUKAMI, D. P. TEW AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

Pure rotational spectra of the ground vibrational states of six isotopologues of OC$\cdots$AgI have been measured by chirped-pulse Fourier transform microwave spectroscopy. The spectra are assigned to determine the rotational constant, B_0, and the centrifugal distortion constant, D_J, of the complex. The nuclear quadrupole coupling constant of the iodine atom, χ_{aa}(I), has also been measured. The complex is linear. The length of the C—O bond, r(CO), in the r_0 geometry for OC$\cdots$AgI is 0.008 Å shorter than that found in the free CO molecule. The length of the Ag—I bond, r(AgI), is 0.013 Å shorter than in free AgI. The nuclear quadrupole coupling constant of the iodine atom is determined to be -769.84(22) MHz for OC$\cdots{}^{107}$AgI implying an ionic character of 0.66 for the metal halide bond. The molecular structure and spectroscopic parameters determined from the experimental data are presented alongside the results of calculations at the explicitly-correlated CCSD(T) level. The design features of a laser ablation source constructed for the present work will be described.

MH02 **15 min 1:47**

MICROWAVE SPECTRUM AND GEOMETRY OF $H_3P\cdots$AgI

N. R. WALKER, S. L. STEPHENS, W. MIZUKAMI, D. P. TEW AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

The pure rotational spectrum of the vibrational ground state of $H_3P\cdots$AgI has been measured by chirped-pulse FTMW spectroscopy. The complex is generated via laser ablation (532 nm) of a silver rod in the presence of CF_3I, PH_3 and argon. It is subsequently stabilized and interrogated in the cold environment of a supersonic jet. The rotational constant, B_0, and the centrifugal distortion constant, D_J, have been measured for $H_3P\cdots{}^{107}$AgI and $H_3P\cdots{}^{109}$AgI. The spectrum of the complex is consistent with a C_{3v} geometry and a linear arrangement of the P, Ag and C atoms. The measured rotational constants allow a preliminary determination of the geometry of the molecule. The nuclear quadrupole coupling constant of the iodine atom, χ_{aa}(I) , is also established. The experimental results are compared with theory performed at the explicitly-correlated coupled-cluster singles, doubles and perturbative triples level.

MH03 **15 min 2:04**

MICROWAVE SPECTROSCOPY AND INTERNAL DYNAMICS OF THE Ne-NO_2 VAN DER WAALS COMPLEX

BRIAN J. HOWARD, GEORGE ECONOMIDES and LEE DYER, *Department of Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, United Kingdom.*

The rotational spectrum of the open-shell complex Ne-NO_2 in the 6 - 18 GHz region is reported. Both fine and hyperfine structure are observed. However, the spectrum does not fit a semi-rigid model as well as the related species Ar-NO_2 [a], Kr-NO_2 [b] and Xe-NO_2 [c]. This is almost certainly a result of the "floppy" nature of this species.

In order to model the dynamics of the complex and to reproduce the observed spectrum, we have obtained an accurate intermolecular potential surface using the RCCSD(T) method and aug-cc-pV(D/T)Z basis sets (extrapolated to the complete basis set limit). Full quantum dynamics calculations were then performed on this surface to give the rotational energy levels and the effective fine and hyperfine structure constants.

---

[a] R.J. Low, M.D. Brooks, C.J. Whitham and B.J. Howard *J. Chem. Phys.*, **105**, 6756 (1996).

[b] S. Blanco, C.J. Whitham, H. Qian and B.J. Howard, *PCCP.*, **3**, 3895 (2001).

[c] C.J. Whitham, R.J. Low and B.J. Howard, *Chem. Phys. Lett.*, **286**, 408 (1998).

MH04 **15 min 2:21**

FTMW SPECTROSCOPY AND DETERMINATION OF THE 3-D POTENTIAL ENERGY SURFACE FOR Ar-CS

CHISATO NIIDA, MASAKAZU NAKAJIMA, YASUKI ENDO, *Department of Basic Science, The University of Tokyo, Tokyo 153-8902, Japan*; YOSHIHIRO SUMIYOSHI, *Department of Chemistry and Chemical biology, Gunma University, Maebashi Gunma, 371-8510, Japan*; YASUHIRO OHSHIMA, *Department of Photo-Molecular Science, Institute for Molecular Science, Okazaki, 444-8585, Japan*; HIROSHI KOHGUCHI, *Department of Chemistry, Hiroshima University, Higashi-Hiroshima, 739-8511, Japan.*

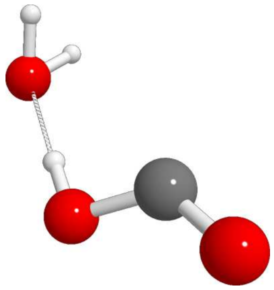
Pure rotational transitions of the Ar-CS complex have been observed by FTMW spectroscopy for the normal species with $v_{CS} = 0, 1, 2$ and for $C^{34}S$ in the ground vibrational state. All the observed transition frequencies have been utilized to determine a 3-Dimentional potential energy surface for the complex, explicitly considering the dependence of the CS stretcing for the intermolecular potential between Ar and CS, which is indispensable to analyze the transitions for the excited vibrational states and those of the ^{34}S species simultaneously. High-level *ab initio* calculations have been performed to obtain the initial 3-D potential. The *ab initio* poteintial has been fitted to an analytical function with determinable parameters. The parameters have been improved by fitting the observed transition frequencies. All the observed transition frequencies have successfully been fitted almost within their experimental accuracies.

MH05 **15 min 2:38**

OBSERVATION OF THE PURE ROTATIONAL SPECTRA OF THE H_2O-$trans$-HOCO COMPLEX

TAKAHIRO OYAMA, MASAKAZU NAKAJIMA, YASUKI ENDO, *Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan*; and YOSHIHIRO SUMIYOSHI, *Department of Chemistry and Chemical Biology, Gunma University, 4-2 Aramaki-machi, Maebashi City, Gunma, 371-8510 Japan.*

Rotational spectra of the H_2O-*trans*-HOCO complex have been observed using a Fourier transform microwave (FTMW) spectrometer. The complex was produced in a supersonic jet by discharging a gas mixture of CO and H_2O diluted in Ar. The observed lines show that the ground state of the complex is split into two by the exchange symmetry of the two equivalent protons of H_2O. The molecular constants including the hyperfine coupling constants have been precisely determined for the two states. The Fermi contact constants of the two states are smaller than that of the *trans*-HOCO monomer. This result indicates that there is an induced effect for the spin density on the hydrogen nucleus of HOCO by the complex formation.



MH06 **15 min 2:55**

STRUCTURE AND INVERSION MOTIONS OF THE WEAKLY BOUND $CH_2F_2 \cdots CO_2$ DIMER

REBECCA A. PEEBLES, AMELIA J. THOMAS, MICHAL M. SERAFIN and SEAN A. PEEBLES, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920.*

The rotational spectrum of the $CH_2F_2 \cdots CO_2$ dimer has been measured using chirped-pulse and resonant cavity Fourier-transform microwave (FTMW) spectroscopy, with the broadband spectrum playing an essential role in allowing identification of the tunneling splittings. The observed a-type transitions were doubled by a few megahertz, while c-type transitions were split by around 200 MHz, suggesting a tunneling motion that inverts the μ_c dipole moment component. A Pickett-type coupled Hamiltonian has been used to analyze the spectra, giving an energy difference (ΔE) between the tunneling states for the normal isotopologue of $115.140(2)$ MHz, and rotational constants of $A_0 = 5567.8604(27)$ MHz, $B_0 = 1832.9676(5)$ MHz, $C_0 = 1828.6132(5)$ MHz, $A_1 = 5567.8540(26)$ MHz, $B_1 = 1831.7711(4)$ MHz, $C_1 = 1828.6106(4)$ MHz. It was also necessary to include a Coriolis coupling term ($G_b = 7.740(6)$ MHz) as well as fourth and sixth order centrifugal distortion constants to obtain a satisfactory spectroscopic fit. The rotational constants and planar moments are consistent with a C_s symmetry structure in which the C_2 axis of CH_2F_2 makes an angle of roughly 23° with the axis of the CO_2, with the fluorine atoms of CH_2F_2 straddling the CO_2 carbon atom. The spectra of five additional isotopologues were analyzed, providing detailed structural information, and all except the mixed $C^{18}O^{16}O$ species showed inversion splittings similar to the normal species. The observation of unsplit spectra for two distinct $C^{18}O^{16}O$ isotopologues confirms that the internal motion involves movement of the CH_2F_2 subunit between the two ends of the CO_2 molecule.

MH07 10 min 3:12

ANALYSIS OF MICROWAVE SPECTRUM, INTERNAL ROTATION AND C–H$\cdots$F INTERACTIONS OF THE $CHF_3\cdots C_2H_3F$ WEAKLY BOUND COMPLEX

LENA F. ELMUTI, DANIEL A. OBENCHAIN, REBECCA A. PEEBLES, SEAN A. PEEBLES, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920.*

C–H$\cdots$X hydrogen bonds with systematic variation of halogens (X = F, Cl, Br) have been examined using Fourier-Transform Microwave (FTMW) spectroscopy. Rotational constants for trifluoromethane–vinyl fluoride (TFM$\cdots$VF) were consistent with a C_S symmetry structure that exhibited both bifurcated and single C–H$\cdots$F interactions between the TFM and VF. This near prolate asymmetric top exhibited three-fold internal rotation of the CF_3 group causing characteristic doubling in its spectra. Initial assignments were completed using chirped-pulse FTMW spectroscopy with additional measurements made using a resonant-cavity FTMW spectrometer. Rotational constants from ab initio calculations at the MP2/6-311++G(2d,2p) level were in agreement with preliminary experimental values ($A = 4828$ MHz, $B = 1049$ MHz, $C = 1018$ MHz). XIAM[a] was used to provide the barrier to internal rotation ($25(5)$ cm^{-1}) and other spectral information. Spectroscopic parameters for the normal isotopic species as well as preliminary structural results on the C–H$\cdots$F interactions in this complex will be presented.

---

[a] H. Hartwig and H. Dreizler, *Z. Naturforsch*, **51a**, (1996), 923-932.

MH08 15 min 3:24

STRUCTURAL STUDIES OF CH_3SiF_2-X (X = NCO, Cl) BY MICROWAVE SPECTROSCOPY

GAMIL A. GUIRGIS, KORREDA K. GAUSE, *Department of Chemistry & Biochemistry, College of Charleston, Charleston, SC 29424 USA*; NATHAN A. SEIFERT, DANIEL P. ZALESKI, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319*; MICHAEL H. PALMER, *School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*; REBECCA A. PEEBLES, SEAN A. PEEBLES, LENA F. ELMUTI, DANIEL A. OBENCHAIN, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL, 61920 USA.*

The structures of CH_3SiF_2-NCO and CH_3SiF_2-Cl have been studied by molecular rotational spectroscopy in the 6.5-18 GHz band. The rotational spectrum was measured by cavity Fourier transform microwave (FTMW) and chirped-pulse FTMW spectroscopy. The experiment targeted the study of CH_3SiF_2-NCO, but CH_3SiF_2-Cl was also observed as an impurity. Due to the dynamic range achieved on these spectra, all isotopologs with natural abundance $\geq 0.2\%$ were assigned, which includes two doubly-substituted isotopologs for the chloride (^{29}Si/^{37}Cl and ^{30}Si/^{37}Cl). Strategies for obtaining the molecular structure for these two molecules using either a Kraitchman analysis (to obtain a partial substitution structure) or r_0 analysis (with additional constraints on the structure supplied by the theoretical structure) will be discussed. Derived structural parameters for the CH_3-SiF_2-X base structure are the same for the two compounds. The hyperfine and internal rotation effects in the spectra have been analyzed for all isotopologs and the Hamiltonian parameters are in very good agreement with ab initio results. The barriers to methyl group internal rotation for the two compounds 446(50) cm^{-1} and 463(3) cm^{-1} and are independent of the isotopic structure of the heavy atom frame.

Intermission

MH09 **15 min 4:00**

MICROWAVE SPECTRA AND GEOMETRIES OF $H_2C_2\cdots AgCl$ AND $H_2C_2\cdots CuCl$

N. R. WALKER, S. L. STEPHENS, W. MIZUKAMI, D. P. TEW AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.*.

Pure rotational spectra of the vibrational ground states of $H_2C_2\cdots AgCl$ and $H_2C_2\cdots CuCl$ have been measured by chirped-pulse FTMW spectroscopy. Each complex is generated via laser ablation of the metal in the presence of small percentages of CCl_4 and C_2H_2 in argon. The complexes are stabilized and interrogated in the cold environment of a supersonic jet. Rotational constants (B_0, C_0) and the centrifugal distortion constant, Δ_J, have been measured for six isotopologues of $H_2C_2\cdots AgCl$ and three isotopologues of $H_2C_2\cdots CuCl$ with substitutions at the metal, chlorine and carbon atoms in each case. The spectrum of each complex is consistent with a C_{2v} structure in which the metal atom is coordinated by the π-orbital of ethyne. The measured rotational constants allow determination of the length of the bond between the metal and chlorine atoms, *r*(M—Cl), and the distance between the metal atom and the centre of the ethyne double bond, *r*(M—*). Nuclear quadrupole coupling constants have been measured for the chlorine atom in each complex and also for copper in $H_2C_2\cdots CuCl$.

MH10 **15 min 4:17**

MICROWAVE SPECTRA, MOLECULAR STRUCTURES AND INTERNAL DYNAMICS OF $H_2S\cdots ICF_3$ and $H_2O\cdots ICF_3$ REVEALED BY BROADBAND ROTATIONAL SPECTROSCOPY

N. R. WALKER, S. L. STEPHENS AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.*.

The rotational spectra of three isotopologues of $H_2S\cdots ICF_3$ and four isotopologues of $H_2O\cdots ICF_3$ have been measured between 7 and 18.5 GHz by chirped-pulse Fourier transform microwave spectroscopy. The rotational constant, B_0, the centrifugal distortion constants, D_J and D_{JK}, and the nuclear quadrupole coupling constant of ^{127}I, $\chi_{aa}(I)$, are precisely determined for $H_2S\cdots ICF_3$ and $H_2O\cdots ICF_3$ by fitting observed transitions to the Hamiltonians appropriate to *symmetric* tops. The measured rotational constants allow determination of the molecular geometries. The C_2 axis of H_2O / H_2S intersects the C_3 axis of the CF_3I sub-unit at the oxygen atom. The r_0 lengths of halogen bonds identified between iodine and sulphur, *r*(S$\cdots$I), and iodine and oxygen, *r*(O$\cdots$I), are determined to be 3.5589(2) Å and 3.0517(18) Å respectively. The angle, ϕ, between the local C_2 axis of the H_2S / H_2O sub-unit and the C_3 axis of CF_3I is found to be 93.7(2)° in $H_2S\cdots ICF_3$ and 34.4(20)° in $H_2O\cdots ICF_3$. The observed symmetric top spectra imply nearly free internal precession of the C_2 axis of the hydrogen sulphide/water unit about the C_3 axis of CF_3I in each of these complexes. Additional transitions of $H_2{}^{16}O\cdots ICF_3$, $D_2{}^{16}O\cdots ICF_3$ and $H_2{}^{18}O\cdots ICF_3$ can only be assigned using Hamiltonians appropriate to asymmetric tops, suggesting that the effective rigid-rotor fits employed do not completely represent the internal dynamics of $H_2O\cdots ICF_3$.

MH11 15 min 4:34

FOURIER TRANSFORM MICROWAVE SPECTRUM OF CO_2 -$(CH_3)_2$ S

YOSHIYUKI KAWASHIMA and TAKAYUKI MORITANI, *Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN*; EIZI HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.*

In spite of the fact that the oxygen and sulfur atoms belong to the same group in the periodic table, oxygen-containing molecules and their corresponding sulfur analogues often exhibit characteristic differences in their chemical and physical properties. We have been interested in these differences and have investigated, in a systematic way using Fourier transform microwave (FTMW) spectroscopy combined with ab initio molecular orbital calculations, complexes consisting of dimethyl ether (DME)/dimethyl sulfide (DMS) and ethylene oxide (EO)/ ethylene sulfide (ES), each being attached to either one of rare gas atoms (Rg), CO, N_2, or CO_2[a]. Among others the CO_2-DMS complex should be mentioned, which, in sharp contrast with its counterpart: CO_2-DME [b]. behaves anomalously, presumably because of low-frequency internal motions, and we have decided to explore it in detail by a FTMW spectrometer. We have generated the CO_2-DMS complex by supersonic expansion of a CO_2 and DMS mixture diluted with Ar, and have scanned the frequency region from 5 to 24 GHz to record the rotational spectra of the complex. We have found it difficult to fit the observed transition frequencies to the ordinary rotational Hamiltonian, but have succeeded to assign 75 transitions by sum rules among the observed transition frequencies. We are suspecting the anomalous behavior of the complex to be caused by a low-frequency torsion of the moieties. In the case of the CO_2-DME, the internal rotations of the two methyl groups of the DME were shown to be locked to the CO_2 by hydrogen bonding, whereas, for the CO_2-DMS, we have observed internal-rotation splittings of the two methyl groups of the DMS, indicating the structure of the CO_2-DMS complex being considerably different from that of the CO_2-DME. We will report the structure at the potential minima and the internal motion of the CO_2-DMS, in comparison with the results predicted by quantum chemical calculations.

---

[a] Y. Kawashima, A. Sato, Y. Orita, and E. Hirota *J. Phys. Chem. A* **116**, 1224 2012.

[b] J. J. Newby, R. A. Peebles, and S. A. Peebles *J. Phys. Chem. A* **108**, 11234 2004.

MH12 15 min 4:51

MICROWAVE SPECTROSCOPY AND PROTON TRANSFER DYNAMICS IN THE FORMIC ACID-ACETIC ACID DIMER

B.J. HOWARD, E. STEER, F. PAGE, M. TAYLER, B. OUYANG, *Department of Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, United Kingdom*; H.O. LEUNG, M.D. MARSHALL, *Department of Chemistry, Amherst College, Amherst, MA 01002*; and J.S. MUENTER, *Department of Chemistry, University of Rochester, Rochester, NY 14627.*

The rotational spectrum of the doubly hydrogen-bonded *hetero* dimer formed between formic acid and acetic acid has been recorded between 4 and 18 GHz using a pulsed-nozzle Fourier transform microwave spectrometer. Each rigid-molecule rotational transition is split into four as a result of two concurrent tunnelling motions, one being proton transfer between the two acid molecules, and the other the torsion/rotation of the methyl group within the acetic acid.

We present a full assignment of the spectrum for $J = 1$ to $J = 7$ for these four torsion/tunnelling states. Spectra have been observed for the main isotopic species [a], with deuterium substitution at the C of the formic acid and all ^{13}C species in natural abundance, The observed transitions are fitted to within a few kilohertz using a molecule-fixed effective rotational Hamiltonian for the separate A and E vibrational species of the G_{12} permutation-inversion group which is applicable to this complex. To reduce the effects of internal angular momentum, a non-principal axis system is used throughout. Interpretation of the internal motion uses an internal-vibration and overall rotation scheme, and full sets of rotational and centrifugal distortion constants are determined.

The proton tunnelling rates and the internal angular momentum of the methyl group in the E states is interpreted in terms of a dynamical model which involves coupled proton transfer and internal rotation. The resulting potential energy surface not only describes these internal motions, but can also explain the observed shifts in rotational constants between A and E species, and the deviations of the tunnelling frequencies from the expected 2:1 ratio. It also permits the determination of spectral constants free from the contamination effects of the internal dynamics.

---

[a] M.C.D. Tayler, B. Ouyang and B.J. Howard, *J. Chem. Phys.*, **134**, 054316 (2011).

MH13 **15 min 5:08**

STRUCTURE OF THE SEVOFLURANE-BENZENE COMPLEX AS DETERMINED BY CHIRPED-PULSE FTMW SPECTROSCOPY

NATHAN A. SEIFERT, DANIEL P. ZALESKI, JUSTIN L. NEILL, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319*; ALBERTO LESARRI, MONTSERRAT VALLEJO, *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; EMILIO J. COCINERO, FERNANDO CASTANO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Campus de Leioa, Ap. 644, E-48080 Bilbao, Spain.*

Following previous microwave studies on sevoflurane monomer by Suenram *et al.*[a] and Vega-Toribio *et al.*[b] we report the broadband rotational spectrum of sevoflurane clustered with benzene. The structure assigned is consistent with a C-H$\cdots\pi$ interaction between the benzene ring and the $(CF_3)_2C$-H hydrogen on sevoflurane. The spectrum of this species is complicated by the six-fold internal rotation of the benzene ring over the C_1 framework of sevoflurane. The six-fold tunneling falls into a high effective barrier case where there are several bound torsional levels. The tunneling spectrum has been successfully analyzed using the BELGI internal rotation program and a barrier to internal rotation of the benzene against sevoflurane of 32.5 cm^{-1} has been determined. Structural information about the complex has been obtained by studying the complex of sevoflurane with benzene-d_1. For this complex, six unique isomers are observed making it possible to determine the positions of the benzene H-atoms in the complex. Combination of these hydrogen r_s positions with the sevoflurane monomer r_s coordinates reported by Lesarri *et al.*[c] results in a substitution structure in excellent agreement with the ab initio results. Finally, initial microwave results on two sevoflurane dimer species will also be presented.

---

[a] R. D. Suenram, D. J. Brugh, F. J. Lovas and C. Chu, 51st OSU Int. Symp. On Mol. Spectrosc., Columbus, OH, 1999, RB07.

[b] A. Vega-Toribio, A. Lesarri, R.D. Suenram, J. Grabow, 64th OSU Int. Symp. On Mol. Spectrosc., Columbus, OH, 2009, MH07.

[c] A. Lesarri, A. Vega-Toribio, R. D. Suenram, D. J. Brugh, J.-U. Grabow, Phys. Chem. Chem. Phys., 12, 9624-9631 (2010).

MH14 **15 min 5:25**

STRUCTURE OF HIGH-ORDER WATER CLUSTERS OF β-PROPIOLACTONE BY BROADBAND MICROWAVE SPECTROSCOPY

JUSTIN L. NEILL, *University of Michigan. Department of Astronomy 830 Dennison Bldg. 500 Church St. Ann Arbor, MI 48109-1042*; CRISTOBAL PEREZ, MATT T. MUCKLE, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904*; ISABEL PENA, JUAN C. LOPEZ, JOSE L. ALONSO, *Grupo de Espectroscopía Molecular (GEM). Edificio Quifima, Laboratorios de Espectroscopía y Bioespectroscopía. Parque Científico Uva Universidad de Valladolid. 47011 Valladolid, Spain.*

The rotational spectra of β-propiolactone-$(H_2O)_n$ (n=1-5) adducts have been extensively analyzed by broadband microwave spectroscopy (CP-FTMW). Unambiguous identification of their structures has been achieved from the spectra of the parent species and $H_2^{18}O$ single substitution clusters and Stark effect measurements. In addition to our previous work, the substitution structures for two n=4 and one n=5 complexes are presented. The three structures show a cyclic arrangement in the oxygen framework. For both n=4 structures, the water molecules form a quasiplanar ring that sits above the BPL unit. The structural differences between these two n=4 complexes are discussed in terms of the water oxygen atom positions and dipole moment orientations, enabling to distinguish between isomers with certainty by CP-FTMW spectroscopy. For n=5, a cyclic arrangement similar to n=4 was found with water molecules making a puckered five-water ring. Substitution coordinates for the oxygen framework support the assignment. Our results show that complexation with BPL induces measurable structural changes in the $(H_2O)_n$ (n = 3, 4, 5) pure water clusters. This fact is also discussed in terms of the variation in O-O distances within pure and complexed water clusters.

MI. MINI-SYMPOSIUM: PHOTODETACHMENT AND PHOTOIONIZATION

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: CAROLINE JARROLD, Indiana University-Bloomington, Bloomington, Indiana

MI01 ***INVITED TALK*** **30 min 1:30**

SLOW-ELECTRON VELOCITY-MAP IMAGING OF NEGATIVE IONS: APPLICATIONS TO SPECTROSCOPY AND DYNAMICS

DANIEL NEUMARK, *Department of Chemistry, University of California at Berkeley, B64 Hildebrand Hall, Berkeley, CA 94720.*

Slow electron velocity map imaging (SEVI) of negative ions is a high resolution variant of negative ion photoelectron spectroscopy that can be used with great effect to investigate spectroscopy and dynamics in radicals, clusters, and transition states. It is particularly powerful when combined with ion trapping and cooling. Several examples will be presented.

MI02 **15 min 2:05**

STATE-RESOLVED PREDISSOCIATION DYNAMICS OF THE FORMYLOXYL RADICAL BY DISSOCIATIVE PHOTODETACHMENT OF HCO_2^- / DCO_2^-

AMELIA W. RAY, BEN B. SHEN, BERWYCK L. J. POAD and ROBERT E. CONTINETTI[a], *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093.*

Near threshold dissociative photodetachment dynamics of HCO_2^- and DCO_2^- were studied using photoelectron-photofragment coincidence spectroscopy in a cryogenically cooled ion beam trap. The combination of colder precursor ions and lower kinetic energy electrons has enabled us to record higher resolution state-resolved dissociation dynamics for the $HCO_2^-/DCO_2^- + h\nu \rightarrow$ H/D + CO_2 + e^- reaction, complementing and extending our earlier study of this system.[b] For $h\nu = 4.27$ eV, photodetachment accesses the three lowest-lying electronic states ($^2B_2$, $^2A_1$, and $^2A_2$) of the formyloxyl radical, with the resulting vibrational features dominated by the OCO bending mode. Excitation of this OCO bend in the transient formyloxyl neutral couples to the bending excitation observed in the state-resolved translational energy distribution for the CO_2 product. Each vibrational state of the nascent neutral is observed to predissociate to several CO_2 product states leading to pronounced vibrational predissociation sequence bands in the photoelectron-photofragment coincidence spectra for both HCO_2^- and DCO_2^-.

---

[a] This work is supported by the US Department of Energy under Grant Number DE-FG03-98ER14879

[b] T.G. Clements and R.E. Continetti, J. Chem. Phys., 115, 5345 (2001)

MI03 15 min 2:22

PHOTOELECTRON-PHOTOFRAGMENT COINCIDENCE SPECTROSCOPY OF TERT-BUTOXIDE AND THE CARBANION ISOMER

BEN B. SHEN, BERWYCK L. J. POAD, AMELIA W. RAY, and ROBERT E. CONTINETTI[a], *Department of Chemistry and Biochemistry, University of California, San Diego, CA 92093.*

The photodetachment dynamics of the $C_4H_9O^-$ anion, produced by proton abstraction from tert-butanol has been studied using a cryogenically-cooled linear electrostatic ion trap to store a fast ion beam[b]. The ion trap is coupled with a Photoelectron-Photofragment Coincidence spectrometer for a kinematically complete experiment in which dissociative neutral intermediates of known internal energy are created by photodetachment of a stable molecular anion. By collecting all resultant neutral fragments from the dissociation event in coincidence with the detached electron using time- and position-sensitive detectors, the correlated momenta and energies of all products can be determined. At 388, 537, and 600nm, both stable and dissociative photodeatchment processes of $C_4H_9O^-$ are observed. The stable channel is consistent with previous photodetachment spectrum from *tert*-butoxide anion[c] as well as a Franck-Condon simulation of the photoelectron spectrum. The dissociative channel is consistent with a methyl loss from an alkylhydroxy radical. Results will be analyzed in the context of calculations employing MP2/6-311++G(d,p) and CBSQ level of theory.

---

[a] This work is supported by the United States Department of Energy under grant number DE-FG03-98ER14879

[b] C. J. Johnson, B. B. Shen, B. L. J. Poad, and R. E. Continetti, *Rev. Sci. Instrum., 82, 105105 (2011)*

[c] T. M. Ramond, G. E. Davico, R. L. Schwartz, W. C. Lineberger, *J. Chem. Phys., 112, 1158 (2000)*

MI04 15 min 2:39

VIBRATIONAL AUTODETACHMENT: INTRAMOLECULAR VIBRATIONAL RELAXATION TO ELECTRONIC MOTION

CHRISTOPHER L. ADAMS, BENJAMIN J. KNURR and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

If a negative ion has vibrational energy in excess of the binding energy of its most weakly bound electron, the anion can undergo vibrational autodetachment (VAD), similar to thermionic emission. When VAD occurs after targeted infrared excitation of a specific vibrational mode in the anion, it encodes information on the intramolecular vibrational relaxation (IVR) processes that take place between excitation and electron emission. Analyzing the kinetic energy distribution of electrons emitted in VAD processes, can yield some information on the IVR process. The photoelectron spectra can be modeled, and we will present an analysis of vibrational autodetachment photoelectron spectra after excitation of CH stretching modes as a case study.

MI05 **15 min 2:56**

PHOTOELECTRON SPECTROSCOPY OF RARE-GAS SOLVATED NUCLEOBASE ANIONS

ANGELA M. BUONAUGURIO, JING CHEN, AND KIT H. BOWEN, *Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218.*

Gas-phase polar molecular anions [uracil (U^-), thymine (T^-), 1-3 dimethyluracil (DMU^-)] solvated by rare gas atoms were studied by means of negative ion photoelectron spectroscopy[a]. The photoelectron spectrum (PES) of U^-, T^-, and DMU^- each exhibit a distinctive dipole-bound (DB) spectral signature. The spectra of U^-, U^- $(Ar)_{1,2}$ and U^- $(Kr)_1$ also only displayed the DB anion feature. Upon the solvation of more rare gas atoms, the spectra of U^- $(Ar)_3$, U^- $(Kr)_2$, and U^- $(Xe)_{1-3}$ not only retained the DB signature but also exhibited the valence anion features. Moreover, the DB and the valence features shifted together to higher electron binding energies (EBEs) with increasing numbers of rare gas solvent atoms. Therefore, the co-existing DB and the valence anions appeared to be strongly coupled with each other, i.e. they effectively form a single state that is a superposition of both DB and valence anion states. For both U^- and T^- series, the “onset size" of the Xe, Kr, and Ar solvents for the co-existing of the two anionic states was 1, 2, and 3 respectively. In addition, a minimum of 2 methane (CH_4) molecules or 1 ethane (C_2H_6) molecule were required to induce the coupling between the two states in the T^- series. Thus, the nucleobase anion interaction with non-polar solvent atoms tracks as the sum of the solvent polarizabilities. However for the DMU- series, the DB and the valence anions of $DMU^-(Xe)_1$, $DMU^-(Kr)_2$, and $DMU^-(Ar)_3$ were completely absent in both the mass spectra and the PES. Beyond these “holes", their PES displayed the similar behaviors to the U^- and T^- series. Extrapolated EA values for these missing species were at or very close to zero, which may explain why they were not seen. However, why this was the case is not clear. With better Franck-Condon overlap between the origins of the NB^- $(Rg)_n$ valence anion and the neutral NB(Rg)n than between those of the NB^- (H2O)n valence anion and the neutral NB(H2O)n, extrapolation of the valence electron affinities, measured from the $NB(Rg)_n^-$ valence anions, should lead to significantly improved estimations of the valence electron affinity values of canonical, molecular nucleobases. $EA_v(U) = 36 \pm 3$ meV, $EA_v(T) = 32 \pm 7$ meV, EA_v(1,3-DMU) = -34 ± 8 meV, and $EA_v(A)$ = -80 meV, are our best recommended extrapolated EA_v values from our experiments.

---

[a] J. Chen, A. M. Buonaugurio and K. H. Bowen, TBA

Intermission

MI06 **15 min 3:30**

A STUDY OF NbMo AND $NbMo^-$ BY ANION PHOTOELECTRON SPECTROSCOPY

PRAVEENKUMAR BOOPALACHANDRAN, SRIJAY S. RAJAN, MELISSA A. BAUDHUIN, and DOREEN G. LEOPOLD , *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.*

We report the 488 and 514 nm anion photoelectron spectra of $NbMo^-$. R2PI spectroscopic studies have established that neutral NbMo has a $^2\Delta_{5/2}$ ground state and a short bond length [a]. We find that the $NbMo^-$ anion has a $^1\Sigma^+$ ground state in which the "extra" electron occupies the (4d)δ bonding orbital, giving a $1\sigma^2 1\pi^4 1\delta^4 2\sigma^2$ valence electron configuration. Thus, $NbMo^-$ has a formal bond order of 6, and is isoelectronic with Mo_2. Low-lying excited states of NbMo ($^2\Sigma^+$) and $NbMo^-$ ($^3\Delta$) are also observed. The spectra provide the electron affinity of NbMo, energies of the $^2\Sigma^+$ and $^3\Delta$ excited states, vibrational frequencies in the anion and neutral molecule ground states and the $^2\Sigma^+$ state, $^2\Delta$ and $^3\Delta$ spin-orbit splittings, and (from Franck-Condon analyses) bond length measurements for the anion ground state and the observed excited states. These results are compared with previous anion photoelectron spectroscopic data for the Group 5/6 congeners VCr and VMo, and with density functional theory predictions.

---

[a] R. Nagarajan and M. D. Morse, J. Chem. Phys. 127, 164305 (2007).

MI07 15 min 3:47

RESONANT TWO-PHOTON DETACHMENT OF WO_2^-

JENNIFER E. MANN, SARAH E. WALLER, DAVID W. ROTHGEB, AND CAROLINE CHICK JARROLD, *Dept. of Chemistry, Indiana University, Bloomington, Indiana, 47405.*

The resonant two-photon detachment spectrum of WO_2^- in the $1.75 - 2.41$ eV range exhibits at least two electronic transitions near the detachment continuum of WO_2^-. The states are assigned to valence-bound states of the anion, rather than dipole bound states, in part because the observed bending frequencies are considerably lower than those in the neutral. One band exhibits doublets, which is attributed to spin-orbit splitting in the two $E_{1/2}$ sub-states of a quartet anion state. A qualitative assignment of the spectrum is made based on comparison with the photoelectron spectrum of WO_2^-, as well as density functional theory calculations.

MI08 15 min 4:04

ELECTRONIC STRUCTURES OF $MoAlO_y^-$ ($y = 1 - 4$) DETERMINED BY PHOTOELECTRON SPECTROSCOPY AND DFT CALCULATIONS

SARAH E. WALLER, JENNIFER E. MANN, EKRAM HOSSIAN, AND CAROLINE CHICK JARROLD, *Dept. of Chemistry, Indiana University, Bloomington, Indiana, 47405.*

Vibrationally-resolved photoelectron spectra of $MoAlO_y^-$ ($y = 1 - 4$) are presented and analyzed within the context of Density Functional Theory computational results. The structures reflect the relative stability of the Mo$-$O versus Al$-$O bond, with the Mo center in a higher oxidation state than Al. The highest occupied and partially occupied orbitals in the anions and neutrals can be described as Mo atomic-like orbitals, so while the Mo center is in a higher oxidation state, the most energetically accessible electrons are localized on the molybdenum center.

MI09 15 min 4:21

ANION PHOTOELECTRON ANGULAR DISTRIBUTIONS: ELECTRON SCATTERING RESONANCES IN PHOTODETACHMENT

RICHARD MABBS, *Washington University in St. Louis, St. Louis, Mo, 63130.*

To a large degree the photoelectron angular distributions (PAD) of anionic species represent signatures of the bound parent orbital. However, these angular distributions are also influenced by interaction of the outgoing electron with the neutral (atomic, molecular or cluster) residue. The electron kinetic energy evolution (eKE) of the PAD is presented for a number of different species (from molecular to cluster anion), showing the often striking effect of excitation of temporary excited anionic states. These cases highlight the influence of different types of electron-molecule scattering resonances in photodetachment dynamics. Additionally, the possibility of using the eKE evolution of the PAD for structural elucidation is discussed.

MI10 15 min 4:38

C-O AND O-H BOND ACTIVATION OF METHANOLE BY LANTHANUM

RUCHIRA SILVA, DILRUKSHI HEWAGE AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

The interaction between methanol (CH_3OH) molecules and laser-vaporized La atoms resulted in the cleavage of C-O and O-H bonds and the formation of three major products, LaH_2O_2, $LaCH_4O_2$ and $LaC_2H_6O_2$, in a supersonic molecular beam. These products were identified by time-of-flight mass spectrometry, and their electronic spectra were obtained using mass-analyzed threshold ionization (MATI) spectroscopy. From the MATI spectra, adiabatic ionization energies of the three complexes were measured to be 40136 (5), 39366 (5) and 38685 (5) cm^{-1} for LaH_2O_2, $LaCH_4O_2$ and $LaC_2H_6O_2$, respectively. The ionization energies of these complexes decrease as the size of the coordinated organic fragments increases. The most active vibrational transitions of all three complexes were observed to be the M-O stretches in the ionic state. A metal-ligand bending mode with a frequency of 127 cm^{-1} was also observed for $[LaH_2O_2]^+$. However, the spectra of the other two complexes were less resolved, due to the existence of a large number of low frequency modes, which could be thermally excited even in the supersonic molecular beams, and of multiple rotational isomers formed by the free rotation of the methyl group in these systems. The electronic transitions responsible for the observed spectra were identified as $^1A_1$ (C_{2v}) $\leftarrow$ $^2A_1$ (C_{2v}) for LaH_2O_2 and ^1A (C_1) $\leftarrow$ ^2A (C_1) for $LaCH_4O_2$ and $LaC_2H_6O_2$.

MI11 **15 min 4:55**

APPLICATION OF EQUATION-OF-MOTION COUPLED-CLUSTER THEORY TO PHOTODETACHMENT CROSS SECTION CALCULATIONS

TAKATOSHI ICHINO and JOHN F. STANTON, *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712.*

Photodetachment cross sections of atomic anions have been calculated with equation-of-motion coupled-cluster (EOM-CC) theory. Two techniques have been examined. One of them treats the photodetached electron as a plane wave, and the transition moment integral is evaluated with the Dyson orbital obtained from EOMIP-CC calculations. In the other technique, the EOM-EE method is utilized to calculate the oscillator strengths for photodetachment processes within the framework of moment theory. The results of these calculations are compared with experimental results, and the pros and cons of the two techniques are discussed.

MI12 **15 min 5:12**

ELECTRON PROPAGATOR THEORY OF AQUEOUS HALIDE PHOTOELECTRON SPECTRA

J. V. ORTIZ, *Department of Chemistry and Biochemistry*
Auburn University
Auburn, Alabama 36849-5312.

Electron binding energies and corresponding Dyson orbitals of solvated anions have been examined with *ab initio* electron propagator calculations on clusters that are embedded in a model electrostatic potential. Spectral predictions represent averages over solvent configurations that are generated by Monte–Carlo simulations with classical potentials. Predicted photoelectron spectra of aqueous alkali halide solutions are stable with respect to cluster size, basis set and self–energy approximations, and the sampling of solvent configurations. Dyson orbitals reveal a fundamental difference in electronic structure between fluoride and other halide solutions. Strong hydrogen bonding in the former case is responsible for delocalization of Dyson orbitals over many solvent molecules near the ionization threshold and for the dispersion of the fluoride contribution to the density of states over the inner–valence region of the spectrum. For other halides, Dyson orbitals near the ionization threshold are more localized on the anionic center.

MJ. MATRIX/CONDENSED PHASE

MONDAY, JUNE 18, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: MICHAEL HEAVEN, Emory University, Atlanta, Georgia

MJ01 **15 min 1:30**

IDENTIFICATION OF α- AND β-PROTONATED NAPHTHALENE ($C_{10}H_9{}^+$) AND THEIR NEUTRAL COUNTERPARTS ISOLATED IN SOLID PARA-HYDROGEN

MOHAMMED BAHOU, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*; YU-JONG WU, *National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan*; YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

We report the infrared (IR) spectra of protonated naphthalene ($C_{10}H_9{}^+$) and hydronaphthyl radical ($C_{10}H_9$) in both α- and β-forms trapped in solid para-hydrogen (p-H_2). These species were produced on electron bombardment of a mixture of p-H_2 and naphthalene during deposition. The IR features of α-$C_{10}H_9{}^+$ were identified on observing the decay of IR lines, whereas those of α-$C_{10}H_9$ and β-$C_{10}H_9$ were identified with the increased intensity after the matrix sample was maintained in darkness for an extended period. IR features of α-$C_{10}H_9$ and β-$C_{10}H_9$ were further characterized on irradiation of a matrix sample with UV or visible light. Irradiation of the matrix sample with visible light (495-700 nm) generated neutral $C_{10}H_9$ in both forms, whereas irradiation with light at 365 nm generated only α-$C_{10}H_9$. Lines due to β-$C_{10}H_9{}^+$ were observed only during the initial period of acquisition of an IR spectrum after secondary photolysis of the matrix sample. Observed wavenumbers and relative intensities agree satisfactorily with the anharmonic vibrational wavenumbers and IR intensities predicted for these species with the B3LYP/6-311++G(2d,2p) method. Compared with literature spectra recorded previously with IR photodissociation of Ar-tagged compounds[a] or IR multiphoton dissociation,[b] our method has the advantages of producing IR spectra with high resolution, true intensity and wide spectral coverage for both protonated polycyclic aromatic hydrocarbons and their neutral counterparts with little interference from other fragments. With these advantages, the IR spectra of α-$C_{10}H_9{}^+$ and β-$C_{10}H_9{}^+$ were clearly distinguished.

---

[a] A. M. Ricks, G. E. Douberly and M. A. Duncan, *Astrophys. J.* **702**, 301 (2009).

[b] U. J. Lorenz, N. Solcá, J. Lemaire, P. Maître and O. Dopfer, *Angew. Chem. Int. Ed,* **46**, 6714 (2007).

MJ02 **15 min 1:47**

INFRARED SPECTRA OF THE 2-CHLOROPROPYL RADICAL IN SOLID PARA-HYDROGEN

JAY C. AMICANGELO, *School of Science, Penn State Erie, Erie, PA 16563*; BARBARA GOLEC and YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

The reaction of chlorine atoms with propylene and one of its deuterium isotopomers in solid $para$-hydrogen (p-H_2) matrices at 3.2 K has been studied using infrared spectroscopy. Irradiation at 365 nm of a co-deposited mixture of Cl_2, C_3H_6, and p-H_2 at 3.2 K produces a series of new lines in the infrared spectrum. Several of the new lines are readily assigned to the gauche and trans conformers of 1,2-dichloropropane ($CH_3CHClCH_2Cl$) resulting from the addition of two Cl atoms to C_3H_6. Weak lines observed at 802 and 975 cm^{-1} and at 813 and 981 cm^{-1} that become more prominent upon secondary irradiation at 254 and 214 nm are assigned to the allyl radical (C_3H_5) and an HCl-allyl radical complex (HCl-C_3H_5), respectively[a]. Of the remaining lines, a strong line at 650 cm^{-1} and weaker lines at 532, 1008, 1133, 1150, 1215 and 1382 cm^{-1} are concluded to be due to a single carrier based on their behavior upon subsequent annealing to 4.5 K and irradiation at 254 and 214 nm. When the positions and intensities of these lines are compared to the MP2/aug-cc-pVDZ predicted vibrational spectra of the possible species that could result from the addition and abstraction reactions of one Cl atom with C_3H_6[a], the best agreement is found with the 2-chloropropyl radical ($CH_3CHClCH_2\cdot$). Isotopic experiments were performed with 3,3,3-$C_3H_3D_3$ and the corresponding infrared peaks due to the deuterium isotopomer of this radical ($CD_3CHClCH_2\cdot$) have also been observed. A final set of experiments were performed following irradiation of the $Cl_2/C_3H_6/p$-H_2 mixture at 365 nm, in which the matrix was irradiated with filtered infrared light from a globar source, which has been shown to induce a reaction between isolated Cl atoms and matrix H_2 to produce HCl and H atoms[b]. In our experiments, the major products observed after infrared irradiation are HCl, 2-chloropropane ($CH_3CHClCH_3$) and the isopropyl radical ($CH_3CH\cdot CH_3$) and the possible mechanisms of formation of these species will be discussed.

---

[a] P. Brana and J. A. Sordo, J. Comput. Chem. 24, 2044 (2003)

[b] P. L. Raston and D. T. Anderson, Phys. Chem. Chem. Phys. 8, 3124 (2006)

MJ03 **15 min 2:04**

DIFFUSION OF HYDROGEN FLUORIDE IN SOLID PARAHYDROGEN.

H. OOE, Y. MIYAMOTO, J. TANG, K. KAWAGUCHI, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530,Japan*; S. KUMA, K. NAKAJIMA, N. SASAO, T. TANIGUCHI, *Research Core for Extreme Quantum World, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530,Japan*; I. NAKANO and M. YOSHIMURA, *Faculty of Science, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530,Japan.*

In general, atoms and molecules diffuse thermally in solid with rate which has Arrhenius-type temperature dependence. On the other hand, it is known that diffusion rate at low temperature sometimes shows non-Arrhenius behavior, which is called ÂĄgquantum diffusionÂĄh[a]. We have studied hydrogen fluoride (HF) in solid parahydrogen (p-H_2) by FTIR absorption spectroscopy and found that HF diffuses in solid p-H_2 even at 3.6 K[b]. In this study, dependence of the rate on temperature, HF concentration and IR irradiation was investigated. Assuming Arrhenius-type dependence, activation energy of the diffusion is less than a few Kelvin, which suggests that the diffusion has the quantum nature. Recent experimental results and a possible mechanism of the diffusion will be discussed.

---

[a] Y. Kagan and A. J. Leggett *ÂĄgQuantum Tunneling In Condensed MediaÂĄh*, North Holland, 1992.

[b] Y. Miyamoto et al. *J. Phys. Chem. A* **115**, 14254 (2011).

MJ04 **15 min 2:21**

SPECTROSCOPIC AND COMPUTATIONAL STUDIES OF MATRIX ISOLATED ISO-$CXBr_3$ (X=F, Cl, Br)

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233*; BRIAN J. ESSELMAN, ROBERT J. MCMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

Iso-polyhalomethanes are important reactive intermediates in the condensed and gas-phase chemistry of halomethanes. Building upon our recent study of iso-bromoform, in this work the substituted iso-tribromomethanes (iso-$CXBr_3$; X = F, Cl, Br) were characterized by matrix isolation infrared and UV/Visible spectroscopy, supported by *ab initio* calculations, to further probe the structure, spectroscopy, properties, and photochemistry of these important intermediates. Selected wavelength laser irradiation of $CXBr_3$ samples in an inert rare gas (typically Ar; mixing ratio 1:500) held at ~5 K yielded iso-$CXBr_3$ (XBrC-Br-Br or Br_2C-Br-X). The observed infrared and UV/Visible absorptions are in excellent agreement with computational predictions, and the energies of various stationary points on the $CXBr_3$ Potential Energy Surfaces (PESs) were characterized computationally using DFT, MP2, and CCSD(T) methods in combination with triple and quadruple-zeta quality basis sets. These calculations show that the isomers are minima on the PESs that lie ~200 kJ/mol above the global $CXBr_3$ minimum, yet are bound by some 60 kJ/mol in the gas-phase with respect to the $CXBr_2$ + Br asymptote. Laser irradiation of the isomers resulted in back photoisomerization to $CXBr_3$, and intrinsic reaction coordinate (IRC) calculations confirmed the existence of a first order saddle point connecting the two isomers. Calculations of important stationary points on the $CXBr_3$ PESs show that in the gas-phase the isomerization barrier lies energetically near the threshold for simple bond fission. The iso-$CXBr_3$ species are significantly stabilized in the condensed phase, due to the high degree of ion-pair character, as revealed by Natural Resonance Theory analysis.

MJ05 **15 min 2:38**

SPECTROSCOPY OF AND PHOTOINDUCED ELECTRON TRANSFER IN THE COMPLEXES OF C_2H_4 WITH I AND I_2

LISA GEORGE, AIMABLE KALUME AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

The charge-transfer complex of ethylene and iodine was isolated in a neon matrix and characterized by infrared and electronic spectroscopy, supported by *ab initio* and Density Functional Theory (DFT) calculations which predict the spectra, structure, and binding energy of the complex. The intense charge transfer band of the complex was observed at 247 nm, in good agreement with Time Dependent DFT predictions. Photoinduced electron transfer initiated by laser irradiation at 240 nm gave rise to an intense band at 373 nm which is assigned to bridged ethylene-I atom radical complex. It is postulated that, following excitation of the charge transfer band, rapid back electron transfer leaves the neutral I_2 fragment on an excited repulsive potential surface, which leads to rapid cleavage of the I-I bond. This is consistent with previous gas-phase studies of arene-I_2 complexes. The photolysis of the radical complex, initiated by laser irradiation at 355 nm, led to the reappearance of absorptions due to the ethylene-I_2 complex and the appearance of both the *anti−* and *gauche−* conformers of the electrophilic addition product, 1,2-diiodoethane, indicating the importance of a radical addition mechanism.

MJ06 **15 min 2:55**

CALCULATION OF RAMAN FREQUENCIES AS FUNCTIONS OF TEMPERATURE AND PRESSURE IN PHASES OF SOLID I, II AND III (III') OF BENZENE

H. YURTSEVEN, *Department of Physics, Middle East Technical University, 06531 Ankara-Turkey*; O. TARI, *Department of Mathematics, Istanbul Arel University, Istanbul, Turkey*.

The Raman frequencies of the lattice modes (A,B and C) are calculated as a function of temperature at constant pressures of 0, 1.4 and 3.05 GPa in the solid phase I of benzene using the volume data through the mode Grüneisen parameter. The Raman frequencies of those lattice modes (A, B and C) are also calculated as a function of pressure at constant temperatures of 274 and 294K in the solid phase I of benzene using the volume data.
Finally, calculation of the Raman frequencies of the lattice modes (A, B and C) studied here are calculated at various pressures (T=294 K) in the solid phases of II, III and III' of benzene using the volume data from the values of the Grüneisen parameter of the lattice modes.
Our calculated frequencies of the Raman modes studied decrease with increasing temperature and they increase with increasing pressure in phase I, as observed experimentally. The calculated Raman frequencies of the lattice modes A, B and C also increase as the pressure increases in the phases II, III and III', as reported experimentally. This shows that our method of calculating the Raman frequencies from the volume data is satisfactory to predict the observed behavior in the solid phases of I, II, III and III' in benzene.

Intermission

MJ07 **15 min 3:30**

HELIUM NANODROPLET ISOLATION OF IONIC LIQUID VAPOR: INRARED LASER SPECTROSCOPY OF [EMIM][Tf_2N]

STEVEN D. FLYNN, GARY E.DOUBERLY, *Department of Chemistry, University of Georgia, Athens, Georgia, USA 30602*.

The Infrared spectrum of the vapor produced upon thermal vaporization of the [emim][Tf_2N][a] ionic liquid has been obtained using the helium nanodroplet isolation method. Despite the low vapor pressure of [emim][Tf_2N], sufficient gas phase densities are produced, allowing for efficient helium nanodroplet pick-up. The mass spectrum of the emim[Tf_2N] doped droplet beam shows signatures[b] that have been attributed in gas phase measurements to the presence of isolated, intact [emim][Tf_2N] ion-pairs. Furthermore, the mass spectrometry results indicate that emim[Tf_2N] does not undergo thermal decomposition at 410 K. Comparisons are made between the experimental measurements and *ab initio* calculations (mp2/6-311++g(d,p)) of the CH stretch vibrational bands and permanent electric dipole moments for several [emim][Tf_2N] low energy isomers. The helium nanodroplet infrared spectrum of this species provides rather definitive support to the previously suggested vaporization mechanism of ionic liquids.[c]

---

[a] [emim][Tf_2N] is defined as 1-ethyl-3-methylimidazolium[bis(trifluoromethylsulfonyl)imide]

[b] Armstrong, J.P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. *Physical Chemistry Chemical Physics* **2007**, *9*, 982.

Strasser, D.; Goulay, F.; Belau, L.; Kostko, O.; Koh, C.; Chambreau, S. D.; Vaghjiani, G. L.; Ahmed, M.; Leone, S. R. textitJournal of Physical Chemistry A **2010**, textit114, 879.

[c] Strasser, D.; Goulay, F.; Kelkar, M. S.; Maginn, E. J.; Leone, S. R. *Journal of Physical Chemistry A* **2007**, *111*, 3191.

Chambreau, S. D.; Vaghjiani, G. L.; To, A.; Koh, C.; Strasser, D.; Kostko, O.; Leone, S. R. *Journal of Physical Chemistry B* **2010**, 114, 1361.

Maginn, E. J.; Kelkar, M. S. *Journal of Physical Chemistry B* **2007**, *111*, 9424.

MJ08 15 min 3:47

C_{60}^+ AND C_{60}^- IN NEON AND ARGON MATRICES

BASTIAN KERN, DMITRY STRELNIKOV, PATRIK WEIS, ARTUR BÖTTCHER and MANFRED M. KAPPES, *KIT Karlsruhe Institute for Technology, Division of Physical Chemistry of Microscopic Systems, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany.*

Mass-selected C_{60} anions have been deposited in noble gas matrices (Ne,Ar) kept at 6K. The vibronic properties of the species (C_{60}^+, C_{60}^0, C_{60}^-) were determined by NIR and MID-IR absorption spectroscopy. By co-depositing electrons without the addition of electron scavengers or donors to the host matrix, we were able to vary the C_{60}^+/C_{60}^- ratio. By changing the C_{60}^+/C_{60}^- ratio, previously known vibrational data of the C_{60}^+ and C_{60}^- species could be confirmed and also extended further. DFT calculations performed on isolated C_{60}^+ and C_{60}^- ions support the experimental assignment.

MJ09 10 min 4:04

FTIR OF METHYL PYRUVATE CONFORMERS IN AN ARGON MATRIX

ALLISON B. COMBS, JORDAN L. PRESTON, SARA E. LILLY, COURTNEY D. HATTEN, and LAURA R. MCCUNN, *Department of Chemistry, One John Marshall Drive, Huntington, WV 25755.*

Methyl pyruvate has been isolated in a low-temperature argon matrix and its vibrational spectrum recorded by FTIR. The spectrum is compared to results from B3LYP/6-311++G** optimization and frequency calculations for the s-cis and s-trans conformers of methyl pyruvate. The s-cis conformer of methyl pyruvate is predicted to have an energy of 1.03 kcal/mol relative to the s-trans conformer, with a barrier height of 2.66 kcal/mol for interconversion between the two conformers. Unique bands of both conformers have been identified in the FTIR spectrum and then compared to the simulated spectra to determine that matrix-isolated methyl pyruvate is composed of approximately 92% s-trans conformer.

MJ10 15 min 4:16

FTIR AND DFT STUDY OF THE VIBRATIONAL SPECTRUM OF SiC_5 TRAPPED IN SOLID Ar

T. H. LE, and W. R. M. GRAHAM, *Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX 76129.*

This paper follows preliminary results on the SiC_5 molecule presented earlier. An absorption at 936.9 ± 0.2 cm^{-1} has been identified as the $\nu_4(\sigma)$ Si-C stretching fundamental of linear SiC_5. Its assignment has been confirmed by the close agreement between DFT predicted and observed ^{13}C isotopic shifts. DFT-B3LYP calculations predict that two other C-C fundamentals, $\nu_1(\sigma)$ and $\nu_2(\sigma)$ of SiC_5 should have intensities 10 to 15 times stronger than $\nu_4(\sigma)$, but would appear in the C-C stretching frequency regions.

Refinements of the Si-C laser ablation techniques have helped to reveal the isotopic ^{13}C shifts for two additional absorptions at 2045.0 and 1992.9 cm^{-1}. Comparison of their observed isotopic shifts with the predictions of DFT calculations at the MPW1PW91/6-311+G(3fd) level have led to their assignment to the $\nu_1(\sigma)$ and $\nu_2(\sigma)$ fundamentals of SiC_5.

MJ11 **15 min 4:33**

VIBRATIONAL SHIFT OF ADSORBED CARBON DIOXIDE WITHIN A METAL-ORGANIC FRAMEWORK

S. FITZGERALD, C. PIERCE, J. SCHLOSS, B. THOMPSON, *Department of Physics and Astronomy, Oberlin College, Oberlin, OH 44074*; J. ROWSELL, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*.

There is much interest in a class of materials known as Metal-Organic Frameworks (MOFs). While practical applications center on hydrogen storage and carbon sequestration, these highly porous, crystalline materials also provide an excellent opportunity for performing matrix isolation experiments. In this talk we will present data on MOF-74, a honey-comb structure consisting of metal-oxide units linked by aromatic rings. Infrared spectra show that for a series of different metal cations, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} the vibrational modes of adsorbed CO_2 are all red shifted relative to the gas phase values. In contrast the ν_3 mode of CO_2 adsorbed within the Mg version of MOF-74 is unique in showing a blue shift. It is accompanied by broader sidebands associated with librational or center of mass motion of the adsorbed CO_2. Spectra obtained below 100 K show the emergence of a second ν_3 band indicating a further distortion of the CO_2 molecule. These results will be discussed in terms of the interaction mechanisms of the different metal cations and in particular the fact that the Mg version of MOF-74 has a very strong affinity for CO_2 with a binding enenergy of 47 kJ/mol, more than 5 kJ/mol greater than any other MOF.

MJ12 **5 min 4:50**

SYMMETRY PECULIARITIES OF THE INTRACRYSTALLINE FIELDS LAYERED SEMICONDUCTOR CRYSTALS $(PbI_2)_{(1-x)}$ $(BiI_3)_{(x)}$

IGOR VERTEGEL, EUGENE CHESNOKOV and ALEKSANDR OVCHARENKO, *Institute of Physics National Academy of Sciences of Ukraine 46, Prospect Nauki, 03680 Kiev, Ukraine*.

In this work the results of the investigation of the ^{127}I NQR spectra at 77K for mixed layered semiconductor crystals $(PbI_2)_{(1-x)}$ $(BiI_3)_{(x)}$ in a wide range of value (0 <x <0.50) are presented. It is shown that in the range 0.05 <x <0.20 of admixture PbI_2 the observed behavior of parameters of the ^{127}I NQR spectra testify about entrance of admixture atoms PbI_2 into the crystal layers. It is shown, that at 0.05 <ă x <0.20 clusters from groups of atoms PbI_2 insular type can be formed, which lay within the limits of the layers of crystal $(PbI_2)_{(1-x)}$ $(BiI_3)_{(x)}$. Upon further increasing of the containing of admixture PbI_2 in crystal BiI_3 the ÂŞnewÂŤ ^{127}I NQR line is appearing. The observed at x ~ 0.20 the new line in spectrum ^{127}I NQR can testify that the mixed crystal $(PbI_2)_{(1-x)}$ $(BiI_3)_{(x)}$ undergoes structural phase transition. It is concluded that at x>0.20 a new crystal presents a solid mixture glassy crystal of substitution type in which of PbI_2 atoms are fully or partially are ordering and lay between crystal[a] .

---

[a] A.I.Barabash, I.G.Vertegel, E.D.Chesnokov et.al., Ukr. J.Phys., 2011,vol.56, No.2, p.158-160.

MJ13 **15 min 4:57**

COMBINED EXPERIMENTAL AND THEORETICAL STUDIES ON THE VIBRATIONAL SPECTRA OF SOME QUINOLINECARBOXALDEHYDE MOLECULES-I

MUSTAFA KUMRU, *Department of Physics, Faculty of Arts and Sciences, Fatih University, 34500 Büyükçekmece, Istanbul, Turkey, mkumru@fatih.edu.tr*.

Combined experimental and theoretical studies have been performed on the structure and vibrational spectra (FT-IR, FT-Raman, Dispersive Raman spectra including far region) of some quinolinecarboxaldehyde molecules. Hartree-Fock (HF) and density functional B3LYP calculations have been employed with the 6-311++G(d,p) basis set for investigating the structural and spectroscopic properties of the *cis* and *trans* conformers of quinolinecarboxaldehyde. The B3LYP frequencies are closer to the experimental frequencies than the HF frequencies, but scaled frequencies of both HF and B3LYP agree almost perfectly with the experimental frequencies. The *cis* conformer has been found more stable than the *trans* conformer. The scaled vibrational frequencies of *cis* conformer also agree slightly better than those of the *trans* conformer with the experimental frequencies.

1. V. Kçük, A. Altun, M. Kumru, Spectrochimica Acta Part A 85(2012)92-98
2. M. Kumru, V. Küçük, T. Bardakç, Spectrochimica Acta Part A 90(2012)28-34

We thank the Turkish Scientific and Technical Research Council (TÜBÍTAK) for their financial support through National Postdoctoral Research Scholarship Programme and Scientific Research Fund of Fatih University under the project number P50011001_G (1457).

TA. ATMOSPHERIC SPECIES

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 160 MATH ANNEX

Chair: LINDA BROWN, Jet Propulsion Laboratory, Pasadena, California

TA01 **15 min 8:30**

FREQUENCY COMB-REFERENCED MEASUREMENTS OF SELF- AND NITROGEN-PERTURBED LINE SHAPE PARAMETERS IN THE $\nu_1 + \nu_3$ BAND OF ACETYLENE

MATTHEW J. CICH, GARY V. LOPEZ, TREVOR J. SEARS[a], *Department of Chemistry, Stony Brook University, Stony Brook, New York 11794*; C. P. MCRAVEN, *Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973*; A. W. MANTZ, *Department of Physics, Astronomy, and Astrophysics, Connecticut College, New London, CT 06320*; and DANIEL HURTMANS, *Service de Chimie Quantique et de Photophysique(Atoms, Molecules et Atmospheres), Universite Libre de Bruxelles, Bruxelles, Belgium B-10050.*

Using an extended cavity diode laser locked to a single component of an Er-fiber-based femtosecond frequency comb, we have made precise measurements of absorption spectral line shapes in a temperature controlled cell. Varying pressures of acetylene and nitrogen were used to determine the N_2 pressure-dependent parameters for the P(11) line in the $\nu_1 + \nu_3$ combination band of acetylene at 195 739.649 513(8) GHz. The temperature dependence of the line shape was determined from measurements at several temperatures, varying from 296 K to 125 K. With the absolute frequency positions at each point on the frequency scale determined by the comb, each experimental data set has better than 10^{-4} fractional error. Parameters describing the line shape, such as pressure-dependent broadening, narrowing and shift coefficients, can be obtained with standard deviations less that 0.1%. The data have been used to test various line shape models beyond the standard Voigt approximation including those with narrowing parameters (Rautian and Galatry models) and those with speed-dependence (Speed-dependent Voigt and Speed-dependent Nelkin-Ghatak models). Fitting results will be presented and the relative performance of the models will be discussed.

Acknowledgements:Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. CPM gratefully acknowledges support by DOE EPSCoR grant DOE-07ER46361 for work conducted at the University of Oklahoma. The measurements and analyses were performed under grants NNX09AJ93G and NNX08AO78G from the NASA Planetary and Atmospheres program.

---

[a] also: *Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973*

TA02 **15 min 8:47**

HIGH ACCURACY MEASUREMENTS OF NEAR-INFRARED CO_2 AND O_2 TRANSITIONS TO SUPPORT ATMOSPHERIC REMOTE SENSING

DAVID A. LONG, JOSEPH T. HODGES, *Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA*; and CHARLES E. MILLER, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.*

Recent remote sensing missions such as NASA's Orbiting Carbon Observatory (OCO-2) have aimed to measure carbon dioxide mixing ratios with a precision of 1 ppm (0.25%) in order to elucidate carbon sources and sinks. This daunting mission objective will require some of the most accurate spectroscopic reference data ever assembled. To address this need we have utilized frequency-stabilized cavity ring-down spectroscopy (FS-CRDS), an ultraprecise refinement of traditional cw-cavity ring-down spectroscopy, to measure CO_2 and O_2 transitions in the near-infrared. We will discuss new line lists as well as observations of subtle line shape effects such as Dicke narrowing, speed-dependence, and line mixing. The effects of line list and line shape on O_2 A-band atmospheric retrievals were assessed using simulated atmospheric transmission spectra. Furthermore, we will discuss a series of enhancements we have made to our spectrometer including high-bandwidth Pound-Drever-Hall locking and the use of a self-referenced optical frequency comb as an absolute frequency reference.

TA03 **15 min 9:04**

TRACE GAS MEASUREMENTS WITH A MULTIPLEXED INTRA-PULSE QUANTUM CASCADE LASER SPECTROMETER

D. WILSON, G. DUXBURY and N. LANGFORD, *Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland,UK.*

Quantitative measurements of the equilibrium concentrations of nitrogen dioxide and dinitrogen-tetroxide have been made using a multiplexed intra-pulse QC laser spectrometer. The measurements were made using long duration pulses from 7.84 and 7.46 micron Quantum Cascade (QC) lasers in the QC laser spectrometer. For double pulse operation the pulse signal from the first laser controller is used to generate a delayed optical pulse from the second laser by using a digital delay pulse generator.This allows two spectra to be recorded sequentially using the 2 Gs high speed digitiser. The spectra are compared with the dimer spectra recorded by J Vander Auwera and his colleagues using using a high resolution Fourier transform spectrometer at the Free University of Brussels.

TA04 **15 min 9:21**

ISOTOPICALLY INVARIANT DUNHAM FIT FOR THE $X^3\Sigma_g^-$, $a^1\Delta_g$, AND $b^1\Sigma_g^+$ STATES OF OXYGEN

SHANSHAN YU, CHARLES E. MILLER AND BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; HOLGER S.P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.*

At the last meeting, we reported the preliminary results on an isotopically invariant Dunham-type fit of the six oxygen isotopologues including experimental data for $v = 0 - 18$ in $X^3\Sigma_g^-$, $v = 0 - 10$ in $a^1\Delta_g$, $v = 0 - 12$ in $b^1\Sigma_g^+$. At this meeting we report the the results of our complete fit, with additional experimental data for $v = 7 - 23$ and $26 - 31$ in $X^3\Sigma_g^-$. A total of 11879 transitions were collected and fitted with a reduced RMS near unity. We made empirical adjustments to remove apparent offsets between datasets by adding/subtracting individual values based on comparison of repeated measurements and/or our model prediction. It was found that the parameters describing the breakdown of the Born-Oppenheimer approximation were of the expected order of magnitude and showed little variation among the electronic states. Dunham potentials were derived and will be presented. To the best of our knowledge, this is the first analysis that simultaneously fits spectra from all six oxygen isotopologues.

TA05 **15 min 9:38**

THE ROTATIONAL SPECTRA OF O-17 SUBSTITUTED OXYGEN SINGLET DELTA

BRIAN J. DROUIN, HARSHAL GUPTA, SHANSHAN YU, CHARLES E. MILLER, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099*; HOLGER S. P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937, Köln, Germany.*

As part of a comprehensive review on molecular oxygen spectroscopy we have measured rotational spectra of isotopic forms of molecular oxygen in its $a^1\Delta_g$ electronic state with high resolution THz spectroscopy. A previously described static discharge cell has been utilized to record spectra of rare isotopologues of excited oxygen[1]. In this work the data set is extended to include all of the ^{17}O substituted isotopologues of O_2 $^1\Delta$. The spectral features were detected in close proximity to predicted positions. Due to the high resolution and good signal to noise ratio, the fundamental hyperfine parameters eQq and C_I are determinable for ^{17}O substituted species for the first time. A refined nuclear spin-orbit coupling constant, $a = -211.9328(283)$ MHz, was determined, and is roughly two orders of magnitude more precise than values determined from near infrared spectroscopy or electron spin resonance studies. Weak signals of vibrationally excited oxygen in the $a^1\Delta_g$ electronic state were also observable for many of the rotational transitions.

[1] H. Gupta, S. Yu, B.J. Drouin, C.E. Miller - RC03, International Symposium on Molecular Spectroscopy, Ohio State University, 2010.

TA06 **10 min 9:55**

LINE MIXING EFFECTS OF O_2 A-BAND WITH PHOTOACOUSTIC SPECTROSCOPY IN SUPPORT OF REMOTE SENSING

THINH Q. BUI[a], DANIEL HOGAN, PRIYANKA M. RUPASINGHE, MITCHIO OKUMURA, *California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125*; DAVID A. LONG and JOSEPH T. HODGES, *NIST, 100 Bureau Drive, Stop 1070, Gaithersburg, MD 20899-1070*; CHARLES E. MILLER, *Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109.*

To achieve NASA's strategic scientific mission of monitoring global atmospheric CO_2 at an unprecedented precision of ÂÂś0.25%, we perform laser based measurements and lineshape studies of the reference atmospheric target O_2 A-band at 760nm to meet the precision requirements of current (ACOS/GOSAT/TCCON) and future (OCO-2/OCO-3/ASCENDS) remote sensing applications. We utilize a novel, high precision (ÂÂś0.01% uncertainty) photoacoustic spectrometer (PAS), at high spectral resolution with a large dynamic range, to provide unique measurements of unsaturated lineshapes of the O_2 A-band to study line-mixing effects currently unaccounted for in spectroscopic databases like HITRAN. Line mixing effects along with other non-Voigt features (Dicke narrowing, collisional induced absorption) will be captured for remote sensing relevant pressures (0.1atm-5atm) and incorporated into a new spectral line profile. We discuss our progress towards this goal.

---

[a] Support from NSF Graduate Fellowship and NASA OCO Funding are gratefully acknowledged

Intermission

TA07 **10 min 10:30**

BROADBAND OZONE ABSORPTION CROSS SECTIONS IN NEAR UV - NEAR IR

ANNA SERDYUCHENKO, VICTOR GORSHELEV, MARK WEBER and JOHN P. BURROWS, *Institute of Environmental Physics, University of Bremen, Germany.*

The global monitoring of the ozone concentration using both satellite borne and ground based instruments plays a key role in the determination of the long-term trends for the stratospheric ozone layer and air quality related studies. The requirement to measure small changes in stratospheric and tropospheric ozone places strong demands on the accuracy of the ozone absorption cross-sections used in retrievals of the spectra delivered by remote sensing spectrometers.

We report on the new dataset, which uniquely combines spectral resolution as high as 0.02 nm with a broad spectral coverage from 220 nm to 1100 nm for convenient use in various current and future projects. The new dataset enables the accurate convolution with the slit functions of all currently relevant ground based and satellite based remote sensing instruments. The absolute accuracy of about three percent or better for most of the spectral range, and wavelength accuracy better than 0.005 nm, has been achieved at eleven temperatures from 195 to 293K.

New dataset includes regions poorly covered so far. In overlapping regions comparison of the new ozone cross-sections with the previously available datasets shows good agreement within the uncertainty limits. We provide analysis of the consistency of our dataset and report on the impact of the new data on the ozone retrievals based on tests performed by different groups.

We believe that the new cross-sections have inherited and combined the advantages over the previous datasets to the maximum possible extent. New dataset is available for scientific community. We hope that groups working on the ozone observations will find new dataset useful on a long-term basis.

TA08 **15 min 10:42**

AIR-BROADENED LINE PARAMETERS FOR THE 2←0 BANDS OF $^{13}C^{16}O$ AND $^{12}C^{18}O$ AT 2.3 μm

V. MALATHY DEVI, D. CHRIS BENNER, *The College of William and Mary, Williamsburg, VA 23187*; M. A. H. SMITH, *Science Directorate, NASA Langley Research Center, Hampton, VA 23681*; A. W. MANTZ, *Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320*; K. SUNG and L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*.

Air-broadened line shape parameters were determined for the first time in the 2←0 bands of $^{13}C^{16}O$ near 4166.8 cm^{-1} and $^{12}C^{18}O$ near 4159.0 cm^{-1}. Spectra were recorded at 0.005 cm^{-1} resolution using a coolable absorption cell[a] in the sample compartment of the Bruker IFS 125HR Fourier transform spectrometer at Jet Propulsion Laboratory. Gas temperatures and pressures ranged from 150 to 298 K and 20 to 700 Torr, respectively. Line parameters were determined by broad-band multispectrum least-squares fitting[b] of the 4000-4360 cm^{-1} region in 16 spectra simultaneously; each set included 4 isotope-enriched pure sample scans and 12 air+CO samples (^{13}CO or $C^{18}O$, as appropriate). The air-broadened parameters measured were Lorentz half-width coefficients, their temperature dependence exponents; pressure-induced shift coefficients, their temperature dependences; and off-diagonal relaxation matrix elements. Speed dependence parameters were included to minimize the fit residuals. For both isotopologues the individual line positions and intensities were constrained to their theoretical relationships in order to obtain the rovibrational (G, B, D, and H) and band intensity parameters, including Herman-Wallis coefficients[c]. The results for $^{13}C^{16}O$ and $^{12}C^{18}O$ are compared with those for the $^{12}C^{16}O$ 2←0 band[d] and discussed.[e]

---

[a] K. Sung, A. W. Mantz, M. A. H. Smith, et al., *JMS* **262** (2010) 122-134.

[b] D. C. Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. A. Atkins, *JQSRT* **53** (1995) 705-721.

[c] V. Malathy Devi, D. C. Benner, L. R. Brown, C. E. Miller and R. A. Toth, *JMS* **242** (2007) 90-117.

[d] V. Malathy Devi, D. C. Benner, M. A. H. Smith, et al., *JQSRT* (2012) in press.

[e] Research described in this paper was performed at Connecticut College, the College of William and Mary, NASA Langley Research Center and the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

TA09 **15 min 10:59**

SPEED DEPENDENT LINE SHAPES IN 1.61 μm AND 2.07 μm CO_2 ATMOSPHERIC RETRIEVALS FOR THE OCO-2 MISSION

DAVID R. THOMPSON, LINDA R. BROWN, DAVID CRISP, YIBO JIANG, FABIANO OYAFUSO, KEEYOON SUNG, CHARLES E. MILLER, VIJAY NATRAJ, DEBRA WUNCH, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr.,Pasadena, CA 91109, U.S.A.*; D. CHRIS BENNER, V. MALATHY DEVI, *The College of William and Mary, Williamsburg, VA 23187, U.S.A.*.

We are validating line parameters for CO_2 at 1.61 μm and 2.07 μm using high resolution atmospheric spectra and a new retrieval algorithm [1, 2] being developed for the Orbiting Carbon Observatory (OCO-2) in order to estimate column-averaged mixing ratio of CO_2, X_{CO2}, to a sub-1% precision. This requirement demands highly accurate molecular line shape models. We tested a combination of line mixing [3] with speed dependent Voigt shapes [4,5] obtained from laboratory spectra using a state of the art multi-spectrum fitting procedure [6, 7]. The atmospheric tests were made with a diverse set of over 400 soundings including upward- and downward-looking FT-IR data from the Total Carbon Column Observing Network (TCCON), and the data from TANSO-FTS spectrometer aboard the Greenhouse gases Observing SATellite (GOSAT), respectively. The new absorption cross sections significantly reduced residuals in the spectral fit in the 2.07 μm region, while the effects on the 1.61 μm band are less definitive but still suggest some improvement. Overall these tests favor the adoption of the new models.[ab]

---

[a] [1] O'Dell C.W., et al. *AMT* 2012; 5:99-121. [2] Crisp, D., et al. *AMTD* 2012; 5:1 - 60. [3] Hartmann, J. M., et al. *ACP* 9:7303-7312. [4] Devi et al., *J. Mol.Spec.* 2007; 245:52-80. [5] Benner et al. 66th International Symposium on Molecular Spectroscopy, Columbus OH (2011). [6] Benner, D.C., et al., *JQSRT* 1995; 53(6):705 - 721. [7] Letchworth, K.L., et al. *JQSRT*, 107: 173 - 192.

[b] The research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology and at The College of William and Mary under contracts with National Aeronautics and Space Administration. US Government Support Acknowledged.

TA10 **15 min 11:16**

THE ν_3 AND ν_4 BANDS OF NITRIC ACID (HNO_3) AT 7.6 μm FOR ATMOSPHERIC STUDIES

A.PERRIN, J.M.FLAUD, *Laboratoire Inter Universitaire des Systemes Atmosphériques, CNRS, Université Paris EST-Créteil, 61 Av du General de Gaulle, 94010 Créteil Cedex France*; M.RIDOLFI, M.CARLOTTI, *Dipartimento di Chimica Fisica e Inorganica (DCFI), Universiy of Bologna, Viale del Risorgimento, 4 - 40136 - Bologna, Italy.*

Nitric acid (HNO_3) plays an important role as a reservoir molecule of the NO_x (nitrogen oxides) species in the stratosphere. The three strongest infrared bands of nitric acid are located at 11 μm (ν_5 and $2\nu_9$ bands), 7.6 μm (the ν_3 and ν_4 bands at 1326 and 1303 cm^{-1}) and 5.8 μm (ν_2 band). Although two times weaker than those located at 7.6 and 5.8 μm, the 11 μm region is the only one which is used for nitric acid retrievals in the atmosphere by several satellite instruments like MIPAS (Michelson Interferometer for Passive Atmospheric Sounding on ENVISAT) or ACE-FTS (ACE Fourier transform spectrometer on SCISAT). This is because the available spectroscopic parameters for HNO_3 in the HITRAN [a] and GEISA [b] databases are of very good quality in this spectral region. Of the two remaining bands, the 7.6 μm one is only partly masked by water, and therefore can be used also for nitric acid retrievals in the upper stratosphere. Moreover, because of their large difference in band intensity, combining measurements at 11 μm and 7.6 μm could maximize informations on the vertical distribution of HNO_3 in the atmosphere. However at 7.6 μm the spectroscopic parameters available in the HITRAN and GEISA databases are are not so good. Indeed, these parameters originate from a list generated more than 20 years ago [c]. The low quality of the list at 7.6 μm prevents HNO_3 retrievals and severely affects the retrievals of several species absorbing in the 7.5-7.7 μm region, like SO_2. This work is a new and more accurate investigation of the line positions and intensities for the ν_3 and ν_4 bands of nitric acid located at 1326.187 and 1303.074 cm^{-1}). For this task, we used new infrared laboratory data combined with a new theoretical model. Examples showing substantial improvements will be given.[d]

---

[a] Rothman et al. J. Quant. Spectrosc. Radiat. Transf., 110, 533-572, 2009

[b] Jacquinet et al. J. Quant. Spectrosc. Radiat. Transf., 112, 2395-2445, 2011

[c] A. Perrin, O. Lado-Bordowski, and A.Valentin, Mol. Physics. 67, 249 (1989)

[d] Financial support from the GDRI HiResMIR is gratefully acknowledged

TA11 **15 min 11:33**

FIRST HIGH RESOLUTION ANALYSIS OF THE $5\nu_3$ BAND OF NITROGEN DIOXIDE NEAR 1.3 μm

D.MONDELAIN, S.KASSI, A.CAMPARGUE, *Laboratoire Interdisciplinaire de Physique (LIPhy), UMR-CNRS 5588, Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France*; A. PERRIN, *Laboratoire Inter Universitaire des Systemes Atmosphériques (LISA), CNRS, Universités Paris Est and Paris 7, 61 Av du Général de Gaulle, 94010 Créteil Cedex France.*

The first high-resolution absorption spectrum of the $5\nu_3$ band of the ^{14}N^{16}O$_2$ molecule at 7766.071 cm^{-1} was recorded by high sensitivity CW-Cavity Ring Down Spectroscopy between 7674 and 7795 cm^{-1}. The noise equivalent absorption of the recordings was α_{min}=5 Œ10^{-11}cm^{-1}. The assignments involve energy levels of the (0,0,5) vibrational state with rotational quantum numbers up to K_a=9 and N=47. The set of the spin-rotation energy levels were reproduced within their experimental uncertainty using a theoretical model which takes explicitly into account the Coriolis interactions between the spin rotational levels of the (0,0,5) vibrational state and those of the (0,2,4) dark state together with the electron spin-rotation resonances within the (0,0,5) and (0,2,4) states. Precise values were determined for the (0,0,5) vibrational energy rotational, spin-rotational constants and for the (0,2,4)↔(0,0,5) coupling constants. In addition the (0,2,4) vibrational energy and rotational, spin-rotational constants were estimated. Using these parameters and the value of the transition dipole moment operator determined from a fit of a selection of experimental line intensities, the synthetic spectrum of the $5\nu_3$ band was generated.

TB. DYNAMICS

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 170 MATH ANNEX

Chair: SCOTT KABLE, University of Sydney, Sydney, Australia

TB01 **15 min 8:30**

LIFETIMES OF THE Ã STATES OF C_3, C_3-NE, AND C_3-AR

YI-JEN WANG, CHIAO-WEI CHEN, LIUZHU ZHOU, ANTHONY J. MERER, YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei 10617, Taiwan, R. O. C.*.

The fluorescence lifetimes of the Ã states of C_3, C_3-Ne and C_3-Ar have been measured under supersonic molecular beam conditions. To minimize possible collisional quenching, the lifetimes of all three species were measured at a distance of about 42 nozzle diameters from the orifice. For all the vibrational levels of the Ã state of the C_3 monomer, only $J'=1$ lifetimes were recorded, using R(0) lines. The accuracy of the lifetimes obtained was estimated to be better than 3ns. General features of the lifetimes of the C_3 monomer are as follows: with increasing excitation of the symmetric stretching vibration, the lifetimes increase to a maximum at $v_1=4$. Bending excitation reduces the lifetimes, though exceptions occur for the 0 v 0 and 1 v 0 levels. Among all the vibrational levels, $0\ 2^-\ 0$, $0\ 4^-\ 0$, and $0\ 2^+\ 0$ have the shortest lifetimes, similar to that of the origin level [a]. Lifetimes of the Ã state of C_3-Ne and C_3-Ar have only been measured for features 1.5-2 and 11-14 cm^{-1}, respectively, to the red of the R(0) lines of the Ã−X̃ bands of free C_3. It is not possible to reduce the backing pressure while measuring lifetimes of the complexes; we therefore reduced the average pressure of the chamber to 1-2x10^{-5} torr by lowering the repetition rate. No sign of predissociation was found in the Ne complex except for the level $0\ 12^+\ 0$. The lifetimes of the complexes did not vary with vibration in the manner found for C_3 itself. The lifetime of the $0\ 2^-\ 0$ level, one of the lowest vibrational levels of the Ã state, was not affected by complexing with either Ne or Ar, consistent with the observation that the least van der Waals shifts were observed for this vibrational level [b].

---

[a] G. Zhang, K.-S. Chen, A. J. Merer, Y.-C. Hsu, W.-J. Chen, S. Shaji, and Y.-A. Liao, J. Chem. Phys. 122, 244308 (2005).

[b] G. Zhang, B.-G. Lin, S.-M. Wen, and Y.-C. Hsu, J. Chem. Phys. 120, 3189 (2004).

TB02 **15 min 8:47**

ACTION SPECTROSCOPY AND DISSOCIATION ENERGY OF AMMONIA TRIMER

CORNELIA G. HEID, AMANDA S. CASE, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*; COLIN M. WESTERN, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.*; F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*.

We have investigated the energy dependence for the vibrational predissociation of ammonia trimer, $(NH_3)_3 \rightarrow (NH_3)_2 + NH_3$, using infrared-action spectroscopy. The action spectra come from detecting specific rovibrational states of the monomer fragment via (2+1) resonance enhanced multiphoton excitation (REMPI) while scanning the IR excitation laser over the NH stretch transitions of the trimer as well as the dimer. The relative intensities of the dimer and trimer features in the action spectra depend on the amount of energy available for breaking the hydrogen bonds in the clusters. For example, the action spectra of ammonia fragments with large amounts of internal energy ($v_2=3$) show almost no trimer contribution since there is not enough energy available to break two bonds in the cyclic trimer. The action spectra for fragments with low internal energies ($v_2=1$), on the other hand, exhibit a substantial trimer component as more energy remains available to dissociate the cluster. Using the threshold at which the trimer feature becomes apparent in our spectra as an upper limit ($E_{diss}^{max} = h\nu_{vib} - E_{int}(NH_3)$), we determine the dissociation energy of ammonia trimer to be in the range between 1700-1800 cm^{-1}. This range agrees well with theoretical predictions.

TB03 **15 min 9:04**

VIBRATIONAL ENERGY RELAXATION OF CHOLOROIODOMETHANE IN COLD ARGON

A.JAIN and E.L.SIBERT, *Department of Chemistry, University of Wisconsin, Madison, 53706.*

Electronically exciting the C-I stretch in the molecule chloroiodomethane CH_2ClI embedded in a matrix of argon at 20K can lead to an isomer, iso-chloroiodomethane CH_2Cl-I, that features a chlorine iodine bond [T. J. Preston *et al.*, J. Chem. Phys. **135**, 114503 (2011)]. By temporally probing the isomer at two different frequencies of 435 nm and 485 nm, three timescales for isomerization were inferred. The first and second timescales correspond to formation and initial relaxation of the isomer, with a decay rate of 0.45 ps^{-1}. The third timescale is attributed to further energy loss as the molecule cools to its local minima, with a decay rate of 0.07 ps^{-1}. To gain further mechanistic insights into this process, we studied the isomerization theoretically using molecular dynamics. Initial energy of 37,500 cm^{-1} (corresponding to electronic excitation of C-I stretch) is provided to the C-I bond. As in the experiment, three timescales are observed. First the molecule loses energy through collisions with a few argon atoms, which leads to a loss of about 10,000 cm^{-1} in 100 fs. Subsequent energy loss follows a bi-exponential decay, with decay rates of 1.16 ps^{-1} and 0.21 ps^{-1}. The implications of our results to the interpretation of the spectroscopic results will be discussed.

TB04 **15 min 9:21**

ULTRAFAST PHOTOPHYSICS OF SIMPLE AROMATIC CHROMOPHORES

RAUL MONTERO, ALVARO PERALTA CONDE, MARTA FERNÁNDEZ-FERNÁNDEZ, FERNANDO CASTANO and ASIER LONGARTE, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Ap. 644, E-48080 Bilbao, Spain.*

It is known that the photophysical properties of chromophores is decisively conditioned by the existence of $\pi\sigma^*$ transitions with repulsive character, in the vicinity of the characteristic bright $\pi\pi^*$ absorptions. The interplay between these two types of states triggers a complex dynamics that takes place in the femto-picoseconds scale.[a] Our group is interested in understanding the ultrafast relaxation mechanisms involving $\pi\sigma^*$ surfaces in a set of isolated aromatic chromofores including: aniline, indole, phenol and pyrrole. In the research carried out, the dynamical signature of the $\pi\sigma^*$ states has been tracked directly on the parent molecules photoexcited in a broad range of their near UV absorption specta, by multiphoton delayed ionization at several wavelengths. For the studied molecules, the work provides a detailed view on the relaxation pathways available, while permits to relate their photophysical behavior with the relative location of the $\pi\sigma^*$ and $\pi\pi^*$ states.

---

[a] W. . Domcke et. al., *Science*, **302**, 1693, 2003.

TB05 **15 min 9:38**

FEMTOSECOND TIMESCALE EVOLUTION OF PYRROLE ELECTRONIC EXCITATION

RAUL MONTERO, ALVARO PERALTA CONDE, VIRGINIA OVEJAS, FERNANDO CASTANO and ASIER LONGARTE, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Ap. 644, E-48080 Bilbao, Spain.*

Pyrrole is a simple aromatic molecule with relevant chromophoric properties in biology. Although its apparent simplicity, it shows a complicated dynamics after excitation in the near part of the UV absorption spectrum, which results from the interplay between the bright $\pi\pi^*$ and the dark dissociative $\pi\sigma^*$ electronic transitions.[a] Herein, we present a time resolved study with ultrafast resolution on the relaxation dynamics of isolated pyrrole, after excitation in the 265-217 nm range. Two lifetimes of 19 and 15 fs, which are associated with the internal conversion from the bright $^1B_2$ $\pi\pi^*$ state and the propagation of the wavepacket on the $\pi\sigma^*$ state, respectively, are found in the studied energy interval. The work also explores the consequences of non resonant adiabatic excitation of the system when broadband femtosecond pulses are employed to prepare the molecule in the targeted electronic states, revealing the key implication of this type of coherent phenomena. The collected data reveal that the bright $^1B_2$ $\pi\pi^*$ state is adiabatically populated at excitation wavelengths far away from resonance, providing an efficient way to reach the $\pi\sigma^*$ state. The recorded transients are fit employing a coherent model that provides a comprehensive view of the dynamical processes pyrrole undergoes after excitation by ultrashort light pulses.

---

[a] M. N. R. Ashfold, B. Cronin, A. L. Devine, R. N. Dixon and M. G. D. Nix *Science*, **312**, 1637-1640, 2006.

TB06 **15 min 9:55**

DEVELOPMENT OF FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY AS A PROBE OF PHOTOISOMERIZATION DYNAMICS

RYAN D. KIEDA, ADAM D. DUNKELBERGER, JAEYOON SHIN, TRACY OUDENHOVEN, and F. FLEMING CRIM, *Department of Chemistry, Universtiy of Wisconsin-Madison, Madison, WI 53706.*

Femtosecond stimulated Raman spectroscopy (FSRS) has proven to be a reliable probe of condensed phase dynamics by simultaneously achieving both exceptional temporal and frequency resolution. We report on preliminary attempts to utilize FSRS as a probe of the photoisomerization of dMe-OMe-NAIP (N-alkylated indanylidene pyrroline Schiff base) which is a mimic of the chromophore in Rhodopsin. We implement a 400 nm Raman pump/continuum probe process following a 400 nm actinic pump pulse which initiates photoisomerization. This initial work appears to corroborate previous transient absorption studies of NAIP while granting a vibrational mode specific look at the dynamics involved in relaxation from its excited state and subsequent vibrational relaxation.

Intermission

TB07 **15 min 10:30**

PHOTOISOMERIZATION DYNAMICS OF dMe-OMe-NAIP, A MODEL FOR THE RETINAL CHROMOPHORE

ADAM D. DUNKELBERGER, RYAN D. KIEDA, JAEYOON SHIN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*; RICARDO ROSSI PACCANI, STEFANIA FUSI, *UniversitÃÂă di Siena, Siena, I-53100, Italy*; MASSIMO OLIVUCCI, *UniversitÃÂă di Siena, Siena, I-53100, Italy and Bowling Green State University, Bowling Green, OH 43403*; and F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

The N-alkylated indanylidene pyrroline Schiff bases (NAIP) mimic the speed and efficiency of photoisomerization of retinal, whose photoisomerization is a key step in the molecular mechanism of vision. We present here a study of the ultrafast isomerization and subsequent relaxation of dMe-OMe-NAIP, a newly synthesized compound in the NAIP class with less steric congestion near the reactive double bond. We show that the excited-state dynamics of dMe-OMe-NAIP are slower than in previously studied NAIP compounds. This simpler compound also lacks the pronounced coherent vibrational motion observed in retinal and other NAIP compounds. We attribute these differences to pre-twisting about the double bond in the ground state of the previously studied compounds that is absent in dMe-OMe-NAIP. The speed of the isomerization and structure of the electronically excited potential energy surface in NAIP compounds make them attractive targets for studies of vibrationally mediated photochemistry. Previous studies from our group have shown that vibrational excitation before promotion to reactive electronic states can influence the course of reactions in isolated molecules. We seek to extend these experiments to molecules in more complicated environments, specifically the solution phase. To that end, we also present preliminary results of experiments probing the timescale of vibrational energy transfer in dMe-OMe-NAIP and other photoreactive Schiff bases.

TB08 15 min 10:47

ELECTRON TUNNELING PATHWAY AND ROLE OF ADENINE IN REPAIR OF DAMAGED DNA BY PHOTOLYASE

ZHEYUN LIU, CHUANG TAN, XUNMIN GUO, YA-TING KAO, JIANG LI, LIJUAN WANG, and DONGPING ZHONG, *Department of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210..*

Through electron tunneling, photolyase, a photoenzyme, restores damaged DNA into normal bases.[a][b] Here, we report our systematic characterization and analyses of three electron transfer processes in thymine dimer restoration by following the entire dynamical evolution during enzymatic repair with femtosecond resolution. We observed the complete dynamics of the reactants, all intermediates and final products, and determined their reaction time scales. Using (deoxy)uracil and thymine as dimer substrates, we unambiguously determined the electron tunneling pathways for the forward electron transfer to initiate repairing and for the final electron return to restore the active cofactor and complete the repair photocycle. Significantly, we found that the adenine moiety of the unusual bent cofactor is essential to mediating all electron transfer dynamics through a super-exchange mechanism, leading to a delicate balance of time scales. The active-site structural integrity, unique electron tunneling pathways and the critical role of adenine assure these elementary dynamics in synergy in this complex photorepair machinery to achieve the maximum repair efficiency close to unity.

---

[a] Z. Liu, C. Tan, X. Guo, Y.-T. Kao, J. Li, L. Wang, A. Sancar, and D. Zhong, *Proc. Natl. Acad. Sci. USA* **108**, 14831 (2011)

[b] J. Li, Z. Liu, C. Tan, X. Guo, L. Wang, A. Sancar, and D. Zhong, *Nature* **466**, 887 (2010)

TB09 15 min 11:04

MOLECULAR UNDERSTANDING OF EFFICIENT DNA REPAIR MACHINERY OF PHOTOLYASE

CHUANG TAN, ZHEYUN LIU, JIANG LI, XUNMIN GUO, LIJUAN WANG and DONGPING ZHONG, *Departments of Physics, Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Biochemistry, The Ohio State University, Columbus, Ohio, 43210.*

Photolyases repair the UV-induced pyrimidine dimers in damage DNA with high efficiency, through a cylic light-driven electron transfer radical mechanism. We report here our systematic studies of the repair dynamics in $E.coli$ photolyase with mutation of five active-site residues. The significant loss of repair efficiency by the mutation indicates that those active-site residues play an important role in the DNA repair by photolyase. To understand how the active-site residues modulate the efficiency, we mapped out the entire evolution of each elementary step during the repair in those photolyase mutants with femtosecond resolution. We completely analyzed the electron transfer dynamics using the Sumi-Marcus model. The results suggest that photolyase controls the critical electron transfer and the ring-splitting of pyrimidine dimer through modulation of the redox potentials and reorganization energies, and stabilization of the anionic intermediates, maintaining the dedicated balance of all the reaction steps and achieving the maximum function activity.

TB10 15 min 11:21

TRANSITION METAL ASSISTED DECOMPOSITION KINETICS OF ORGANIC MOLECULES: MODELS FOR CATALYSIS

DARRIN BELLERT, IVANNA LABOREN, and OTSMAR VILLARROEL, *Department of Chemistry, Baylor University, Waco, TX 76798.*

Instrumentation has been developed for measuring kinetic parameters for gas phase decomposition reactions activated by transition metal cations. This technique combines laser spectroscopy with mass spectrometry and fragment energy analysis. These reactions occur on the microsecond timescale. Reactants are formed as binary clusters in a jet-cooled expansion. Tunable laser radiation delivers well-defined energy impulses to the reactants. Kinetic information is gleaned from the ensuing unimolecular decomposition reaction. This talk focuses on a comparison study of the low-energy decomposition dynamics of acetone activated by the nickel and cobalt cations.

TB11 **15 min 11:38**

TRANSIENT ABSORPTION AND TIME-RESOLVED FLUORESCENCE STUDIES OF SOLVATED RUTHENIUM DI-BIPYRIDINE PSEUDO-HALIDE COMPLEXES

R. COMPTON, *National Research Council, Postdoctoral Fellow*; D. WEIDINGER, *Schafer Corporation*; J. C. OWRUTSKY, *Chemistry Division, Naval Research Laboratory*.

Time-resolved IR and fluorescence measurements were performed to probe the vibrational and electronic properties, respectively, of ruthenium di-bipyridine pseudo-halide ($Ru(Bpy)_2(X)_2$ (where X = CN, N_3 or NCS)) complexes. Vibrational energy relaxation (VER) times were determined for the complexes dissolved in dimethyl sulfoxide (DMSO) with a trend in VER time of NCS $>$ CN $>$ N_3. A similar trend and comparable absolute rates for NCS^- and $N3^-$ were previously observed by our group and others for simple inorganic anions in solution, suggesting a minimal contribution due to complexation. Measurements of the VER time of the CN complex in various solvents provide VER times in ethanol (42.3 ps) and DMSO (53.3 ps), which shows that protic solvents promote the relaxation. Time-resolved fluorescence measurements indicate a strong ligand dependence, with a factor of five decrease in the excited electronic state decay time from the CN (215 ns) to the NCS (39 ns) complex. A solvent dependence of the CN complex reveals a nearly 3-fold increase in the fluorescence decay time from acetonitrile (70 ns) to DMSO (215 ns).

TC. MICROWAVE

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 1000 MCPHERSON LAB

Chair: PHILLIP SHERIDAN, Canisius College, Buffalo, New York

TC01 **10 min 8:30**

PURE ROTATIONAL SPECTROSCOPY OF PANHs I: 1,10-PHENANTHROLINE. IMPLICATIONS OF PANHs IN ASTROPHYSICAL ENVIRONMENTS AND OBSERVATIONAL SPECTRA

BRETT A. MCGUIRE, IAN A. FINNERAN, P. BRANDON CARROLL, *Department of Chemistry, California Institute of Technology, Pasadena, CA 91125*; and GEOFFREY A. BLAKE, *Divisions of Geological & Planetary Sciences and Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.*

Polycyclic aromatic hydrocarbons (PAHs) have been proposed as possible carriers of the diffuse interstellar bands, the unidentified infrared features, and as likely precursors for the recently-observed C_{60} and C_{70} fullerenes. While PAHs have been well studied in the laboratory, and ultraviolet through infrared spectral simulations of PAHs can reproduce astronomical spectra reasonably well, several discrepancies still exist. Nitrogen-substituted PAHs, PANHs, have been proposed as a possible explanation for one of the major differences: the peak position of the 6.2 μm feature. While identification of individual PAH and PANH species from infrared spectra alone is extremely difficult, identification in the mm and sub-mm regimes using heterodyne spectroscopy is far more feasible. The frequently low (or zero) dipole moment of PAHs makes pure-rotational laboratory measurements and astronomical observation difficult. PANHs, however, often have substantial dipole moments, making them ideal targets for laboratory and astronomical studies. We present here the results of a laboratory study of the PANH 1,10-phenanthroline using direct absorption mm/sub-mm spectroscopy. We discuss implications of these results for the astrochemistry of PAHs and PANHs and astronomical searches for such species at radio through (sub)mm wavelengths.

TC02 **10 min 8:42**

PURE ROTATIONAL SPECTROSCOPY OF PANHs II: ACRIDINE. POSSIBLE APPLICATIONS IN THz COHERENT CONTROL SPECTROSCOPY

IAN A. FINNERAN, P. BRANDON CARROLL, BRETT A. MCGUIRE, *Department of Chemistry, California Institute of Technology, Pasadena, CA 91125*; and GEOFFREY A. BLAKE, *Divisions of Geological & Planetary Sciences and Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.*

Recent developments in THz pulse generation have allowed for the synthesis of short (sub-ps), high power (>10 MV/cm) pulses capable of controlling low energy vibrations, such as large amplitude torsions or bending modes. Clusters of polycyclic aromatic nitrogen heterocycles (PANHs) with water are good candidates for this research since a significant amount of theoretical and experimental work has already been undertaken on these species. A thorough understanding of the rotational spectra of these molecules is essential for assessing their suitability in far-IR/THz coherent control studies and is also of astrochemical interest. A promising target in this regard is the PANH acridine. Here we present the pure-rotational spectrum of the acridine monomer recorded with a direct absorption mm/sub-mm wave spectrometer and discuss the results in the context of future applications to coherent control of large amplitude motions of small aromatic water clusters.

TC03 **10 min 8:54**

PURE-ROTATIONAL SPECTROSCOPY OF PANHs III: PHENANTHRIDINE. POSSIBLE APPLICATIONS TO THE SPECTROSCOPY OF PROTONATED AROMATIC SPECIES

P. BRANDON CARROLL, BRETT A. MCGUIRE, IAN A. FINNERAN, *Department of Chemistry, California Institute of Technology, Pasadena CA, 91125*; GEOFFREY A. BLAKE, *Divisions of Geological and Planetary Sciences and Chemistry and Chemical Engineering, California Institute of Technology, Pasadena CA, 91125.*

Protonated species are believed to play a key role in the physical and chemical processes at work in the interstellar medium (ISM). The predicted abundances of precursor polycyclic aromatic nitrogen heterocycles (PANHs), and the stability of aromatic systems, make protonated PANHs a particularly important class of protonated species for ISM chemistry. Gas-phase protonation of simple PANHs, such as phenanthridine, is an excellent starting point for studying these systems. As a first step, we have obtained the pure-rotational spectrum of neutral phenanthridine using a direct absorption, mm/sub-mm spectrometer. We present the results of this study, and discuss applications of these result to future spectroscopic and dynamical studies of phenanthridine-H^+ and other protonated aromatic systems.

TC04 **15 min 9:06**

A PURE ROTATIONAL STUDY OF TWO NEARLY-EQUIVALENT STRUCTURES OF HEXAFLUOROACETONE IMINE

DANIEL A. OBENCHAIN, DANIEL J. FROHMAN, G. S. GRUBBS II, B. E. LONG, WALLACE C. PRINGLE, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

The rotational spectrum of hexafluoroacetone imine, $(CF_3)_2C{=}NH$, has been observed on a chirped pulse Fourier transform microwave spectrometer. Each of the singly substituted ^{13}C isotopologues and the ^{15}N isotopologue have been observed in natural abundance on a Balle-Flygare cavity type spectrometer. The r_0 and r_S structures have been determined for the heavy atom backbone. Both *a*-type and *b*-type transitions exhibit doubling with a spacing of about 15 kHz to 40 kHz. A change in an $\angle$NCCF dihedral angle appears to be the source of the doubling, and each set of transitions can be fit to two unique conformers of hexafluoroacetone imine. This structural difference produces two sets of rotational constants that have differences in experimental values on the order of kHz.

TC05 **15 min 9:23**

A ROTATIONAL STUDY OF 2H−3H−PERFLUOROPENTANE AND ITS ISOTOPOLOGUES

CHINH H. DUONG, DANIEL A. OBENCHAIN, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

The chirped pulse Fourier transform microwave spectrum of 2H−3H−perfluoropentane has been observed and assigned. Given a racemic mixture sample of the four available structural isomers, only the (S,S) structure was observed in the broadband spectrum. Attempts at observing the ^{13}C isotopologues on a Balle−Flygare cavity type spectrometer and their assignments will be discussed, along with an examination of the theoretical predictions for the structure and rotational constants of the molecule against their experimental values. Structural results of the monomer will also be compared with those of the helical structure of C_2 perfluoropentane.[a]

---

[a] Joseph A. Fournier, Robert K. Bohn, John A. Montgomery Jr., Masao Onda. *J. Phys. Chem.* **114** (1118), 2010.

TC06 **15 min 9:40**

CONFORMATIONS AND BARRIERS TO METHYL GROUP INTERNAL ROTATION IN TWO ASYMMETRIC ETHERS: PROPYL METHYL ETHER AND BUTYL METHYL ETHER

B. E. LONG, *Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Ave, Middletown, CT 06459-0180*; F. DeCHIRICO, S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

The conformational preferences of the O-C-C-C unit are important in many biological systems[a] with the unit generally preferring a gauche configuration compared to an anti configuration. Butyl methyl ether and propyl methyl ether provide very simple systems for this phenomenom to manifest. Pure rotational spectra of the title molecules have been recorded using chirped pulse Fourier transform microwave spectroscopy (CP-FTMW). In the case of butyl methyl ether, only one conformer has been observed. This conformer has torsional angles of COCC = 180°, OCCC = 62° and CCCC = 180° (anti-gauche-anti) and rotational constants of A = 10259.4591(33) MHz, B = 1445.6470(13) MHz, and C = 1356.2944(14) MHz. The rotational spectrum was doubled and has been analyzed to produce an effective barrier to methyl group internal rotation of 780(35) cm^{-1}. A prior rotational spectroscopic study on propyl methyl ether had focused only on the high energy anti-anti conformer.[b] We have analyzed spectra from the lowest energy anti-gauche conformer and the spectroscopic constants will be presented. A summary of the differences in conformational energies and methyl group internal rotation barriers for the class of aliphatic asymmetric ethers will be presented.

---

[a] K. N. Houk, J. E. Eksterowicz, Y.-D. Wu, C. D. Fuglesang, D. B. Mitchell. *J. Am. Chem. Soc.* **115** (4170), 1993.

[b] Hiroshi Kato, Jun Nakagawa, Michiro Hayashi. *J. Mol. Spectrosc.* **80** (272), 1980.

TC07 **15 min 9:57**

MW SPECTROSCOPY COUPLED WITH ULTRAFAST UV LASER VAPORIZATION: RIBOSE FOUND IN THE GAS PHASE

EMILIO J. COCINERO, PATRICIA ECIJA, FRANCISCO J. BASTERRETXEA, JOSÉ A. FERNÁNDEZ, FERNANDO CASTANO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Ap. 644, E-48080 Bilbao, Spain*; ALBERTO LESARRI, *Departamento de Química-Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Spain*; JENS-UWE GRABOW, *Institut für Physikalische Chemie, Lehrgebiet A, Universität Hannover, Callinstraße. 3A, D-30167 Hannover, Germany.*

Sugars are aldoses or ketoses with multiple hydroxy groups which have been elusive to spectroscopic studies. Here we report a rotational study of the aldopentose ribose. According to any standard textbook aldopentoses can exhibit either linear forms, cyclic five-membered (furanose) structures or six-membered (pyranose) rings, occurring either as α- or β- anomers depending on the orientation of the hydroxy group at C-1 (anomeric carbon). β-Furanose is predominant in ribonucleosides, RNA, ATP and other biochemically relevant derivatives, but is β-furanose the native form also of free ribose? Recent condensed-phase X-ray[a] and older NMR[b] studies delivered conflicting results. In order to solve this question we conducted a microwave study on D-ribose that, owing to ultrafast UV laser vaporization[c], has become the first C-5 sugar observed with rotational resolution. The spectrum revealed six conformations of free ribose, preferentially adopting β-pyranose chairs as well as higher-energy α-pyranose forms. The method also allowed for unambiguous distinction between different orientations of the hydroxy groups, which stabilize the structures by cooperative hydrogen-bond networks. No evidence was observed of the α-/β-furanoses or linear forms found in the biochemical derivatives.

---

[a] i) D. Šišak, L. B. McCusker, G. Zandomeneghi, B. H. Meier, D. Bläser, R. Boese, W. B. Schweizer, R. Gylmour and J. D. Dunitz *Angew. Chem. Int. Ed.* **49**, 4503, 2010. ii) W. Saenger *Angew. Chem. Int. Ed.* **49**, 6487, 2010.

[b] i) M. Rudrum, and D. F. Shaw, *J. Chem. Soc.* **52**, 1965. ii) R. U. Lemieux and J. D. Stevens *Can. J. Chem.* **44**, 249, 1966. iii) E. Breitmaier and U. Hollstein *Org. Magn. Reson.* **8**, 573, 1976.

[c] E. J. Cocinero, A. Lesarri, P. Écija, F. J. Basterretxea, J. U. Grabow, J. A. Fernández and F. Castaño *Angew. Chem. Int. Ed.* in press: DOI: 10.1002/anie.201107973, 2012.

TC08 **15 min 10:14**

FOURIER TRANFORM MICROWAVE STUDIES OF BI-MOLECULES OF CARBOXYLIC ACIDS

LUCA EVANGELISTI, GANG FENG, GOU QIAN, ASSIMO MARIS and W. CAMINATI, *Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy*; LAURA B. FAVERO, *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, Via Gobetti 101, I-40129 Bologna, Italy*; EMILIO COCINERO, PATRICIA EJICA, JOSE' A. FERNANDEZ and FERNANDO CASTANO, *Departamento de Quimica Fisica, Facultad de Ciencia y Tecnologia, Universidad del Pais Vasco, E-48080 Bilbao, Spain*; ALBERTO LESARRI, *Departamento de Quimica Fisica y Quimica Inorganica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; ROLF MEYER, *Sonnenbergstrasse 18, CH-5621 Zufikon, Switzerland.*

We recorded the molecular beam Fourier transform microwave spectra of several isotopic species of several homo and hetero dimers of carboxylic acids (R-COOH). Several tunnelling splittings have been measured with the accuracy underlying microwave spectroscopy. These splittings have been originated by the concerted double proton transfer of the two protons, but in some cases also by internal motions within the R chain in R-COOH. When the splittings were due to the double proton transfer, they were considerably decreasing upon mono- or bi-deuteration of the two carboxylic protons. The splittings due to the proton transfer have been used to determine the barrier to the proton transfer by applying a flexible model suited to take into account the coupling of the proton motions with the skeletal motions. The potential energy surfaces of the lateral chain motions have also been estimated. A full frame structure has been determined for some bimolecules, obtaining details of the Ubbelohde effect associated to the double hydrogen bond.

Intermission

TC09 **15 min 10:45**

THE ROTATIONAL SPECTRA OF PERFLUOROPROPIONIC ACID AND ITS HYDRATES

WEI LIN, AGAPITO SERRATO III, *Department of Chemistry and Environmental Sciences, University of Texas at Brownsville, 80 Fort Brown, Brownsville, TX 78520*; DANIEL A. OBENCHAIN, G. S. GRUBBS II, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577.*

The pure rotational spectrum of perfluoropropionic acid, CF_3CF_2COOH, has been studied using a chirped pulse Fourier transform microwave spectrometer in the frequency range of 8−14 GHz. A total of 81 transitions, including *a*-type, *b*-type, and *c*-type transitions have been observed and analyzed. The rotational constants and the five quartic centrifugal distortion constants have been determined for the first time. Quantum chemical calculations and the spectral analysis indicate that the observed conformer is the *gauche* form of perfluoropropionic acid with calculated dihedral angles $\angle$CCCO = 106° and 107° completed at the MP2/6-311G++(3df, 3pd) and MP2/aug-cc-pVDZ level, respectively. The rotational spectrum of the perfluoropropionic acid monohydrate has been assigned from the broadband spectrum. Most of the transitions exhibit doubling patterns belonging to the tunneling motion of the water molecule. Progress on the assignment of the perfluoropropionic acid dihydrate will also be presented.

TC10 **10 min 11:02**

THE MILLIMETER WAVE SPECTRUM OF LINALOOL

COREY J EVANS, STEPHANIE M ALLPRESS, *Department of Chemistry, University of Leicester, Leicester, LE17RH, United Kingdom*; PETER D GODFREY, DON MCNAUGHTON, *School of Chemistry, Monash University, 3800, Victoria, Australia.*

The millimeter wave spectrum (48-72 GHz) of linalool has been recorded for the first time. Over 40 conformers of S-(+) and R-(-)-linalool have been investigated using computational chemistry techniques, with 10 conformers predicted to be within 400 cm^{-1} of the lowest lying isomer at the B3LYP/aug-cc-pVTZ level of theory. The observed lines can be assigned to two conformers of (S)-(+)-linalool. Precise rotational and centrifugal distortion constants have been determined for both conformers.

TC11 **15 min 11:14**

THE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM AND POTENTIAL ENERGY CALCULATIONS FOR AN AROMATIC CLAISEN REARRANGEMENT MOLECULE, ALLYL PHENYL ETHER

G. S. GRUBBS II, *Department of Chemistry, Wesleyan University, 52 Lawn Ave., Middletown, CT 06459-0180*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577*; and STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, 52 Lawn Ave., Middletown, CT 06459-0180.*

Claisen rearrangement ethers are a fundamental organic, pericyclic rearrangement reaction reagent. In the mechanism of a Claisen rearrangement, a vinyl allyl ether is needed to provide the necessary Lewis acid/base sites on the molecule for the rearrangement and are simply heated. This rearrangement was first discovered by heating up the title molecule, allyl phenyl ether.[a] However, much like the Diels-Alder, Cope, and other pericyclic reactions, conformation and coordination of chemical groups is key to the Claisen mechanism. In this study, the authors present some structural characteristics of allyl phenyl ether from an analysis of the microwave spectra in the 8-14 GHz region using a CP-FTMW spectrometer. This is, to the authors knowledge, the first known microwave region study of the title molecule. Three conformers have been observed and assigned to date and will be discussed. Along with the rotational spectra, geometry calculations and potential energy surfaces performed at the MP2/6-311G++(3d,2p) level will be discussed and compared to the experimental results. Modeling the Claisen aromatic rearrangement mechanism using CP-FTMW spectroscopy will also be discussed.

---

[a] L. Claisen *Chemische Berichte* **45**, 3157, October 1912.

TC12 **15 min 11:31**

ROTATIONAL SPECTRUM AND LARGE AMPLITUDE MOTIONS OF 3,4-, 2,5- and 3,5-DIMETHYL-BENZALDEHYDE

I. KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris Diderot et Paris Est, 61 av. Général de Gaulle, 94010, Créteil, France*; M. TUDORIE, *Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, 50 av. F-D. Roosevelt, 1050 Bruxelles, Belgique*; M. JAHN, J.-U. GRABOW, *Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany*; M. GOUBET, *Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, F-59655 Villeneuve d'Ascq, France.*

The microwave spectra of the 3,4-, 2,5- and 3,5-Dimethyl-Benzaldehyde (DMBA) molecules have been recorded for the first time in the 2-26.5 GHz frequency range, using the COBRA-FTMW spectrometer in Hannover, with an instrumental uncertainty of 0.5 kHz for unblended lines. The experimental assignments and fits are supplemented by *ab initio* quantum chemical calculations,conformational energy landscape, and dipole moment components. The analysis of the spectra for the three isomers are in progress. The latest results, including spectroscopic constants and large amplitude motion parameters, will be presented. This investigation[a] follows the study of the spectra of the 4-Methyl-Benzaldehyde molecule[b]. The DMBA isomers belong to a similar series of molecules formally obtained by adding a second methyl group at the aromatic ring.

These molecules serve as prototype systems for the development of the theoretical model of asymmetric top molecules having C_s symmetry while containing two inequivalent methyl tops (C_{3v}), exhibiting different barrier heights and coupling terms to methyl internal rotation. Thus, the DMBA isomers represent benchmark species for testing the two-top internal rotors BELGI program written recently[c]

---

[a] Supported by the ANR-08-BLAN-0054 contract (France), the Deutsche Forschungsgemeinschaft, and the Land Niedersachsen (Germany).

[b] H. Saal, W. Caminati, I. Kleiner, A. R. Hight-Walker, J. T. Hougen, J.-U. Grabow, to be published.

[c] M. Tudorie, I. Kleiner, J. T. Hougen, S. Melandri, L. W. Sutikdja, W. Stahl, J. Mol. Spectrosc., 269 (2011), 211-225

TC13 **15 min 11:48**

SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURES FOR THE EQUATORIAL CONFORMERS OF N-METHYLPIPERIDONE AND TROPINONE BY THE MIXED ESTIMATION METHOD

JEAN DEMAISON, *Laboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France*; NORMAN C. CRAIG, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*; EMILIO J. COCINERO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Ap. 644, E-48080 Bilbao, Spain*; JENS-UWE GRABOW, *Institut für Physikalische Chemie and Elektrochemie, Lehrgebiet A, Gottfried-Wilhelm-Leibniz Universität, Callinstrasse 3A, D-30167 Hannover, Germany*; ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; H. D. RUDOLPH, *Department of Chemistry, University of Ulm, D-89069 Ulm, Germany*.

N-methylpiperidone and tropinone, which contain a structural motif found in numerous alkaloids, are too large for determining an accurate equilibrium structure either by ab initio methods or by experiment. However, the ground state rotational constants of the parent species and of all isotopologues with a substituted heavy atom (^{13}C, ^{15}N, ^{18}O) are known from microwave spectroscopy.[ab] These constants have been corrected for the rovibrational contribution calculated from an ab initio cubic force field. These semiexperimental equilibrium rotational constants have been supplemented by carefully chosen structural parameters from medium level ab initio calculations. In the mixed estimation method, the two sets of data have been used in a weighted least-squares fit to determine a reliable equilibrium structure for both molecules. This work shows that it is possible to determine reliable equilibrium structures for large molecules (34 degrees of freedom in the case of tropinone). The method could be applied without too much difficulty to still larger molecules.

---

[a] L. Evangelisti, A. Lesarri, M. K. Jahn, E. J. Cocinero, W. Caminati, J.-U. Grabow J. Phys. Chem. A 115, 9545-9551 (2011)

[b] E. J. Cocinero, A. Lesarri, P. Écija, J.-U. Grabow, J. A. Fernández, F. Castaño PCCP 12, 6076-6083 (2010)

TD. MINI-SYMPOSIUM: PHOTODETACHMENT AND PHOTOIONIZATION

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 1015 MCPHERSON LAB

Chair: RICHARD MABBS, Washington University in St. Louis, St. Louis, Missouri

TD01 *INVITED TALK* **30 min 8:30**

TRANSITION-METAL-DOPED PLANAR BORON CLUSTERS: A NEW CLASS OF AROMATIC COMPOUNDS WITH HIGH COORDINATION

LAI-SHENG WANG, *Department of Chemistry, Brown University, Providence, Rhode Island.*

Photoelectron spectroscopy in combination with computational studies over the past decade has shown that boron clusters possess planar or quasi-planar structures, in contrast to that of bulk boron, which is dominated by three-dimensional cage-like building blocks. All planar or quasi-planar boron clusters are observed to consist of a monocyclic circumference with one or more interior atoms. The propensity for planarity has been found to be due to both σ and π electron delocalization throughout the molecular plane, giving rise to concepts of σ and π double aromaticity. We have found further that the central boron atoms can be substituted by transition metal atoms to form a new class of aromatic compounds, which consist of a central metal atom and a monocyclic boron ring (M©B$_n$). Eight-, nine-, and ten-membered rings of boron have been observed, giving rise to octa-, ennea-, and deca-coordinated aromatic transition metal compounds [1-3].
References:
[1] "Aromatic Metal-Centered Monocyclic Boron Rings: Co©B_9^- and Ru©B_9^-" (Constantin Romanescu, Timur R. Galeev, Wei-Li Li, A. I. Boldyrev, and L. S. Wang), Angew. Chem. Int. Ed. **50**, 9334-9337 (2011).
[2] "Transition-Metal-Centered Nine-Membered Boron Rings: M©B_9 and M©B_9^- (M = Rh, Ir)" (Wei-Li Li, Constantin Romanescu, Timur R. Galeev, Zachary Piazza, A. I. Boldyrev, and L. S. Wang), J. Am. Chem. Soc. **134**, 165-168 (2012).
[3] "Observation of the Highest Coordination Number in Planar Species: Decacoordinated Ta©B_{10}^- and Nb©B_9^- Anions" (Timur R. Galeev, Constantin Romanescu, Wei-Li Li, L. S. Wang, and A. I. Boldyrev), Angew. Chem. Int. Ed. **51**, 2101-2105 (2012).

TD02 **15 min 9:05**

ELECTRON SPIN STATES AND STRUCTURES OF LANTHANIDE (Ce, Pr, and Nd) COMPLEXES OF CYCLOOCTATERAENE

SUDESH KUMARI, YANG LIU, MOURAD ROUDJANE AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

1,3,5,7Cyclooctatetraene (COT, C_8H_8) is one of the most versatile ligands used in organometallic chemistry, with coordination modes ranging from η^2 to η^8. COT is anti-aromatic with a tub conformation in its ground state; however, the dianion ($C_8H_8^{2-}$) is aromatic and planar. In this paper, we report a study of M(COT) (M = Ce, Pr, and Nd) using pulsed-field ionization zero electron kinetic energy (ZEKE) spectroscopy and density functional theory. The ZEKE spectra of the Ce, Pr, and Nd-COT complexes show multiple electronic transitions from the neutral ground state to various ion states, and each transition exhibits a major metal-ligand stretching progression. From the ZEKE spectra, the neutral ground states were determined as triplet, quartet, and quintet, and the ion states were doublet, triplet, and quartet for M = Ce, Pr, and Nd, respectively. In both neutral and ion states, the complexes are in C_{8v} symmetry, and COT is planar. The conformational change of COT from a tub shape to a plane is induced by two electron transfer from the metal atoms to the ligand orbitals. It is noted that the spectra of these complexes are very much different from those of the Sc, Y, La, and Gd complexes previously studied in our group, for which only single transition was observed.[a][b]

---

[a] J. S. Lee, Y Lei, S. Kumari, and D.-S. Yang, J . Chem. Phys. 131, 104304, (2009)
[b] M. Roudjane, S. Kumari, and D.-S. Yang, J. Phys. Chem. A 116, 839, (2012)

TD03 15 min 9:22

CYCLOPOLYMERIZATION OF ACETYLENE TO BENZYNE AND NAPHTHALENE

DILRUKSHI HEWAGE, RUCHIRA SILVA AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

Reactions of acetylene (C_2H_2) with laser-vaporized La atoms produced La(C_6H_4) and La ($C_{10}H_8$) in supersonic molecular beams. The organic fragments in these complexes were benzyne and naphthalene. The benzyne species was produced by the La-mediated cyclotrimerization of three acetylene molecules, whereas naphthalene was formed likely by the cyclization of the transient benzyne with two additional acetylene molecules. These cyclized products were identified by mass-analyzed threshold ionization mass spectroscopy, which measured adiabatic ionization energies and several vibrational frequencies. The measured ionization energies were 40875 (5) cm^{-1} for La(C_6H_4) and 36767 (5) cm^{-1} for La($C_{10}H_8$). The most active vibrational transitions of both complexes were metal-ligand stretching with 326 cm^{-1} for La(C_6H_4) and 286 cm^{-1} for La ($C_{10}H_8$). By combining the spectra with theoretical calculations, the ground electronic states of the neutral complexes were determined to be $^2A_1$ (C_{2v}) and $^2A'$ (C_s) and those of the corresponding ions were $^1A_1$ (C_{2v}) and $^1A'$ (C_s) for La (C_6H_4) and La($C_{10}H_8$), respectively.

TD04 15 min 9:39

ELECTRONIC RELAXATION OF THE PHENYLALANINE RESIDUE IN GAS PHASE PEPTIDES: ROLE OF THE NEIGHBOURING AMIDE GROUPS IN THE PHOTOPHYSICS

Y. LOQUAIS, H.S. BISWAL, B. TARDIVEL, V. BRENNER, M. MONS, *CEA, IRAMIS, SPAM, Lab. Francis Perrin, URA 2453, Gif-sur-Yvette, F-91191, France*; E. GLOAGUEN, *CNRS, INC & INP, Lab. Francis Perrin, URA 2453, Gif-sur-Yvette, F-91191, France*; C. JOUVET, M. BROQUIER, *CNRS, INP, ISMO, CLUPS, UMR 8214, Orsay, F-91405, France*; M. MALIS, I. LJUBIC and N. DOSLIC, *Ruder Bošković Institute, Department of Physical Chemistry, Zagreb, 10000, Croatia.*

Protein absorption in the near UV is mainly due to the presence of aromatic systems on the side chain of three residues: phenylalanine, tryptophan and tyrosine. It is generally expected that the photophysics of these UV chromophores depends on their immediate environment within the molecule and thus on the conformation of these flexible molecules. This property may in particular be used as an optical diagnostic of the conformational state of the peptide chain.

The structure of peptide chains isolated in the gas phase can be characterized by UV and IR laser spectroscopy[a]. These measurements allow us to distinguish the spectral contributions of the different conformers and thus provide us with an elegant way to address the issue of the conformational dependence on the photophysics. For this purpose, the dynamics of relaxation of the $\pi\pi^*$ excited state of several peptides containing a phenylalanine residue have been studied using two-colour resonant two-photon ionization (2C-R2PI) in the ns time scale at CEA and ps at CLUPS and laser-induced fluorescence as well. The lifetime of the $\pi\pi^*$ excited state is found to strongly depend on the conformation adopted by the molecule and on the excess energy in the excited state, with measured lifetimes ranging from 1 ns to 80 ns.

The nature of the end caps of the phenylalanine residue (Ac-Phe-NH_2 vs. Ac-Phe-NHMe) or the deuteration of the amide groups induce different behaviours. The substitution of some atoms of the molecule provide additional information on their role in the relaxation dynamics and can be used to tell which relaxation pathways found by quantum chemistry calculations are compatible with the experiments.The first results suggest the occurrence of a conical intersection between the excited $\pi\pi^*$ state and backbone local excitation states.

---

[a] W. Chin; F. Piuzzi; I. Dimicoli and M. Mons, Phys. Chem. Chem. Phys., 8, pp 1033-1048 (2006)

TD05 15 min 9:56

PROTON TRANSFER IN NEUTRAL PEPTIDES EXAMINED BY CONFORMATIONAL SPECIFIC IR AND UV SPECTROSCOPY

SANDER JAEQX, JOS OOMENS, *FOM institute Rijnhuizen, Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands*; ANOUK M. RIJS, *Radboud University Nijmegen, Institute of Molecules and Materials (molecular & biophysics), Toernooiveld 7, 6525 ED Nijmegen, the Netherlands.*

The combination of UV and IR spectroscopy offers a powerful probe to study molecular structure and intramolecular interactions. With resonance enhanced multi photon ionization (REMPI), the electronically excited state of biomolecules can be probed. As different conformations have different excited state energies, peaks in the REMPI spectrum can be attributed to different conformations. This allows us to perform conformation specific IR absorption spectroscopy using IR-UV ion-dip spectroscopy (IR-IDS) in the 1800-1000 cm^{-1} region by employing the free electron laser FELIX. IR-IDS in combination with DFT calculations allows us to determine the gas phase conformations of biomolecules. Here, we used these techniques on Z-Glu-OH and Z-Arg-OH to reveal their conformational structure and the possible presence of proton transfer. There is an ongoing debate on the gas phase structure of arginine. Proton transfer has been suggested to occur from the C-terminal COOH group to the guanidium side chain of arginine to form a zwitterion. Moreover, there can be two tautomers of canonical arginine. Here, we will elucidate the gas phase structure of arginine. In order to promote intramolecular proton transfer, we designed a peptide which contains both the most acid (Glu) as well as the most basic residue (Arg): Z-Glu-Arg-NHMe and Z-Glu-Ala$_n$-Arg-NHMe. Here, the occurrence of proton transfer will be probed via the carboxylic acid C=O stretch vibration.

Intermission

TD06 15 min 10:30

SURPRISING COMPLEXITY OF A SMALL MOLECULE: PHOTOFRAGMENTATION DYNAMICS OF ICN, ICN·Ar$_n$ and ICN·(CO$_2$)$_n$

ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*; AMANDA S CASE, JOSHUA P. MARTIN, and W. CARL LINEBERGER, *JILA and Department of Chemistry and Biochemistry University of Colorado, Boulder, CO 80309.*

The photofragmentation dynamics of ICN^- in isolation and in complexes with argon or CO_2 are investigated through a combination of experimental and theoretical studies. Experimentally, we probe the excited state dynamics of ICN^- following excitation to the lowest energy state that correlates to I^- + CN products. In the absence of solvating atoms or molecules, most of the excess charge localizes on I^-, although $\approx 3\%$ of the products have the charge localized on the CN^-. The introduction of a single CO_2 or argon atom changes the branching ratio between the three possible product channels (I^- , CN^- or ICN^-). Interestingly when one argon atom is introduced roughly 5% of the products undergo cage recombination to form ICN^-, providing an example of single atom caging.[a] When CO_2 is introduced, cage recombination is only seen in larger complexes, but a significant fraction of the photoproducts obtained following excitation of $ICN^- \cdot CO_2$ have the charge localized on the CN. These results will be discussed and analyzed using potential surfaces evaluated at the MR-SOCISD level of theory.[b]

---

[a] A. S. Case, E. M. Miller, J. P. Martin, Y.-J. Lu, L. Sheps, A. B. McCoy and W. C. Lineberger, Angew. Chem. Int. Ed. **51**, 2651 (2012)

[b] A. B. McCoy, IJQC, (in press).

TD07 **15 min 10:47**

NONRADIATIVE DECAY DYNAMICS OF METHYL-4-HYDROXYCINNAMATE AND ITS MONOHYDRATED COMPLEX REVEALED BY PICOSECOND PUMP-PROBE SPECTROSCOPY

T. EBATA, D. SHIMADA, R. KUSAKA, and Y. INOKUCHI, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; M. EHARA, *Institute for Molecular Science, 38 Myodaiji, Okazaki 444-8585, Japan.*

The lifetimes of methyl 4-hydroxycinnamate (OMpCA) and its mono-hydrated complex (OMpCA-H_2O) in the S_1 state have been measured by picosecond pump-probe spectroscopy in a supersonic beam. For OMpCA, the lifetime of the S_1 - S_0 origin is 8 - 9 ps. On the other hand, the lifetime of OMpCA-H_2O complex at the origin is 930 ps, which is 100 times longer than that. Furthermore, in the complex the S_1 lifetime shows rapid decrease at an energy of $200\ \mathrm{cm}^{-1}$ above the origin and becomes as short as 9 ps at $500\ \mathrm{cm}^{-1}$. Theoretical calculations with symmetry-adapted cluster-configuration interaction (SAC-CI) method suggest that in OMpCA, the trans - cis isomerization occurs smoothly without a barrier on the S_1surface, while in OMpCA-H_2O complex, there exists a barrier along the isomerization coordinate. The calculated barrier height of OMpCA-H_2O is in good agreement with that estimated from the lifetime measurements.

TD08 **15 min 11:04**

DEUTERATION EFFECT STUDY ON THE VIBRATIONAL DYNAMICS OF PHENOL AND PHENOL-WATER COMPLEX BY PICOSECOND TIME-RESOLVED IR-UV PUMP-PROBE SPECTROSCOPY IN A SUPERSONIC MOLECULAR BEAM

YASUNORI MIYAZAKI, YOSHIYA INOKUCHI, and TAKAYUKI EBATA, *Department of Chemistry, Graduate School of Science, Hiroshima University, Japan.*

The vibrational energy relaxations of the OH and OD stretch of phenol-d_0 and phenol-d_0-(H_2O) complex and phenol-d_1 and phenol-d_1-(D_2O) complex, respectively, are investigated by picosecond IR-UV pump-probe spectroscopy. The key to understand their dynamic is well-suited to a two-step Tier model. For phenol-d_0, an energy flow is described by the intramolecularVR steps: $''OH\ stretching\ level'' \rightarrow ''doorway\ state'' \rightarrow ''bath\ state''$. The intramolecularVR lifetime of phenol-d_0 is obtained to be 14 ps. On the other hand, the OD stretching vibration of phenol-d_1 exhibits quantum beats, followed by the intramolecularVR with a lifetime of 90 ps. In contrast, for the phenol-water complex, the intramolecularVR lifetime of OH(OD) stretch becomes 4.3 ps(12 ps) and an energy flow is described by the intramolecular and intermolecular processes, which lead to VP (vibratinal predisocciation). Although the energy difference is $1000\ \mathrm{cm}^{-1}$, no remarkable change of intermolecularVR and VP lifetimes is found in the hydrogen-bonded phenol-water complexes.

TD09 **15 min 11:21**

PICOSECOND TIME-RESOLVED IR-UV PUMP-PROBE SPECTROSCOPIC STUDY ON VIBRATIONAL ENERGY RELAXATION OF BENZENE DIMER AND TRIMER IN THE CH STRETCHING REGION

RYOJI KUSAKA, YOSHIYA INOKUCHI, and TAKAYUKI EBATA, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan.*

Vibrational energy relaxation (VER) in the CH stretching region of benzene dimer (Bz_2) and trimer (Bz_3) has been studied by IR-UV pump-probe spectroscopy in supersonic beams. Firstly, we investigated isotope-substituted *hd* heterodimer, where h=C_6H_6 and d=C_6D_6, because the Stem and Top sites in the *hd* dimer can be site-selectively excited, different from *hh* homodimer. The two *h*(stem)*d*(top) and *h*(top)*d*(stem) isomers show remarkable difference in the lifetimes of intracluster vibrational energy redistribution (IVR). In the transient UV spectra, we observed a broad electronic transition due to the bath modes. The time evolutions of the bath modes can be described by a three step VER model involving IVR and vibrational predissociation (VP). This model was also confirmed by the observed rise profile of the Bz fragment. Secondly, we investigated *hh* homodimer. The *hh* homodimer shows the stepwise VER process with time constants similar to those of the *hd* dimer, suggesting a very weak excitation-exchange coupling of the vibrations between the two sites of the *hh* dimer. Finally, we found that Bz_3 also exhibits the stepwise VER process, though each step is faster than Bz_2.

TD10 **15 min 11:38**

PHOTOELECTRON SPECTROSCOPY OF ALUMINUM DOPED BORON CLUSTERS

WEI-LI LI, CONSTANTIN ROMANESCU, LAI-SHENG WANG, *Brown University, Chemistry Department, 324 Brook Street,Providence, RI 02912, USA.*

Anionic boron clusters have been shown to be planar or quasi-planar up to B_{21}^{-} from a series of combined photoelectron spectroscopy and theoretical studies. All these boron clusters consist of a peripheral ring characterized by strong two-center-two-electron (2c-2e) B-B bonds and one or more interior atoms. The propensity for planarity is due to σ- and π-electron delocalizations throughout the molecular plane, giving rise to concepts of σ- and π-aromaticity. The quasi-planarity, on the other hand, can be mechanical in nature - the circumference of the cluster is too small to fit the inner atoms - even for doubly aromatic clusters. Two questions arise: firstly, can isoelectronic substitution by a single aluminum atom on the outer ring enhance the planarity of quasi-planar structures, and, secondly, can the interior boron atoms be replaced by aluminum? A series of aluminum isoelectronic substitution of boron clusters have been investigated ranging from B_{7}^{-} to B_{12}^{-}. Aluminum turns out to avoid the central position in the all these clusters and enhance the planarity of AlB_{6}^{-} and AlB_{11}^{-} clusters by expanding the peripheral ring.

References:
[1] C. Romanescu, A. P. Sergeeva, W. L. Li, A. I. Boldyrev and L. S. Wang, *J. Am. Chem. Soc.* **133** (22), 8646-8653 (2011)
[2] T. R. Galeev, C. Romanescu, W. L. Li, L. S. Wang and A. I. Boldyrev, *J. Chem. Phys.* **135**, (8) 104301 (2011)
[3] W. L. Li, C. Romanescu, T. R. Galeev, L. S. Wang and A. I. Boldyrev, *J. Phys. Chem. A* **115** (38), 10391-10397 (2011)

TE. MINI-SYMPOSIUM: SPECTROSCOPY OF INTERFACES

TUESDAY, JUNE 19, 2012 – 8:30 AM

Room: 2015 MCPHERSON LAB

Chair: MICHAEL DUNCAN, University of Georgia, Athens, Georgia

TE01 *INVITED TALK* **30 min 8:30**

SELECTIVE ADSORPTION OF IONS TO AQUEOUS INTERFACES AND ITS EFFECTS ON EVAPORATION RATES

RICHARD J. SAYKALLY, *Department of Chemistry, University of California and Chemical Sciences Division, Lawrence Berkeley National Laboratory Berkeley, CA 94720-1460.*

By exploiting the strong UV charge-transfer-to-solvent (CTTS) resonances of selected anions in aqueous electrolytes, their interfacial adsorption properties are measured by UV-SHG spectroscopy. Temperature and concentration dependences are determined, with the goal of establishing a molecular description of selective ion adsorption. A study of prototypical chaotrope thiocyanate reveals that its strong adsorption is driven by enthalpic forces and impeded by entropy. A study of nitrite indicates even stronger adsorption as an ion pair with sodium. Evaporation rates are measured by combining liquid microjet technology and Raman thermometry. The relationship between surface propensities of ions and evaporation rates is investigated. A detailed molecular mechanism for aqueous evaporation is sought.

W. S. Drisdell, R. J. Saykally, R. C. Cohen Effect of Surface Active Ions on the Rate of Water Evaporation, J. Phys. Chem. C 114, 11880-11885 (2010).

D.E. Otten, R. Onorato, R. Michaels, J. Goodknight, R. J. Saykally "Strong Surface Adsorption of Aqueous Sodium Nitrite as an Ion Pair," Chem. Phys. Lett. 519-520, 45-48 (2012).

D.E. Otten, P. Shaffer, P. Geissler, R.J. Saykally "Elucidating the Mechanism of Selective Ion Adsorption to the Liguid Water Surface," PNAS 109 (3), 701-705 (2012).

TE02 **10 min 9:05**

BISULFATE (HSO_4^-) DEHYDRATION AT THE VAPOR/SOLUTION INTERFACE PROBED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

AARON M. JUBB and HEATHER C. ALLEN, *Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

With perspective towards atmospheric chemistry, ion behavior at vapor/solution interfaces has important implications for understanding aqueous aerosols as reactions at this interface control the growth and uptake of the aerosol. Sulfate species are a major ionic component of aqueous acidic tropospheric aerosols with bisulfate (HSO_4^-) being the major sulfate species at pH values lower than 2. The application of inherently interface specific spectroscopic methods such as vibrational sum frequency generation (VSFG) allows for resolution of interfacial chemical species versus the bulk species facilitating a clearer understanding of chemical phenomena taking place at vapor/solution interfaces. Here we present VSFG results on the effects that cation identity have toward the molecular environment experienced by bisulfate anions residing within the vapor/solution interface for aqueous H_2SO_4, Na_2SO_4, and $MgSO_4$ solutions. By probing the ν_{SS}-SO_3 vibrational mode of interfacial bisulfate anions directly we are able to elucidate the influence that Na^+ and Mg^{2+} ions have toward bisulfate hydration within the interface. Our results indicate that Na^+ and Mg^{2+} perturb the hydration of interfacial bisulfate anions but do not form ion-pair complexes. Mg^{2+} is found to exhibit a larger net influence on bisulfate hydration relative to Na^+.

TE03 **10 min 9:17**

INTERFACIAL WATER STRUCTURE AND CATION BINDING WITH THE DPPC PHOSPHATE AT AIR /AQUEOUS INTERFACES STUDIED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

WEI HUA, HEATHER C. ALLEN, *Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

Molecular-level knowledge of water structure and cation binding specificity to lipid headgroups at lipid/water interfaces plays a key role in many relevant chemical, biological, and environmental processes. To obtain information on the molecular organization at aqueous interfaces, vibrational sum frequency generation (VSFG) has been applied extensively as an interface-specific technique. Dipalmitoylphosphocholine (DPPC) is a major component of cell membranes and has been used as a proxy for the organic coating on fat-coated aerosols. In the present work, in addition to conventional VSFG studies on cation interaction with the phosphate headgroup moiety of DPPC, we employ phase-sensitive vibrational sum frequency generation (PS-VSFG) to investigate the average direction of the transition dipole moment of interfacial water molecules. The average orientation of water structure at DPPC/water interfaces is inferred. DPPC orients interfacial water molecules on average with their net transition dipole moment pointing towards the surface. The influence of Na^+, K^+, Mg^{2+}, Ca^{2+} is identified in regard to interfacial water structure and DPPC headgroup organization. Ca^{2+} is observed to have greater impact on the water structure and a unique binding affinity to the phosphate headgroup relative to other cations tested. In highly concentrated Ca^{2+} regimes the already disturbed interfacial hydrogen-bonding network reorganizes to resemble that of the neat salt solution interface.

TE04 **15 min 9:29**

THE SPECTROSCOPIC STUDY OF ESTROGEN AND ITS HYDRATED CLUSTERS IN A SUPER SONIC JET

FUMIYA MORISHIMA, YOSHIYA INOKUCHI and TAKAYUKI EBATA, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-hiroshima, 739-8526, Japan.*

Structures of estrogen and its hydrated clusters have been studied by several laser spectroscopies in supersonic jet. The electronic spectrum of estrogen shows several origin bands. By observing UV-UV hole-burning and IR-UV spectra, it is concluded they are due to different conformers originating from difference of orientation of OH group(s). We also observed electronic and IR spectra of estrogen-H_2O. By aids of DFT calculations, the conformations and hydrated structures are determined.

Intermission

TE05 **15 min 10:15**

INFRARED SPECTROSCOPY OF LARGE-SIZED NEUTRAL AND PROTONATED METHANOL CLUSTERS

TOMOHIRO KOBAYASHI, RYUNOSUKE SHISHIDO, ASUKA FUJII, *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*; JER-LAI KUO, *Institute of Atomic and Molecular Science, Academia Sinica, Taipei 10617, Taiwan.*

The OH stretch region of infrared spectra of size-selected $(CH_3OH)_n$ and H^+ $(CH_3OH)_n$ clusters were measured in the size range of n=10-50. While the neutral clusters show the similar spectral features in all the observed size range, the spectral features of the protonated clusters largely depend on the size and finally converge to those of the neutral clusters at n=40. The decomposition of the hydrogen-bonded OH stretch band demonstrates that the contribution of the 3-coordinated sites is less than 10 percent of the 2-coordinated sites. This means that the hydrogen bond network of the methanol clusters is basically a single chain and branching of the chain is scarce.

TE06 10 min 10:32

INFRARED SPECTROSCOPY OF $(CH_3)_3N\text{-}H^+\text{-}(H_2O)_n$ (n = 1-22)

RYUNOSUKE SHISHIDO, ASUKA FUJII, *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*; and KUO JER-LAI, *Institute of Atomic and Molecular Sciences Academia Sinica, Taipei, Taiwan.*

The magic number behavior of $H^+(H_2O)_{21}$ has been well known. Futhermore, this magic number is observed even in the mixed clusters $H^+(H_2O)_m(NH_3)_n$ and $H^+(H_2O)_m(MeOH)_n$ (m + n = 21). This means that NH_3 or MeOH molecules are compatible with water molecules in the hydrogen bond network of the magic number cluster.

In the present study, infrared spectroscopy is applied to $(CH_3)_3N\text{-}H^+\text{-}(H_2O)_n$ (n = 1-22), and structures of these clusters are determined with help of density functional theory calculations. As a result, it is demonstrated that no magic number is seen in the case of $(CH_3)_3N\text{-}H^+\text{-}(H_2O)_n$. $(CH_3)_3N$ is not a spectator to the hydrogen bond network of protonated water clusters, and it is largely changes the network structure.

TE07 15 min 10:44

INVESTIGATING ELECTRONIC PROPERTIES OF IONIZED PAH CLUSTERS

C. JOBLIN, D. KOKKIN, A. BONNAMY, D. TOUBLANC, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*; M. RAPACIOLI, A. SIMON, L. DONTOT, A. GAMBOA, F. SPIEGELMAN, *LCPQ, Université de Toulouse, UPS; CNRS; 118 Route de Narbonne, 31062 Toulouse Cedex 09, France*; P. PARNEIX, T. PINO, O. PIRALI, G. FÉRAUD, H. FRIHA, C. FALVO, P. BRÉCHIGNAC, *ISMO; Université Paris-Sud 11; CNRS; Bât. 210, 91405 Orsay Cedex, France*; G. GARCIA, L. NAHON, *Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, B.P. 48, 91192 Gif sur Yvette, France*; G. MULAS, *INAF; Osservatorio Astronomico di Cagliari, Strada n. 54, Loc. Poggio dei Pini, 09012 Capoterra, CA, Italy*.

Polycyclic aromatic hydrocarbon (PAH) clusters have been proposed as candidates for evaporating very small grains that are revealed by their mid-IR emission at the surface of UV-irradiated clouds in interstellar space[a]. This motivates studies on the photostability and spectroscopic signatures of such species to validate their presence in interstellar environments and constrain their survival therein. We have used the molecular beam chamber SAPHIRS and the photoelectron-photoion coincidence spectrometer DELICIOUS II[b] at the SOLEIL synchrotron facility to characterize the electronic properties of cationic coronene ($C_{24}H_{12}$) clusters up to the pentamer. These experimental results are analysed in the light of electronic structure calculations[c]. In particular a Density Functional Tight Binding + Configuration Interaction scheme[d] is developed to describe charge delocalization in these large systems and calculate the ionization potential, vibrational spectra, and charge transfer excited states. For the coronene dimer cation, complementary measurements are performed with the PIRENEA set-up to quantify some of the electronic transitions, in particular their oscillator strengths that cannot be extracted from the photoelectron spectroscopy. Emphasis will be put on the evolution of the spectra with cluster size.

---

[a] M. Rapacioli, C. Joblin and P. Boissel *Astron. & Astrophys.* **429** (2005), 193-204.

[b] G. Garcia, H. Soldi-Lose and L. Nahon *Rev. Sci. Instrum.* **80** (2009), 023102.

[c] Joint ANR project GASPARIM, ANR-10-BLAN-501

[d] M. Rapacioli, A. Simon, L. Dontot and F. Spiegelman *Phys. Status Solidi B* **249** (2) (2012), 245-258.

TE08 **15 min 11:01**

QUANTUM STATE-RESOLVED REACTIVE AND INELASTIC SCATTERING AT GAS-LIQUID AND GAS-SOLID INTERFACES

MONIKA GRÜTTER, DANIEL J. NELSON AND DAVID J. NESBITT, *JILA, University of Colorado and National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, U.S.A..*

Quantum state-resolved reactive and inelastic scattering at gas-liquid and gas-solid interfaces has become a research field of considerable interest in recent years[abc]. The collision and reaction dynamics of internally cold gas beams from liquid or solid surfaces is governed by two main processes, impulsive scattering (IS), where the incident particles scatter in a few-collisions environment from the surface, and trapping-desorption (TD), where full equilibration to the surface temperature $(T_{\mathrm{TD}} \approx T_{\mathrm{s}})$ occurs prior to the particles' return to the gas phase. Impulsive scattering events, on the other hand, result in significant rotational, and to a lesser extent vibrational, excitation of the scattered molecules, which can be well-described by a Boltzmann-distribution at a temperature $(T_{\mathrm{IS}} >> T_{\mathrm{s}})$. The quantum-state resolved detection used here allows the disentanglement of the rotational, vibrational, and translational degrees of freedom of the scattered molecules.

The two examples discussed are (i) reactive scattering of monoatomic fluorine from room-temperature ionic liquids (RTILs) and (ii) inelastic scattering of benzene from a heated ($\sim$ 500 K) gold surface. In the former experiment, rovibrational states of the nascent HF beam are detected using direct infrared absorption spectroscopy, and in the latter, a resonace-enhanced multi-photon-ionization (REMPI) scheme is employed in combination with a velocity-map imaging (VMI) device, which allows the detection of different vibrational states of benzene excited during the scattering process.

---

[a] M. E. Saecker, S. T. Govoni, D. V. Kowalski, M. E. King and G. M. Nathanson *Science* **252**, 1421, 1991.

[b] A. M. Zolot, W. W. Harper, B. G. Perkins, P. J. Dagdigian and D. J. Nesbitt *J. Chem. Phys* **125**, 021101, 2006.

[c] J. R. Roscioli and D. J. Nesbitt *Faraday Disc.* **150**, 471, 2011.

TE09 **15 min 11:18**

PROBING THE STRUCTURE OF IONIC LIQUID SURFACES BY ROTATIONALLY AND ELECTRONICALLY INELASTIC SCATTERING OF NO

M. P. ZIEMKIEWICZ, A. ZUTZ, and D. J. NESBITT , *JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado, USA.*

Room temperature ionic liquids (RTILâĂŹs) are a highly diverse class of materials with many potential technological applications. They are candidates for use in advanced electrolytes, green solvents, and supported liquid membranes for CO_2 sequestration. We present studies where inelastic scattering of high or low velocity nitric oxide provides insight into the microscopic structure of these complex surfaces. As an open shell diatomic, jet-cooled NO $[^2\Pi_{1/2}(\mathrm{J} = 0.5)]$ features both molecular and electronic collision dynamics as seen by probing scattered rotational and spin-orbit distributions respectively. These studies show substantial variation in degree of rotational and electronic excitation as ionic liquid identity is varied. Also, surface heating is found to have a strong effect on scattered spin-orbit branching, possibly due to the dependence of surface structure on temperature. This is discussed in terms of a picture where the electronic degree of freedom may serve as a sensitive measure of the cationic versus anionic nature of the top few layers of this material.

TE10 **10 min 11:35**

PHOTOELECTRON SPECTROSCOPY OF SOLVATED ELECTRONS IN LIQUID MICROJETS

MADELINE ELKINS, ALEXANDER STREVE, and DANIEL NEUMARK, *Department of Chemistry, University of California - Berkeley, Berkeley, CA 94720.*

The solvated electron is a bare electron in solution. Lacking any internal degrees of freedom, it can be thought of as the simplest possible quantum mechanical solute, thus this relative simplicity makes the solvated electron an excellent model system for studying chemistry in solution. Furthermore, the solvated electron has proven to be an important transient in radiation chemistry and biology where it acts as an extremely reactive reductant. Research in the Neumark group over the past 10 years has contributed much to the understanding of the solvated electron via the study of anionic solvent clusters, the gas-phase analogues of the bulk solvated electron. By extrapolation to the limit of infinite cluster size, these results have been used to infer the binding energies and internal conversion lifetimes of the solvated electron in various bulk solvent systems; however, some controversy exists over this extrapolation method. Liquid microjets allow us to test these extrapolations by direct investigation of the bulk solvated electron in the liquid phase.

First measurements of the vertical binding energy (VBE) of the solvated electron in water were performed in 2010 and are in remarkable agreement with the predictions from anionic water clusters. Investigations into the binding energies of the solvated electron in methanol, ethanol, and tetrahydrofuran are presented, which yield some surprising results. Like in water, results in tetrahydrofuran are consistent with the VBE extrapolated from the cluster data; however, in methanol the result is significantly different from the predicted value. Moving on from the vertical binding energy experiments, we are beginning a study of the dynamics of the electron in aqueous solution. There are three known timescales for the relaxation of the solvated electron following excitation to its single, bound excited state; however, the transient absorption experiments used to measure these timescales originally are unable to conclusively determine a relaxation mechanism. We propose to repeat these measurements using time resolved photoelectron spectroscopy. These measurements are currently in progress and preliminary results are presented.

TF. INFRARED/RAMAN

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: KEEYOON SUNG, JPL-CalTech, Pasadena, California

TF01 **15 min 1:30**

THE HIGH-RESOLUTION FAR-INFRARED SPECTRA OF SULFUR DI-CYANIDE, $S(CN)_2$ AND THE PURSUIT OF THAT OF CYANOGEN ISO-THIOCYANATE, NCNCS

MANFRED WINNEWISSER, BRENDA P. WINNEWISSER, FRANK C. De LUCIA, *Department of Physics, The Ohio State University, Columbus Ohio, 43210-1106, USA*; DENNIS W. TOKARYK, DAMIEN FORTHOMME, SEPHEN C. ROSS, *Department of Physics and Centre for Laser, Atomic, and Molecular Sciences, University of New Brunswick, P.O. Box 4400, Fredericton NB E3B 5A3, Canada*; BRANT E. BILLINGHURST, *Canadian Light Source, Inc., University of Saskatchewan, Saskatoon, SK, Canada*.

There are only pellet low resolution infrared spectra reported in the literature for sulfur di-cyanide $S(CN)_2$, and none at all for cyanogen iso-thiocyanate, NCNCS. These two molecules are linked by a thermal isomerization reaction: NCSCN plus heat yields mainly NCNCS. Despite its difficult synthesis and its short kinetic life time, NCNCS is the best example so far of a quasi-linear molecule which clearly exhibits the distinctive monodromy-induced dislocation of the ro-vibrational energy levels. The momentum maps (monodromy plots) of various physical quantities, such as effective rotational constants, ro-vibrational energies, dipole moment components etc. for NCNCS show at the top of the punt of the two-dimensional champaign-bottle potential energy function[a] all the effects of quantum monodromy and exited state quantum phase transitions[b]. For that reason it would be highly interesting to observe for NCNCS the high-resolution FIR bands of the lowest quasi-linear bending vibration. At the Canadian Light Source in May-June 2011 we first had to obtain the far-infrared spectrum of the precursor molecule $S(CN)_2$ with the IFS125HR Bruker Fourier transform spectrometer. Six of the fundamental vibrational modes of this molecule have been observed and measured with the maximum resolution of 0.00096 cm^{-1}. The analysis of the measured and assigned band systems is presently being carried out and will be reported in this contribution. The experimental strategy for synthesizing NCNCS and observing its FIR bands in a flow system through a multi-pass infrared absorption cell will also be discussed.

---

[a] B. P. Winnewisser, M. Winnewisser, I. R. Medvedev, F. C. De Lucia, S. C. Ross and J. Koput, Phys. Chem. Chem. Phys., 2010, **12**, 8158-8189.

[b] D. Larese and F. Iachello, J. Mol. Struct., 1006 (2011) 611-628

TF02 **15 min 1:47**

COMBINATION BANDS OF THE NONPOLAR OCS DIMER INVOLVING INTERMOLECULAR MODES

M. REZAEI, J. NOROOZ OLIAEE, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada*; A.R.W. MCKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*.

Spectra of the nonpolar carbonyl sulfide in the region of the OCS ν_1 fundamental band were observed in a supersonic slit-jet apparatus. The expansion gas was probed using radiation from a tunable diode laser employed in a rapid-scan signal averaging mode. Three bands centered at 2085.906, 2103.504, and 2114.979 cm^{-1} were observed and anlysed. The rotational assignment and fitting of the bands were made by fixing the lower state parameters to those for the ground state of nonpolar $(OCS)_2$, thus confirming that they were indeed combination bands of the of the most stable isomer of OCS dimer. The band centered at 2085.906 cm^{-1} is a combination of the forbidden A_g intramolecular mode plus the geared bend intermolecular mode and that centered at 2114.979 cm^{-1} is a combination of the allowed B_u intramolecular mode plus the intermolecular van der Waals stretch. The combination at 2103.504 cm^{-1} can be assigned as a band whose upper state involves four quanta of the intramolecular bend or the B_u intramolecular mode plus two quanta of the intermolecular torsional mode. Isotopic work is needed to conclusively identify the vibrational assignment of this band. Our experimental frequencies for the geared bend and van der Waals modes are in good agreement with a recent high level ab initio calculation by Brown et al. [a]

---

[a] J. Brown, Xiao-Gang Wang, T. Carrington Jr. and Richard Dawes, Journal of Chemical Physics, submitted.

TF03 **15 min 2:04**

PHOTOIONIZATION INDUCED WATER MIGRATION OF 4-AMINOBENZONITRILE-$(H_2O)_1$ CLUSTER

TAKASHI NAKAMURA, *Chemical Resources Laboratory, Tokyo Tech, 4259 Nagatsuta-machi, Midori-ku, Yokohama-shi, Kanagawa, 226-8503, Japan*; MITSUHIKO MIYAZAKI, MASAAKI FUJII, *Chemical Resources Laboratory, Tokyo Tech, 4259 Nagatsuta-machi, Midori-ku, Yokohama-shi, Kanagawa, 226-8503, Japan*; and KOICHI TSUKIYAMA, *Department of Chemistry, Faculty of Science Division I, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan.*

4-Aminobenzonitrile-water cluster has two competitive hydration isomers at the S_0 state. One is NH isomer in which water binds to the NH group and the other is CN isomer in which water binds to the CN group. We applied IR dip spectroscopy to investigate how the interaction changes in the D_0 state. The IR spectra showed the same feature that was assigned to the NH isomer though the two isomers were selectively ionized. This observation means water molecule bonded to the CN group migrates to the NH group induced by the photoionization.

TF04 **15 min 2:21**

ISOLATION OF ION-DRIVEN CONFORMATIONS IN DIPHENYLACETYLENE MOLECULAR SWITCHES USING CRYOGENIC INFRARED SPECTROSCOPY

ARRON B. WOLK, *Yale University, 225 Prospect Street, New Haven, CT 06520*; ETIENNE GARAND, *Yale University, 225 Prospect Street, New Haven, CT 06520*; IAN M. JONES, *Yale University, 225 Prospect Street, New Haven, CT 06520*; MICHAEL Z. KAMRATH, *Yale University, 225 Prospect Street, New Haven, CT 06520*; ANDREW HAMILTON, *University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA*; and MARK A. JOHNSON, *Yale University, 225 Prospect Street, New Haven, CT 06520.*

We report the infrared predissociation spectra of a family of ionic diphenylacetylene molecular switch complexes.[a] The electrosprayed complexes were trapped and cooled in a cryogenic (10K) quadrupole ion trap and tagged with molecular deuterium. The infrared spectra of the vibrationally cold species reveal sharp transitions over a wide energy range (800 - 3800 cm^{-1}), facilitating comparison to harmonic spectra. The evolution of the band pattern upon derivatization of the complexes exposes the signatures of the amide, urea, and carbonyl functionalities, enabling unambiguous identification of the non-covalent interactions that control the secondary structure of the molecule. Complexation with the tetramethylammonium cation reveals a conformation analogous to that of the neutral molecule, while halide ion attachment induces a conformational change similar to that observed earlier in solution. In several cases, both the donor and acceptor groups involved in the multidentate H-bonds are observed, providing a microscopic mechanical picture of the interactions at play.

---

[a] I. Jones, and A. Hamilton, *Angew. Chem. Intl. Edit.* **50**, 4597 (2011).

TF05 **15 min 2:38**

INFRARED SPECTROSCOPY OF COLD, HYDRATED ALKALINE EARTH-HYDROXIDE CLUSTERS

CHRISTOPHER JOHNSON, CHRISTOPHER LEAVITT, JOSEPH FOURNIER, MARK JOHNSON, *Department of Chemistry, Yale University, New Haven, CT 06520.*

Hydrated, singly-charged $[MOH]^+$ (M=Mg,Ca) clusters have been investigated using mass-selective cryogenic infrared spectroscopy. Spectra of $[MOH]^+ \cdot (H_2O)_n$ reveal broad features beginning at $n = 3$ that approach 1000 cm^{-1} in width at $n = 5$, indicative of large amplitude motion in the water network despite ion temperatures below 40 K. Comparison to calculated structures and spectra help to elucidate the structural and charge-separation dynamics occurring in these clusters.

TF06 **15 min 2:55**

A HIGH RESOLUTION FAR INFRARED STUDY OF LOW LYING VIBRATIONAL BANDS OF 3-OXETANONE

ZIQIU CHEN AND JENNIFER VAN WIJNGAARDEN, *Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada.*

Rotationally resolved vibrational spectra of the four lowest frequency bands of the four-membered heterocycle 3-oxetanone (c-$C_3H_4O_2$) have been collected with a resolution of 0.00096 cm^{-1} using the far infrared beamline at the Canadian Light Source synchrotron. The modes observed correspond to motions best described as: ring puckering v_{21} at 139.55 cm^{-1}, C=O deformation (out-of-plane) v_{20} at 399.59 cm^{-1}, C=O deformation (in-plane) v_{16} at 448.19 cm^{-1}, and the ring deformation v_7 at 684.99 cm^{-1}. The observed spectra exhibit rich spectroscopic features including hot bands originating from the low energy ring puckering band and a first order *a-type* Coriolis interaction between the closely spaced v_{16} and v_{20} bands. The assignment and analysis of these dense spectra will be presented.

Intermission

TF07 **15 min 3:30**

GAS-PHASE SPECTROSCOPY OF TYROSINE BY LASER DESORPTION SUPERSONIC JET TECHNIQUE - STABILIZATION MECHANISM OF THE MOST STABLE CONFORMER

YOKO SHIMOZONO, SHUN-ICHI ISHIUCHI, MASAAKI FUJII , *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama 226-8503 Japan*; and KOICHI TSUKIYAMA , *Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601 Japan.*

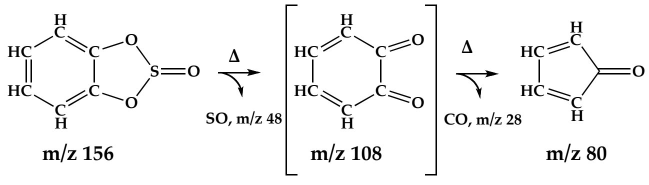
Gas-phase spectroscopy of tyrosine, which is one of the aromatic amino acids, has been reported by many researchers, however, their conclusions of the number of conformers and the assignments of their structures do not consistent with each other. In this work, electronic and infrared spectra of tyrosine were measured by laser desorption supersonic jet technique, and number of the conformers and their structures were reassigned by comparison with quantum chemical calculations. It was found that electrostatic interaction between phenolic OH and amino-acid chain is specifically enhanced in the most stable conformer.

TF08 **15 min 3:47**

POLARIZED MATRIX INFRARED SPECTRA OF CYCLOPENTADIENONE

THOMAS K. ORMOND, ADAM M. SCHEER, G. BARNEY ELLISON, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215*; MARK R. NIMLOS, *Center for Renewable Chemical, Technologies & Materials, NREL, 1617 Cole Blvd., Golden, CO 80401*; JOHN W. DAILY, *Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309-0427*; JOHN F. STANTON, *Institute for Theoretical Chemistry, Department of Chemistry, University of Texas, Austin, TX 78712.*

We are developing a resistively-heated SiC μtubular reactor with a 100 μsec residence time to study the thermal cracking of biomass monomers. The decomposition products are identified by two independent techniques: 118.2 nm VUV photoionization mass spectrometry (PIMS) and matrix infrared spectroscopy. Many lignins thermally crack[a] to produce cyclopentadienone (m/z 80) and its derivatives. Subsequent decomposition of these cyclopentadienones results in formation of substituted acetylenes which are known precursors to polycyclic aromatic hydrocarbons and soot. Due to its anitaromatic character, cyclopentadienone is highly reactive and presents an interesting spectroscopic system. Pyrolysis of *o*-phenylene sulfite (m/z 156) is a convenient precursor for cyclopentadienone. In this work we report the polarized matrix infrared absorption spectra of cyclopentadienone and d_4-cyclopentadienone. The PIMS results corroborate the thermal decomposition steps of phenylene sulfite. *Ab initio* coupled-cluster anharmonic force field calculations are used to guide the vibrational assignments.



---

[a] A. M. Scheer, C. Murkarakate, D. J. Robichaud, M. R. Nimlos, and G. B. Ellison *J. Phys. Chem. A* 115, 13381 (2011)

TF09 **15 min 4:04**

MIXED HELICES IN THE GAS PHASE: CONFORMATION-SPECIFIC UV AND IR SPECTROSCOPY OF POLYGLYCINE Z-(GLY)$_n$ (n=1,3,5)

JACOB C. DEAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

The intrinsic conformational preferences of peptide backbones have long been of fundamental importance to biochemical understanding of protein folding and its structure-function relationship. As such, the simplest naturally-occurring amino acid, glycine, is a model building block for understanding backbone structure in peptides due to its flexible nature (no side chain to hinder folding) and unmatched range of potential Ramachandran angles to be sampled. In aqueous solution, polyglycine is thought to form a loose 3_1 helix (PGII) that has been a challenge to characterize, and depends intimately on the aqueous solvent for its stability. What is not established is the fundamental conformational preferences for glycine-rich peptides in the absence of solvent. This talk will present a detailed study of the single-conformation spectroscopy of a series of glycine peptides that begins to address this subject, using Z-(Gly)$_n$-OH with n=1,3,5 and Z-(Gly)$_5$-NHMe. Double-resonance UV and IR methods were used to obtain conformation-specific spectra, and conformational assignments were made using the NH/OH stretch, Amide I, and Amide II regions of the infrared spectrum. The observed conformers exhibit a common backbone structure that evolves with increasing number of glycines. In eludicating the helical structure of Z-(Gly)$_5$, -OH and -NHMe capped pentaglycines were investigated, and with the aid of ab initio calculations it was found that a mixed helix conformation was preferred in both cases completely dominating the population sampled in the jet. IR-UV holeburning spectroscopy was employed to demonstrate the existence of only one conformation for both Z-(Gly)$_5$ molecules. These structures use 7-membered H-bonded rings to produce turns along the backbone while 14-membered and 16-membered rings tie the structure together into a mixed helix. Such helices differ from the PGII helix in having a smaller dipole due to alternating direction of the 14- and 16-membered rings.

TF10 **15 min 4:21**

UTILIZING FORCE FIELD METHODS TO EXPLORE POTENTIAL ENERGY LANDSCAPES OF FLEXIBLE BIOMOLECULES

ZACHARY S. DAVIS, *Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*; JOANNE M. CARR, IVAN Y. W. TAN, DAVID J. WALES, *Cambridge University Center for Computational Chemistry, Lensfield, Cambridge, United Kingdom CB2 1EW*; TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.*

Spectroscopic studies of single conformations of flexible biomolecules are providing considerable new physical insight to their conformational preferences. Such studies are done against a backdrop of a full potential energy surface (PES) that has great complexity, often containing thousands of minima and an even greater number of transition states separating them. Often the relationship between experiment and the full PES is unclear. In this context, it would be extremely helpful to have predictions and summaries of the PES that enable comparisons from one molecule to the next, and of one molecule under different conditions. By utilizing the speed of force field calculations, the potential energy surface may be thoroughly explored, including both minima and transition states, in a computationally inexpensive manner. As minima and transition states are found, they are added to a disconnectivity graph, a summary of the entire potential energy surface in which the different minima are connected to one another by one or more transition states, which are grouped by energy. Disconnectivity graphs have been prepared for the flexible hexamide Z-(Gly)$_5$-NHMe (where the Z-cap is a benzocarboxy substituent), which has been studied experimentally in isolated form using single-conformation spectroscopy. Disconnectivity graphs of both the isolated and solvated molecule provide insight to the solvent-induced conformational differences. In addition, the peptide Ac-Phe-Ala-NHMe has been modeled using all α-amino acids, all β-amino acids, and all γ-amino acids. As the flexibility and complexity of the triamide increases, the disconnectivity graphs illuminate changes in the relationships between different conformational families as well as any changes in the height of the barriers between those families. These results will be compared to previous results from single-conformation spectroscopy on this series.

TF11 10 min 4:38

BINDING OF Na^+ AND K^+ TO THE HEADGROUP OF PALMITIC ACID MONOLAYERS STUDIED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

ZISHUAI HUANG and HEATHER C. ALLEN, *Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

Alkali cations are critical in biological systems due to their electrical interaction with cell membranes. While Na^+ and K^+ share similar chemical and physical properties, they can exhibit differences when interacting with biological membranes. These phenomena may be modeled using a Langmuir monolayer of surfactant on alkali chloride solutions. Vibrational sum frequency generation (VSFG) spectroscopy is an interface specific technique that is widely employed to study molecular organization at surfaces and interfaces. VSFG spectroscopy was used to probe the CO_2^- vibrational mode for the carboxylic acid headgroup of palmitic acid (PA) spread on the surface of NaCl and KCl solutions in the vibrational region between 1400 and 1500 cm^{-1}. The ability of Na^+ and K^+ to bind with the carboxylic headgroup of PA is revealed by observing peak positions ($\sim$1410 cm^{-1} and $\sim$1470 cm^{-1}) and relative intensity for the CO_2^- peaks. These results are compared and discussed with perspective toward elucidating interfacial PA headgroup organization. The time evolution for the PA CO_2^- peaks is also monitored after monolayer spreading via VSFG and these results are presented as well.

TF12 15 min 4:50

CONFORMATIONAL AND STRUCTURAL STUDIES OF ISOPROPYLAMINE FROM TEMPERATURE DEPENDENT RAMAN SPECTRA OF XENON SOLUTIONS AND *AB INITIO* CALCULATIONS

JOSHUA J. KLAASSEN, IKHLAS D. DARKHALIL, JAMES R. DURIG, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110, USA.*

The Raman and infrared spectra (4000 to 50 cm^{-1}) of the gas, liquid or solution, and solid have been recorded of isopropylamine, $(CH_3)_2CHNH_2$. Variable temperature (-50 to -100^{o}C) studies of the Raman spectra (3500 to 100 cm^{-1}) dissolved in liquid xenon have been carried out. From these data, both the *trans* and *gauche* conformers have been identified and their relative stability obtained. The enthalpy difference has been determined from 20 band pairs at 6 temperatures to be 113 +/- 11 cm^{-1} (1.35 +/- 0.13 kJ mol^{-1}) with the *trans* conformer the more stable form. The percentage of the *gauche* conformer is estimated to be 54 +/- 1 percent at ambient temperature. The conformational stabilities have been predicted from *ab initio* calculations utilizing several different basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. By utilizing previously reported microwave rotational constants along with *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained for the *trans* conformer. The determined heavy atom and NH_2 distances in angstroms are C-C = 1.530(3), C-N = 1.465(3), N-H = 1.019(3) and angles in degrees NCC = 108.9(5), CCC = 111.0(5), HNC = 110.3(5). The structural parameters for the *gauche* conformer were estimated by using the same adjustment differences to the *gauche* form as those obtained for the corresponding *trans* parameters. Vibrational assignments have been provided for the observed bands for both conformers which are supported by MP2(full)/6-31G(d) *ab initio* calculations to predict harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for both conformers. The results are discussed and compared to the corresponding properties of some related molecules.

TG. ELECTRONIC

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: JOSH BARABAN, Massachusetts Institute of Technology, Cambridge, Massachusetts

TG01 **10 min 1:30**

IMPROVED EXPERIMENTAL LINE POSITIONS FOR THE (1,1) BAND OF THE $b^1\Sigma^+$ - $X^3\Sigma^-$ TRANSITION OF O_2 BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

LEAH C. O'BRIEN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652*; EMILY C. O'BRIEN, JAMES J. O'BRIEN, *Department of Chemistry & Biochemistry and Center for NanoScience, University of Missouri, St. Louis, MO 63121-4400.*

We report improved experimental line positions for the (1,1) band of the $b^1\Sigma^+$ - $X^3\Sigma^-$ transition of O_2. Results are comparised with previous experimental measurements and predicted values. Additionally, a new method of producing vibrationally hot molecules for use in absorption spectroscopy of stable gas phase molecules is described.

TG02 **15 min 1:42**

SPECTROSCOPY OF CuN IN THE NEAR INFRARED BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

LEAH C. O'BRIEN, KAITLIN A. WOMACK, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652*; JAMES J. O'BRIEN, *Department of Chemistry & Biochemistry and Center for NanoScience, University of Missouri, St. Louis, MO 63121-4400.*

Transitions with red-degraded bandheads have been identified at 13005, 12963, 12957, and 12948 cm^{-1}. One P and one R branch are identified in each transition. We have tentatively assigned these transitions as absorption from the X $^3\Sigma^-$ ground state of CuN. Rotational analyses of these bands are in progress, and results will be presented. A strong perturbation is observed in one of the excited states. The electronic structure of CuN will be discussed and compared with predicted electronic states from theoretical calculations. The gas phase CuN molecules were produced using a copper hollow cathode in a plasma discharge.

TG03 **15 min 1:59**

THE SOLUTION TO THE ELECTRONIC SPECTRUM OF THE CHLORINE CATION (Cl_2^+)

MOHAMMED A. GHARAIBEH and DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*; APOSTOLOS KALEMOS, *National and Kapodistrian University of Athens, School of Natural Sciences, Department of Chemistry, Laboratory of Physical Chemistry, P.O. Box 64 004, 157 10 Zografou, Athens, Greece*; ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.*

The highly perturbed $A^2\Pi_i$ - $X^2\Pi_i$ electronic band system of the chlorine cation (Cl_2^+) had previously been extensively studied, but no satisfactory vibrational analysis had been achieved. Although rotationally quite regular, the bands show substantial vibrational perturbations, irregular chlorine isotope splittings, and numerous weak extra features. We have succeeded in obtaining LIF spectra of jet-cooled Cl_2^+ that extend the known spectrum some 3000 cm^{-1} to the red of all previous measurements. The very weak 0 - 0 band has been positively identified and the v′= 0 - 3 levels are found to be unperturbed. Higher levels exhibit significant perturbations, which we have shown by high level ab initio studies of the relevant potential energy curves to be due to a homogeneous spin-orbit interaction between the $A^2\Pi_{3/2}$ and $B^2\Delta_{3/2}$ states. Non-adiabatic effects have been introduced using the coupled equations, which have been solved to yield the energies of the vibronic levels. The computed vibronic states are in good quantitative agreement with the experimental data, allowing assignments to be made for both the strong main bands as well as the weaker transitions to the interloper levels. After more than 80 years of study, the electronic spectrum of the chlorine cation can now be understood in considerable detail.

TG04 15 min 2:16

CAVITY RINGDOWN ABSORPTION SPECTRUM OF THE $T_1(n, \pi^*) \leftarrow S_0$ TRANSITION OF ACROLEIN: ANALYSIS OF THE 0_0^0 BAND ROTATIONAL CONTOUR

NIKOLAUS C. HLAVACEK, MICHAEL O. MCANALLY, and STEPHEN DRUCKER, *Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702.*

Acrolein (propenal, CH_2=CH—CH=O) is the simplest conjugated enal molecule and serves as a prototype for investigating the photochemical properties of larger enals and enones. Acrolein has a coplanar arrangement of heavy atoms in its ground electronic state. Much of the photochemistry is mediated by the $T_1(\pi, \pi^*)$ state, which has a CH_2–twisted equilibrium structure. In solution, the $T_1(\pi, \pi^*)$ state is typically accessed via intersystem crossing from an intially prepared planar $S_1(n, \pi^*)$ state. An intermediate in this photophysical transformation is the lowest $^3(n, \pi^*)$ state, a planar species with adiabatic excitation energy below S_1 and above $T_1(\pi, \pi^*)$. The present work focuses on this $^3(n, \pi^*)$ intermediate state; it is designated $T_1(n, \pi^*)$ as the lowest-energy triplet state of acrolein having a planar equilibrium structure.

The $T_1(n, \pi^*) \leftarrow S_0$ band system, with origin near 412 nm, was first recorded in the 1970s at medium (0.5 cm^{-1}) resolution using a long-path absorption cell. Here we report the cavity ringdown spectrum of the 0_0^0 band, recorded using a pulsed dye laser with 0.1 cm^{-1} spectral bandwidth. The spectrum was measured under both bulk-gas (room-temperature) and jet-cooled conditions. The band contour in each spectrum was analyzed by using a computer program developed[a] for simulating and fitting the rotational structure of singlet-triplet transitions. The assignment of several resolved sub-band heads in the room-temperature spectrum permitted approximate fitting of the inertial constants for the $T_1(n, \pi^*)$ state. The determined values (cm^{-1}) are $A = 1.662$, $B = 0.1485$, $C = 0.1363$. For the parameters A and $(B + C)/2$, estimated uncertainties of ±0.003 cm^{-1} and ±0.0004 cm^{-1}, respectively, correspond to a range of values that produce qualitatively satisfactory global agreement with the observed room-temperature contour. The fitted inertial constants were used to simulate the rotational contour of the 0_0^0 band under jet-cooled conditions. Agreement with the observed jet-cooled spectrum was optimized by varying the homogeneous linewidth of the rovibronic transitions as well as the rotational temperature. The optimal FWHM was about 0.20 cm^{-1}, leading to an estimate of 25 ps for the lifetime of the $T_1(n, \pi^*)$ state of acrolein ($v = 0$) under isolated-molecule conditions.

---

[a] R. H. Judge *et al.*, *J. Chem. Phys.* **103**, 5343 (1995).

TG05 15 min 2:33

COMPUTATIONAL APPROACHES TO THE DETERMINATION OF THE MOLECULAR GEOMETRY OF ACROLEIN IN ITS $T_1(n, \pi^*)$ STATE

MICHAEL O. MCANALLY, NIKOLAUS C. HLAVACEK, and STEPHEN DRUCKER, *Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702.*

The spectroscopically derived inertial constants for acrolein (propenal) in its $T_1(n, \pi^*)$ state[a] were used to test predictions from a variety of computational methods. One focus was on multiconfigurational methods, such as CASSCF and CASPT2, that are applicable to excited states. We also examined excited-state methods that utilize single reference configurations, including EOM-EE-CCSD and TD-PBE0. Finally, we applied unrestricted ground-state techniques, such as UCCSD(T) and the more economical UPBE0 method, to the $T_1(n, \pi^*)$ excited state under the constraint of C_s symmetry. The unrestricted ground-state methods are applicable because at a planar geometry, the $T_1(n, \pi^*)$ state of acrolein is the lowest-energy state of its spin multiplicity. Each of the above methods was used with a triple zeta quality basis set to optimize the $T_1(n, \pi^*)$ geometry. This procedure resulted in the following sets of inertial constants:

Inertial constants (cm^{-1}) of acrolein in its $T_1(n, \pi^*)$ state

Method	*A*	*B*	*C*	Method	*A*	*B*	*C*
CASPT2(6,5)[b]	1.667	0.1491	0.1368	UCCSD(T)[b]	1.668	0.1480	0.1360
CASSCF(6,5)	1.667	0.1491	0.1369	UPBE0	1.699	0.1487	0.1367
EOM-EE-CCSD	1.675	0.1507	0.1383				
TD-PBE0	1.719	0.1493	0.1374	**Experiment**[a]	1.662	0.1485	0.1363

The two multiconfigurational methods produce the same inertial constants, and those constants agree closely with experiment. However the sets of computed bond lengths differ significantly for the two methods. In the CASSCF calculation, the lengthening of the C=O and C=C bonds and the shortening of the C—C bond are more pronounced than in CASPT2.

---

[a] Previous talk

[b] O. S. Bokareva *et al.*, *Int. J. Quant. Chem.* **108**, 2719 (2008).

Intermission

TG06 **15 min 3:10**

CONSISTENT ASSIGNMENTS OF THE VIBRATIONS OF SUBSTITUTED BENZENES

ADRIAN M. GARDNER and TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

When substituted benzene molecules become the subject of a spectroscopic study, one is often haunted by the knowledge of the confusion that awaits owing to the various vibrational labeling schemes, conventions and assignments that have been employed in the past are unraveled. Here, we attempt to alleviate this frustration through the development of a scheme which unites the normal modes of vibration of all mono-substituted benzene molecules based on those of fluorobenzene.[a]

---

[a] A. M. Gardner and T. G. Wright, *J. Chem. Phys.*, **135**, 114305 (2011)

TG07 **15 min 3:27**

ELECTRONIC AND PHOTOELECTRON SPECTROSCOPY OF TOLUENE

ADRIAN M. GARDNER, ALISTAIR M. GREEN, VICTOR TAMÉ-REYES and TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

Electronic and photoelectron spectra of toluene are presented and discussed. The utilization of a recently reported scheme for assigning the normal vibrations of substituted benzenes allows these spectra to be compared to those of other molecules with unprecedented clarity.[a] Changes in vibrational activity within a series of substituted benzene molecules will be discussed, specifically the increased rate of intramolecular vibrational energy redistribution observed in molecules where the substituent is a methyl group.

---

[a] A. M. Gardner and T. G. Wright, *J. Chem. Phys.*, **135**, 114305 (2011)

TG08 **15 min 3:44**

RESONANCE ENHANCED MULTIPHOTON IONIZATION (REMPI) SPECTROSCOPY OF WEAKLY BOUND COMPLEXES

LLOYD MUZANGWA, SILVER NYAMBO, BRANDON UHLER AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

We have recently implemented Resonance Enhanced Multiphoton Ionization (REMPI) spectroscopy in our laboratory as a spectroscopic probe of transient species. We will report on initial gas-phase studies of the spectra of weakly bound van der Waals and halogen bonded complexes involving aromatic organic donors. The complexes are formed in the rarified environment of a supersonic molecular beam, which is skimmed prior to passing into the differentially pumped flight tube of a linear time-of-flight mass spectrometer. Ionization is initiated both by 1+1 and 1+1' REMPI schemes; the latter is used to minimize fragmentation. Our initial studies have examined van der Waals and halogen bonded complexes involving the phenol and toluene chromophores. Progress in the coupling of a discharge source into this apparatus will also be discussed.

TG09 15 min 4:01

CONFORMATION-SPECIFIC INFRARED AND ULTRAVIOLET SPECTROSCOPY OF α-METHYLBENZYL RADICAL: PROBING THE STATE-DEPENDENT EFFECTS OF METHYL ROCKING AGAINST A RADICAL SITE

NATHANAEL M. KIDWELL, DEEPALI N. MEHTA, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*; NEIL J. REILLY, DAMIAN L. KOKKIN, and MICHAEL C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.*

Combustion processes involve a myriad of complex reaction pathways which connect smaller precursors to larger polyaromatic hydrocarbons, many of which are still unknown. In particular, benzyl-type radicals play an important role in combustible fuels due to their intrinsic resonance stabilization and consequent increase in relative concentration. Here, we present a study of the vibronic spectroscopy of α-Methylbenzyl radical (α-MeBz), in which the orientation of the methyl group adjacent to the radical site responds to the electronic interaction extending from the conjugated π-system. Probing the isolated radical, produced in an electrical discharge under jet-cooled conditions, the two-color resonant two-photon ionization, fluorescence excitation, and dispersed fluorescence spectra were obtained in order to determine the ground and excited state barriers to internal rotation and the angular change associated with electronic excitation. Resonant ion-dip infrared spectroscopy (RIDIRS) has also been implemented to elucidate the infrared signatures in the alkyl and aromatic CH stretch regions in order to probe in a complementary way the state-dependent conformational preferences of α-MeBz. We will show that the D_0- and D_1-RIDIR spectra report sensitively on the strong coupling between the CH stretch vibrations and the C_α-C_β torsional geometry. Furthermore, photoionization efficiency scans were carried out to reveal the adiabatic ionization threshold of α-MeBz and the quantized levels present in the radical cation state.

TG10 15 min 4:18

VIBRONIC SPECTROSCOPY OF PHENYLVINYLNITRILE

DEEPALI N. MEHTA, POLINA NAVOTNAYA, ALEX PAROBEK, RACHEL CLAYTON, VANESA VAQUERO VARA, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084 U.S.A.*

This talk will present results of a gas phase, jet-cooled vibronic spectroscopy study of phenylvinylnitrile (C_6H_5-CH=CH-CâL'ąN, PVN). This molecule is seen as a potential photochemical precursor to nitrogen heteroaromatics, and therefore is particularly relevant to Titan's atmosphere, where nitriles exist in significant abundance. As a first step towards such photochemical studies, a fluorescence excitation spectrum of PVN spanning the range 33,500-35,840 cm^{-1} (298.5-279.0 nm) has been recorded, and dispersed fluorescence spectra that uncover and characterize the vibronic activity have been acquired. The S_0-S_1 origin is a prominent band located at 33,826 cm^{-1}, and the excitation spectrum is characterized by significant vibronic activity leading to spectral congestion. Hole-burning in the region of 33,500-35,840 cm^{-1} has also been completed, and the excitation spectrum can be assigned solely to (E)-PVN. As PVN is the nitrogen-containing counterpart to phenylvinylacetylene (PVA), a comparison of the vibronic spectroscopy between the two molecules will be made.

TH. MICROWAVE

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: SHANSHAN YU, Jet Propulsion Laborabory, Pasadena, California

TH01 **15 min 1:30**

PROTIC ACID HYDROGEN BONDING IN CHLOROFLUOROETHYLENES: THE HYDROGEN FLUORIDE-VINYL CHLORIDE COMPLEX

HELEN O. LEUNG AND MARK D. MARSHALL, *Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.*

Our studies of intermolecular complexes formed in the gas phase between protic acids (HX) and chlorofluoroethylene complexes to date have demonstrated a preference for HX binding to a F atom over hydrogen bond formation with the Cl atom. *Ab initio* calculations suggest that this may not be true for species with an increased degree of halogen substitution on the ethylene. To characterize the nature of hydrogen bond formation with the less electronegative, but more polarizable Cl atom, we have obtained the microwave spectrum of HF-vinyl chloride complex. Analysis of the spectra for the ^{35}Cl and ^{37}Cl isotopologues demonstrate that the complex is planar and provides structural parameters for this species. This allows comparisons to be made between the HX hydrogen bond to Cl and that to F.

TH02 **15 min 1:47**

BROADBAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND MOLECULAR STRUCTURE OF THE ARGON-*(Z)*-1-CHLORO-2-FLUOROETHYLENE COMPLEX

HELEN O. LEUNG AND MARK D. MARSHALL, *Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.*

A chirped-pulse Fourier transform microwave spectrometer is used to obtain the 6–18 GHz rotational spectrum of the gas-phase complex formed between argon and *(Z)*-1-chloro-2-fluoroethylene. Both the ^{35}Cl and ^{37}Cl isotopologues are observed in natural abundance, and analysis of these spectra provides predictions for both singly-substituted ^{13}C species with sufficient precision to allow their observation with minimal searching using the more sensitive narrow band Balle-Flygare cavity technique. The non-planar structure of the complex is similar to previously observed argon-fluoroethylene complexes with the argon atom closer to the fluorine than to the chlorine. In contrast to the argon-vinyl chloride and argon-*cis*-1,2-difluoroethylene complexes, tunneling of the argon atom between the two equivalent, non-planar geometries is not observed.

TH03 15 min 2:04

ROTATIONAL SPECTRUM OF Ar...PROPARGYL ALCOHOL COMPLEX

DEVENDRA MANI, ABHISHEK SHAHI and E. ARUNAN, *Department of Inorganic and Physical Chemistry, Indian Institute of Science Bangalore, India-560012.*

Pure rotational spectrum for Ar...Propargyl alcohol complex has been observed and fitted. Fitted rotational constants for the complex are : A=4346.17307(90) MHz, B=1617.15317(19)MHz and C= 1245.42065(15) MHz. These rotational constants are very close to the ab-initio rotational constants for the geometry, in which propargyl alcohol exists in gauche conformation and Ar interacts with both, the hydroxyl group and the acetylenic group of propargyl alcohol. Rotational spectrum of deuterated isotopologue (-OD) of the complex further confirms the existence of the above mentioned geometry. In previous studies tunneling frequency corresponding to -OH tunneling motion in propargyl alocohol monomer was determined to be 652.4 GHz and for -OD tunneling motion in mono-deuterated species, it was 213.5 GHz[ab]. In Ar...Propargyl alcohol complex also, a-type and c-dipole transitions show tunneling splitting. In the parent complex, for a-type transitions, tunneling splitting was 10 KHz and for c-type transitions (c-dipole of the complex is in the same direction as in propargyl alcohol monomer, and it is antisymmetric with respect to OH tunneling motion in both monomer and the complex), it was 2.59 MHz. In deuterated complex (OD) splitting was not resolvable for a-type transitions while for c-type it reduces to 900 KHz. Search for C-13 isotopologues is in progress. Moreover, propargyl alcohol offers several possibilities for H-bonding and we are planning to study its complexes with water in near future. Results will be presented in the talk.

---

[a] E. Hirota,J. Mol. Spectrosc. 26 (1968) 335-350.
[b] J.C. Pearson, B.J. Drouin, J. Mol. Spectrosc. 234 (2005) 149-156.

TH04 15 min 2:21

ROTATIONALLY-RESOLVED SPECTRA OF 2-METHYLFURAN FROM THE CM-WAVE TO THE FAR INFRARED

STEVEN T. SHIPMAN and IAN A. FINNERAN, *Division of Natural Sciences, New College of Florida, Sarasota, FL 34243*; SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; JENNIFER VAN WIJNGAARDEN, *Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada.*

Rotationally-resolved spectra of 2-methylfuran have been acquired in several spectral regions. Spectra from 8.7 to 26.5 GHz were collected with a waveguide chirped-pulse Fourier transform microwave spectrometer at New College of Florida. Spectra from 75 to 960 GHz were collected with a single-pass direct absorption mm-/submm-wave spectrometer at Emory University. Spectra in selected regions from 200 to 700 cm^{-1} were collected using far infrared radiation from the Canadian Light Source synchrotron facility coupled to a Bruker IFS125HR Fourier transform spectrometer. A complete analysis of the combined data set is ongoing. Here, we will present our current results, which include assignments of over 25,000 transitions from the ground vibrational state and the first excited state of the methyl torsional mode.

TH05 15 min 2:38

THE FOURIER TRANSFORM MICROWAVE (FTMW) SPECTRA OF CYCLOHEXENE OXIDE AND ITS ARGON COMPLEX

DANIEL J. FROHMAN, STEWART E. NOVICK, and WALLACE C. PRINGLE, *Department of Chemistry, Wesleyan University, 52 Lawn Ave., Middletown, CT 06459-0180.*

The microwave spectrum of cyclohexene oxide and its isotopologues have been observed and assigned, improving upon previous rotational studies of this molecule.[a,b] Additionally, the ^{17}O isotopomer of cyclohexene oxide and the Ar complex of the normal isotopologue of cyclohexene oxide have been fit for the first time. Fits for the ^{13}C-cyclohexene oxide Ar complexes will also be presented.

---

[a] Tatsuya Ikeda, Roger Kewley, and R. F. Curl, Jr. *J. Mol. Spectrosc.*, **44** (1972), 459-469.
[b] Raquel Sánchez, Susana Blanco, Juan C. López, and José L. Alonso. *J. Mol. Struct.*, **780-781** (2006), 57-64.

TH06 15 min 2:55

MICROWAVE SPECTRA OF DEUTERIUM ISOTOPOLOGUES OF *cis*-HEXATRIENE

NORMAN C. CRAIG, HANNAH A. FUSON, HENGFENG TIAN, and HERMAN VAN BESIEN, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*; ANDREW A. CONRAD AND MICHAEL J. TUBERGEN, *Department of Chemistry, Kent State University, Kent, OH 44242*.

Several deuterium isotopologues of *cis*-hexatriene have been synthesized in sub-millimole amounts. They include a mixture of the 1,1-d_2, *cis*-1-d_1, and *trans*-1-d_1 species and a sample of the 2-d_1 species. Microwave spectra for *b*-type transitions were observed in the 12-21 GHz range on the jet-beam, mini-cavity FT instrument at Kent State University. *cis*-Hexatriene has a small dipole moment of approximately 0.05 D. For the 1,1-d_2 species, 11 lines were found, and for each of the two 1-d_1 species, 9 lines were observed. For the 2-d_1 species, 10 lines were measured. Ground state rotational constants were fitted to the transitions using quartic centrifugal distortion constants computed with the B3LYP/cc-pVTZ model for each isotopologue. In prior work, rotational constants for the ^{13}C species of *cis*-hexatriene were observed in natural abundance.[a] Thus, we are close to having sufficient experimental information for determining a semiexperimental equilibrium structure for *cis*-hexatriene. The principal goal is to assess the effect of pi-electron delocalization on the C_6 backbone in comparison with butadiene.

---

[a] R. D. Suenram, B. H. Pate, A. Lesarri, J. L. Neill, S. Shipman, R. A. Holmes, M. C. Leyden, N. C. Craig J. Phys. Chem. A 113, 1864-1868 (2009).

TH07 15 min 3:12

THE CONFORMATIONS AND STRUCTURES OF 1H-NONAFLUOROBUTANE

JOSEPH A. FOURNIER, ROBERT K. BOHN, *Dept. of Chemistry, Univ. of Connecticut, Storrs, CT 06269-3060*; JOHN A. MONTGOMERY, JR., *Dept. of Physics, Univ. of Connecticut, Storrs, CT 06269-3046*.

The all trans conformers of perfluorocarbons, unlike hydrocarbons, are helical with C-C-C-C dihedral angles about 164^0. Fluorocarbons with H substitution can replace chlorofluorocarbons as propellants and compressor fluids without the disadvantage of causing ozone depletion in the upper atmosphere. 1H-perfluorobutane, $CHF_2CF_2CF_2CF_3$, has been studied by pulsed-jet Fourier transform microwave spectroscopy. The spectrum is very rich. Quantum chemical calculations identify five stable conformers with relative energies up to 1.1 kcal/mol. Thus far three conformers have been characterized and many lines remain unassigned. The assigned species have CCCCanti/CCCH gauche as well as the anti/anti and gauche/anti forms. Rotational constant values are 1428.9501(2) MHz, 593.323877(6) MHz, and 546.43578(6) MHz for the anti/gauche species, 1323.664(3) MHz, 617.6051(5) MHz for the ant/anti species, and 1066.9384(4) MHz, 768.4736(4) MHz, and 671.3145(4) MHz for the gauche/anti form.

TH08 15 min 3:29

ROTATIONAL SPECTRA AND STRUCTURES OF THE MONO- AND DI-FLUORINATED PYRIDINES

CODY W. VAN DIJK, MING SUN AND JENNIFER VAN WIJNGAARDEN, *Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada*.

The ground state rotational spectra of a series of fluorinated pyridines have been measured using a Balle-Flygare Fourier transform microwave (FTMW) spectrometer and a chirped pulse Fourier transform microwave (cp-FTMW) instrument between 8 and 23 GHz. The species under investigation include 2- and 3-fluoropyridine as well as 2,3-, 2,4-, 2,5-, 2,6- and 3,5-difluoropyridine. In addition to the parent species, the spectra of the ^{13}C and ^{15}N singly-substituted isotopologues were recorded in natural abundance and used to calculate relevant geometric parameters of the pyridine ring backbone. Analysis of the ^{14}N hyperfine structure provided an additional source of information about the electronic structure surrounding the nitrogen atom as a function of fluorine substitution. The experimental results are compared with those from *ab initio* theory and are consistent with a bonding model that involves donation of electron density from fluorine into the π-system of pyridine.

Intermission

TH09 **15 min 4:00**

MILLIMETER AND SUBMILLIMETER-WAVE SPECTRUM OF AMINOACETONITRILE (NH_2CH_2CN)

YUTA MOTOKI, YUKARI TSUNODA, HIROYUKI OZEKI, *Department of Environmental Science, Toho University, 2-2-1 Miyama, Funabashi, 274-8510, Japan*; KAORI KOBAYASHI, *Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555, Japan.*

Aminoacetonitrile (NH_2CH_2CN) draws an attention with respect to a synthesis of amino acid in interstellar space, as it is considered to be a direct precursor of the simplest amino acid, glycine. Recently the molecule was detected toward SgrB2(N) [a], in which spectral line frequencies are predicted on the basis of the previous millimeter-wave study[b]. We have measured pure rotational spectrum of aminoacetonitrile in the millimeter and the submillimeter-wave region. About 300 spectral lines including both a-type and b-type transitions were recorded up to 661 GHz, and centrifugal distortion constants up to the octic term were precisely determined. We had to reinvestigate most of the b-type transition lines due to wrong assignments in the previous study. The updated frequency catalogue of the aminoacetonitrile are now accurate enough for astronomically search up to 1000 GHz.

---

[a] A. Belloche et al., *A&A*, 482, 179 (2008)

[b] M. Bogey, H. Dubus and J. C. Guillmin, *J. Mol. Spectrosc.*, 143, 180 (1990)

TH10 **15 min 4:17**

PERTURBATIONS AND VIBRATIONAL ENERGIES IN ACRYLONITRILE FROM GLOBAL ANALYSIS OF ITS MM-WAVE TO THZ ROTATIONAL SPECTRUM

ZBIGNIEW KISIEL, LECH PSZCZÓŁKOWSKI, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; BRIAN J. DROUIN, CAROLYN S. BRAUER, SHANSHAN YU, JOHN C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA*; IVAN R. MEDVEDEV, *Department of Physics, Wright State University, Dayton, OH 45435, USA*; SARAH FORTMAN, CHRISTOPHER NEESE, *Department of Physics, The Ohio State University, Columbus, OH 43210, USA.*

The rotational spectrum of acrylonitrile has recently been studied in some detail up to THz frequencies.[a,b] The perturbation between the ground state and $v_{11} = 1$ that was initially identified in the parent[a] has also been observed in other isotopologues.[b] The considerable energy difference between these states (228.29991(2) cm^{-1} in the parent) was, in all cases, determined entirely from perturbations in rotational transitions.

Many other perturbations in rotational transitions have been identified, allowing the $v_{15} = 1$ level to be added to the analysis.[c] We have now extended the broadband coverage of the rotational spectrum even further, and have been able to add the fourth vibrational state, v_{11}=2, to the global analysis. The current coupled fit encompasses well over 12000 transition frequencies and delivers precise vibrational energy information entirely on the basis of many fitted perturbations in rotational transitions. The present work was used to further refine the features for identifying perturbations built into the AABS package for Assignment and Analysis of Broadband Spectra.[d]

---

[a] Z.Kisiel, L.Pszczółkowski, B.J.Drouin, C.S.Brauer, S.Yu, J.C.Pearson, *J. Mol. Spectrosc.*, **258**, 26 (2009).

[b] A. Krasnicki, Z.Kisiel, B.J.Drouin, J.C.Pearson, *J. Mol. Struct.*, **1006**, 20 (2011).

[c] Z.Kisiel *et al.*, MH09, 66th OSU International Symposium on Molecular Spectroscopy (2011)

[d] Z.Kisiel, L.Pszczółkowski, I.R.Medvedev, M.Winewisser, F.C.De Lucia, E.Herbst, *J. Mol. Spectrosc.*, **233**, 231 (2005).

TH11 15 min 4:34

STRUCTURE AND ROTATIONAL DYNAMICS OF ISOAMYL ACETATE AND METHYL PROPIONATE STUDIED BY MICROWAVE SPECTROSCOPY

W. STAHL, H. V. L. NGUYEN, L.W. SUTIKDJA, D. JELISAVAC, H. MOUHIB, *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany*; I. KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris Diderot et Paris Est, 61 av. Général de Gaulle, 94010, Créteil, France*.

The microwave spectra of a number of organic aliphatic esters have been recorded for the first time in the 3-26.5 GHz frequency range, using the molecular beam Fourier-transform microwave (MB-FTMW) spectrometer in Aachen, with an instrumental uncertainty of a few kHz for unblended lines. The combined use of *ab initio* quantum chemical calculations and spectral analysis allowed us to determine the spectroscopic parameters and potential barriers to internal rotation of the methyl groups for the lowest energy conformers.

We will compare here the results from *ab initio* calculations and from two different hamiltonian methods (the XIAM and BELGI codes) for isoamyl acetate H_3C-COO-(CH$_2$)$_2$-CH(CH$_3$)$_2$, an one-top internal rotor molecule with a C_1 symmetry and for methyl propionate CH_3CH_2COOCH_3 containing two inequivalent methyl tops (C_{3v}), with different barrier heights.

This study is part of a larger project which aims at determining the structures of the lowest energy conformers for a serie of organic esters and ketones which are of interest for flavour or perfume applications.

TH12 15 min 4:51

ROTATIONAL ENERGIES IN VARIOUS TORSIONAL LEVELS OF CH$_2$DOH[a]

L. H. COUDERT, A. EL HILALI, *LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France*; L. MARGULÈS, R. A. MOTIYENKO, *Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; and S. KLEE, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany*.

Using an approach accounting for the hindered internal rotation of a monodeuterated methyl group,[b] an analysis of the torsional spectrum of the monodeuterated species of methanol CH$_2$DOH has been carried out recently and led to the assignment of 76 torsional subbands in its microwave, FIR, and IR spectra. Although this approach also allowed us to account for subband centers, the rotational structure of the torsional subbands is not well understood yet.

In this paper, we will deal with the rotational energies of CH$_2$DOH. Analyses of the rotational structure of the available subbands[b] have been performed using the polynomial-type expansion introduced in the case of the normal species of methanol.[c] For each subband, FIR or IR transitions and a-type microwave lines, within the lower torsional level, were fitted. The frequencies of the latters were taken from previous investigations[d] or from new measurements carried out from 50 to 950 GHz with the submillimeterwave solid state spectrometer in Lille. Subbands involving lower levels with $v_t = 0$ and $K \geq 3$ could be satisfactorily analyzed. For levels characterized by lower K-values, the expansion fails. In the case of the $K = 1, v_t = 1$ level, the frequencies of a-type microwave transitions involving the lower member of the K-type doublet cannot be well reproduced. For $K = 0$ levels with $v_t = 1$ and 2, a large number of terms is needed in the expansion.

We will try to understand why the rotational energies of these levels cannot be reproduced. The results of the analyses will be compared to those obtained with a global approach based on the rotation-torsion Hamiltonian of the molecule.[e]

---

[a] Work supported by the CNES, the INSU program PCMI, and the ANR-08-BLAN-0225 and ANR-08-BLAN-0054 contracts.

[b] El Hilali, Coudert, Konov, and Klee, *J. Chem. Phys.* **135** (2011) 194309.

[c] Ioli, Moruzzi, Riminucci, Strumia, Moraes, Winnewisser, and Winnewisser, *J. Mol. Spec.* **171** (1995) 130.

[d] Quade and Suenram, *J. Chem. Phys.* **73** (1980) 1127; and Su and Quade, *J. Mol. Spec.* **134** (1989) 290.

[e] Lauvergnat, Coudert, Klee, and Smirnov, *J. Mol. Spec.* **256** (2009) 204.

TH13 **15 min 5:08**

INTENSITIES IN THE ROTATIONAL-TORSIONAL SPECTRUM OF METHANOL

SARAH M. FORTMAN, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, *Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210, USA.*

Traditionally, intensities of rotational spectra are calculated rather than measured. Dipole moments (accurately calculated from Stark Effect measurements) and spectroscopic analyses of the rotational spectra (to define the wavefunctions) underlie these calculated intensities. However, the suitability of this approach for molecules with internal motion, especially if the rotational-torsional spectroscopic analysis is semi-empirical, is less clear. An astrophysically important example is methanol.

We have recently taken intensity calibrated methanol data in the 560-650 GHz region and compared our experimental results with calculated intensities. Several trends of intensity differences stand out, with some nearing 50%.

TH14 **15 min 5:25**

ROTATIONAL SPECTRUM OF NEOPENTYL ALCOHOL, $(CH_3)_3CCH_2OH$

ZBIGNIEW KISIEL, LECH PSZCZÓŁKOWSKI, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; ZHIFENG XUE, MARTIN A. SUHM, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6, 37077 Göttingen, Germany.*

The rotational spectrum of neopentyl alcohol (2,2-dimethyl-1-propanol, $(CH_3)_3CCH_2OH$) has been investigated for the first time. This molecule differs from ethanol only in having the ^{t}Bu group instead of the methyl group, and is likewise anticipated to exhibit two spectroscopic species, with $trans$ and $gauche$ hydroxyl orientation. Quantum chemistry computations predict the $trans$ to be the more stable species. Rotational transitions of both species have now been assigned in supersonic expansion cm-wave FTMW experiment and in room temperature, mm-wave spectra up to 280 GHz. The supersonic expansion measurements with Ar carrier gas confirm that $trans$ is the global minimum species. The $trans$ spectrum is predominantly b-type, while the $gauche$ is predominantly a-type and the frequencies of rotational transitions in both species appear to be perturbed in different ways. The results from effective and from coupled Hamiltonian fits for neopentyl alcohol are presented, and are compared with predictions from $ab\ initio$ calculations.

TI. RADICALS AND IONS

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: JINJUN LIU, University of Louisville, Louisville, Kentucky

TI01 **15 min 1:30**

MODERATE RESOLUTION JET COOLED CAVITY RINGDOWN SPECTRA OF THE $\tilde{A}$ STATE OF NO_3 RADICAL

TERRANCE J. CODD, MING-WEI CHEN[a], MOURAD ROUDJANE and TERRY A. MILLER, *Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.*

The $\tilde{A}$-$\tilde{X}$ spectrum of NO_3 has been previously observed using cavity ringdown spectroscopy (CRDS) by Andrei Deev *et. al* under ambient conditions.[a] There the authors assigned a number of vibronic bands in the spectrum. However, under these conditions, hot-bands may be present and the spectrum becomes very congested at frequencies higher than ~8700 cm^{-1} due to the density of vibronic states and the overlap of their rotational contours. In order to obtain more information about the $\tilde{A}$ state of NO_3 we recently obtained spectra from 7550 cm^{-1} to over 10000 cm^{-1} using our moderate resolution ($\simeq$ 0.05 cm^{-1}) jet cooled CRDS apparatus. Jet cooling in our apparatus reduces the rotational temperature to <30 K and eliminates vibrational hot bands greatly simplifying the spectrum. We are able to resolve and assign more than 15 vibronic features including a new assignment of the 3_0^1 band. Analysis of the ν_4 progression shows weak Jahn-Teller coupling in this mode. Anomalous band contours and anharmonic spacings are observed for the $\nu_1\nu_4$ combination bands and the cause is being investigated. We also see some features that could belong to vibronically forbidden transitions which may be magnetic dipole allowed.

---

[a] present address: University of Illinois at Urbana-Champaign, Urbana, IL 61801

[a] A. Deev, J. Sommar, and M. Okumura, J. Chem. Phys. 122, 224305 (2005)

TI02 **15 min 1:47**

HIGH RESOLUTION JET COOLED CAVITY RINGDOWN SPECTROSCOPY OF THE $\tilde{A}$ STATE 3_0^1 BAND OF THE NO_3 RADICAL

TERRANCE J. CODD, MOURAD ROUDJANE and TERRY A. MILLER, *Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.*

The $^2E''\tilde{A}$ state of NO_3 is doubly degenerate and is therefore subject to Jahn-Teller (JT) distortion. In the $\tilde{A}$ state there are two JT active modes, ν_3 and ν_4 (e' stretch and in plane bend respectively). Theoretical work has predicted that the JT effect in the $\tilde{A}$ state should be quite strong and approach the static case (D$\geq$1) where the molecule is permanently distorted to a lower symmetry geometry.[abc] A moderate resolution spectrum of the $\tilde{A}$ state showed a feature that we tentatively assigned as the 3_0^1 band based on position and band contour.[d] Using high resolution cavity ringdown spectroscopy we have now obtained a rotationally resolved spectrum of this band. The analysis of this band has been commenced using an oblate symmetric top Hamiltonian with spin-rotation terms. This analysis supports the assignment of this band to the a_1'' vibronic component of the 3_0^1 band. So far, the spectrum shows no evidence of a large geometric distortion of the molecule. Some lines appear to be split, as was previously observed in the 4_0^1 and 4_0^2 bands,[e] and the possible sources of this splitting are being investigated.

---

[a] J.F. Stanton, 66th OSU International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus Ohio, 2011, TJ-03

[b] W. Eisfeld, K. Morokuma, J. Chem. Phys. 114, 9430 (2001)

[c] S. Faraji, H. Köppel, W. Eisfeld, S. Mahapatra, J. Chem. Phys. 347, 110 (2008)

[d] T.J. Codd, M.W. Chen, T.A. Miller, 66th OSU International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus Ohio, 2011, TD-06

[e] M.W. Chen, T.J. Codd, G. Just, T.A. Miller, OSU International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus Ohio, 2011, TD-07

TI03 **15 min 2:04**

HIGH RESOLUTION CAVITY RING DOWN SPECTROSCOPY OF THE 4^3_0 BAND OF THE $\tilde{A}^2E''$ STATE OF NO_3 RADICAL.

MOURAD. ROUDJANE, TERRANCE J. CODD and TERRY A. MILLER, *Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.*

The NO_3 radical is expected to exhibit a Jahn-Teller effect in its degenerate $\tilde{A}^2E''$ electronic state.[a] A more comprehensive understanding of its structure can be achieved using high resolution rotationally resolved absorption spectroscopy of its different vibronic bands. The high resolution absorption spectra of 4^3_0 vibronic band of the $\tilde{A}\ ^2E''$ excited state of NO_3 have been successfully recorded for the first time using our jet cooled cavity ring down apparatus. The parallel 4^3_0 band is a vibronically allowed transition and shows the same contour as the one observed previously for 4^n_0 (n=1,2).[b] The oblate symmetric top model Hamiltonian including both centrifugal distortion and spin rotation terms is used to analyze the spectrum. The rotational analysis of this band, supported by combination differences, demonstrate the existence of doubled lines as were observed for 4^n_0 (n=1,2) bands.The possible sources of this splitting are being investigated.

---

[a] E. Hirota, T. Ishiwata, K. Kawaguchi, M. Fujitake, N. Ohashi, and I. Tanaka, *J. Chem. Phys.*, **107**, 2829, 1997.

[b] Chen, M.W. et al. 66 th OSU International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, 2011, talk WJ-04.

TI04 **10 min 2:21**

FTIR SPECTROSCOPY OF THE ν_4 BANDS OF $^{14}NO_3$ and $^{15}NO_3$

R. FUJIMORI, N. SHIMIZU, J. TANG, K. KAWAGUCHI, *Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan*; T. ISHIWATA, *Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, Japan,.*

High-resolution Fourier transform infrared spectra of the NO_3 ν_4 bands of ^{14}N and ^{15}N isotopic species were observed in the 365 and 360 cm^{-1} region. Observed lines were used to determine ΔK=3 combination differences of the ground state coupled with transition frequencies of the ν_3 hot band $\nu_3 + \nu_4 - \nu_4$ in 1127 cm^{-1} region[a] and $\nu_3 + \nu_4$ band in 1492 cm^{-1} region, which made it possible to determine the rotational C_0 constants of 0.228 6321(67) cm^{-1} and 0.228 674(11) cm^{-1} for $^{14}NO_3$ and $^{15}NO_3$, respectively. Inertial defects of several vibrational states were calculated by using a formula of Jagod and Oka[b] and compared with the observed values. Although the observed Coriolis coupling constants ζ_4=-0.188 ($^{14}NO_3$) and -0.156 ($^{15}NO_3$) are largely different from the expected value of -0.7 from a force field calculation, observed inertial detects are in good agreement with calculated values, for example, Δ_{obs}(Gr.)= 0.206 [0.223] amuÅ^2, (v_4=1) 0.434[0.437] amuÅ^2 etc, where calculated values are given in square brackets.

---

[a] K. Kawaguchi, N. Shimizu, R. Fujimori, J. Tang, T. Ishiwata, and I. Tanaka, *J. Mol. Spectrosc.* **268**, 85 (2011).

[b] M.-F. Jagod and T. Oka, *J. Mol. Spectrosc.* **139**, 313 (1990).

TI05 **15 min 2:33**

FTIR SPECTRUM AND PERTURBATION ANALYSIS OF THE ν_2 BAND OF $^{15}NO_3$

N. SHIMIZU, R. FUJIMORI, J. TANG, K. KAWAGUCHI, *Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan*; T. ISHIWATA, *Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, Japan,.*

In 1987, Friedl and Sander[a] reported observation of the FTIR spectrum of the ν_2 band of $^{14}NO_3$ in 762 cm^{-1} region, and rotational analysis was carried out for only transitions with K=3. The obtained negative centrifugal distortion constant D_N implied presence of perturbation from other states, but the perturbation analysis has not been carried out. In the present study, the ν_2 band of $^{15}NO_3$ was first observed in 742 cm^{-1} region. In contrast to the case of $^{14}NO_3$, rotational assignments were carried out for K=0, 3, 6, 9, 12, and 15, and transitions with N≤12 were fitted with usual energy level expression for D_{3h} molecule. However, when we included higher N transitions up to N=22, an effect of Coriolis interaction from v_4=2 appeared in negative D_N for K=0 and staggering in K=3. An energy matrix including ℓ=0 and ℓ=±2 of v_4=2 and ℓ=0 of v_2 =1 was used to obtain the energy values of v_2 =1 , including the Corilis and ℓ-type resonance terms. From the determined interaction constant between v_2 =1 and v_4=2 , anharmonic constant k_{444} was estimated, by assuming a mixing of v_4=1 and v_4=2.

---

[a] R. R. Friedel and S. P. Sander, *J. Phys. Chem.* **91**, 2721 (1987).

TI06 **15 min 2:50**

DISPERSED FLUORESCENCE SPECTROSCOPY OF THE $\tilde{B}\ {}^2E'$ – $\tilde{X}\ {}^2A_2'$ TRANSITION OF NO_3

MASARU FUKUSHIMA and TAKASHI ISHIWATA, *Faculty of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.*

We have generated NO_3 in supersonic free jet expansions and observed laser induced fluorescence (LIF) of the $\tilde{B}\ {}^2E'$ – $\tilde{X}\ {}^2A_2'$ transition. We have measured LIF excitation spectrum and dispersed fluorescence (DF) spectra from the single vibronic levels (SVL) of the $\tilde{B}\ {}^2E'$ state. Comparing with the vibrational structures of the DF spectra, vibrational structure of the $\tilde{X}\ {}^2A_2'$ state has been analyzed. It is especially concluded that the 1,492 cm^{-1} level in the $\tilde{X}\ {}^2A_2'$ state has no contribution of the ν_4 (e') mode, though there are two opinions in which the level is attributed to the ν_3 (e') fundamental or the $\nu_3 + \nu_4$ combination level.

TI07 **15 min 3:07**

ENERGY LEVELS OF THE NITRATE RADICAL BELOW 2000 CM^{-1}

J.F. STANTON AND C.S. SIMMONS, *Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.*

Highly sophisticated quantum chemistry techniques have been employed to build a three-state diabatic Hamiltonian for the nitrate radical (NO_3). Eigenvalues of this Hamiltonian (which includes effects beyond the Born-Oppenheimer approximation) are consistent with the known "vibrational" levels of NO_3 up to *ca.* 2100 cm^{-1} above the zero-point level; with a small empirical adjustment of the diabatic coupling strength, calculated levels are within 20 cm^{-1} of the measured level positions for those that have been observed experimentally. Of the eleven states with e' symmetry calculated below 2000 cm^{-1}, nine of these have been observed either in the gas phase by Hirota and collaborators as well as Neumark and Johnston, or in frozen argon by Jacox. However, the Hamiltonian produces two levels that have not been seen experimentally: one calculated to lie at 1075 cm^{-1} (which is the third e' state, above ν_4 and $2\nu_4$) and another at 1640 cm^{-1} which is best assigned as one of the two e' sublevels of $4\nu_4$. A significant result is that the state predicted at 1075 cm^{-1} is not far enough above the predicted $2\nu_4$ level (777 cm^{-1} *v. ca.* 760 cm^{-1} from experiment) to be plausibly assigned as $3\nu_4$ (which is at 1155 cm^{-1}: experimental position: 1173 cm^{-1}), nor is its nodal structure consistent with such an idea. Rather, it is quite unambiguously the ν_3 level. Given the fidelity of the results generated by this model Hamiltonian as compared to experiment, it can safely be concluded that the prominent infrared band seen at 1492 cm^{-1} (corresponding to a calculated level at 1500 cm^{-1}) is *not* ν_3, but rather a multiquantum state best viewed as a sublevel of the $\nu_3 + \nu_4$ combination.

Intermission

TI08 **15 min 3:40**

OXYGEN-18 STUDIES OF HOCO AND HONO FORMATION

OSCAR MARTINEZ, JR. and MICHAEL C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138.*

Using isotopically-enriched samples of $H_2^{18}O$ and $C^{18}O$, the singly- and doubly-substituted ^{18}O isotopic species of both *cis* and *trans* isomers of HOCO and HONO have been studied by FT microwave spectroscopy. Although both molecules appear to be formed by simple bimolecular reactions involving the OH radical in our discharge source, the relative abundances of different ^{18}O isotopic species suggest that only HONO undergoes extensive oxygen atom exchange, in agreement with earlier studies[a]. More accurate molecular structures have also been derived for isomers of both molecules from this and other new ($HO^{13}CO$) isotopic data.

---

[a] G. D. Greenblatt and C. J. Howard, J. Phys. Chem. **93**, 1035-1042 (1989)

TI09 **15 min 3:57**

A UV+VUV MULTIPHOTON IONIZATION SCHEME FOR OH RADICALS[a]

JOSEPH M. BEAMES, FANG LIU and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

OH radicals are of significant atmospheric interest as a dominant oxidizing agent in day-time tropospheric chemistry. In this study, a 1+1′ multiphoton ionization (MPI) scheme is employed to record rotationally-resolved spectra of OH radicals via the $A^2\Sigma^+$ resonant intermediate state.[a] UV excitation is used to prepare OH $A^2\Sigma^+$(v=1, J, F_i), which is subsequently ionized by a second photon of fixed frequency VUV (118.3 nm), generated by tripling the 355 nm output of a Nd:YAG laser. The mass-selected OH^+ ion signal from 1+1′ MPI is detected using time-of flight mass spectrometry and compared with the laser-induced fluorescence (LIF) signal arising from OH $A^2\Sigma^+$-$X^2\Pi$(1,0) excitation. The MPI signal is observed over a range of UV+VUV total energies, corresponding to various OH $A^2\Sigma^+$ (v=1, J, F_i) intermediate states, with relative intensities that differ considerably from LIF. The ion signal is enhanced relative to LIF at combined UV + VUV photon energies consistent with an autoionizing 3*d* Rydberg state that converges on the OH^+ $A^3\Pi$ ion core;[b] direct ionization into OH^+ $X^3\Sigma^-$ is forbidden in a one-photon electric-dipole transition from OH $A^2\Sigma^+$. The MPI intensities have been quantified relative to LIF over the OH $A^2\Sigma^+$-$X^2\Pi$(1,0) region such that this scheme is now applicable for quantitative state-selective detection of OH $X^2\Pi$.

---

[a] This research was supported by the Office of Basic Science of the Department of Energy.

[a] J. M. Beames, F. Liu, M. I. Lester and C. Murray, *J. Chem. Phys.* **134**, 241102 (2011).

[b] J. D. Barr, A. De Fanis, J. M. Dyke, S. D. Gamblin, N. Hooper, A. Morris, S. Stranges, J. B. West, and T. G. Wright, *J. Chem. Phys.* **110**, 345 (1999).

TI10 **15 min 4:14**

CONFIRMED ASSIGNMENTS OF ISOMERIC DIMETHYLBENZYL RADICALS GENERATED BY CORONA DISCHARGE

YOUNG WOOK YOON, SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Korea.*

Polymethylbenzyl radicals, multi-methyl-substituted benzyl radicals, have been believed to be an ideal model for understanding the torsional effect of methyl group and substitution effect on electronic transition. These radicals are mainly generated from polymethylbenzenes by electric discharge for spectroscopic observation. However, the existence of several methyl groups on the benzene ring may produce several isomeric polymethylbenzyl radicals by removing one of the C-H bonds of each methyl group at different substitution position, which makes the assignment of spectrum ambiguous. In this work, the controversial vibronic assignments of isomeric dimethylbenzyl radicals were clearly resolved by using different precursors. By using corresponding dimethylbenzyl chlorides as precursors, we identified the origins of the vibronic bands of the dimethylbenzyl radicals generated by corona discharge of precursors 1,2,3- and 1,2,4-trimethylbenzenes. From the analysis of the spectra observed from the dimethylbenzyl chlorides in a corona excited supersonic expansion using a pinhole-type glass nozzle, we revised previous assignments of the 2,6- and 2,3-dimethylbenzyl radicals as well as the 3,4-, 2,4-, and 2,5-dimethylbenzyl radicals. In addition, spectroscopic data of electronic transition and vibrational mode frequencies in the ground electronic state of each isomer were accurately determined by comparing them with those obtained by an *ab initio* calculation and with the known vibrational data of precursors.

TI11 15 min 4:31

CAVITY-RINGDOWN SPECTROSCOPY OF THE VIBRONICALLY MIXED $\tilde{A}\,^2A_2 - \tilde{B}\,^2B_2$ EXCITED STATES OF THE BENZYL RADICAL AND THE $\tilde{1}\,^2A_2 \leftarrow \tilde{X}\,^2B_1$ TRANSITION OF THE PHENOXY RADICAL IN A SUPERSONIC JET EXPANSION

MICHAEL N. SULLIVAN, KEITH FREEL, J. PARK, M.C. LIN, and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

The benzyl and phenoxy radicals are hydrocarbon combustion intermediates that influence the formation of polyaromatic hydrocarbons (PAH's). By this means they impact the earliest stages of soot formation. Detection and characterization of the highly reactive intermediate species in PAH formation reactions can help us to describe the mechanisms involved. However, the low concentrations associated with these radicals require special detection techniques.

This study combines an electrical discharge to produce radicals, a supersonic jet expansion for collisional cooling, and utilizes cavity ringdown spectroscopy (CRDS) for detection. We report the absorption spectra for the vibronically mixed $\tilde{A}\,^2A_2 - \tilde{B}\,^2B_2$ excited states of the benzyl radical ($\approx$ 450nm) and the $\tilde{1}\,^2A_2 \leftarrow \tilde{X}\,^2B_1$ electronic transition of the phenoxy radical. Rotationally structure is somewhat resolved, and as such a contour fit was performed using the PGOPHER program. Rotational temperatures of 20 and 30 K were indicated for benzyl and phenoxy, respectively. Molecular constants were extracted using a least squares contour fitting procedure. Homogeneous line broadening was observed for phenoxy, and the excited state lifetime was estimated for various vibronic states. Summaries of the data for both radicals, along with comparisons to the results from electronic structure calculations, will be presented.

TI12 15 min 4:48

THE CYCLOPENTADIENYL RADICAL REVISITED: THE EFFECTS OF ASYMMETRIC DEUTERATION OF JAHN-TELLER MOLECULES

SAMANTHA STROM, JINJUN LIU, *University of Louisville, Department of Chemistry, Louisville, KY 40292.*

Asymmetric deuteration of Jahn-Teller active molecules partially lifts the vibronic degeneracy and hence provides a unique approach to understanding the Jahn-Teller effect. Previously, a spectroscopic model was proposed and used to simulate the spectra of the asymmetrically deuterated isotopomers of the methoxy radical.[a][b] The same model has been implemented and successfully simulated the previously reported high-resolution laser-induced fluorescence (LIF) spectra of the asymmetrically deuterated cyclopentadienyl radical (C_5H_4D and C_5HD_4).[c] A joint fitting of the transitions from both of the zero-point levels of the $\tilde{X}^2E_1''$ ground electronic state, split by the asymmetric deuteration, to the $\tilde{A}^2A_2''$ state yields one set of molecular constants for both levels, which, when combined with molecular constants of C_5H_5 and C_5D_5, can be used to determine the molecular geometry and magnitude of the Jahn-Teller distortion. The main goal of this new investigation is to resolve the discrepancy between the experimentally determined and the ab initio calculated Jahn-Teller distortion.[d] In addition, a theoretic model is proposed to quantitatively reproduce the splitting of the zero-point level due to the asymmetric deuteration and zero-point energies for the Jahn-Teller distorted structures around the conical intersection.

---

[a] D. G. Melnik, J. Liu, R. F. Curl, and T. A. Miller, *Mol. Phys.* **105**, 529 (2007).

[b] D. G. Melnik, J. Liu, M.-W. Chen, T. A. Miller, and R. F. Curl, *J. Chem. Phys.* **135**, 094310 (2011)

[c] L. Yu, D.W. Cullin, J.M. Williamson, and T.A. Miller, *J. Chem. Phys.* **98**, 2682 (1993).

[d] M. J. Bearpark, M. A. Robb, and N. Yamamoto, *Spectrochim. Acta Part A* **55**, 639 (1999).

TI13 15 min 5:05

THE PHENALENYL FREE RADICAL - A JAHN-TELLER-HERZBERG-TELLER D3H PAH

G. D. O'CONNOR, T. P. TROY, D. A. ROBERTS, N. CHALYAVI, B. FÜCKEL, M. J. CROSSLEY, K. NAUTA, T.W. SCHMIDT, *School of Chemistry, The University of Sydney, NSW 2006, Australia*; and J. F. STANTON, *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165, United States.*

After benzene and naphthalene, the smallest polycyclic aromatic hydrocarbon bearing six-membered rings is the threefold-symmetric phenalenyl radical. Despite the fact that it is so fundamental, its electronic spectroscopy has not been rigorously scrutinized, in spite of growing interest in graphene fragments for molecular electronic applications. Here we used complementary laser spectroscopic techniques to probe the jet-cooled phenalenyl radical *in vacuo*. Its spectrum reveals the interplay between four electronic states that exhibit JahnâĂŞTeller and pseudo-JahnâĂŞTeller (Herzberg-Teller) vibronic coupling. The coupling mechanism has been elucidated by the application of various *ab initio* quantum-chemical techniques.

TI14 15 min 5:22

LASER INDUCED FLUORESCENCE STUDY OF $\widetilde{B}$ - $\widetilde{A}$ TRANSITION OF ISOPROPOXY RADICAL

RABI CHHANTYAL-PUN, JINJUN LIU[a] and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

Alkoxy radicals are important intermediates in combustion and atmospheric chemistry. Alkoxy radicals are also of significant spectroscopic interest for the study of Jahn-Teller and pseudo-Jahn-Teller effects, involving the $\widetilde{X}$ and $\widetilde{A}$ states. Isopropoxy ($CH_3CH(O)CH_3$) radical is the simplest secondary alkoxy radical. High resolution laser induced fluorescence (LIF) studies of the $\widetilde{B}$ - $\widetilde{X}$ transition have been performed previously.[b] In this talk we will present results obtained from a moderate resolution LIF study of the $\widetilde{B}$ - $\widetilde{A}$ transition whose analysis should complement the $\widetilde{B}$ - $\widetilde{X}$ analysis. The separation between the $\widetilde{A}$ and $\widetilde{X}$ band origin was found to be 58(±3) cm^{-1} which is more precise but consistent with the previous dispersed fluorescence experiment.[c] We are also able to observe transitions corresponding to CO stretch progressions and a low frequency fundamental vibrational mode. The origin band and CO stretch progressions were found to have similar rotational contours which differ from the $\widetilde{B}$ - $\widetilde{X}$ origin band contour. Analysis of the different band contours of $\widetilde{B}$ - $\widetilde{A}$ transitions and their implications will be presented.

---

[a] Present address: Department of Chemistry, University of Louisville, 2320 South Brook Street, Louisville, Kentucky 40292

[b] J. Liu and T. A. Miller, 65th OSU International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, 2010, TG-14

[c] J. Jin, I. Sioutis, G. Tarczay, S. Gopalakrishnan, A. Bezant, and T. A. Miller, J. Chem. Phys. 121, 11780 (2004)

TI15 15 min 5:39

ANALYSIS OF THE ROTATIONALLY-RESOLVED SPECTRA OF ISOPROPOXY RADICAL USING MULTIMODE VIBRONIC CALCULATIONS

DMITRY G. MELNIK, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210*; JINJUN LIU, *Department of Chemistry, University of Louisville, 2320 South Brook Street, Louisville, Kentucky 40292.*

We have recorded the high resolution spectra of $\tilde{B} \leftarrow \tilde{X}$ of isopropoxy radical. The isopropoxy radical can be qualitatively viewed as a "chemically substituted" methoxy (with two methyl groups playing roles of "isotopes" of hydrogen), and the calculations[a] indicate the methyl substitution only moderately removes the degeneracy of the $\tilde{X}^2E$ state of methoxy. Therefore, isopropoxy is expected to exhibit the effects of the vibronic coupling within near-degenerate electronic state twofold. Such a coupling can affect the selection rules of vibronic transitions as well as the observed parameters of the effective rotational Hamiltonian. These effects can be understood if the details of the vibronic eigenstates are available. To obtain such information we used a simple semi-quantitative model which accounts for spin-orbit and vibronic coupling involving several vibrational modes. We have subsequently use these results to predict the effects of the vibronic coupling on the observed parameters of the molecule. The results of these calculations will be discussed.

---

[a] R. A. Young and D. R. Yarkony, *J. Chem. Phys.*, **125**, 234301 (2006)

TJ. MINI-SYMPOSIUM:SPECTROSCOPY OF INTERFACES

TUESDAY, JUNE 19, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: ASUKA FUJII, Tohoku University, Sendai, Japan

TJ01 *INVITED TALK* **30 min 1:30**

ION ORGANIZATION AND REVERSED ELECTRIC FIELD AT AIR/AQUEOUS INTERFACES REVEALED BY HETERODYNE-DETECTED SUM FREQUENCY GENERATION SPECTROSCOPY

WEI HUA, ZISHUAI HUANG, AARON M. JUBB, HEATHER C. ALLEN, *Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210.*

Sum frequency generation (SFG) is a second order optical spectroscopy that probes regions of non centrosymmetry, interfaces, and allows for the understanding of molecular organization at air/aqueous interfaces. An overview of our work in this area is presented with emphasis on phase-sensitive SFG (PS-SFG) spectroscopy. PS-SFG is a variant of SFG and is used in our laboratory to investigate the average direction of the transition dipole of interfacial water molecules. The orientation of water at air/aqueous inorganic salts interfaces of $CaCl_2$, NaCl, Na_2SO_4, $(NH_4)_2SO_4$, and Na_2CO_3 is inferred from the direct measurement of the transition dipole moment. We find that charge separation at the air/water interface is most obvious for the aqueous ammonium sulfate solution where the local electric field has a greater magnitude at this interface relative to the other salt solutions. The magnitude of the electric field in the surface extending to the subsurface regions decreases in the order: $(NH_4)_2SO_4 > Na_2SO_4 > Na_2CO_3 \geq CaCl_2 >$ NaCl; the electric field is opposite in direction for the sulfates and carbonate relative to the chloride salts.

TJ02 **15 min 2:05**

BROADBAND SUM-FREQUENCY GENERATION SPECTROSCOPY OF HIGH-FREQUENCY VIBRATIONS OF WATER MOLECULES AT SILICA SURFACES

OLEKSANDR ISAIENKO, SATOSHI NIHONYANAGI, DEVIKA SIL and ERIC BORGUET, *Temple University, Department of Chemistry, 1901 North 13th Street, Philadelphia, Pennsylvania, 19122 USA.*

Building on our discovery of a method to extend noncollinear optical parametric amplification to a broad class of materials, we developed one of the first sources generating ultrabroadband infrared pulses with bandwidths $\Delta\nu > 2500$ cm^{-1} in the near-IR (λ = 1.1-1.6 μm)[a] and $\Delta\nu > 1000$ cm^{-1} in the mid-IR (λ = 1.7-3.5 μm; ν = 2800-6000 cm^{-1})[b]. The ultra-broadband IR source enabled surface-sensitive sum-frequency generation (SFG) vibrational spectroscopy of mineral-water interfaces crucial in many natural and man-made processes such as ion exchange in geochemical environments and oil extraction from tar sands. This novel ultrabroadband IR source allowed the acquisition of SFG spectra of water OH stretch (spanning 3000-3800 cm^{-1}) from mineral surfaces without tuning the IR frequency, in 60 sec or less.

The high signal-to-noise ratio of the broadband-IR SFG setup allowed the extension of SFG spectroscopy of interfacial hydroxyls at mineral/water surfaces to the low cross-section vibrational modes found in the high frequency range (4000-7000 cm^{-1}). We performed, what we believe to be, the first surface-specific vibrational SFG spectroscopic measurements of the stretch+bend combination band, $\nu_{comb} = \nu_{OH}+\delta_{HOH}$ of liquid water at silica surfaces near 5200 cm^{-1} [c]. SFG of the ν_{comb} mode allows in-situ probing of surface-bound, e.g., SiOH, and H-OH hydroxyls separately. This provides access to the interfacial water bending mode δ (near 1600 cm^{-1}), which has not been observed directly in SFG.

---

[a] O. Isaienko and E. Borguet *Opt. Express* **16**(6), 3949-3954 March 2008.

[b] O. Isaienko and E. Borguet *Opt. Express* **20**(1), 547-561 January 2012.

[c] O. Isaienko, S. Nihonyanagi, D. Sil and E. Borguet (*in preparation*).

TJ03 **15 min 2:22**

STRUCTURE, ENERGETICS AND FINITE TEMPERATURE OH-STRETCH SPECTROSCOPY OF THE WATER HEXAMER

C. J. TAINTER, J. L. SKINNER, *Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, WI 53706.*

We use a newly developed and recently reparameterized classical empirical simulation model for water that involves explicit three-body interactions to study the water hexamer. The lowest energy isomer is found to be one of the cage structures, in agreement with vibration-rotation-tunneling experiments. Furthermore, the relative energy ordering of the different isomers is in good agreement with CCSD(T) calculations. The OH-stretch spectra calculated for the low-energy structures is compared to *ab initio* and density functional theory calculations. Finally, replica-exchange molecular dynamics were performed from 40 to 194 K, showing the cage isomer has the lowest free energy from 0 to 70 K, and the book isomer has the lowest free energy from 70 to 194 K. The OH-stretch spectra were calculated from these simulations, leading to a re-assignment of the peaks in recent experimental spectra.

TJ04 **15 min 2:39**

INFRARED SPECTROSCOPY OF PROTONATED BENZENE-WATER NANOCLUSTERS: HYDRONIUM, ZUNDEL AND EIGEN AT A HYDROPHOBIC INTERFACE

T. C. CHENG, B. BANDYOPADHYAY, and M. A. DUNCAN, *University of Georgia, Dept. of Chemistry, 1001 Cedar St, Athens, GA 30602.*

Mixed protonated nanocluster cations of benzene and water are produced in a pulsed discharge/supersonic expansion source, mass-selected in a time-of-flight spectrometer, and studied with infrared laser photodissociation spectroscopy. Small cluster ions with strong bonding are studied via the method of "tagging" with argon atoms, while larger clusters dissociation by the elimination of neutral benzene molecules. Vibrational patterns in these systems are studied with computational chemistry, and they are also compared to the known IR spectra of protonated water or protonated benzene clusters. Vibrations assigned to shared proton motions, π-hydrogen bonds, free-OH stretches, hydrogen bonded O-H stretches, and free C-H stretches are measured for clusters containing 1-4 benzene or water molecules. In each system, the structures detected are those for protonated water clusters solvated by neutral benzene, rather than protonated benzene ions solvated by water. Binding at the hydrophobic surface of benzene induces significant shifts on the vibrations of zundel and eigen ions at positions once and twice removed from the point of contact, illustrating the importance of inductive interactions in these systems.

TJ05 **15 min 2:56**

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF VANADIUM-CARBON DIOXIDE CATIONS: EVIDENCE FOR AN INTRACLUSTER REACTION.

ANTONIO D. BRATHWAITE, ALLEN M. RICKS, MICHAEL A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602-2256*; ,.

Cationic vanadium-carbon dioxide clusters, consisting of up to ten carbon dioxide ligands, are produced in a molecular beam via laser vaporization in a pulsed nozzle source. The cations are mass selected and studied via infrared photodissociation spectroscopy in the 600-4000 cm^1 region. The number of infrared active bands, their frequency positions and their relative intensities, allows us to gain insight into the structure and bonding of these species. The sudden appearance of new infrared bands in the spectra of complexes having seven or more ligands provides evidence for an intracluster reaction. We explore possible reaction products by comparing these spectra to those of vanadium and vanadium oxide-carbonyls. Low frequency measurements and DFT calculations have allowed us to identify complexes containing a metal atom bonded to an oxalate-like structure as the product of these reactions.

Intermission

TJ06 **15 min 3:30**

UV AND IR SPECTROSCOPIC STUDIES OF COLD ALKALI METAL ION-BENZO CROWN ETHER COMPLEXES IN THE GAS PHASE

YOSHIYA INOKUCHI, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; OLEG V. BOYARKIN, *Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland*; RYOJI KUSAKA, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; TAKEHARU HAINO, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; TAKAYUKI EBATA, *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; and THOMAS R. RIZZO, *Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland.*

We measured UV photodissociation and IR-UV double-resonance spectra of benzo-crown ether complexes with alkali metal ions (Li^+, Na^+, K^+, Rb^+, and Cs^+) in a cold, 22-pole ion trap[a]. All the complexes show a number of vibronically resolved UV bands in the 36000-38000 cm^{-1} region. We used the IR-UV spectra in the CH stretching region to distinguish peaks in the UV spectra that belong to different conformers. The use of density functional theory allows us to determine the conformation of the complexes.

---

[a] Y. Inokuchi, O. V. Boyarkin, R. Kusaka, T. Haino, T. Ebata and T. R. Rizzo *J. Am. Chem. Soc.* **133**(31), 12256 July 2011.

TJ07 **15 min 3:47**

GAS PHASE HYDRATION OF MODEL PEPTIDE CHAINS: FAR/MID INFRARED SIGNATURE OF WATER INTERMOLECULAR MOTIONS IN THE MONOHYDRATE

M. CIRTOG, Y. LOQUAIS, V. BRENNER, B. TARDIVEL, M. MONS, *CEA, IRAMIS, SPAM, Lab. Francis Perrin, URA 2453, F-91191, Gif-sur-Yvette, France*; E. GLOAGUEN, *CNRS, INC & INP, Lab. Francis Perrin, URA 2453, F-91191, Gif-sur-Yvette, France*; A. M. RIJS, *Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 7, 6525 ED Nijmegen, the Netherlands*.

The far/mid infrared region (100 - 800 cm^{-1}) of two hydrated conformations of the model peptide chain N-acetyl-phenylalanine-amide (Ac-Phe-NH_2) have been investigated in a supersonic jet expansion by conformational selective double-resonance IR/UV spectroscopy, using the free electron laser FELIX for the far IR tunability. The two folded conformations (identified in a previous work[a]) share the same H-bonding network, with the water molecule bridging the peptide ends as a donor and acceptor but differ by the orientation of the free hydrogen. By comparison with the isolated peptide, hydration gives rise to new spectroscopic features locate in three different spectral regions namely around 160, 400 and 600 cm^{-1}. The analysis of a series of quantum chemical harmonic frequency calculations using various approaches (DFT and DFT-D) suggests that this spectral region constitutes a real challenge to the theory. As expected, the low frequency modes present a strong anharmonicity[b] and sensitivity to the position of the water molecule. It has nevertheless allowed us to assign the new experimental signatures to a direct excitation of normal modes widely involving intermolecular libration and wagging motions of the water molecule in the complex, and revealed an extended coupling with the peptide backbone deformation motions.

---

[a] H.S. Biswal, Y. Loquais, B. Tardivel, E. Gloaguen and M. Mons, J. Am. Chem. Soc. 133, 3931 (2011).

[b] S. Jaeqx, M. Schmit, W.J. van der Zande, and A.M. Rijs, manuscript in preparation

TJ08 **15 min 4:04**

IR SPECTROSCOPY OF $Au^-{\cdot}(CO_2)_n$ CLUSTERS: STRONG CLUSTER SIZE DEPENDENCE OF METAL-LIGAND INTERACTION

BENJAMIN J. KNURR and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

Gold is a widely used catalyst in many reactions. For example, negatively charged gold clusters have been shown to catalyze the oxidation of CO to CO_2 [1], although the precise role of negative charge has not been understood. A previous study from our laboratory has shown that the binary complex $[AuCO_2]^-$ has the CO_2 ligand covalently bound to the gold, leading to significant charge transfer onto the CO_2 unit and concomitant decrease of the OCO bond angle and weakening of the CO bonds [2]. The structure of this aurylformate anion is reminiscent of structural motifs assumed to play a role in a recent approach towards production of solar fuels using reductive activation of CO_2 [3].

We report infrared spectra of $Au^-{\cdot}(CO_2)_n$ clusters highlighting solvation mediated changes in the infrared signatures of the ligands. These results are discussed in the framework of quantum chemistry calculations.

1. U. Heiz and W.D. Schneider, J. Phys. D - Appl. Phys., 33 (2000) R85- R102.
2. A.D. Boese, H. Schneider, A.N. Gloess, and J.M. Weber, J. Chem. Phys., 122 (2005) 154301.
3. E.E. Barton, D.M. Rampulla, and A.B. Bocarsly, J. Am. Chem. Soc., 130 (2008) 6342.

TJ09 **15 min 4:21**

THE THZ SPECTRUM OF LANTHANIDE AND TRANSITION METAL HALIDES - EFFECTS ON THE WATER SPECTRUM

G. SCHWAAB, VINAY SHARMA AND MARTINA HAVENITH, *Physical Chemistry II, Department of Chemistry and Biochemistry, Ruhr University Bochum, D-44780 Bochum, Germany.*

Recently, we were able to show that aqueous solutions of alkali and earth-alkali halides show strong resonances in the THz range that may be attributed to movements of individual ions in their surrounding water cage. Here, we extend this study to bromides and chlorides of selected lanthanides and transition metals. The effects of these strong ions on the water network as well as the detectability of contact ion complexes will be discussed.

WA. PLENARY SESSION

WEDNESDAY, JUNE 20, 2012 – 8:30 AM

Room: AUDITORIUM, INDEPENDENCE HALL

Chair: ANNE B. MCCOY, The Ohio State University, Columbus, Ohio

WA01 **40 min 8:30**

THE ATACAMA LARGE MILLIMETER/SUBMILLIMETER ARRAY (ALMA): EARLY RESULTS

ALWYN WOOTTEN, *National Radio Astronomy Obsy, 520 Edgemont Rd, Charlottesville, Va 22903.*

New radioastronomical instruments, such as ALMA or the Jansky VLA, have increased spectral throughput by orders of magnitude over previously available capabilities. ALMA brings orders of magnitude increases in spectral sensitivity and spatial resolution over what has previously been available. These increased capabilities open new possibilities for studies of complex molecules in the interstellar medium.

Complex interstellar molecules may form on the surfaces of interstellar grains, after which they may be liberated into the gas phase by shocks, radiation, or other external influences. Emission from complex molecules may be diluted owing to the large number of transitions large molecules may undergo, particularly in warm regions of interstellar clouds. High sensitivity and spatial resolution are necessary to explore the distributions and relationships of these molecules. Of particular interest are the distributions of large organic molecules. Observations which establish the relationships between various large molecules are now emerging from these new instruments and will be discussed.

WA02 **40 min 9:15**

TERAHERTZ SPECTROSCOPY OF MOLECULES, RADICALS AND IONS USING EVENSON-TYPE TUNABLE FIR SPECTROMETER

FUSAKAZU MATSUSHIMA, *Department.of Physics, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan.*

Frequencies of pure rotational transitions of neutral molecules, free radicals, and ionic molecules in the terahertz region have been measured precisely by using a frequency tunable far-infrared spectrometer in Toyama for more than 2 decades. The spectrometer (sometimes called as TuFIR in short) was developed by K.M. Evenson about 30 years ago [a] [b]. The terahertz light source is generated by synthesizing difference frequency of two mid-infrared CO_2 laser lines using a MIM diode as a photo mixer. A microwave radiation is added so that the tunable sidebands are obtained. The molecules and ions investigated up to now in Toyama are; 1) neutral molecules or radicals (LiH, KH, ^{18}OH, NH, N^{18}O, NH_3), 2) molecule with internal rotation (CH_3OH including transitions between different torsional states), 3) water molecules ($H_2{}^{16}O$ including v_2=1 excited state, $H_2{}^{17}O$, $H_2{}^{18}O$, D_2O), 4) molecular cation (protonated rare gas atoms such as HeH^+, NeH^+, ArH^+, KrH^+, XeH^+ including their isotopic species, H_2D^+, N_2H^+, H_2F^+), 5) molecular anion (OH^-, OD^-). The following topics are picked up in the talk. 1) principle and properties of TuFIR spectrometer with its history of developments, 2) some efforts to extend the properties of the spectrometer, 3) extended negative glow discharge cell: its property and recent application to investigate molecular ions.

---

[a] K.M. Evenson, D.A. Jennings, and F.R. Peterson, Appl. Phys. Lett. **44**, 576 (1984)

[b] I.G. Nolt et al., J. Mol. Spectrosc., **125**, 274 (1987)

Intermission

WA03 40 min 10:20

FEMTOSECOND ROTATIONAL RAMAN FOUR-WAVE MIXING SPECTROSCOPY

SAMUEL LEUTWYLER and HANS-MARTIN FREY, *Departement für Chemie und Biochemie, Freiestrasse 3. CH-3012 Bern, Switzerland.*

Femtosecond time-resolved rotational Raman four-wave mixing (fs-RR-FWM) is a background-free rotational coherence spectroscopic (RCS) technique. Broadband rotational Raman scattering is achieved using fs pulses with a typical spectral bandwidth of 40-120 cm^{-1}, thereby covering the range of rotational Raman transitions without exciting low-lying vibrational Raman bands. This allows the direct determination of the ground state rotational and centrifugal constants. Unlike other RCS techniques, RR-FWM does not depend on the existence of bound excited electronic states, and in contrast to microwave and millimeter-wave spectroscopy it does not require the existence of a molecular dipole moment. Thus, fs-RR-FWM can be generally applied for the determination of the rotational constants of vibrational ground states and of low-lying vibrational states of nonpolar gas-phase molecules with a relative accuracy of $\sim 10^{-7}$.

After an introduction into the method and experimental setups (both gas-cell and supersonic jet), fs-RR-FWM rotational coherence measurements of cycloalkanes (cyclopropane, cyclopentane and cyclohexane) and n-alkanes will be discussed.

WA04 40 min 11:05

CALCULATING RO-VIBRATIONAL SPECTRA USING AN ECKART FRAME

XIAOGANG WANG and TUCKER CARRINGTON, JR., *Chemistry Department, Queen's University, Kingston, Canada.*

Using normal coordinates and an Eckart molecule-fixed frame it is possible, for some molecules, to compute ro-vibrational spectra with either perturbation theory or variational methods. A compact normal coordinate Eckart kinetic energy operator (KEO) has been known for decades. The Eckart frame minimises Coriolis coupling and thereby reduces the number of basis functions required to achieve converged energy levels. It, however, is almost always used with normal coordinates which are poorly suited to the description of large amplitude vibrations. For molecules with large amplitude motion, it is common to use, as vibrational coordinates, polar coordinates associated with a set of vectors specifying the position of the atoms of the molecule. The vectors may be bond vectors, Jacobi vectors, Radau vectors etc. It would clearly be advantageous to use polar (polyspherical) coordinates and an Eckart frame. Instead, polar coordinates are generally used with a frame attached to a small number of the vectors. Unfortunately, the Eckart polyspherical KEO is complicated. It has been derived only for three-atom molecules. Using finite difference methods it is possible, without deriving a KEO, to work with polyspherical vibrational coordinates and an Eckart frame. We demonstrate that this allows us to deal with large amplitude motion and at the same time exploit the fact that an Eckart frame facilitates the choice of good basis functions.

WF. INFRARED/RAMAN

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: ISABELLE KLEINER, CNRS, University Paris 7, Paris Est, Creteil, France

WF01 15 min 1:30

HIGH RESOLUTION INFRARED SPECTRA OF AR-WATER AND NE-WATER AT 6 μm

X. LIU and Y. XU, *Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2.*

Ar- and Ne-water are highly floppy van der Waals complexes where the water subunit experiences nearly free internal rotation. Their ro-vibrational energy levels are characterized by the internal rotor states of the water subunit within the complex and a pseudo-diatomic rotational energy Hamiltonian. Large amplitude motions of the complexes lead to strong perturbations, such as Coriolis coupling and angular-radial coupling among the internal rotor states and the van der Waals bending and stretching states. Mid-infrared spectra of Ar- and Ne-water were measured with a direct absorption spectrometer with an external cavity quantum cascade laser at 6 μm and a 366-pass astigmatic absorption cell.[a] The scan-to-scan frequency instability of the laser was addressed with a "on-the-fly" calibration procedure.

The infrared spectrum of Ar-water has been studied by Weida and Nesbitt,[b] in which the $\Sigma 1_{10}$ and $\Pi 1_{10}$ states have been identified. At least three new overlapping bands at 1630 cm^{-1} have been observed and two of them have been tentatively assigned to the $n = 1, \Sigma 1_{01} \leftarrow \Pi 1_{10}$ and $\Sigma 1_{10} \leftarrow \Sigma 1_{01}$ bands. The $n = 1, \Pi 1_{01} \leftarrow \Sigma 1_{01}$ band that was missing in the previous study was found at 1639 cm^{-1}. Four new bands in the 1645-1665 cm^{-1} region have been observed and assigned to the $\Pi 2_{12} \leftarrow \Pi 1_{01}$, $\Sigma 2_{12} \leftarrow \Sigma 1_{01}$, $\Pi 2_{12} \leftarrow \Sigma 1_{01}$, and $n = 1, \Sigma 1_{11} \leftarrow \Sigma 0_{00}$. A global fit of the microwave, far-infrared, near-infrared and mid-infrared data was performed with Pickett's SPFIT program to determine the spectroscopic constants of these levels. Infrared spectrum of Ne-water is analogous to that of Ar-water. The Ne-water PES[c] is much shallower than that Ar-water. As a result, there are fewer number of internal rotor states supported by the surface. Indeed, only the $\Pi 1_{10} \leftarrow \Sigma 1_{01}$, $\Sigma 1_{10} \leftarrow \Pi 1_{01}$, $n = 1, \Sigma 0_{00} \leftarrow \Sigma 0_{00}$, and $\Pi 1_{11} \leftarrow \Sigma 0_{00}$ bands were observed in our measurements. Severe spectral perturbations have been detected and analyzed. No infrared transitions of He-water were detected in the same frequency region. This is consistent with the previous theoretical calculation which predicted that the He-water potential supports only one bound state and no infrared transitions could be observed in this region because of the $b-$ type selection rule.

---

[a] X. Liu, Y. Xu, Z. S., W. S. Tam, I. Leonov, *Appl. Phys. B*, **102**, 629, 2011

[b] M. Weida, D. Nesbitt, *J. Chem. Phys.* **106**, 3078, 1997

[c] A. Haskopoulos, *J. Phys. Chem. A*, **114**, 8730, 2010

WF02 15 min 1:47

DIODE LASER SPECTROSCOPY OF N2–D2O COMPLEX IN THE V2 BEND REGION OF D2O

SONG LI, RUI ZHENG, YU ZHU, YU YANG, and CHUANXI DUAN, *College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China.*

The rovibrational spectrum of N2–D2O complex was measured in the v2 bend region of D2O using a rapid-scan diode laser spectrometer to probe a pulsed supersonic slit jet. Three subbands, namely Ka = 1–0, 0–0, and 0–1, were recorded. All the transitions in the spectrum are doubled, due to D2O tunneling within the complex. The spectrum was analyzed in terms of a standard asymmetric rotor Hamiltonian, yielding band origins, rotational and centrifugal distortion constants for the upper and lower tunneling levels. The band origin of N2–D2O is slightly blue-shfited from the monomer, indicating that the intermolecular bond becomes weaker upon vibrational exciation of the v2 bend mode of D2O. The tunneling dynamics within the complex will be discussed.

WF03 15 min 2:04

ANALYSIS OF THE HIGH-RESOLUTION MID-INFRARED SPECTRUM OF DEUTERATED WATER CLUSTERS

BRADLEY M. GIBSON and JACOB T. STEWART, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

We have obtained rotationally-resolved infrared spectra of fully deuterated water clusters and Ar-D_2O clusters in the D_2O bending region near 1185-1205 cm^{-1} using a continuous-wave cavity ringdown spectrometer (cw-CRDS) with a quantum cascade laser (QCL) light source. These clusters were produced in a continuous supersonic expansion from a 150 μm x 1 cm slit using argon carrier gas, giving rovibrational transitions with a full width at half maximum of approximately 20 MHz. We will present our assignment of the Ar-D_2O spectra and preliminary analysis of spectra of other clusters (particularly our results for $(D_2O)_2$).

WF04 15 min 2:21

OVERTONE VIBRATIONAL SPECTROSCOPY AND DYNAMICS IN H_2-H_2O COMPLEXES: A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

MICHAEL P. ZIEMKIEWICZ, CHRISTIAN PLUETZER, DAVID J. NESBITT, *JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado*; YOHANN SCRIBANO, *CNRS-Université de Bourgogne, Dijon, France*; ALEXANDRE FAURE, *CNRS, Institut de Planétologie et d'Astrophysique de Grenobleï£¡(IPAG), France*; AD VAN DER AVOIRD, *Radboud University, 6525 AJ Nijmegen, The Netherlands.*

H_2 is the most abundant molecule in the universe and also H_2O occurs in relatively high concentrations in various interstellar environments. Processes that occur through the interaction of these molecules may, for example, play a role in the mechanism producing the observed H_2O maser activity. Spectroscopic studies of the H_2-H_2O complex in different stable and metastable states will be reported in the accompanying talk; theoretical studies will be presented here. The latter involve calculations of the bound rovibrational levels of the complex with both monomers in their vibrational ground state, as well as of the metastable levels with H_2O in its OH stretch overtone state, on the appropriate *ab initio* five-dimensional intermolecular potential surfaces. Also the line strengths of all the allowed transitions between these levels that may occur in combination with the $v_{\mathrm{OH}} = 2 \leftarrow 0$ overtone transition were computed, for all four ortho/para H_2 and ortho/para H_2O variants of the complex. The spectrum simulated with these data agrees very well with the measured spectrum and was used to assign this spectrum. In addition, the information obtained from the theory was useful to understand the observed predissociation dynamics of the complex.

WF05 15 min 2:38

OVERTONE VIBRATIONAL SPECTROSCOPY AND DYNAMICS IN H_2-H_2O COMPLEXES: A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

MICHAEL P. ZIEMKIEWICZ, CHRISTIAN PLUETZER and DAVID J. NESBITT , *JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado, USA*; YOHANN SCRIBANO, *CNRS-UniversitÂÂt'e de Bourgogne, Dijon, France*; ALEXANDRE FAURE, *CNRS, Institut de PlanÂÂt'etologie et dâĂŹAstrophysique de Grenoble(IPAG), France*; and AD VAN DER AVOIRD, *Radboud University, Nijmegen, The Netherlands.*

We present spectroscopic studies on the H_2-H_2O complex, providing information on the binding of these astrochemically-significant molecules. Understanding this interaction is crucial for further understanding the production of H_2 from atomic hydrogen on interstellar dust grain surfaces, which are often covered with an icy mantel. We generate these clusters using a slit supersonic jet expansion which cools to below 5 K, a temperature which is sufficiently low for observing this species whose binding energy is 60 cm^{-1}. The experimental detection method consists of an infrared vibrational excitation followed by a 193 nm pulse to photolyze H_2O and laser induced fluorescence on the OH product. In conjunction with theoretical studies presented in the accompanying talk, we identify two overtone bands associated with excitation of the $|02-\rangle \leftarrow |00+\rangle$ transition in the water moiety. Theory and experiment agree to within 0.2 cm^{-1}, which attests to the accuracy of the method used to make predictions, as shown in the accompanying talk. Additional time and frequency domain measurements are performed with this three laser experiment to obtain information on predissociation dynamics, where internal H_2O vibration is transferred to the intermolecular coordinate. Theoretically-generated excited state wavefunctions are used to obtain further insight into the significant dependence of predissociation lifetime on the upper state in the infrared cluster transition.

Intermission

WF06 **15 min 3:10**

INFRARED SPECTRA OF He-, Ne-, AND Ar-C_2D_2 COMPLEXES

M. REZAI, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N 1N4, Canada*; A.R.W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*; BERTA FERNÁNDEZ, *Department of Physical Chemistry and Center for Research in Biological Chemistry and Molecular Materials (CIQUS), University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain*; DAVID FARRELLY, *Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300.*

Remarkably, there are no previously published experimental spectra of the helium-acetylene van der Waals complex. Apparently, infrared spectra of He-C_2H_2 were recorded around 1990 in Roger Miller's lab, but a detailed rotational assignment was not possible even with the help of two extensive sets of theoretical predictions.[a] Here, we study rare gas-C_2D_2 complexes in the ν_3 region (∼2439 cm^{-1}) using a rapid-scan tuneable diode laser spectrometer to probe a pulsed supersonic slit-jet expansion. The He-C_2D_2 assignment problem is readily apparent: most of the absorption is piled-up in a very narrow region around 2440.85 cm^{-1}, close to the $R(0)$ line of the C_2D_2 monomer. This pile-up is a signature of very weak anisotropy in the helium-acetylene intermolecular potential, leading to almost free internal rotation of the C_2D_2. We are able to achieve a convincing rotational assignment with the help of theoretical energy level calculations based on the intermolecular potential surface of Munteanu and Fernández.[b] So far the results are limited to He-C_2D_2 transitions which correlate with the monomer $R(0)$ transition.

Ne-C_2D_2 also shows a free-rotation pile-up of lines near $R(0)$ which makes assignment tricky. In contrast, Ar-C_2D_2 exhibits more conventional behavior and a normal asymmetric rotor analysis is possible.

---

[a] T. Slee, R.J. Le Roy, and C.E. Chuaqui, *Mol. Phys.* **77**, 111 (1992); R. Moszynski, P.E.S. Wormer, and A. van der Avoird, *J. Chem. Phys.* **102**, 8385 (1995).

[b] R. Munteanu and B. Fernández, *J. Chem. Phys.* **123**, 014309 (2005).

WF07 **15 min 3:27**

COMBINATION BANDS OF THE NONPOLAR N_2O DIMER AND INFRARED SPECTRA OF $(C_2D_4)_2$ AND $(C_2D_4)_3$ USING A QUANTUM CASCADE LASER

M. REZAEI, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada*; A.R.W. MCKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada*; K.H. MICHAELIAN, *Natural Resources Canada, CANMET Western Research Center, 1 Oil Patch Drive, Suite A202 Devon Alberta T9G 1A8, Canada..*

Our pulsed-jet supersonic apparatus has been retrofitted by an infrared cw external-cavity quantum cascade laser (QCL) manufactured by Dayligh Slutions to study infrared spectra of weakly-bound complexes. The QCL is used in the rapid-scan signal-averaging mode. Although the repetition rate of the QCL is limited by its PZT scan rate, which is 100 Hz, we describe a simple technique to increase the effective repetition rate to 625 Hz. In addition, we have significantly reduced the long term frequency drift of the QCL by locking the laser frequency to the sides of a reference line. Performance of the apparatus is illustrated by recording spectra of the combination bands of the nonpolar $(^{14}N_2O)_2$ and $(^{15}N_2O)_2$ and infrared spectra of ethylene dimer and trimer.

Spectra of ethylene dimer and trimer were studied in the ν_{11} fundamental band region of C_2D_4 (∼ 2200 cm^{-1}). The dimer spectrum is that of a prolate symmetric top perpendicular band, with a distinctive appearance because the A rotational constant is almost exactly equal to six times the B constant. The analysis supports the previously determined cross-shaped dimer structure with D_{2h} symmetry. Ethylene trimer has not previously been observed with rotational resolution. The spectrum is that of an oblate symmetric top parallel band. It leads to a proposed trimer structure which is barrel shaped and has C_{3h} or C_3 symmetry, with the ethylene monomer CÂŮC axes approximately aligned along the trimer symmetry axis.

WF08 15 min 3:44

HIGH RESOLUTION OVERTONE SPECTROSCOPY OF ACETYLENE-WATER VAN DER WAALS COMPLEXES

K. DIDRICHE, T. FOLDES, M. HERMAN, *Service de Chimie quantique et Photophysique CP160/09, Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Av. Roosevelt, 50, B-1050, Bruxelles, Belgium.*

The FANTASIO+ set-up[a] (for 'Fourier trANsform, Tunable, diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn') was upgraded by implementing a pulsed nozzle and a liquid injector. Experiments were performed to test the new capacities of this improved set-up. The first results will be presented, among which the CW-cavity ring down spectra of the $^{12}C_2H_2$-H_2O and $^{12}C_2H_2$-D_2O absorption bands in the 2CH excitation range (1.5 μm). The first analyses of these spectra will be presented.

---

[a] Didriche *et al.*, *Mol. Phys.* 2010, **108**, 2158-2164

WF09 10 min 4:01

HIGH RESOLUTION INFRARED SPECTRA OF JET-COOLED FORMAMIDE AND FORMAMIDE DIMER IN THE C=O STRETCH REGION

FUMIE X. SUNAHORI, YUNJIE XU, *Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.*

Formamide (FA) is the simplest molecule with a peptide bond. It has attracted considerable theoretical and spectroscopic attention as a model peptide. The structure of the FA monomer in the ground state was determined to be planar by rotational spectral analyses of several isotopic species.[a] Its high resolution FIR spectrum and IR spectrum in the symmetric N-H stretching region were reported previously.[b] Both matrix isolation[c] and jet-cooled FTIR[d] studies of FA dimer reported spectral evidence for the cyclic C_{2h} symmetric FA dimer bonded by two NH—O bonds, which was predicted to be the most stable structure by ab initio calculations. No high-resolution spectrum of FA dimer, however, has been recorded so far. Our aim in the present study is to study high-resolution IR absorption spectra of both FA and its dimer in the C=O stretching region in order to gain information about the peptide-peptide interactions.

IR spectrum of the FA monomer was measured using a rapid scan infrared laser spectrometer equipped with an astigmatic multipass cell. While the monomer band centers at 1754 cm^{-1}, the lines most likely belonging to FA dimer were observed around 1740 cm^{-1}. The spectral assignment of the C=O stretching band of the monomer was made by the means of ground state combination differences. Further data collection and spectral analysis of FA dimer are currently underway. The results will be updated at the conference.

---

[a] E. Hirota, R. Sugisaki, C. J. Nielsen, G. O. SÃÂÿrensen, J. Mol. Spectrosc. 49, 251, 1974.

[b] C. L. Brummel, M. Shen, K. B. Hewett, L. A. Philips, J. Opt. Soc. Am. B, 11, 176, 1994; D. McNaughton, C. J. Evans, S. Lane, C. J. Nielsen, J. Mol. Spectrosc., 193, 104, 1999.

[c] A. Mardyukov, E. Sanchez-Garcia, P. Rodziewicz, N. L. Doltsinis, W. Sander, J. Phys. Chem. A., 111, 10552, 2007.

[d] M. Albrecht, C. A. Rice, M. A. Suhm, J. Phys. Chem. A., 112, 7530, 2008.

WF10 15 min 4:13

ANALYSIS OF AB INITIO NORMAL-MODE DISPLACEMENT VECTORS ALONG THE INTERNAL ROTATION PATH FOR THE THREE C-H STRETCHING VIBRATIONS IN METHANOL

LI-HONG XU, RONALD M. LEES, *Centre for Laser, Atomic and Molecular Sciences (CLAMS) Physics Department University of New Brunswick, 100 Tucker Park Road, Saint John, NB, Canada E2L 4L5*; JON T. HOUGEN, *Sensor Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

Stemming from the observation of inverted A/E splittings for the ν_2 and ν_9 asymmetric CH-stretching modes in methanol, there has been much theoretical interest in attempting to explain the nature of the inversion. We have recently examined the ab initio normal-mode vibrational displacement vectors along the internal rotation path for the three C-H stretching vibrations in methanol, both in the symmetrized and non-symmetrized PAM coordinates. Graphical representations of the Cartesian atomic normal mode displacement vectors $d_i(\gamma)$ determined by the Gaussian suite of programs for the three CH stretching motions, $\nu_2(A_1), \nu_3(A_1)$ and $\nu_9(A_2)$, along the steepest-descent internal rotation path γ in methanol (CH$_3$OH) will be presented and discussed, where A_1 and A_2 are notations in permutation-inversion group G_6. These modes are interesting because the symmetry environment of each C-H bond changes significantly during the internal rotation, i.e., each of the methyl bonds takes turns passing (twice for a complete torsional revolution) through the plane of symmetry of the COH frame of the molecule. We present some simple theoretical models which can be used to help understand these displacement vectors. Although this is work in progress, some explanation is already possible for the rather irregular (avoided-crossing-like) behavior of these displacement vectors.

WF11 15 min 4:30

TWO MODEL HAMILTONIANS FOR TORSION-INVERSION TUNNELING IN THE CH-STRETCH VIBRATIONALLY EXCITED STATES OF METHYLAMINE

MAHESH B DAWADI, AND DAVID S PERRY, *Department of Chemistry, The University of Akron, OH 44325-3601.*

In methylamine (CH$_3$NH$_2$), there are six equivalent mimina that are connected by torsion and inversion tunneling. In the G_{12} molecular symmetric group, there are four species, $A = \{A_1, A_2\}$, $B = \{B_1, B_2\}$, E_1 and E_2 that combine with distinct nuclear states. The ground vibrational state of CH$_3$NH$_2$ is split by torsion and inversion tunneling into a multiplet pattern of four distinct energy levels[a]. The experimental tunneling pattern for CH$_3$NH$_2$ in the ν_{11} asymmetric CH-stretch fundamental has been previously reported at this meeting. In the experimental pattern, the degenerate species (E_1 and E_2) are at the top and bottom of the multiplet and the non-degenerate species (B and A) are between them. In this work, we present two models for the torsion-inversion tunneling behavior in the CH-stretch excited states. Each model includes the lowest order torsion-inversion-vibration interactions available in the context of the model. The first model, which extends Hougen's treatment of methanol,[b] couples the two vibrational angular momentum components of the asymmetric CH-stretches to the large-amplitude motion to yield predicted tunneling patterns for the ν_2 and ν_{11} fundamentals. This model gives similar patterns for ν_2 and ν_{11}, in which E_1 and E_2 are in the middle of the multiplet and the non-degenerate species are at the top and bottom. The second model, which follows conceptually Wang and Perry's local mode treatment of methanol,[c] couples the three local CH-stretches to each other and to the large-amplitude motion to yield the tunneling patterns for the ν_2, ν_3 and ν_{11} fundamentals. For this model, we found that, for ν_2 and ν_{11}, both E_1 and E_2 are at the bottom of the multiplet, in contrast to ν_3 and the ground state where they are at the top. The fact that neither model reproduces the observed tunneling pattern for ν_{11}, suggests that additional isolated perturbations or systematic interactions are present in the experimental spectra.

---

[a] V.V. Ilyshin et al.*J. Mol. Spectrosc.* **251**(56-63), 2008.

[b] J.T. Hougen *J. Mol. Spectrosc.* **207**(60-65), 2001.

[c] X. Wang and D.S. Perry *J. Chem. Phys.* **109**(10795-10805), 1998.

WF12 **15 min 4:47**

ELUCIDATING THE COUPLING IN THE CH STRETCH SPECTRAL REGION

EVAN G. BUCHANAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804*; EDWIN L. SIBERT, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706-1322.*

An important aspect of single conformation spectroscopy, aided by vibrational frequency calculations, is analyzing and assigning observed spectra to particular conformational isomers. However, certain infrared spectral regions have traditionally been considered less diagnostic, even ambiguous, despite the rich information content contained in the chromophores. One such chromophore, prevalent in most molecules, is the CH stretch vibration, where the CH stretch and bend overtone often participate in Fermi resonance. We have employed a parameterized reduced dimension Hamiltonian that incorporates cubic terms due to stretch/bend coupling, using the comparison with single-conformation spectra on a series of test molecules which include 1,2-diphenylethane, 2,2,2-tricyclophane, 1,2-diphenoxyethane, and dibenzo-15-crown-5 ether. This has led to excellent fits of the alkyl CH stretch region, particularly for tricyclophane, leading to a firm assignment for the conformations observed, and to a quantitative determination of the stretch-stretch and stretch-bend coupling present in the molecules. Details specific to the methodology as well as the success of the strategy will be discussed.

WG. ELECTRONIC

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: J. MATHIAS WEBER, University of Colorado, Boulder, Colorado

WG01 **15 min 1:30**

UNGERADE POLYADS IN THE $45800 - 46500$ CM^{-1} REGION OF THE S_1 STATE OF C_2H_2

J. H. BARABAN, P. B. CHANGALA, R. G. SHAVER, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

We present an analysis of *ungerade* vibrational polyads in the $45800 - 46500$ cm^{-1} region of the S_1 state of C_2H_2. This congested region is expected to hold at least 22 highly interacting vibrational levels. The polyads were observed in IR-UV double resonance LIF spectra, using $\nu_3''(\sigma_u^+)$, $\nu_3 + \nu_4''(\Pi_u)$, and $\nu_1 + \nu_5''(\Pi_u)$ as ground state vibrational intermediates. The assignments of the levels will be discussed, as well as a comparison between the observed structure and that predicted by effective constants from lower energy polyads, supplemented by *ab initio* theory where such constants are not available. We will also discuss local regions of interest, including perturbations. The goals of this analysis are to enable an extension of our understanding of the level structure to higher energies, nearing the *cis-trans* transition state, as well as to establish the *trans* level structure comprehensively, thereby permitting the identification of interloper states belonging to the *cis* manifold.

WG02 **15 min 1:47**

IDENTIFICATION OF NEW *CIS* VIBRATIONAL LEVELS IN THE S_1 STATE OF C_2H_2

J. H. BARABAN, P. B. CHANGALA, R. G. SHAVER, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

Although the S_1 ($\tilde{A}\ ^1A_u$) state of the $trans$ conformer of acetylene has been known for many years, the corresponding S_1 ($\tilde{A}\ ^1A_2$) state of the cis conformer was only discovered recently.[a] Transitions to it from the ground state are electronically forbidden, but its vibrational levels acquire intensity by tunneling through the isomerization barrier and interacting with levels of the $trans$ conformer. We have recently identified two new vibrational levels (3^2 and 4^16^1) of the *cis* conformer of S_1 C_2H_2, bringing the total number of levels observed to six out of an expected ten up to the energies studied in this work. The appearance of these levels in IR-UV double resonance LIF spectra will be discussed, along with their vibrational assignments. Experimentally determined vibrational parameters and *ab initio* anharmonic force fields for both the *trans* and *cis* conformers will be presented as part of the evidence supporting these assignments. These results shed new light on the vibrational level structure of both conformers in this isomerizing system.

---

[a] A. J. Merer, A. H. Steeves, J. H. Baraban, H. A. Bechtel, and R. W. Field. *J. Chem. Phys.*, 134(24):244310, 2011.

WG03 **15 min 2:04**

UNUSUAL ANHARMONICITIES IN ISOMERIZING SYSTEMS: THE S_1 STATE OF C_2H_2

J. H. BARABAN, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

Low-barrier *cis-trans* isomerization profoundly affects the $\tilde{A}$-$\tilde{X}$ spectrum of acetylene. We present extensions of the usual effective Hamiltonian model that capture these effects, and thereby enable fits of the complete $\tilde{A}\ ^1A_u$ state $J = K = 0$ level structure up to 4300 cm^{-1} above the *trans* zero point level. The relationship between these new additions to the model and spectroscopic indicators of the transition state energy will also be discussed. One dimensional models will be used to illustrate both the effects of the isomerization dynamics on the spectrum and how they can be exploited to reveal the isomerization barrier height.

WG04 **15 min 2:21**

UNKNOWN BANDS OBSERVED IN THE 266 NM PHOTOLYSIS OF IODOMETHANES

JIA-JEN DU, CHIA-HSIN CHEN, and BOR-CHEN CHANG, *Department of Chemistry, National Central University, 300 Jhongda Road, Jhongli 32001, Taiwan.*

Unknown bands that were not seen in the nascent emission spectra following the near-UV photolysis of bromomathanes ($CHBr_{3-n}Cl_n$, n= 0, 1, 2 and CH_2Br_2)[a] were observed in the 520-820 nm region of the nascent emission spectra following the 266 nm photolysis of iodomethanes (CHI_3, CH_2I_2, and CH_3I) in a slow flow system at ambient temperature.[b] We have dramatically improved the signal-to-noise (S/N) ratios of these unknown bands for further data analyses. Pressure dependence and temporal waveforms of the unknown bands were also recorded. The analyses show that these bands have the vibrational intervals of roughly 400 cm^{-1} and possibly originate from the same upper level with emission to different lower levels. Moreover, the nascent emission spectra of photolyzing the deuterated or ^{13}C-substituted isotopomers (CD_2I_2, CD_3I, and $^{13}CH_2I_2$) were also acquired, and the results indicate that the carrier molecule probably does not contain any hydrogen or carbon atoms. Our current progress will be presented.

---

[a] S.-X. Yang, G.-Y. Hou, J.-H. Dai, C-.H. Chang, and B.-C. Chang, J. Phys. Chem. A **114**, 4785 (2010).

[b] C.-N. Liu, H.-F. Liao, G.-Y. Hou, S-.X. Yang, and B.-C. Chang, 65^{th} OSU International Symposium on Molecular Spectroscopy, MI10 (2010).

WG05 **15 min 2:38**

UV AND 532 NM PHOTODISSOCIATION OF O-NITROTOLUENE: DETECTION OF ELECTRONICALLY EXCITED NITRIC OXIDE IN NITROGEN AND ARGON

HELENA DIEZ-Y-RIEGA and HERGEN EILERS, *Applied Sciences Laboratory, Institute for Shock Physics, Washington State University, Spokane, WA 99210-1495, USA.*

It is well known that NO is one of the main fragments produced by photodissociation of o-nitrotoluene. We detected vibrationally-excited NO in ground and electronically excited states using LIF. We also observed emission due to the formation of C(I) which is overlapping with NO emission. In the presence of N_2, longer lifetime of the NO emission is observed showing evidence of energy transfer from highly excited N_2. In the presence of Ar, evidence of o-nitrotoluene-Ar cluster formation was observed.

WG06 **15 min 2:55**

FLUORESCENCE EMISSION AND EXCITATION SPECTRA OF PHOTO-FRAGMENTED NITROBENZENE.

CHRISTOPHER J. LUE, CHAKREE TANJAROON, J. BRUCE JOHNSON, SUSAN D. ALLEN, SCOTT W. REEVE, *Arkansas Center for Laser Applications and Science and Department of Chemistry and Physics, P.O. Box 419 State University, AR 72467.*

Upon absorption of a UV photon, nitrobenzene readily dissociates into C_6H_5, NO_2, C_6H_5NO, O, C_6H_5O, and NO through three different channels.[a] We have recorded high resolution emission and excitation spectra of the NO resulting from photo-fragmented nitrobenzene using a pulsed picosecond tunable laser and a nanosecond dye laser. Specifically, the lasers probed the $A^2\Sigma^+ \rightarrow X^2\Pi_{(1/2,3/2)}$ NO band system between 225-260 nm using an one or two color process. In a one color process, the same energy (wavelength) photon is used to dissociate nitrobenzene and excite NO. In a two color process, photons of a particular energy are used to dissociate the nitrobenzene while photons of a different energy are used to probe the resultant NO. We have determined the rotational and vibrational temperatures of the nascent NO. And, we have examined the effect of the relative timing of the two photons on the fluorescence spectra to extract information about the photodissociation dynamics.

---

[a] Lin, M.-F.; Lee, Y. T.; Ni, C.-K.; Xu, S. and Lin, M. C. J. Chem. Phys., AIP, 2007, 126.

WG07 **15 min 3:12**

MIMICKING TRIMERIC INTERACTIONS IN THE AROMATIC SIDE CHAINS OF THE PROTEINS: A GAS PHASE STUDY OF INDOLE...(PYRROLE)$_2$ HETEROTRIMER

ALOKE DAS and SUMIT KUMAR, *Indian Institute of Science Education and Research, 900 NCL Innovation Park, Dr. Homi Bhabha Road, Pune-411008, Maharashtra, India.*

Aromatic trimeric interactions are extremely important in the stabilization of the specific structures of the proteins as well as protein-protein, and protein-ligand interactions. Here I will present a direct evidence of the observation of a cyclic asymmetric structure of indole...(pyrrole)$_2$ trimer bound by three N-H...π hydrogen bonding interactions in a supersonic jet. The experiment has been performed by using resonant two-photon ionization (R2PI), IR-UV, and UV-UV double resonance spectroscopic techniques. Density functional theory (DFT) calculations nicely corroborate the experimental results showing one weakly allowed IR-active band due to symmetric stretch of the N-H bonds and two strongly allowed IR-active bands due to two types of asymmetric stretches of the N-H bonds in the trimer. The most significant finding of the present investigation is that there is a direct IR spectral signature for the determination of the geometry of a trimer if it has a cyclic asymmetric structure.

Intermission

WG08 **15 min 3:45**

VIBRONIC COUPLING IN A FLEXIBLE BICHROMOPHORE: 1,2-DIPHENOXYETHANE

EVAN G. BUCHANAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804*; DAVID F. PLUSQUELLIC, *National Institute of Standards and Technology, Radiation and Biomolecular Physics Division, Gaithersburg, MD 20899-8443.*

Investigations of isolated flexible bichromophores through single conformation spectrocopy have provided tremendous insights into the intrinsic properties of close lying, vibronically coupled electronic states. However, the S_2 origin is often elusive, requiring a gambit of experimental techniques aided by high level calculations to pin down its location and the excitonic splitting. Here, we expand our studies on flexible bichromophores to 1,2-diphenoxyethane (C_6H_5-O-CH_2-CH_2-O-C_6H_5, DPOE). Ultraviolet hole-burning identified two confomrers present in the supersonic jet expansion with C_{2h} and C_2 symmetry. Both experimental and computational results suggest a small excitonic splitting of no more than a few cm^{-1}. The vibrationally and rotationally resolved spectra of DPOE conformational isomers will be discussed with regard to the vibronic coupling and excitonic splitting. Finally, the perturbation to the DPOE excited states due to a single water molecule will be discussed.

WG09 **15 min 4:02**

COMPREHENSIVE SPECTROSCOPIC CHARACTERIZATION OF MODEL AROMATIC SUBSTITUENTS OF LIGNIN

JACOB C. DEAN, VANESA VAQUERO VARA, KELLY M HOTOPP, BRIAN C. DIAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

2,6-Dimethoxyphenol (2,6-DMP) is a model compound with aromatic substitution similar to that in sinapyl alcohol, one of the three monomers that make up lignin. 2,6-DMP has been studied combining several spectroscopic techniques that span the microwave, infrared and ultraviolet regions. Spectra from laser-induced fluorescence excitation, IR-UV hole-burning, fluorescence dip IR, dispersed fluorescence and rotational spectra have allowed us to develop more insight to the structural details, intramolecular H-bonding and electronic excited states of this sinapyl alcohol analog. Coupling in the CH stretch region, broadening effects in the IR spectra and Coriolis coupling due to the OH tunneling coordinate in the rotational spectrum will be shown as we present this diverse set of experimental data involving transitions between different vibronic, vibrational and rotational levels of the molecule. These features will be compared to those in 2-methoxyphenol and 4-methyl-2,6-DMP during the discussion.

WG10 **15 min 4:19**

SPECTROSCOPIC INVESTIGATION OF LIGNIN LINKAGES: UV AND IR SIGNATURES OF PRIMARY DILIGNOLS

JACOB C. DEAN, PATRICK S. WALSH, JOSEPH R. GORD, BIDYUT BISWAS, P. V. RAMACHANDRAN, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

Lignin is an abundant, aromatic biopolymer ubiquitous to all plant matter; its properties are vital to the structural rigidity of plants as well as protection of the cell wall from degradation. As the major structural framework for plants, the breakdown of lignin for harvestable biomass is a formidable challenge. At a fundamental level, the characterization of lignin sequences and structures lag far behind those of proteins. One of the unique aspects of lignin is that it is composed of only three monolignols which are themselves structurally similar, all of which are aromatic derivatives. The structural complexity of lignin is in large measure due to the unique variety of chemical linkages between these three sub-units. As a result, there is a need for spectroscopic characterization of individual lignin linkages, and for elucidating potential fragmentation pathways and the relative energetics associated with those linkages in the polymer network. In this light, spectroscopic interrogation of these dilignol bichromophores yield signatures characteristic of their specific linkages which can also be found in high-order lignin oligomers. The β-O-4 and β-β linkages have been studied and their UV and IR signatures have been uncovered on a single-conformation basis in a supersonic expansion by use of IR/UV-UV HB and RIDIR spectroscopy. Fragmentation following resonant two-photon ionization of the neutral species was also explored and evidence for linkage-specific fragmentation has been revealed.

WG11 **15 min 4:36**

SYNERGISTIC TWO-PHOTON ABSORPTION ENHANCEMENT IN PHOTOSYNTHETIC LIGHT HARVESTING

KUO-MEI CHEN, YU-WEI CHEN and TING-FONG GAO, *National Sun Yat-sen University, Kaohsiung, Taiwan, Republic of China.*

The grand scale fixation of solar energies into chemical substances by photosynthetic reactions of light-harvesting organisms provides Earth's other life forms a thriving environment. Scientific explorations in the past decades have unraveled the fundamental photophysical and photochemical processes in photosynthesis. Higher plants, green algae, and light-harvesting bacteria utilize organized pigment-protein complexes to harvest solar power efficiently and the resultant electronic excitations are funneled into a reaction center, where the first charge separation process takes place. Here we show experimental evidences that green algae (*Chlorella vulgaris*) *in vivo* display a synergistic two-photon absorption enhancement in their photosynthetic light harvesting. Their absorption coefficients at various wavelengths display dramatic dependence on the photon flux. This newly found phenomenon is attributed to a coherence-electronic-energy-transfer-mediated (CEETRAM) photon absorption process of light-harvesting pigment-protein complexes of green algae. Under the ambient light level, algae and higher plants can utilize this quantum mechanical mechanism to create two entangled electronic excitations adjacently in their light-harvesting networks. Concerted multiple electron transfer reactions in the reaction centers and oxygen evolving complexes can be implemented efficiently by the coherent motion of two entangled excitons from antennae to the charge separation reaction sites. To fabricate nanostructured, synthetic light-harvesting apparatus, the paramount role of the CEETRAM photon absorption mechanism should be seriously considered in the strategic guidelines.

WG12 **15 min 4:53**

EMISSION AND fs/ns-TRANSIENT ABSORPTION OF ORGANOMETALLIC COMPLEXES BOUND TO A DINUCLEAR METAL CENTER

CHRISTOPHER B. DURR, SAMANTHA E. BROWN-XU and MALCOLM H. CHISHOLM, *The Ohio State University, Department of Chemistry and Biochemistry, Columbus, Ohio 43210.*

Compounds containing a MM quadruple bond (M = Mo or W) of the form $M_2L_2L'_2$, where L and L$'$ are conjugated organic ligands, show interesting photophysical properties along with a metal-to-ligand charge transfer (MLCT) band that is tunable throughout the UV-Vis-NIR spectra. Recently, our attention has shifted towards ligands that incorporate a secondary transition metal complex bound to an organic moiety. Along with allowing for a second tunable MLCT band for better coverage of the solar spectrum, these hybrid molecules show unique spectroscopic properties that were explored using fs/ns-transient absorption and UV-Vis/NIR emission. These techniques allow for the elucidation of the electronic character of the excited states as well as their lifetimes. This knowledge will be put to use in the design of new materials that could later be incorporated into next generation photovoltaic devices.

WG13 **15 min 5:10**

TUNING FÖRESTER RESONANCE ENERGY TRANSFER (FRET) IN DNA-FLUOROPHORE CONSTRUCTS

MARVIN POLLUM and CARLOS E. CRESPO HERNÁNDEZ, *Department of Chemistry and Center for Chemical Dynamics, Case Western Reserve University, Cleveland, OH 44106.*

According to Förester's equations, the efficiency (E_{FRET}) of resonance energy transfer between fluorophores is governed by three factors: separation distance, relative orientation of transition dipole moments, and the spectral overlap integral. We've designed an ideal architecture for controlling each of these parameters by covalently linking FRET fluorophore pairs into complementary DNA helices. Steady-state absorption and emission spectroscopies are used to determine E_{FRET} in a range of environments, while time-resolved techniques are used to reveal any decreases in FRET due to competing electronic relaxation pathways.

WH. ASTRONOMICAL SPECIES AND PROCESSES

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: ERIC HERBST, University of Virginia, Charlottesville, Virginia

WH01 **15 min 1:30**

A CONFUSION LIMITED SPECTRAL SURVEY OF ORION

J. CERNICHARO, B. TERCERO, N. MARCELINO, T. BELL, *CAB. Dpt Astrophysics. Crta Torrejón Km 4. 28850 Torrejón de Ardoz. Madrid. Spain*; A. PALAU, *ICE, Campus UAB, Torre C5, 08193 Bellaterra. Spain.*

A line survey of Orion KL has been carried out with the 30m IRAM radio telescope. In addition to the central position, which was observed across the whole frequency range covered by the 30m telescope (80-280 GHz), a 2-D line survey over a region of 2’x2’ has been performed between 200-282 GHz. Spectral features with intensities below 0.05 K, 0.1 K and 0.1 K in the 3mm, 2mm and 1mm ranges respectively are considered to belong to the confusion limit of the survey. More than 15000 lines have been detected above these confusion limits, of which more than 10000 have been assigned to 44 molecules and their isotopologues. A particular effort has been made in the laboratory to characterize isotopic species of abundant molecules such as CH_3CH_3CN and CH_3OCOH and their vibrationally excited states. We present the results for some abundant species and their isotopologues (SO, CS, SiS, SiO, SO_2), the status of the identifications and the possible carriers for the 5000 remaining unidentified lines.

The thousands of well defined spectral features below the confusion limits at 3 and 2 mm are also awaiting identification. Above 200 GHz these features make a "pseudocontinuum" whose assignment is hopeless. The implications for line surveys in the ALMA era will be discussed.

WH02 **15 min 1:47**

HERSCHEL OBSERVATIONS OF EXTRAORDINARY SOURCES (HEXOS).

J. L. NEILL, N. R. CROCKETT, E. A. BERGIN, *Department of Astronomy, University of Michigan, 500 Church St, Ann Arbor, MI 48109, USA*; and THE HEXOS TEAM, *http://www.hexos.org/team.php/.*

The HEXOS guaranteed-time key program consists of high-resolution, high-sensitivity spectral line surveys of five sources within the Orion and Sagittarius B2 molecular clouds in the mostly unexplored frequency regime of the HIFI and PACS instruments on board the Herschel Space Observatory. Transitions with an unprecedented range of excitation energies are observed in these spectra, leading to robust constraints on the physical conditions of a large number of molecular species. This talk will present key results in the analysis of these surveys over the past year. We have completed a full-band analysis of the HIFI spectrum towards Orion KL, estimated to contain over 100,000 spectral features, revealing distinctions between molecules that probe hot ($\sim$ 300 K) gas and those that are detected in cooler ($\sim$ 100 K) environments. A total of 31 molecules and their isotopologues have been modeled in this spectrum. The analysis of the Sagittarius B2(N) HIFI spectrum, which has similar complexity to that of Orion KL and also contains spectral features coming from a range of physical environments, is currently underway and early results will be presented.

WH03 **15 min 2:04**

UNRAVELING THE MYSTERIES OF COMPLEX INTERSTELLAR ORGANIC CHEMISTRY USING HERSCHEL/HIFI SPECTRAL LINE SURVEYS

SHIYA WANG, MARY L. RADHUBER, JACOB C. LAAS, JAY A. KROLL, JAMES L. SANDERS, AND SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; DARIUSZ C. LIS, *Division of Physics, Mathematics, and Astronomy, California Institute of Technology, Pasadena, CA 91125*; ERIC HERBST, *Departments of Chemistry, Physics, and Astronomy, University of Virginia, Charlottesville, VA 22904*.

The goal of our ongoing Herschel Space Observatory OT1 program is to probe the influence of physical environment on molecular complexity through spectral line surveys. These observations target a sample of 10 sources, probe a range of physical environments, and include frequency windows that contain transitions from a set of known complex organic molecules. From these results, we have determined the fractional abundances of a set of organic molecules that are predicted by models to trace key chemical mechanisms in interstellar clouds. We are examining correlations between classes of molecules, as well as correlations between the physical properties of the source (i.e. temperature, density, age, etc.) and each molecular target. These results can be used as benchmarks to improve astrochemical models to the point where accurate predictions of complex molecular inventory can be based on the physical and chemical environment of a given source. Here we will report on preliminary results from these observations and discuss these results in the context of the effect that physical environment has on the chemical complexity of interstellar clouds.

WH04 **15 min 2:21**

ANALYSIS OF OH^+, H_2O^+, AND H_3^+ IN A DIFFUSE MOLECULAR CLOUD TOWARD W51

NICK INDRIOLO, DAVID A. NEUFELD, *Department of Physics & Astronomy, Johns Hopkins University, Baltimore, MD 21218*; MARYVONNE GERIN, *LERMA, CNRS UMR 8112, 24 rue Lhomond, 75231 Paris Cedex 05, France*; THOMAS R. GEBALLE, *Gemini Observatory, Hilo, HI 96720*.

Absorption lines from the molecules OH^+, H_2O^+, and H_3^+ have all been observed in a diffuse molecular cloud along a line of sight near W51 IRS2. We present the first chemical analysis that combines the information provided by all three of these species. Together, OH^+ and H_2O^+ are used to determine the molecular hydrogen fraction (f_{H_2}) in the outskirts of the observed cloud, as well as the product of the cosmic-ray ionization rate of atomic hydrogen and an efficiency factor ($\epsilon\zeta_{\mathrm{H}}$). The efficiency factor (ϵ) describes what fraction of the time ionization of H by cosmic rays eventually leads to OH^+. H_3^+ is used to infer the cosmic-ray ionization rate of H_2 (ζ_2) in the molecular interior of the cloud. By demanding that the two ionization rates are equal, and taking the value inferred from H_3^+ to be correct, we determine ϵ. This is an important step in the future use of OH^+ and H_2O^+ on their own as tracers of the cosmic-ray ionization rate.

WH05 **15 min 2:38**

OBSERVATIONS OF OH^+ AND H_2O^+ ACROSS THE GALAXY WITH HERSCHEL

NICK INDRIOLO, DAVID A. NEUFELD, *Department of Physics & Astronomy, Johns Hopkins University, Baltimore, MD 21218*; MARYVONNE GERIN, *LERMA, CNRS UMR 8112, 24 rue Lhomond, 75231 Paris Cedex 05, France*; THE PRISMAS CONSORTIUM,.

The launch of the Herschel Space Observatory in 2009 opened up the possibility for high resolution spectroscopic astronomical observations at THz frequencies. This has led to the detection of several new species in the interstellar medium, including OH^+ and H_2O^+. Both of these molecules were observed as part of the PRISMAS[a] key programme, and are detected in absorption in eight sight lines that probe material up to distances of 12 kpc away. From these observations we derive column densities of both species, which are then used to determine the molecular hydrogen fraction in multiple velocity components along each line of sight. Additionally, we estimate the ionization rate of atomic hydrogen due to cosmic rays. Finally, we compare molecular hydrogen fractions and cosmic-ray ionization rates inferred for different clouds and sight lines with each other, and with other tracers of both parameters with the intent of searching for variations across the Galaxy.

---

[a] PRobing InterStellar Molecules with Absorption line Studies

WH06 15 min 2:55

MORPHOLOGY OF GAS IN THE GALACTIC CENTER FROM SPECTROSCOPY OF H_3^+

TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637*; THOMAS R. GEBALLE, *Gemini Observatory, Hilo, HI 96720*; NICK INDRIOLO, *Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218*; MIWA GOTO, *Universitäts-Sternwarte München, MüÃÂijnchen Germany 81679.*

Over the last several years our observations of the infrared spectrum of H_3^+ toward the Galactic center (GC) have established a high ionization rate ($\zeta > 2 \times 10^{-15}$ s^{-1}) and the existence of a vast amount of warm ($T \sim 250$ K) and diffuse ($n < 100$ cm^{-3}) gas with a high volume filling factor ($f > 0.3$) in the Central Molecular Zone (CMZ) of the GC, a region of radius $\sim$ 150 pc.[abc] These findings are gradually being assimilated into the astrophysics of the GC.

Determining the morphology of this gas is difficult because the sightlines for study are limited by the uncontrollable locations of background stars suitable for spectroscopy of H_3^+. There are wide longitudinal gaps in the locations of those stars and the precise radial locations of the stars within the CMZ are uncertain. Nevertheless, the velocity profiles of the observed H_3^+ spectra indicate the presence of the Expanding Molecular Ring (EMR), a structure containing mostly diffuse gas expanding from the center with velocities of up to 180 km s^{-1} and bordering the CMZ. On the other hand, the 120 pc Molecular Ring,[d] an inner t ring of cold dust and dense gas with radius $\sim$ 100 pc is not clearly seen in H_3^+. This is possibly because the sightlines that we have observed to date lie close to the Galactic plane and miss the ring, which goes above and below the Galactic plane.[e]

---

[a] Oka, T., Geballe, T.R., Goto, M., Usuda, T., McCall, B.J. 2005, ApJ, 632, 882

[b] Goto, Usuda, Nagata, Geballe, McCall, Indriolo, Suto, Henning, Morong, and Oka, 2008, ApJ, 688, 306.

[c] Geballe, T.R. and Oka, T. 2010, ApJ, 709, L70

[d] Sofue, Y. 1995, PASJ, 47, 527

[e] Molinari, S. et al. 2011, ApJ, 735, L33.

Intermission

WH07 15 min 3:30

CH^+ SPECTRUM AND DIFFUSE INTERSTELLAR BANDS TOWARD HERSCHEL 36 EXCITED BY DUST EMISSION

JULIE DAHLSTROM, *Carthage College*; TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637*; SEAN JOHNSON, DANIEL E. WELTY, LEW M. HOBBS, and DONALD G. YORK, *Department of Astronomy and Astrophysics, University of Chicago, Chicago, IL 60637.*

All electronic CH^+ interstellar absorption lines so far observed had been limited to the $R(0)$ transition starting from the J = 0 ground level; this is because of the very rapid $J = 1 \rightarrow 0$ spontaneous emission with the life time of $\sim$ 140 s. We have observed the $R(1)$ and $Q(1)$ lines of the $A^1\Pi \leftarrow X^1\Sigma$ band from the excited J = 1 level 40.08 K (27.86 cm^{-1}) above the J = 0 level toward Herschel 36 indicating high radiative temperature of T_r = 17.5 K. The high temperature is most likely due to far infrared dust emission from the Her 36 SE.[a] We have also observed the $R_1(3/2)$ line of CH starting from the excited fine structure level J = 3/2 which is 25.76 − 25.57 K above the J = 1/2 level.

The effect of high radiative temperature is also noticed as unique lineshapes of diffuse interstellar bands (DIBs) observed toward Her 36. We have examined seven DIBs including λ 5780.5, λ 5797.1, λ 6190.0, and λ 6613.0 that are correlated with each other with correlation coefficients > 0.93. While for ordinary sightlines the lineshapes of these DIBs are more or less symmetric, those toward Her 36 show a long tail toward the red. This is due to far infrared pumping of high J rotational levels of polar carriers of the DIBs by the dust emission. We have developed a model calculation of relaxation taking into account of both radiative and collisional processes. A linear molecule with about 6 carbon atoms can explain some of the DIBs. For the DIBs we have examined, probably the carriers are of this size since we cannot explain the large difference between the DIBs toward ordinary sightlines and toward Her 36 with larger molecules.

---

[a] Goto, M., Stecklum, B., Linz, H., Feldt, M., Henning, Th., Pascucci, I., and Usuda, T. 2006, ApJ, **649** 299.

WH08 **15 min 3:47**

MOLECULAR CONTENT OF THE HELIX NEBULA

L.N. ZACK, N. R. ZEIGLER, and L.M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

Multiple transitions of H_2CO, HCO^+, and CO were detected at nine positions across the planetary nebula NGC 7293, the Helix Nebula, using the 12m telescope and the Submillimeter Telescope (SMT) of the Arizona Radio Observatory (ARO). A complete map of the nebula has also been made in the J = 1 $\rightarrow$ 0 transition of HCO^+ at 89 GHz. HCO^+ emission was found to be widespread across the Helix, and is coincident with the ionized gas as traced in optical images. A complex velocity structure is apparent in the HCO^+ spectra, as well. The CO and H_2CO data (J = 1 $\rightarrow$ 0, 2 $\rightarrow$ 1, and 3 $\rightarrow$ 2) were modeled using a radiative transfer code at the nine positions observed in the Helix. Kinetic temperatures were typically found to be in the range $T_{kin} \approx 20$ - 45 K and the gas density on the order of $n(H_2) \approx 10^5$ cm^{-3} at these positions. The column densities for CO, H_2CO, and HCO^+ were determined to be 10^{15}, 10^{12}, and 10^{11} cm^{-2} respectively, corresponding to fractional abundances, relative to H_2, of f $\approx 10^{-4}$, 10^{-7}, and 10^{-8}. The extended distribution of HCO^+ suggests that dense clumps may exist throughout the nebula. Hence, the chemistry of evolved planetary nebulae may be more active than previously thought.

WH09 **15 min 4:04**

THE MOLECULAR CONTENT OF PLANETARY NEBULAE: THE DUMBBELL AND THE RED SPIDER

JESSICA L. EDWARDS, LUCY M. ZIURYS, ERIN G. COX, NEVILLE J. WOOLF, *Department of Chemistry and Biochemistry, Department of Astronomy, Steward Observatory, The University of Arizona, Tucson, AZ 85721.*

The molecular content of Planetary Nebulae (PNe) is not well characterized. It is generally thought that as the PN evolves, the ultraviolet radiation from the central star destroys molecular material from the AGB (asymptotic giant branch) shell. Here we present new observations of two interesting nebulae, the Dumbbell (NGC6853) and the Red Spider (NGC6537), carried out with the Sub-Millimeter telescope and the 12-Meter telescope of the Arizona Radio Observatory. The J=1-0 transition of HCO^+ at 89 GHz has been mapped across the face of the Dumbbell Nebula, which is estimated to be about 10,000 years old. HCO^+ appears to be extended by several arcminutes across the Dumbbell, as traced by optical atomic emission, with an abundance relative to H_2 of $f \sim 10^{-7}$. The molecule traces interesting velocity structure apparent in CO as well. In the Red Spider Nebula (age $\sim$ 1,000 years) CS and HCO^+ have been detected with abundances on the order of $f \sim 10^{-6}$ for both. Searches for other molecules are currently being conducted. Most current results will be presented.

WH10 **15 min 4:21**

SPECTRAL LINE SURVEYS OF YOUNG STELLAR OBJECTS USING THE CALTECH SUBMILLIMETER OBSERVATORY

JAMES L. SANDERS III, MARY L. RADHUBER, JACOB C. LAAS, JAY A. KROLL and SUSANNA L. WIDICUS WEAVER, *Emory University, Department of Chemistry, Atlanta, Georgia 30322.*

Advancements in radioastronomical instrumentation have allowed for the identification of approximately 170 interstellar molecules, many of which are complex organic molecules (COMs). Many of the detected COMs, including species such as glycolaldehyde and formamide, are thought to be prebiotic precursors in the chemistry of these star-forming regions. Complex organic chemistry is especially rich in hot cores/corinos, where thermal evaporation during the warm-up phase of star-formation releases molecules from icy grain mantles into the gas phase. Grain surface and gas phase astrochemical models provide predicted abundances of COMs, and these predictions can be tested through observations of a variety of sources. We have used the Caltech Submillimeter Observatory (CSO) to conduct deep λ=1.3mm unbiased line surveys of 8 sources including hot cores, hot corinos, dense molecular clouds, and shocked regions. These line surveys cover frequencies in the range of 215 - 270 GHz with an RMS noise level of $\sim$30 mK, which is sufficiently deep to probe many of the largest COMs that have been identified to date. We have performed detailed spectral analyses for these line surveys targeting a range of COMs that test the chemical mechanisms included in astrochemical models. Here we present the spectra and results of a quantitative analysis of these sources, and discuss the implications of these results for astrochemical models.

WH11 **15 min 4:38**

IDENTIFYING LOCAL CHEMICAL ENVIRONMENTS IN ORION KL BY BROADBAND DATA CUBE ANALYSIS

BRENT J.HARRIS, CLARE YANG, KEVIN K. LEHMANN, BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904*; ANTHONY J. REMIJAN, CRYSTAL L.BROGAN, *National Radio Astronomy Observatory, Charlottesville, VA 22904.*

A method for visualizing large data cubes from broadband radio astronomy has been implemented. Visualizing the cube in"correlation space" where the spatial distribution images for each data channel are correlated, is an effective tool for screening co-spatial features and dumping feature-less pixels out of the data set. The technique is tested using the Expanded Very Large Array Demonstration Science data of Orion KL in the 23.6 GHz to 26.6 GHz spectral range at a spatial resolution of approximately 5"x2.". This frequency range includes the methanol E-symmetry K=2-1 Q-branch (in addition to transitions from other molecules including ammonia, SO_2, OCS, and methyl formate). This observation has a spectral resolution of 133 kHz giving a velocity resolution of 1.6 km/s. Along a particular line of sight, both thermalized and non-thermalized methanol is present in Orion KL, and the spectra can be separately analyzed. The thermalized methanol belongs to the Orion"hot core" and the broadband spectrum can be fit with a rotational temperature of 118K. The non-thermal methanol emission profiles vary throughout the molecular cloud, and each spectrum can be reproduced using a steady-state, local velocity gradient model adapted for integration into this study. Analysis of the temperature and density in different local environments of Orion will be discussed.

WH12 **15 min 4:55**

THE ROTATIONAL SPECTRUM OF HCl^+

HARSHAL GUPTA, B. J. DROUIN, J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology*[a]*, Pasadena, CA 91109.*

The rotational spectrum of the radical ion HCl^+ has been detected at high resolution in the laboratory, supporting conclusively the identification of this ion with the *Herschel Space Observatory's* Heterodyne Instrument for the Far-Infrared (HIFI) in diffuse clouds toward the Galactic star-forming regions W31C and W49N. Three rotational transitions, one in the ground state $^2\Pi_{3/2}$ ladder and two in the $^2\Pi_{1/2}$ ladder (643 cm^{-1} above ground), were observed in a microwave discharge of He and HCl. Well-resolved chlorine hyperfine structure and Λ-doubling, and the detection of lines of $H^{37}Cl^+$ at precisely the expected isotopic shift, provide conclusive evidence for the laboratory identification. The detection of rotational transitions in the $^2\Pi_{1/2}$ ladder of HCl^+ for the first time allows an experimental determination of the individual hyperfine coupling constants of chlorine, and yields a precise value of eQq_2. The spectroscopic constants determined by fitting a Hamiltonian simultaneously to our data and more than 8000 optical transitions are so precise, that they allow calculation of the frequencies of $^2\Pi_{3/2}$ $J = 5/2 - 3/2$ transition observed by HIFI to within 0.2 km s^{-1}, and indeed, those of the strongest rotational transitions of HCl^+ below 7.5 THz to better than 1 km s^{-1}.

---

[a] A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2012© California Institute of Technology. All rights reserved.

WH13 15 min 5:12

HERSCHEL/HIFI IDENTIFICATION OF HCl$^+$ IN THE INTERSTELLAR MEDIUM

M. DE LUCA, M. GERIN, E. FALGARONE, *LERMA-LRA, UMR 8112 du CNRS, Observatoire de Paris, École Normale Supérieure, UPMC & UCP, 24 rue Lhomond, 75231, Paris Cedex 05, France*; HARSHAL GUPTA, B. J. DROUIN, J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology*[a], *Pasadena, CA 91109*; D. A. NEUFELD, *The Johns Hopkins University, Baltimore, MD 21218*; D. C. LIS, R. MONJE, T. G. PHILLIPS, *California Institute of Technology, Pasadena, CA 91125*; D. TEYSSIER, *European Space Astronomy Centre, ESA, Madrid, Spain*; J. R. GOICOECHEA, B. GODARD, T. A. BELL, *Centro de Astrobiología (CSIC/INTA), Madrid, Spain*; A. COUTENS, *Université de Toulouse, UPS-OMP, IRAP, Toulouse, France*.

The radical ion HCl$^+$, a key intermediate in the chlorine chemistry of the interstellar gas, has been identified for the first time in the interstellar medium with the *Herschel Space Observatory's* Heterodyne Instrument for the Far-Infrared. The ground state rotational transition of H^{35}Cl$^+$, $^2\Pi_{3/2}$ $J = 5/2 - 3/2$, showing Λ-doubling and hyperfine structure, is detected in absorption toward the bright Galactic submillimeter-wave continuum regions, W31C (G10.6-0.4) and W49N. The complex interstellar absorption features are modeled by convolving in velocity space the opacity profiles of other molecular tracers of the same sources with the fine and hyperfine structure of HCl$^+$ derived from a combined analysis of recent high-resolution submillimeter-wave measurements and optical data from the literature. The models reproduce well the interstellar absorption, and the frequencies inferred from the astronomical observations are in exact agreement with those calculated from spectroscopic constants derived from the laboratory data. The detection of H^{37}Cl$^+$ toward W31C, with a column density consistent with the expected ^{37}Cl abundance, provides additional evidence for the identification. These observations also yield the surprising result that HCl$^+$ accounts for nearly $3 - 5\%$ of the gas-phase chlorine toward W31C and W49N, values several times higher than the maximum fraction ($\sim 1\%$) predicted by chemical models.

---

[a] A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.

WH14 15 min 5:29

INTEGRAL FIELD SPECTROSCOPY OF THE RED RECTANGLE: UNRAVELING THE CARRIER OF THE RRBs IN 2D

D. L. KOKKIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. Colonel Roche, BP 44346, F-31028 Toulouse Cedex 4, France*; R. G. SHARP, *Research School of Astronomy & Astrophysics, Mount Stromlo Observatory, Cotter Road, Weston Creek, ACT 2611, Australia*; M. NAKAJIMA, *Department of Chemical System Engineering, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*; T. W. SCHMIDT, *School of Chemistry, The University of Sydney, New South Wales, 2006, Australia*.

Following the initial detection of the C_2 Swan origin bands in the Red Rectangle, an unusual biconical protoplanetary nebula, a concerted effort has been undertaken in understanding this key astrophysical molecule from both the theoretical and experimental standpoint. In this talk we will present integral field observations on the Red Rectangle paying particular attention to the Swan Bands and the 5800Å Red Rectangle band (RRB), an unassigned molecular emission feature. Integral field astronomy allows us to spectrally map the nebula, tracing the RRBs and C_2, and how they relate to one another across the object. By analysis of the C_2 Swan bands of the RR, and assuming that the RRBs arise from photoexcitation and emission, we relate the abundance of C_2 to the product of the oscillator strength and the column density of the RRB carrier.

WI. RADICALS AND IONS

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: KENTAROU KAWAGUCHI, Okayama University, Okayama, Japan

WI01 **15 min 1:30**

THE PREDICTED INFRARED SPECTRUM OF THE HYPERMETALLIC MOLECULE CaOCa IN ITS LOWEST TWO ELECTRONIC STATES $\tilde{X}\ ^1\Sigma_g^+$ AND $\tilde{a}\ ^3\Sigma_u^+$

B. OSTOJIĆ, *Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Studentski trg 14-16, 11 000 Belgrade, Serbia*; P. R. BUNKER, P. SCHWERDTFEGER, *Centre for Theoretical Chemistry and Physics (CTCP), The New Zealand Institute for Advanced Study(NZIAS), Massey University Auckland, Private Bag 102904, North Shore City, 0745 Auckland, New Zealand*; ARTUR GERTYCH, PER JENSEN, *FB C – Physikalische und Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany.*

This study of CaOCa is the third in a series by us on Group 2 alkaline-earth M_2O hypermetallic oxides. As with our previous calculations in the series, on BeOBe and MgOMg, the *ab initio* calculations we report here show that CaOCa has a linear $^1\Sigma_g^+$ ground electronic state and a very low lying linear $\tilde{a}\ ^3\Sigma_u^+$ first excited triplet electronic state. For CaOCa we determine that the singlet-triplet splitting $T_e(\tilde{a})$ = 386 cm^{-1}. We calculate the three-dimensional potential energy surface, and the electric dipole moment surfaces, of each of the two states using a multireference configuration interaction (MRCISD) approach in combination with internally contracted multireference perturbation theory (RS2C) based on full-valence complete active space self-consistent field (FV-CASSCF) wavefunctions with a cc-pwCVQZ-DK basis set for Ca and a cc-pCVQZ basis set for O. We simulate the infrared absorption spectra of $^{40}Ca^{16}O^{40}Ca$ in each of these electronic states in order to aid in its eventual spectroscopic characterization.

WI02 **15 min 1:47**

INTERMOLECULAR INTERACTIONS BETWEEN THE SUPEROXIDE RADICAL AND HYDROGEN FLUORIDE

WAFAA M. FAWZY, YUCHENG ZHANG, and MAHMOUD ELSAYED, *Department of Chemistry, Murray State University, Murray, KY 42071.*

This work concerns theoretical characterization of the nature of intermolecular interaction between the superoxide radical and hydrogen fluoride. The long-range intermolecular potential energy surface of the superoxide-HF complex was examined using the CCSD(T)/aug-cc-pVXZ, X=1, 2, 3, 4, and 5, level of theory. Our preliminary results show a minimum energy structure that corresponds to a non-linear planar geometry of Cs symmetry. In this structure, the hydrogen atom of the HF moiety is bonded to one of the oxygen atoms of the superoxide radical via a very strong hydrogen bond that is comparable to ionic bond (D_e = 41.4 kcal/mol). Such an ionic hydrogen bond causes elongation of the H-F bond length in the complex by about 0.1 angstroms. These results as well as those of vibrational frequency calculations will be presented.

WI03 **15 min 2:04**

INTERMOLECULAR INTERACTIONS BETWEEN URACIL AND REACTIVE SPECIES

SIJIN REN and WAFAA M. FAWZY, *Department of Chemistry, Murray State University, Murray, KY 42071.*

We have investigated intermolecular interactions between uracil (U) and each of the fluoride ion, superoxide anion, and the hydroxyl radical. Computational study of these new systems presents several challenges, most importantly is the choice of the proper level of theory and the appropriate size of the basis set. Our investigations on the U-F$^-$ complex showed that the MP2 and density functional method (DFT) with aug-cc-pVDZ and aug-cc-pVTZ basis sets provide results that are consistent with those obtained with highly correlated methods for H_2O-F$^-$. This suggests that these levels of calculations are suitable for exploring the structures and the potential energy surfaces of the U-$O_2{}^-$ and U-OH complexes. Our preliminary results show that each of the F$^-$ and the superoxide ions forms a very strong hydrogen bond with a specific hydrogen atom in the uracil ring. Also, results suggest that proton transfer occurs between the bonding site in uracil and each of the F$^-$ and $O_2{}^-$ ions. On the other hand, preliminary results show that the OH radical chemically reacts with the uracil molecule. Discussion of details of calculations and results will be presented.

WI04 **15 min 2:21**

A NEW APPROACH TO INVESTIGATE PAH DERIVED CATIONS AS DIB CARRIERS

D. L. KOKKIN, C. MARSHALL, A. BONNAMY, and C. JOBLIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*; A. SIMON, *LCPQ, Université de Toulouse, UPS; CNRS; 118 Route de Narbonne, 31062 Toulouse Cedex 09, France*.

Polycyclic aromatic hydrocarbons (PAHs) and their cations are considered as attractive candidates for the Diffuse Interstellar Bands, some discrete absorption features observed throughout the visible and near-infrared spectral range whose origin is still investigated. So far, not a single PAH species has been identified on the basis of a spectral agreement. This indicates either that the molecular diversity is very large or that the candidates that have been considered are not the correct ones. In particular, small/medium-sized PAHs are submitted to photodissociation under UV photons from stars. It is therefore of interest to characterize the spectroscopy of key breakdown products. These spectroscopic studies should be performed in conditions that mimic those found in interstellar space, that leads to additional experimental difficulties. We will describe the approach we are developing with the PIRENEA set-up[a] [b] and present results on 1-methylpyrene cation and derived species. Experimental measurements are guided by calculations based on density functional theory and its time-dependent implementation.

---

[a] F. Useli-Bacchitta, A. Bonnamy, G. Malloci, G. Mulas, D. Toublanc, and C. Joblin, *Chem. Phys.* **371** (2010), 16-23.

[b] Joint ANR project GASPARIM, ANR-10-BLAN-501

WI05 **15 min 2:38**

HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPIC STUDY OF CYCLOPROPENE (c-C_3H_4)

KONSTANTINA VASILATOU, JULIE M. MICHAUD, GUIDO GRASSI, DENITSA BAYKUSHEVA and FREDERIC MERKT, *Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zürich, Switzerland.*

The spectroscopic information available on the cyclopropene radical cation is limited to that contained in low-resolution He I photoelectron spectra [a,b]. To better characterize the structure of this cation, we have recently measured high-resolution PFI-ZEKE photoelectron spectra of c-C_3H_4 and several of its deuterated isotopomers in the vicinity of the adiabatic ionization threshold. Our new data include fully rotationally resolved spectra of the origin band of the $\widetilde{\mathrm{X}}^+ \leftarrow \widetilde{\mathrm{X}}$ transition of c-C_3H_4 and spectra of the low-vibrational levels of c-C_3H_4 and the deuterated isotopomers recorded at lower resolution. Because our efforts at synthesizing the partially deuterated isotopomers always resulted in mixtures of several isotopomers, differing in their number of D atoms and in the location of these atoms, the analysis of the isotopic shifts turned out to be challenging. Combining the information contained in the rotational structure of the origin band of c-C_3H_4 with the ionization energies of the isotopomers measured by photoionization mass spectrometry and the vibrational structure observed in the PFI-ZEKE spectra of the mixtures of deuterated isotopomers, we were able to draw conclusions on the structure of the cyclopropene radical cation based solely on experimental data. The adiabatic ionization energy of c-C_3H_4 was determined to be $77931.8(5)\,\mathrm{cm}^{-1}$.

---

[a] M. B. ROBIN, C. R. BRUNDLE, N. A. KUEBLER, G. B. ELLISON AND K. B. WIBERG, *J. Chem. Phys.* **57**, 1758 (1972).

[b] P. BISCHOF AND E. HEILBRONNER, *Helv. Chim. Acta* **53**, 1677 (1970).

WI06 **15 min 2:55**

SUB-DOPPLER SPECTROSCOPY OF MOLECULAR IONS IN THE MID-INFRARED

JAMES N. HODGES, KYLE N. CRABTREE, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy, and Physics, Univeristy of Illinois, Urbana, IL 61801.*

High precision, high accuracy spectroscopy in the mid-IR plays an important role in many areas of study. It provides benchmarks for *ab initio* calculations, acts as a reference for astronomical searches, and enables the study of highly fluxional ions, such as CH_5^+ and H_5^+. In an effort to advance these interests, we built an instrument that uses Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy to achieve sensitive, high signal-to-noise spectra of molecular ions with sub-Doppler features.

There are four main components of the instrument: a tunable cw-OPO, an optical cavity with a finesse of ~ 200, a liquid nitrogen cooled AC positive column cell, and an optical frequency comb for absolute frequency calibration. The OPO is pumped by a fiber laser at 1064 nm with a signal cavity resonant between 1.5 and 1.6 μm, which corresponds to an idler wavelength tunable between 3.2 and 3.9 μm. The idler is actively locked to the cavity via a Pound-Drever-Hall locking scheme responsible for maintaining the resonance condition of the cavity. Inside the cavity is a AC driven positive column plasma, which produces a high ion density and modulates their velocity providing neutral discrimination. Since the cell can be cooled by liquid nitrogen, the instrument has an extra advantage due to signal enhancement of low J transitions. Saturation spectroscopy is possible because of enhancement of laser power in the cavity, which leads to improved precision with respect to line center determination due to narrow Lamb dips. To achieve sub-MHz accuracy, the signal and pump are roughly calibrated with a near-IR wavemeter and then referenced to a frequency comb. To demonstrate the advantages of this technique, measurements of the ν_2 fundamental band of H_3^+ will be presented.

WI07 **15 min 3:12**

THE INFRARED SPECTRUM OF CH_5^+ REVISITED

KYLE N. CRABTREE, JAMES N. HODGES, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy, and Physics, University of Illinois, Urbana, IL 61801.*

The infrared spectrum of CH_5^+, originally collected and published over a decade ago, remains unassigned to this day owing to its complexity. CH_5^+ is a highly fluxional species that challenges the concept of molecular structure itself, and consequently the spectrum features no obvious patterns that would aid in assignment. Efforts toward extracting rotational energy level spacings using the four-line combination differences technique have been frustrated by the low precision of the spectrum, leading to a large number of coincidences in a combination differences analysis. Knowledge of energy level spacings could guide searches for its microwave spectrum, and consequently its detection in the interstellar medium where it is expected to be an important reactive species.

We have revisited the infrared spectrum of CH_5^+ using Noise Immune Cavity-Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS) with a cw-OPO laser. By combining our spectrometer with an optical frequency comb, we can measure line centers with much greater precision and accuracy than previously possible. In this talk, we will discuss progress toward remeasurement of the previously-published lines with NICE-OHVMS, and the implications of greater precision and accuracy for the combination differences analysis.

Intermission

WI08 15 min 3:45

INFRARED PHOTODISSOCATION SPECTROSCOPY OF ALUMINUM BENZENE CATION COMPLEXES

B. BANDYOPADHYAY, K. N. REISHUS, M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602-2256.*.

$\mathrm{Al}^+ - \mathrm{bz}$ and $\mathrm{Al}^+ - \mathrm{bz}_2$ complexes are produced in a laser vaporization/supersonic expansion source. These complexes are mass selected and their infrared spectra (700-4500 cm^{-1}) are taken using infrared laser photodissociation spectroscopy via the argon tagging method. DFT on both complexes is carried out to obtain the structures and vibrational frequencies. The CH stretch and fingerprint regions of both complexes are compared to theory and the free benzene spectrum. The far infrared spectrum of $\mathrm{Al}^+ - \mathrm{bz}$ (700-1800 cm^{-1}) is compared to the previous spectrum collected using IR-MPD and significant differences in linewidth and line position are observed. The structure of $\mathrm{Al}^+ - \mathrm{bz}_2$ indicated by the vibrational band patterns is investigated and compared to theory, which predicts an asymmetric structure.

WI09 15 min 4:02

STRUCTURES AND SPECTROSCOPIC PROPERTIES CALCULATED FOR $C_6H_7^+$ AND ITS COMPLEXES WITH Ne, Ar, N_2, OR CO_2

P. BOTSCHWINA and R. OSWALD, *Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*.

Explicitly correlated coupled cluster theory at the CCSD(T)-F12x (x = a, b) level[a] in conjunction with the double-hybrid density functional B2PLYP-D[b] has been employed in a study of the benzenium ion ($C_6H_7^+$) and its complexes with simple ligands (L = Ne, Ar, N_2, or CO_2).[c] The ground-state rotational constants of $C_6H_7^+$ are predicted to be A_0 = 5445 MHz, B_0 = 5313 MHz, and C_0 = 2731 MHz. For the complexes with L = Ne, Ar or N_2, the energetically most favourable structure is of π-bonded type, but for the most strongly bound complex $C_6H_7^+ \cdot CO_2$ a conformer with the CO_2 ligand lying in the ring-plane of the $C_6H_7^+$ moiety is slightly lower in energy.

---

[a] T. B. Adler, G. Knizia, and H.-J. Werner, *J. Chem. Phys.* **127**, 221106 (2007);
G. Knizia, T. B. Adler, and H.-J. Werner, *J. Chem. Phys.* **130**, 054104 (2009).

[b] T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.* **9**, 3397 (2007).

[c] P. Botschwina and R. Oswald, *J. Phys. Chem. A* **115**, 13664 (2011);
P. Botschwina and R. Oswald, *J. Chem. Phys.* submitted.

WI10 15 min 4:19

ROVIBRATIONAL STATES OF $ClHCl^-$ ISOTOPOMERS: A JOINT THEORETICAL AND SPECTROSCOPIC INVESTIGATION

P. BOTSCHWINA, P. SEBALD, and R. OSWALD, *Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*; K. KAWAGUCHI, *Department of Chemistry, Okayama University, Tsushimanaka 3-1-1, Okayama 700-8530, Japan*.

Explicitly correlated coupled cluster theory at the CCSD(T*)-F12b level[a] and two precise spectroscopic constants[b] were used to construct an analytical potential energy function (PEF) for highly anharmonic $ClHCl^-$. From variational calculations with that PEF, a large number of rovibrational energies of different isotopomers were obtained. Theory helped with assignments of lines observed by IR diode laser spectroscopy and enabled to elucidate rather complex and unusual patterns of rovibrational interactions. In addition, transition dipole moments were predicted and analyzed.

---

[a] T. B. Adler, G. Knizia, and H.-J. Werner, *J. Chem. Phys.* **127**, 221106 (2007);
G. Knizia, T. B. Adler, and H.-J. Werner, *J. Chem. Phys.* **130**, 054104 (2009).

[b] K. Kawaguchi, *J. Chem. Phys.* **88**, 4186 (1988).

WI11 15 min 4:36

VIBRONIC SPECTROSCOPY OF JET-COOLED 2-FLUORO-m-XYLYL AND 2-CHLORO-m-XYLYL RADICALS GENERATED BY CORONA DISCHARGE

YOUNG WOOK YOON, CHANG SOON HUH, SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Korea.*

By means of a technique of corona excited supersonic expansion (CESE) combined with a pinhole-type glass nozzle developed in this laboratory, we generated vibronically excited but jet-cooled 2-fluoro-m-xylyl and 2-chloro-m-xylyl radicals from precursors 2-fluoro-m-xylene 2-chloro-m-xylene with a large amount of carrier gas He, respectively. The well-resolved vibronic emission spectra of the jet-cooled radical species were recorded with a long-path monochromator in the visible region. From the analysis of the spectrum, we determine an accurate electronic energy of the $D_1 \rightarrow D_0$ transition and the frequencies of vibrational modes in the ground electronic state by comparison with those of *ab initio* calculations and the known spectroscopic data of precursors for the first time. The red-shift of the origin band of each species from parental benzyl radical agrees well with those predicted from synergic effect of each substituent into benzene ring.

WI12 15 min 4:53

SPECTROSCOPY IDENTIFICATION OF BENZYL-TYPE RADICALS GENERATED BY CORONA DISCHARGE OF PRECURSORS OF MIXED SUBSTITUENTS

YOUNG WOOK YOON, CHANG SOON HUH, SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Korea.*

We generated vibronically excited but jet-cooled benzyl-type radicals from corona discharge of precursor of mixed substituents using a technique of corona excited supersonic expansion coupled with a pinhole-type glass nozzle, from which the visible vibronic emission spectra were recorded with a long-path monochromator. The spectra exhibit the intensity variation of each species with discharging voltage, indicating the radical species generated in corona discharge is highly sensitive to excitation. From the analysis of the spectra, we found the Cl substituent is replaced in preference to the F substituent by the hydrogen atoms liberated from the dissociation of the C-H bond of the methyl group of the precursor, from which we proposed the possible mechanism for the elimination reaction of substituent in terms of the bond dissociation energy. Additionally, we obtained an accurate electronic energy in the $D_1 \rightarrow D_0$ transition and the vibrational mode frequencies of newly detected benzyl-type radicals in the ground electronic state by comparison with those of *ab initio* calculations and the known spectroscopic data of precursors for the first time.

WI13 15 min 5:10

JET-COOLED, BROAD RANGE NEAR-IR SCAN OF REACTIVE INTERMEDIATES USING CAVITY RINGDOWN SPECTROSCOPY

NEAL D. KLINE, TERRANCE J. CODD, MING-WEI CHEN[a], And TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210..*

A technique has been developed for obtaining broad range scans of jet-cooled radicals using cavity ringdown spectroscopy. The talk will describe a method that uses a slit jet expansion in tandem with an electrical discharge to produce the reactive intermediates and obtain rotational temperatures of 15-30 K and effective vibrational temperatures of 0 K. The spectrum can be recorded by scanning the second stokes of an H_2 Raman shifted YAG-pumped dye laser with bandwidth of ≈ 0.1 cm^{-1}. This technique has been used to obtain the jet-cooled $\widetilde{A} - \widetilde{X}$ spectra of the NO_3 radical and the 2,1-hydroxypropyl peroxy radical (2,1-HPP). Obtaining the jet-cooled spectra helped to identify hot bands present in the room temperature spectrum of NO_3 and also helped to identify cold, low-frequency fundamental bands present in the 2,1-HPP spectrum.

---

[a] Present Address: Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, 61801

WI14 **15 min 5:27**

SPECTROSCOPIC AND KINETIC MEASUREMENTS OF ORGANIC PEROXY RADICALS BY DUAL-WAEVELENGTH CAVITY RING DOWN SPECTROSCOPY

DMITRY G. MELNIK, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.*

The weakly-absorbing $\tilde{A} \leftarrow \tilde{X}$ transition of organic peroxy radicals in the NIR provides an excellent opportunity for quantitative species-specific measurements. Previously[a] we used the dual-wavelength cavity ring-down spectroscopy (CRDS) technique to accurately measure the absolute peak absorption cross-section of ethyl peroxy radical, $C_2H_5O_2$. In the present work, we extend the capabilities of the dual-wavelength technique to studying kinetics of the self-reaction of ethyl peroxy by utilizing a high duty-factor, time-resolved CW-CRDS. An extension of this technique to study cross-reactions between different species will be discussed.

---

[a] D. Melnik et al., *J. Phys. Chem. A*, **114**, 11583 (2010)

WJ. MINI-SYMPOSIUM: PHOTODETACHMENT AND PHOTOIONIZATION

WEDNESDAY, JUNE 20, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: DONG-SHENG YANG, University of Kentucky, Lexington, Kentucky

WJ01 *Journal of Molecular Spectroscopy Review Lecture* **30 min 1:30**

HIGH-RESOLUTION PHOTOELECTRON AND PHOTOIONIZATION SPECTROSCOPY

F. MERKT, *Laboratorium für Physikalische Chemie, ETH Zurich, CH 8093 Zurich, Switzerland.*

Since its development in the late 1950s and early 1960s [a] [b], photoelectron spectroscopy has established itself as an important method to study the electronic structure of molecules, their photoionization dynamics, and the structure and dynamics of molecular cations. In recent years, and particularly since the development of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy [c], considerable progress has been made in the resolution that can be achieved by photoelectron spectroscopy. This progress relies on the systematic exploitation of the unusual physical properties of high Rydberg states and enables one today to resolve the rotational structure in the photoelectron spectra of even large molecules and the hyperfine structure in the photoelectron spectra of small molecules.

This talk will begin with a brief historical review of photoelectron spectroscopy. Then, the relationship between photoelectron spectroscopy, photoionization spectroscopy and the spectroscopy of high Rydberg states will be discussed. It will be explained how this relationship is currently exploited to improve the resolution achievable by PFI-ZEKE photoelectron spectroscopy. Then, the physical principles that are at the heart of the latest methods related to high-resolution photoelectron spectroscopy will be described together with their fundamental limitations. Depending on the resolution and the spectral range needed to address a specific scientific problem, a choice can be made between several different methods with spectral resolutions ranging from 30 GHz to better than 1 MHz [d].

The talk will summarize the current state of the art in gas-phase photoelectron spectroscopy and be illustrated by several examples, primarily taken from the research in my group, in which photoelectron spectroscopy has contributed to answer questions concerning the structure and dynamics of small-sized molecular cations.

---

[a] F. I. Vilesov, B. C. Kurbatov, and N. Terrenin, Soviet Phys. (Doklady) 6, 490 (1961)

[b] D. W. Turner and M. I. Al-Jobory, J. Chem. Phys. 37, 3007 (1962)

[c] G. Reiser, W. Habenicht, K. Müller-Dethlefs and E. W. Schlag, Chem. Phys. Lett. 152, 119 (1988)

[d] F. Merkt, S. Willitsch and U. Hollenstein, High-resolution photoelectron spectroscopy, in: Handbook of high-resolution spectroscopy, eds. M. Quack and F. Merkt (Wiley, Chichester, 2011), Vol. III, pp 1617-1654

WJ02 **15 min 2:05**

THE GAS-PHASE SPECTROSCOPY STUDY OF ThN and ThN^+

I. O. ANTONOV, B. J. BARKER, M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

The thorium nitride sample was prepared by means of laser ablation of thorium metal in a pulsed supersonic expansion of He seeded with NH_3. Laser induced fluorescence and resonantly enhanced multiphoton ionization techniques were applied to study the spectroscopy of ThN molecule in gas phase for the first time. The ionization energy of ThN has been measured and the ground electronic state ThN^+ ion was probed with pulsed field ionization - zero electron kinetic energy technique. The high level ab initio calculation performed for both ThN and ThN^+ have shown good agreement with experimental data.

WJ03 15 min 2:22

MASS-ANALYZED THRESHOLD IONIZATION OF M_2O_2 (M = Ce and Pr)

LU WU, BENI DANGI, MOURAD ROUNJANE, and DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

M_2O_2 (M = Ce and Pr) is produced in a pulsed laser-vaporization metal-cluster source and studied by mass-analyzed threshold ionization (MATI) spectroscopy. From the MATI spectra, the adiabatic ionization energy is determined to be 37300(5) cm^{-1} for Ce_2O_2, and 37885 (5) cm^{-1} for Pr_2O_2. Like group 3 transition metal M_2O_2 (M=Sc, Y, and La) clusters we reported previously, these lanthanide clusters have a D_{2h} planer structure and the vibrational modes observed are from the in-plane motions. However, the ground and other low-energy electronic states of the lanthanide oxides have a much higher electron spin multiplicity due to the existence of 4f electrons in the Ce and Pr atoms. The 4f electron of Ce atom has significantly lower energies than the 5d or 6s electrons and remain uncoupled in Ce_2O_2. On the other hand, the energy differences between the 4f and 5d/6s electrons of Pr atom are relatively small, and a 4f → 5d electron promotion is required in the formation of Pr_2O_2. The electronic transitions responsible for the observed MATI spectra are tentatively determined to be $^4B_{1u} \leftarrow {}^5A_g$ for Ce_2O_2 and $^6B_{1u} \leftarrow {}^7B_{2g}$ and $^6B_{1u} \leftarrow {}^5B_{1u}$ for Pr_2O_2.

WJ04 15 min 2:39

PREFERRED METAL BINDING SITE OF ANILINE

SUDESH KUMARI, BRAD SOHNLEIN AND DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

Group III metal-aniline complexes, M-aniline (M = Sc, Y, and La), were produced by interactions between laser-vaporized metal atoms and aniline vapor in a pulsed molecular beam source, identified by photoionization time-of-flight mass spectrometry, and studied by pulsed-field ionization zero electron kinetic energy (ZEKE) spectroscopy and density functional theory calculations. Adiabatic ionization energies and several vibrational intervals were measured from the ZEKE spectra. Metal binding sites and electronic states were determined by combining the ZEKE measurements and theoretical calculations. Although aniline has various possible sites for metal coordination, the preferred site was determined to be phenyl ring. The metal binding with the phenyl ring yields *syn* and *anti* conformers. In these conformers, the neutral complexes are in doublet ground states and the corresponding singly charged cations in singlet states.

Intermission

WJ05 15 min 3:10

PHOTOIONIZATION OF ALKALI-DOPED HELIUM NANODROPLETS

MORITZ THEISEN, FLORIAN LACKNER, GÜNTER KROIS, MARKUS KOCH and WOLFGANG E. ERNST, *Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.*

Superfluid helium droplets (He_N) provide a cold, weakly-interacting environment for the investigation of weakly bound molecules. Whereas the host-dopant interaction is weak for neutral molecules, ion impurities may be surrounded by frozen shells of polarized helium atoms. An extreme example of the different behavior is given by alkali metal impurities that stay at the surface of the droplet as neutrals but immerse into the droplet as cations releasing a considerable amount of binding energy. We report measurements of the photoionization efficiency for the rubidium-He_N and cesium-He_N systems [a] and find that the ionization threshold is lowered compared with the free atoms and is in good agreement with Rydberg state spectroscopy of these systems [b]. The corresponding energy shift increases when going from heavy to light alkali metals and from small to large helium droplets. Both effects can be explained by the difference in polarization energies associated with submerged alkali metal cations. The findings agree qualitatively well with recent calculations of helium snowball formation around alkali metal cations [c].

---

[a] M. Theisen, F. Lackner, G. Krois, and W. E. Ernst, J. Phys. Chem. Lett. 2, 2778 (2011).

[b] F. Lackner, G. Krois, M. Theisen, M. Koch, and W. E. Ernst, Phys. Chem. Chem. Phys. 13, 18781 (2011).

[c] D. E. Galli, D. M. Ceperley, and L. Reatto, J. Phys. Chem. A 115, 7300 (2011).

WJ06 **15 min 3:27**

PHOTOIONIZATION SPECTROSCOPY OF ISOLATED Cr ATOMS IN ULTRACOLD HELIUM NANODROPLETS

ANDREAS KAUTSCH, MATTHIAS HASEWEND, MARTIN RATSCHEK, MARKUS KOCH, and WOLFGANG E. ERNST, *Institute of Experimental Physics, TU Graz, Petersgasse 16, 8010 Graz, Austria.*

Recently we succeeded in doping Cr atoms to He nanodroplets (He_N) at 0.4 K[a] and carried out resonance ionization mass spectroscopy (RIMS). Here we present resonant two-photon ionization (R2PI) measurements in the wavelength range from 350 to 361 nm (27700 - 28600 cm^{-1}, 3.43 - 3.54 eV). As one of several possible ionization pathways we allocate a first excitation step to the $y^7P^o \leftarrow a^7S_3$ transition, happening inside the He_N. Due to the interaction with the surrounding He this excitation appears broadened in the spectra and gives the possibility to obtain detailed information about the perturbation upon electronic excitation of the Cr atom in He_N[b]. Subsequently, the dopant atom leaves the He_N and is ionized in the gas phase where discrete free atom autoionization levels are populated leading to additional sharp spectral features.

Future investigations with two photon two color ionization and selective electron energy ionization as well as quantum chemistry calculations will be discussed.

---

[a] M. Ratschek, M. Koch, and W. E. Ernst, J. Chem. Phys., in press (2012)

[b] C. Callegari and W. E. Ernst, Helium Droplets as Nanocryostats for Molecular Spectroscopy - from the Vacuum Ultraviolet to the Microwave Regime, in Handbook of High-Resolution Spectroscopy, eds. M. Quack and F. Merkt, John Wiley & Sons, Chichester, 2011.

WJ07 **15 min 3:44**

PHOTOIONIZATION OF HIGHLY CHARGED ARGON IONS AND THEIR DIAGNOSTIC LINES

SULTANA N. NAHAR, *Department of Astronomy, The Ohio State University, Columbus, OH 43210.*

Lines of highly charged He-like and Li-like ions in the ultraviolet and X-ray regions provide useful diagnostics for the physical and chemical conditions of the astrophysical as well as fusion plasmas. For example, Ar XVII lines in a Syfert galaxy have been measured by the X-ray space observatory Chandra. Results on photoionization of Ar XVI and Ar XVII obtained from relativistic Breit-Pauli R-matrix method and close-coupling approximation will be presented. Important features for level-specific photoionization for the diagnostic w, x, y, z lines of He-like Ar XVII in the ultraviolet region will be illustrated. Although monotonous decay dominates the low energy photoionization for these ions, strong resonances appear in the high energy region indicating higher recombination, inverse process of photoionization, at high temperature. The spectra of the well known 22 diagnostics dielectronic satellite lines of Li-like Ar XVI will be shown produced from the the KLL resonances in photoionization.
[a]

---

[a] Acknowledgement: Partially supported by DOE, NSF; Computational work was carried out at the Ohio Supercomputer Center

WJ08 15 min 4:01

HIGH-RESOLUTION PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF Cl_2: THE GROUND ($X^+\ ^2\Pi_g$) AND FIRST EXCITED ($A^+\ ^2\Pi_u$) ELECTRONIC STATES OF Cl_2^+

SANDRO MOLLET, and FRÉDÉRIC MERKT, *ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang Pauli-Strasse 10, 8093 Zürich, Switzerland.*

Recently, two studies have been devoted to the low-lying electronic states of Cl_2^+, one by PFI-ZEKE photoelectron (PE) spectroscopy of the $X^+ \leftarrow X$ transition[a] and one by laser-induced-fluorescence spectroscopy of the $A^+ \rightarrow X^+$ band system[b]. To complement the information available on the X^+ and A^+ electronic states of Cl_2^+, we have recorded partially rotationally resolved single-photon PFI-ZEKE PE spectra of the $X^+\ ^2\Pi_{g,i} \leftarrow X\ ^1\Sigma_g^+$ and $A^+\ ^2\Pi_{u,i} \leftarrow X\ ^1\Sigma_g^+$ ($i = 3/2,\ 1/2$) photoionizing transitions of Cl_2 in the wavenumber ranges $92\,500 - 96\,500\ \mathrm{cm}^{-1}$ and $106\,750 - 115\,500\ \mathrm{cm}^{-1}$. These regions correspond to transitions to low-lying vibrational levels of the X^+ state with $v^+ = 0 - 5$ and to transitions to vibrational levels of the X^+ state with $v^+ = 25 - 45$ and vibrational levels of the A^+ state with $v^+ \leq 7$.

The analysis of the rotational structure and the isotopic shifts of these spectra has enabled the derivation of an improved value of the first adiabatic ionization energy ($92\,647.7 \pm 0.3\ \mathrm{cm}^{-1}$ for $^{35}Cl_2$). In combination with measurements of ion-pair states with $n \approx 1800$[c], new values for the dissociation energies D_0 of Cl_2 and Cl_2^+ could also be derived. The potential energy function of the X^+ state of Cl_2^+ was determined in a least-squares fitting procedure. Spin-orbit splittings were derived for many vibrational levels of the X^+ and A^+ states. Combining our results with other results[b,d,e,f], several low-lying vibrational levels of the upper spin-orbit component of the A^+ state could be assigned for the first time. The PFI-ZEKE PE spectra also contain a series of as yet unassigned lines and reveal numerous perturbations.

---

[a] J. LI, Y. HAO, J. YANG, C. ZHOU, AND Y. MO, *J. Chem. Phys.* **127**, 104307 (2007).

[b] M. A. GHARAIBEH, AND D. J. CLOUTHIER, 66th *Int. Symposium on Molecular Spectroscopy*, Book of Abstracts, p. 169 (2011).

[c] S. MOLLET, AND F. MERKT, *Phys. Rev. A* **82**, 032510 (2010).

[d] R. P. TUCKETT, AND S. D. PEYERIMHOFF, *Chem. Phys.* **83**, 203 (1984).

[e] L. WU, X. YANG, Y. GUO, L. ZHENG, Y. LIU, AND Y. CHEN, *J. Mol. Spect.* **230**, 72 (2005).

[f] H. VAN LONKHUYZEN, AND C. A. DE LANGE, *Chem. Phys.* **89**, 313 (1984).

WJ09 15 min 4:18

ROTATIONALLY RESOLVED PHOTOELECTRON SPECTROSCOPY OF ArXe AND KrXe

LORENA PITICCO, MARTIN SCHÄFER, and FRÉDÉRIC MERKT, *ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland.*

The high resolution spectroscopic information available on the low-lying electronic states of $ArXe^+$ and $KrXe^+$ is limited to vibrationally resolved emission spectra of the C_2 1/2 → (X 1/2, A_2 1/2), B 1/2 → (X 1/2, A_2 1/2) and C_1 3/2 → A_1 3/2 band systems[a,b] and to vibrationally resolved threshold photoelectron spectra of $ArXe$[c,d] and $KrXe$[e,f]. Recently *ab initio* potential functions for these states have been reported[g].

Rotationally resolved photoelectron spectra of the lowest three electronic states of $ArXe^+$ and $KrXe^+$ have been recorded by PFI-ZEKE photoelectron spectroscopy following $1_{\mathrm{VUV}}+1'$ resonant two-photon excitation from the X 0^+ ground state of ArXe and KrXe via selected rotational levels of the C 1 and D 0^+ excited states (C 0^+ and D 1 in the case of KrXe)[h,i]. The bandwidth of the vacuum-ultraviolet radiation used to access the intermediate states was narrow enough to enable the selection of individual isotopomers. Photoelectron spectra recorded from several rovibrational levels of the intermediate states provided access to the X 1/2 ($v^+ = 0 - 15$), A_1 3/2 ($v^+ = 0 - 3$) and A_2 1/2 ($v^+ = 0 - 8$) levels of $ArXe^+$ and the X 1/2 ($v^+ = 5, 22, 28$) and A_1 3/2 ($v^+ = 3 - 5$) levels of $KrXe^+$. The analysis of the rovibrational structure of the photoelectron spectra led to improved spectroscopic parameters for these states and to a better description of the low-lying electronic states of $ArXe^+$ and $KrXe^+$.

---

[a] K. P. HUBER AND R. H. LIPSON, *J. Mol. Spectrosc.* **119**, 433 (1986).

[b] M. TSUJI, M. TANAKA AND Y. NISHIMURA, *Chem. Phys. Lett.* **262**, 349 (1996).

[c] H. YOSHII, T. HAYAISHI, T. ONUMA, T. AOTO, Y. MORIOKA AND K. ITO, *J. Chem. Phys.* **116**, 7468 (2002).

[d] O. ZEHNDER AND F. MERKT, *J. Chem. Phys.* **128**, 014306 (2008).

[e] H. YOSHII, T. TANAKA, Y. MORIOKA, T. HAYAISHI AND K. ITO, *J. Chem. Phys.* **111**, 10595 (1999).

[f] O. ZEHNDER AND F. MERKT, *Mol. Phys.* **106**, 1215 (2008).

[g] L. A. VIEHLAND, B. R. GRAY AND T. G. WRIGHT, *Mol. Phys.* **108**, 547 (2010).

[h] L. PITICCO, F. MERKT, A. A. CHOLEWINSKI, F. R. W. MCCOURT AND R. J. LE ROY, *J. Mol. Spectrosc.* **264**, 83 (2010).

[i] L. PITICCO, M. SCHÄFER AND F. MERKT, *J. Chem. Phys.* **136**, 074304 (2012).

WJ10 **15 min 4:35**

PROBING THE ADSORPTION OF CARBON MONOXIDE ON TRANSITION METAL CLUSTERS USING IR ACTION SPECTROSCOPY

VIVIKE J. F. LAPOUTRE, JOS OOMENS and JOOST M. BAKKER, *FOM Institute Rijnhuizen, Edisonbaan 14, 3439MN Nieuwegein, The Netherlands.*

The discovery of enhanced catalytic activity of small gold clusters has led to a great interest in size-dependent catalytic properties of metal clusters[a]. To obtain a better understanding of the catalytic mechanisms it is essential to know the structures of these clusters and the nature of their interaction with reactant molecules.

We have studied the structure of gas-phase niobium clusters[b] with a carbon monoxide adsorbed using IR action spectroscopy. We present size-selective IR spectra obtained via IR multiple photon spectroscopy monitoring either photodetachment or photodissociation depending on the charge state. The combination of these spectra with DFT calculations allows for the structural determination of the adsorption product.

---

[a] M. Haruta *et al.*, *Journal of Catalysis* **115** 301-309 (1989).

[b] M. Haertelt *et al.*, *The Journal of Physical Chemistry Letters* **2** 1720-1724 (2011)

RA. ELECTRONIC

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 160 MATH ANNEX

Chair: JOEL TELLINGHUISEN, Vanderbilt University, Nashville, Tennessee

RA01 **15 min 8:30**

ELECTRONIC TRANSITIONS OF PALLADIUM MONOBORIDE AND PLATINUM MONOBORIDE

Y. W. NG, H. F. PANG, Y. S. WONG, YUE QIAN, and A. S-C. CHEUNG , *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*.

Electronic transition spectrum of palladium monoboride (PdB) and platinum (PtB) monoboride have been studied using the technique of laser-ablation/reaction free jet expansion and laser induced fluorescence spectroscopy. The metal monoborides were produced by reacting laser ablated metal atoms and diborane ((B_2H_6) seeded in argon. Five and six vibrational bands were observed respectively for the PdB and PtB molecules. Preliminary analysis of the rotationally resolved structure showed that both molecules have $X^2\Sigma^+$ ground state. Least-squares fit of the measured line positions yielded molecular constants for the electronic states involved. Molecular and electronic structures of PdB and PtB are discussed using a molecular orbital energy level diagram.
Financial support from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 701008P) is gratefully acknowledged.

RA02 **15 min 8:47**

THE OPTICAL STARK SPECTRUM OF THE $[11.9]\Omega = 3/2 - X^3\Pi_{3/2}$ BAND SYSTEM OF PLATINUM MONOFLUORIDE, PtF

CHENGBING QIN AND TIMOTHY C. STEIMLE , *Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287*.

Recently the O'Brien group[a] reported on the field-free detection and analysis of the [11.9]= $3/2 - X^2\Pi_{3/2}$ band system of PtF using intracavity laser absorption. The hollow cathode condition limited the spectral resolution, which was insufficient to fully resolved the hyperfine splitting of ^{195}Pt (I=1/2) and ^{19}F (I=1/2). Here we report laser-induced fluorescence spectra of the 1-0 and 0-0 bands of the [11.9]= $3/2 - X^2\Pi_{3/2}$ transition of PtF, obtained at near natural linewidth resolution (FWHM 40MHz) using supersonic molecular beam techniques. The spectra show a complex, cleraly resolved hyperfine structure which has siginificant contributions from magnetic term in ^{195}Pt and ^{19}F. The spectra of ^{194}PtF, ^{195}PtF, ^{196}PtF, ^{198}PtF isotopogues have been assigned and analyzed. The electric field induced dependence of the R(1.5) branch of the ^{195}PtF isotopogue was analyzed to produce permanent electric dipole moment, μ, of 3.45 D and 2.32 D for the $X^2\Pi_{3/2}$ and $[11.9]\Omega = 3/2$ states, respectively. A comparision with Ab Initio prediction[b,c] will be given.

---

[a] K.G. Handler, R.A. Harris, L.C. O'Brien and J.J.O'Brien *J.Mol. Spectrosc.* **265** 39, 2011.

[b] W. Liu and R. Franke *J. Comput. Chem.* **23** 564, 2001.

[c] W. Zou, Y. Liu and J. E. Boggs *Dalton Transactions*, **39** 2023, 2000

RA03 **15 min 9:04**

X-RAY RESONANT IRRADIATION AND HIGH-Z RADIOSENSITIZATION IN CANCER THERAPY USING PLATINUM NANO-REAGENTS

SULTANA N. NAHAR, *Department of Astronomy, The Ohio State University, Columbus, OH 43210*; S. LIM, *Biophysics Program, The Ohio State University, Columbus, OH 43210*; M. MONTENEGRO, *Catholic University of Chile*; A.K. PRADHAN, *Department of Astronomy, Biophysics Program, Chemical Physics, The Ohio State University, Columbus, OH 43210*; R. BARTH, *Pathology Department, The Ohio State University, Columbus, OH 43210*; E. BELL, *Radiation Oncology, The Ohio State University, Columbus, OH 43210*; C. TURRO, R. PITZER, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

We describe the atomic-molecular-bio physics of X-ray irradiation of High-Z heavy-element nanomaterials as radiosensitizing agents in cancer therapy. Our reports in past few ISMSs showed that compounds of High-Z elements, Pt and Au, embedded in tumors could provide the most efficient therapy and diagnostics (theranostics) when X-rays are targeted at their resonant energies. Harmful damages due to unnecessary broadband radiation from conventional X-ray sources can be reduced considerably by using a monochromatic X-ray source at resonant energy. We will present our recent findings from Monte Carlo simulations, using Geant4 code, for X-ray energy absorption and dose deposition in tissues where the broadband X-ray sources have three different peak voltages, 100 keV, 170 keV and 6 MeV. We use platinum as an agent for killing cancerous cells via increased linear-energy-transfer (LET) and dose enhancement. We find that X-ray energies in the range below 100 keV are most efficient in achieving both the required tissue penetrative depths and deposition of energy. This confirms the previous results for Au that it is only the low-energy component around 100 keV from the 6 MV linear accelerator (LINAC) that is most effective in dose-enhanced cell killing. Preliminary experimental results cancer cells with Pt and results on K_α radiation of Al will also be presented.[a]

---

[a] Acknowledgement: Partially supported by DOE, NSF; Computational work was carried out at the Ohio Supercomputer Center

RA04 **15 min 9:21**

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF SCANDIUM MONOIODIDE

ZHENWU LIAO, MEI YANG, MAN-CHOR CHAN, *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong*; YE XIA, A. S.-C. CHEUNG, *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.*

The laser induced fluorescence spectrum of scandium monoiodide (ScI) between 787 and 814 nm has been recorded. ScI molecule was produced by reacting laser vaporized Sc atoms with methyl iodide (CH_3I). Spectra of eleven vibrational bands of the $C^1\Sigma^+$ - $X^1\Sigma^+$ transition of ScI were obtained and analyzed. A merged least-squares fit of the measured line positions yielded accurate molecular constants for the upper levels of the $C^1\Sigma^+$ state and the v = 1 - 4 levels of the $X^1\Sigma^+$state. One vibrational band observed at 11627 cm^{-1} belongs to a sub-band transition of the $a^3\Delta$ state, which is found to be perturbed by the $X^1\Sigma^+$ state. Details of the perturbation and molecular constants obtained will be reported.

RA05 **15 min 9:38**

THE SPECTROSCOPY STUDY OF UF AND UF$^+$

J. H. BARTLETT, I. O. ANTONOV, M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

Uranium metal has been laser ablated in a pulsed-jet expansion of 0.1% SF_6 in He to generate the fluoride. Spectroscopic data are obtained using the laser-induced fluorescence and resonance-enhanced multiphoton ionization techniques for gas-phase UF for the first time. The pulsed-field ionization zero electron kinetic energy (PFI-ZEKE) technique is used to study the low-lying states of UF$^+$. The ionization potential from PFI-ZEKE for UF is found to be D_e = 51137 cm^{-1}. Ω states up to $\frac{13}{2}$ and vibrational states v^+ = 0-4 are observed in the REMPI and PFI-ZEKE spectra. Assignments of the electronically excited states are based on measured Ω values and high-level ab initio calculations.

RA06 **15 min 9:55**

THE OPTICAL STARK SPECTRUM OF the $[17.8]0^{+}-X^{1}\Sigma^{+}$ BAND OF GOLD MONOFLUORIDE,AuF

RUOHAN ZHANG, CHENGBING QIN, AND TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287*; THOMAS VARBERG, *Department of Chemistry,Macalaster College,1600 Grand Avenue, St. Paul,MN 55105.*

The bonding and electrostatic prperties of gold containig molecules are highly influenced by realtivistic effects[a]. Recently Varberg's group reported[b] on the field-free detection and analysis of the $[17.8]0^{+}-X^{1}\Sigma^{+}$ band system of AuF at Doppler limited resolution. Here we report on the analysis of the same band recorded field free and in the presence of a static electric field for a cold molecular beam sample. The Stark induced shifts of the R(0)(17756.156 cm^{-1}), R(1)(17756.640 cm^{-1}) and P(1)(17755.123 cm^{-1})branch features were analyzed to determine the permanent electric dipole moment, μ_{el}, of 2.025 D and 4.218 D for the $[17.8]0^{+}$ and $X^{1}\Sigma^{+}$ states, respectively. The agreement with the various DFT [c] and wave-function[d] based predictions will be discussed.

---

[a] P.Pyykko; *Angew Chem. Int* **43** 4412, 2004.

[b] E.K. Butler, B. J. Knurr, K. J. Manke, T. R. Vervoot, and T. D. Varberg; *J. Phys. Chem. A* **114** 4831, 2010.

[c] E. Goll, and H. Stoll; *Phys. Rev. A* **76** 032507, 2007.

[d] F. Holka, A. Avramopoulos, O. Loboda, V. Kello, and M.G. Papadopoulos; *Chem.Phys. Lett* **472** 185, 2009.

Intermission

RA07 **15 min 10:30**

LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF JET-COOLED NiF: AN INVESTIGATION OF THE Ω-TYPE DOUBLING IN THE Ω=1/2 STATES OF THE $3d^{9}$ GROUND ELECTRONIC CONFIGURATION

D. L. ARSENAULT, D. W. TOKARYK, C. LINTON, *Department of Physics and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*; A. G. ADAM, *Department of Chemistry and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3.*

A recent paper by Hougen[a] presents the hypothesis that the relative parities of Ω=1/2 levels in the $3d^{9}$ complex of NiF may need to be reconsidered, since the experimental determinations reported in the literature[b c d] via Ω-doubling parameters differ by a sign from those obtained from Hougen's theoretical treatment. We report on an experiment that attempts to resolve the discrepancy via laser-induced fluorescence and dispersed fluorescence spectroscopy of NiF created in the molecular-jet laser-ablation apparatus at the University of New Brunswick. New data involving the $[22.9]^{2}\Pi_{3/2}$–X $^{2}\Pi_{3/2}$ and $[22.9]^{2}\Pi_{3/2}$–[0.25] $^{2}\Sigma_{1/2}$ transitions were obtained, in which several isotopologues of NiF could be resolved and their spectra analyzed. Dispersed fluorescence spectra were obtained by exciting parity-resolved transitions of the $[22.9]^{2}\Pi_{3/2}$–X $^{2}\Pi_{3/2}$ spectrum with a narrow-bandwidth cw laser, then observing the fluorescence to the [0.25] $^{2}\Sigma_{1/2}$ and [1.5] $^{2}\Sigma^{+}_{1/2}$ states with a grating spectrometer. Changes in the dispersed fluorescence pattern as levels of the same J' with different parities were excited will be discussed, and the implications for verifying or refuting Hougen's claim will be presented.

---

[a] J T. Hougen, *J. Mol. Spectrosc.* **267** (2011) 23–35.

[b] C. Dufour and B. Pinchemel, *J. Mol. Spectrosc.* **173** (1995) 70–78.

[c] Y. Krouti, T. Hirao, C. Dufour, A. Boulezhar, B. Pinchemel, and P. F. Bernath, , *J. Mol. Spectrosc.* **214** (2002) 152-174.

[d] M. Tanimoto, T. Sakamaki, and T. Okabayashi, *J. Mol. Spectrosc.* **207** (2001) 66–69.

RA08 10 min 10:47

EXOMOL: MOLECULAR LINE LISTS FOR ASTROPHYSICAL APPLICATIONS. A THEORETICAL LINE LIST FOR NICKEL HYDRIDE.

S. N. YURCHENKO, L. LODI, A. KERRIDGE and J. TENNYSON, *University College London, Department of Physics and Astronomy, London WC1E 6BT, UK.*

Exomol (www.exomol.com) is a database of molecular line lists which can be used for spectral characterisation and simulation of astrophysical enviroments such as exoplanets, brown dwarfs, cool stars and sunspots[a]. New line lists for about 30 small molecules of astrophysical interest which currently lack a complete spectroscopic coverage are being generated. The list includes diatomics (e.g., C_2, O_2, AlO), triatomics (e.g., H_2S, C_3, SO_2), tetratomics (e.g., PH_3, HOOH, H_2CO) and a few larger molecules (most notably CH_4 and HNO_3). We report progress on a new theoretical line list for nickel hydride NiH. The spectra of transition-metal hydrides such as NiH are very complicated due to the large-number of low-lying electronic states, to the importance of correlation, relativistic and spin-orbit effects and of the various couplings between angular momenta. In our study potential energy curves and the relevant couplings were computed *ab initio* and the corresponding coupled-surface ro-vibronic problem was solved using an expansion in Hund's case *(a)* wave functions. Potential curves and couplings were then refined semi-empirically using the available experimental spectroscopic data [b].

---

[a] J. Tennyson and S. N. Yurchenko, Mon. Not. R. Astron. Soc. (submitted)

[b] Vallon R., S.H. Ashworth, P. Crozet, R.W. Field, D. Forthomme, H. Harker, C. Richard and A.J. Ross, J. Chem. Phys. A **113**, 13159-13166 (2009)

RA09 15 min 10:59

LABORATORY MEASUREMENTS OF THE ZEEMAN EFFECT IN THE F–X SYSTEM OF IRON MONOHYDRIDE

PATRICK CROZET, GUILLAUME TOURASSE, AMANDA J. ROSS, *LASIM, Université Lyon 1 & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France*; D. W. TOKARYK, *Department of Physics and Center for Laser, Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, Canada E3B 5A3*; FRÉDÉRIC PALETOU, *Observatoire Midi-Pyrenées (CNRS) 14 Av Edouard Belin, 31400 Toulouse, France*; ARTURO LÓPEZ ARISTE, *THEMIS Telescope, CNRS UPS 853, C/Via Lactea s/n, 38200 La Laguna, Tenerife, Spain.*

We have used a hollow cathode sputtering source, flowing a mixture of 10 % H_2 in Ar $\sim$ 45 standard cm^3/minute to form FeH radicals. Sputtering from iron required currents $\geq$ 250 mA. A permanent magnet was placed 2–3 cm below the cathode, generating magnetic fields 3000–4500 Gauss. Output from a Sirah Matisse Ti:sapphire laser was focused to a beamwaist $<$ 1mm to probe a reasonably homogeneous region of the magnetic field, with the laser operating around 1 μm for the 0-0 band and 890 nm for the 1-0 band of the $F\ ^4\Delta$ă$\leftarrow X\ ^4\Delta$ system in FeH. The magnetic field is calibrated to 0.5 % accuracy from the Zeeman response of the Ar I line at 10958.339 cm^{-1}. Several spectra have been taken for lines of the R branches of the $F\ ^4\Delta_{7/2} \leftarrow X\ ^4\Delta_{7/2}$ and $F\ ^4\Delta_{5/2} \leftarrow X\ ^4\Delta_{5/2}$ sub-bands, showing resolved structures at Doppler resolutions. Unresolved structures are seen for the Q and P transitions. Landé factors have been determined for the upper state (relying on ground state data from LMR work[a]) either from fits to peak positions, or by simulating observed profiles when this was impossible. The Landé factors have been used to deduce a magnetic field of 2200 Gauss in sunspots from lines near 1 μm observed at the solar telescope THEMIS (Tenerife) in July 2011. Stokes V profiles were recorded at the telescope, for optimum sensitivity. The magnetic field deduced from atomic lines (Ti,Fe) is around 10 % higher than that found from FeH, compatible with molecules forming at higher altitudes in the solar atmosphere.

---

[a] J.M. Brown, H. Korsgen, S.P. Beaton, & K.M. Evenson, J. Chem. Phys. 124 234309 (2006)

We gratefully acknowledge financial support from the French agency ANR, and from the CNRS (PNPS programme) for this work.

RA10 15 min 11:16

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $E^2\Pi$–$X^2\Sigma^+$ TRANSITIONS OF SrH, SrD AND BaH.

R.S. RAM, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA*; K. TERESZCHUK, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; P.F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 USA; Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; and K.A. WALKER, *Department of Physics, University of Toronto, Toronto, Ont., M5S 1A7, Canada.*

Emission spectra of SrH, SrD and BaH have been studied at high resolution using a Fourier transform spectrometer. The SrH and SrD molecules have been produced in a high temperature furnace by the reaction of strontium metal vapor with H_2/D_2 in the presence of a slow flow of Ar gas. The spectra observed in the 18000–19000 cm^{-1} region consist of the 0–0 and 1–1 bands of the $E^2\Pi$–$X^2\Sigma^+$ transition of the two isotopologues. A rotational analysis of these bands has been obtained by combining the present measurements with previously available pure rotation and vibration-rotation measurements for the ground state, and improved spectroscopic constants have been obtained for the $E^2\Pi$ state.

The high resolution spectrum of the $E^2\Pi$–$X^2\Sigma^+$ transition of BaH has been observed using a Ba hollow cathode lamp operated with 150 V and 300 mA current with a slow flow of 700 mTorr of Ar and 40 mTorr of H_2 gases. The spectrum in the 14000–15600 cm^{-1} region was recorded at a resolution of 0.015 cm^{-1} with the 1-m Fourier transform spectrometer associated with the McMath-Pierce Telescope of the National Solar Observatory at Kitt Peak. A rotational analysis of the 0–0, 1–1 and 2–2 bands has been performed and improved spectroscopic constants were determined for the $E^2\Pi$ state by combining the data with existing vibration-rotation measurements of the ground state.

RA11 15 min 11:33

NEAR INFRARED LASER SPECTROSCOPY OF SCANDIUM MONOBROMIDE

YE XIA, A. S.-C. CHEUNG, *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.*; ZHENWU LIAO, MEI YANG, MAN-CHOR CHAN, *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong.*

High resolution laser spectrum of scandium monobromide (ScBr) between 787 and 845 nm has been investigated using the technique of laser vaporization/reaction with free jet expansion and laser induced fluorescence spectroscopy. ScBr was produced by reacting laser vaporized Sc atoms with ethyl bromide (C_2H_5Br). Spectra of six vibrational bands of both $Sc^{79}Br$ and $Sc^{81}Br$ isotopomers of the $C^1\Sigma^+$ - $X^1\Sigma^+$ transition and seven vibrational bands of the $e^3\Delta$ - $a^3\Delta$ transition were obtained and analyzed. Least-squares fit of the measured line positions for the singlet transitions yielded accurate molecular constants for the v = 0 âĂŞ 3 levels of the $C^1\Sigma^+$ state and the v = 0 âĂŞ 2 levels of the $X^1\Sigma^+$ state. Similar least-squares fit for the triplet transitions yielded molecular constants for the v = 0 âĂŞ 2 levels of both $e^3\Delta$ and $a^3\Delta$ states. The equilibrium bond length, r_0, of the $a^3\Delta$ state has been determined to be 2.4789 .

Financial support from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 701008P) is gratefully acknowledged

RA12 **15 min 11:50**

MEASUREMENT OF HYPERFINE STRUCTURE AND PERMANENT ELECTRIC DIPOLE MOMENTS IN THE ELECTRONIC SPECTRUM OF IRIDIUM MONOHYDRIDE AND DEUTERIDE

C. LINTON, *Physics Department and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*; A. D. GRANGER and A. G. ADAM, *Chemistry Department and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*; S. E. FREY, A. LE and T. C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287, USA.*.

High resolution spectra of $^3\Phi_4$ - $X^3\Phi_4$ transitions of IrH and IrD were obtained using the laser ablation spectrometer at Arizona State University. With linewidths lower than 50 MHz, hyperfine structure due to the nuclear spin (I = 3/2) of both iridium isotopes ^{193}Ir and ^{191}Ir was resolved. Using the optical Stark effect, which examined the tuning properties of the hyperfine lines when an external electric field was applied, permanent electric dipole moments were determined for both electronic states. The interpretation of the hyperfine parameters and dipole moments in terms of the insights they provide into the electron configurations of the two electronic states will be discussed and the results will be compared with isovalent molecules , CoH and RhH, in the same group.

RB. ATMOSPHERIC SPECIES

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 170 MATH ANNEX

Chair: V. MALATHY DEVI, College of William and Mary, Williamsburg, Virginia

RB01 15 min 8:30

MULTISPECTRUM FITTING OF FTS AND CRDS SPECTRA SIMULTANEOUSLY

D. CHRIS BENNER, V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA*; KEEYOON SUNG, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, U.S.A.*; JOSEPH T. HODGES, *National Institute of Standards and Technology, Gaithersburg, MD 20899.*

Various types of spectra contain different sorts of spectral line information. An FTS spectrum provides broad coverage of an identical sample at all parts of the spectrum, but a cavity ring down spectrometer provides higher resolution, more information about line shapes and greater dynamic range in spectral line intensity. In order to use all of the information available, one should put all the spectra available into a single solution. The multispectrum nonlinear least squares fitting technique has proven successful in doing this with transmission spectra from various spectrometers. However, fitting data from cavity ring down spectrometers that produce cross sections is a problem when combined with transmission spectrometers. The solution is to choose a path length for the CRDS data to produce transmissions and use the uncertainty of each cross section as a means of weighting the transmission in the multispectrum solution. This has been incorporated into our fitting technique[a]. Sample oxygen A band fits of CRDS data from NIST combined with FTS data from a high resolution Fourier transform spectrometer in the Infrared, Bruker IFS125-HR, at JPL, equipped with two multipass White cells (absorption path length extendible to 32.5 m and 148 m, respectively) will be shown[b].

---

[a] D. Chris Benner, C. P. Rinsland, V. M. Devi, M. A. H. Smith, and D. A. Atkins, JQSRT 1995;53:705-21.

[b] Support for the work at William and Mary was provided by JPL and the NIST Greenhouse Gas Measurements and Climate Research Program. Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology under contracts with National Aeronautics and Space Administration. Support for the work at NIST was provided by at the NIST Greenhouse Gas Measurements and Climate Research Program.

RB02 15 min 8:47

CAUSAL CORRELATION FUNCTIONS AND FOURIER TRANSFORMS: APPLICATION IN CALCULATING PRESSURE INDUCED SHIFTS

Q. MA, *NASA/Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025, USA*; R. H. TIPPING, *Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487, USA*; N. N. LAVRENTIEVA, *V. E. Zuev Institute of Atmospheric Optics SB RAS, 1, Akademician Zuev square, Tomsk 634021, Russia.*

By adopting a concept from signal processing, instead of starting from the correlation functions which are even, one considers the causal correlation functions whose Fourier transforms become complex. Their real and imaginary parts multiplied by 2 are the Fourier transforms of the original correlations and the subsequent Hilbert transforms, respectively. Thus, by taking this step one can complete the two previously needed transforms. However, to obviate performing the Cauchy principal integrations required in the Hilbert transforms is the greatest advantage. Meanwhile, because the causal correlations are well-bounded within the time domain and band limited in the frequency domain, one can replace their Fourier transforms by the discrete Fourier transforms and the latter can be carried out with the FFT algorithm. This replacement is justified by sampling theory because the Fourier transforms can be derived from the discrete Fourier transforms with the Nyquis rate without any distortions. We apply this method in calculating pressure induced shifts of H_2O lines and obtain more reliable values[a]. By comparing the calculated shifts with those in HITRAN 2008 and by screening both of them with the pair identity and the smooth variation rules, one can conclude many of shift values in HITRAN are not correct.

---

[a] Q. Ma, R. H. Tipping, and N. N. Lavrentieva, JQSRT dio:10.1016/j.jqsrt.2012.02.012 (2012).

RB03 **15 min 9:04**

EVALUATION OF THE EXPERIMENTAL AND THEORETICAL INTENSITIES OF WATER-VAPOR LINES IN THE 2 μm REGION USING SOLAR-POINTING FTS SPECTRA

I. E. GORDON, L. S. ROTHMAN, *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA*; L. LODI, J. TENNYSON , *University College London, Department of Physics and Astronomy, London, UK*; G. C. TOON, L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA.*

The HITRAN spectroscopic database contains water-vapor absorption lines in a wide spectral range (0-25 000 cm^{-1}). The precision and accuracy of the transition intensities are diverse and strongly depend on the spectral region and dynamic range. Now, a significant volume of new experimental and theoretical studies must be evaluated region by region prior to inclusion in the next update of HITRAN.

For this presentation, we examine the quality of water absorption parameters at 2 μm because they overlap spectral features of prominent CO_2 bands that are important to ongoing and future missions (such as GOSAT and OCO-2) designed to monitor the carbon cycle globally from orbit.

The accurate knowledge of water-vapor spectral parameters is important not only for accounting for water transitions in spectra, but also for evaluating how pressure broadening of the CO_2 lines by water affect atmospheric retrievals.

It was determined (using different air-mass retrievals from the solar-pointing Fourier transform spectrometer at Park Falls, WI) that the new *ab initio* intensities calculated at the University College London[a] have proven to be an improvement over currently tabulated HITRAN intensities, which in the 800-8 000 cm^{-1}region are based on the semi-empirical values from the SISAM database[b]. In addition, it was found that these new *ab initio* intensities provide better consistency between the bands in this region (namely $3\nu_2$, $\nu_2 + \nu_3$ and $\nu_1 + \nu_2$) with respect to previous theoretical attempts.

It was also determined that many SISAM experimental intensities are superior to the SISAM semi-empirical values that are now in HITRAN.

---

[a] Lodi L.,Tennyson J., Polyansky O. L., J Chem Phys, 135, 034113-10 (2011).

[b] http://mark4sun.jpl.nasa.gov/h2o.html.

RB04 **15 min 9:21**

THE COF_2 HOT BANDS IN THE ν_6 REGION AND THE $2\nu_6$ OVERTONE[a]

E. A. COHEN, B. J. DROUIN, and L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

Using results from our analysis of rotational and infrared spectra of $\nu_2,\ \nu_3,\ \nu_5$, and ν_6[b] we have fit the hot bands in the ν_6 region near 774 cm^{-1} originating in ν_2, ν_3, and ν_5 as well as the $2\nu_6$ overtone band. Although the $2\nu_6$ state is perturbed by the nearby and as yet unassigned $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$ states, a set of effective parameters was derived which adequately describes the $2\nu_6$ spectrum as well as the $2\nu_6 - \nu_6$ hot band. These results improve the description of the ν_6 spectrum, particularly in the Q-branch region. The molecular parameters will be presented and examples of spectra will be shown.

---

[a] This work was done at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.

[b] E.A. Cohen, and B.J. Drouin, Abstract TE10, International Symposium on Molecular Spectroscopy, Columbus, OH, 2010.

RB05 **15 min 9:38**

PHOTO-TAUTOMERIZATION OF ACETALDEHYDE TO VINYL ALCOHOL: A NEW MECHANISM FOR ORGANIC ACID FORMATION IN THE TROPOSPHERE

D.U. ANDREWS, B.R. HEAZLEWOOD, A.T. MACCARONE, T. CONROY, R.J. PAYNE, M.J.T. JORDAN and S.H. KABLE , *School of Chemistry, University of Sydney, Sydney, NSW, 2006, Australia.*

We present a detailed kinetic master equation (ME) model of the photochemistry of acetaldehyde under conditions relevant to tropospheric chemistry. The dissociation and isomerization rate constants are benchmarked to collision-free experiments in a supersonic expansion, at wavelengths where reaction is only possible on S_0. Extensive photo-isomerization is observed when irradiated with actinic ultraviolet radiation (310-330 nm). The ME model quantitatively reproduces the experimental observations and shows unequivocally that keto-enol photo-tautomerization, forming vinyl alcohol, is the crucial first step.

When collisions are included into the ME, the model quantitatively reproduces the previously reported quantum yields for photodissociation at all pressures (0 - 1 atm) and wavelengths (295 - 340 nm). Crucially, at 1 atm pressure, and averaged over the intensity distribution of the solar spectrum, our model predicts that 26% of the total CH_3CHO quantum yield is into the collisionally-relaxed vinyl alcohol photo-tautomerization product.

The photochemistry and photophysics of many carbonyls are similar to that of acetaldehyde. Therefore, we expect that photo-tautomerization of carbonyls into their respective enols will be a general phenomenon under atmospheric conditions. Such photo-tautomerization mechanisms are not included in any current tropospheric model and might, given that an enol will react rapidly to form an acid, we propose that they may account for the production of organic acids in the troposphere.

RB06 **15 min 9:55**

HIGH RESOLUTION STIMULATED RAMAN SPECTROSCOPY OF CARBON TETRAFLUORIDE CF_4

V. BOUDON, *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne, 9. Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*; D. BERMEJO, R. Z. MARTÍNEZ, *Instituto de Estructura de la Materia, CSIC Serrano 123, E-28006 Madrid, Spain.*

The spectra of the ν_1, ν_2 and $2\nu_2$ bands were obtained with a quasi-cw stimulated Raman spectrometer. In this technique, two laser beams are focused simultaneously on the sample and their frequency difference scanned, normally by scanning one of them. When this difference matches a Raman transition of the molecule under study, an energy transfer takes place between both beams, so that by monitoring the intensity of one of them throughout a frequency scan a Raman spectrum of the sample can be obtained. In a quasi-cw spectrometer one of the laser beams is continuous and the other one pulsed, providing an optimum compromise between resolution and sensitivity. The apparatus function results from the convolution of the linewidths of the two lasers. In our setup this function is dominated by the contribution of the pulsed beam, resulting in a FWHM of $\sim$ 75 MHz, which sets the limit to the resolution of the spectrometer.
The three bands analyzed in this work were studied at a temperature of 135 K. The spectrum of ν_1 was obtained at a sample pressure of 2 mbar. For the spectra of $2\nu_2$ and ν_2, which are much weaker, pressures of 15 and 20 mbar respectively were used. The analysis has been performed thanks to the XTDS and SPVIEW softwares developed in Dijon for such molecules[a].

---

[a] Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov and J.-P. Champion, *J. Mol. Spectrosc.*, **251** 102–113 (2008).

Intermission

RB07 15 min 10:30

PRELIMINARY MODELING OF CH_3D FROM 4000 TO 4550 cm^{-1}

A. V. NIKITIN, *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russian Federation*; LINDA R. BROWN, K. SUNG, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; M. REY, Vl. G. TYUTEREV, *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France*; M. A. H. SMITH, *Science Directorate, NASA Langley Research Center, Hampton, VA 23681, USA*; A. W. MANTZ, *Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320, USA*.

New line positions, intensities and quantum assignments were obtained for $^{12}CH_3D$ between 4000 and 4550 cm^{-1} using high resolution spectra recorded with two Fourier transform spectrometers and enriched gas samples (98%-Deuterium) at room and cold (80 K) temperatures. The effective Hamiltonian and the effective Dipole moment expansions were expressed in terms of irreducible tensor operators adapted to symmetric top molecules. Over 4000 positions and 1300 line intensities in this region were reproduced with RMS values of 0.007 cm^{-1} and 14%, respectively. With these new results included, the simultaneous modeling of the four lowest polyads of $^{12}CH_3D$ from 0 to 4550 cm^{-1} [Ground State, Triad (1000 ÂŰ 1600 cm^{-1}), Nonad (2000 to 3300 cm^{-1}), and Enneadecad (3400 to 4600 cm^{-1})] permitted over 19000 observed positions to be fitted within 0.003 cm^{-1}. [a]

---

[a] Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, Connecticut College, and NASA Langley Research Center under contracts and cooperative agreements with the National Aeronautics and Space Administration. Support from ÂŞCH4@TitanÂŤ contract (ANR France) and of SAMIA GDRI project for the modeling is acknowledged.

RB08 15 min 10:47

SUBMILLIMETER SPECTRUM OF METHYL CHLORIDE: ANALYSIS OF THE ν_3=1 EXCITED STATE

ALISSA P. FISHER, *Auburn University*; DANE J. PHILLIPS, *Kratos Defense and Security Solutions Digital Fusion, 4904 Research Dr., Huntsville, Al, 35805*; DENNIS G. WILSON, *Massachusetts Institute of Technology*; ELIZABETH RHODES, *University of Alabama Tuscaloosa*; HENRY O. EVERITT, *Army Aviation and Missile RD&E Center, Weapon Sciences Directorate, Redstone Arsenal, AL, 35898.*

A significant source of chlorine in the atmosphere is found in the form of the halogenated species methyl chloride. Atmospheric as well as chemical sensing research of this molecule requires a detailed knowledge of its line position frequencies. The ground vibrational state, as well as the ν_6=1 vibrational state have been well studied using both microwave and infrared spectroscopy. The effort described here is the examination of less completely analyzed ν_3=1vibrational state by means of a frequency tunable microwave source with Schottky diode multipliers and heterodyne detection in the submillimeter region. Doppler limited spectra was obtained for $J \leq 25$, $K \leq 9$ for the ν_3=1 rotational states for both Cl isotopomers. The center frequencies of the hyperfine-split lines where obtained through a non-linear least squares fitting of the measured frequency modulated spectra with the derived lineshapes. These centers were combined with previously measured line frequencies to calculate new hyperfine and sextic rotational constants for the ν_3=1 state.

RB09 **15 min 11:04**

IMPROVED LINE PARAMETERS FOR CH4 AROUND 1.6 MICRONS

VICTOR GORSHELEV, ANNA SERDYUCHENKO, M. BUCHWITZ, , J. BURROWS, *University of Bremen, Germany*; N. HUMPAGE, J. REMEDIOS, *University of Leicester, UK.*

Methane (CH4) is one of the most important greenhouse gases, also being modified by anthropogenic activity. It can be nowadays monitored globally by satellite borne instruments and this is required on the long-term. Although a significant amount of spectroscopic data on CH4 is available, the information on the line parameters in near infrared (NIR) and mid infrared (MIR) spectral regions is inadequate for accurate remote sensing.
The state of the art database for CH4 line parameters is HITRAN 2008. The CH4 line parameters around 1.6 micron in HITRAN 2008 are based on laboratory measurements of the CH4 spectrum at University of Bremen and an analysis scheme used to improve the line parameters of the previous HITRAN version (Frankenberg et al., 2008). However, that analysis was only based on a limited number of measurements (e.g., only room temperature and only using N2 as a buffer gas).
To overcome these limitations, we are performing new laboratory measurements and corresponding data analysis with the goal to further improve the spectroscopic line parameters for CH4 in the critical spectral region around 1.6 microns, which is used to derive methane columns globally by the greenhouse gas satellite sensors SCIAMACHY/ENVISAT and TANSO/GOSAT.
We are using an approach similar to that of Frankenberg et al., 2008, but based on an extended set of measurements at an adequate number of representative atmospheric temperatures and also using air and O2 as buffer gases in addition to N2.
New spectra will be used to obtain information on the broadening coefficients with the accuracy needed for challenging remote sensing applications. Before release, the new data will be tested on GOSAT and SCIAMACHY retrievals.
Updated spectroscopic information for the CH4 bands in the IR spectral region will be available for reprocessing of the GOSAT and SCIAMACHY data as well as for general the scientific community.

RB10 **15 min 11:21**

ANALYTICAL CHEMICAL SENSING IN THE SUBMILLIMETER/TERAHERTZ SPECTRAL RANGE

BENJAMIN L. MORAN, ALYSSA M. FOSNIGHT, IVAN R. MEDVEDEV, *Department of Physics, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA*; CHRISTOPHER F. NEESE, *Department of Physics, Ohio State University, 191 West Woodruff Ave., Columbus, OH 43210, USA.*

Highly sensitive and selective Terahertz sensor utilized to quantitatively analyze a complex mixture of Volatile Organic Compounds is reported. To best demonstrate analytical capabilities of THz chemical sensors we chose to perform analytical quantitative analysis of a certified gas mixture using a novel prototype chemical sensor that couples a commercial preconcentration system (Entech 7100A) to a high resolution THz spectrometer. We selected Method TO-14A certified mixture of 39 volatile organic compounds (VOCs) diluted to 1 part per million (ppm) in nitrogen. 26 of the 39 chemicals were identified by us as suitable for THz spectroscopic detection. Entech 7100A system is designed and marketed as an inlet system for Gas ChromatographyâĂŞMass Spectrometry (GC-MS) instruments with a specific focus on TO-14 and TO-15 EPA sampling methods. Its preconcentration efficiency is high for the 39 chemicals in the mixture used for this study and our preliminary results confirm this. Here we present the results of this study which serves as basis for our ongoing research in environmental sensing and analysis of exhaled human breath.

RC. ASTRONOMICAL SPECIES AND PROCESSES

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 1000 MCPHERSON LAB

Chair: HARSHAL GUPTA, Jet Propulsion Laboratory, Pasadena, California

RC01 **15 min 8:30**

CDMS AND JPL MOLECULAR SPECTROSCOPY CATALOGUES IN A COMMON INFRASTRUCTURE: VAMDC

S. SCHLEMMER, C. P. ENDRES, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; B.J. DROUIN, S. YU, J.C. PEARSON, *Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109* ; H. S. P. MÜLLER, P. SCHILKE, J. STUTZKI, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*.

The virtual atomic and molecular data centre (VAMDC, http://www.vamdc.org/) is a collection of databases with a common data model. It combines molecular spectroscopy databases; like the Cologne Database for Molecular Spectroscopy (CDMS), the Jet Propulsion Laboratory microwave, millimeter and submillimeter spectral line catalogue (JPL) and the HITRAN databases, with other databases, *e.g.*, on molecular collisions (BASECOL, KIDA). VAMDC is open to include other databases adopting the same data structure and access protocols to the data. Due to the common data model all data can be accessed through one portal. The individual databases are located on a system of distributed servers which all can handle a common query language which enables the combined access to the very different data.

In this presentation requests to CDMS and JPL will be used to explain the basic ideas behind the very powerful VAMDC instrument, its portal and the query possibilities. A new portal to CDMS allows access to all old and new spectroscopic data. In addition CDMS has a number of new features, in particular meaningful quantum numbers, references linked to data points, and improved documentation. In addition, fit files are accessible for download and queries to other databases are possible.

Due to the new format the long anticipated unified spectroscopy database including all relevant information is realized. Together with other groups within the VAMDC consortium we are working on common user tools to simplify the access for new customers and to tailor data requests for users with specified needs, e.g. HFS information. The development of CDMS and JPL within the VAMDC infrastructure will allow a much more sophisticated analysis of complex observational data which, *e.g.*, come from the ALMA telescope.

RC02 **15 min 8:47**

CDMS 2012: A DATABASE WITHIN THE FRAMEWORK OF THE VIRTUAL ATOMIC AND MOLECULAR DATA CENTRE – RECENT DEVELOPMENTS

HOLGER S. P. MÜLLER, C. P. ENDRES, J. STUTZKI, S. SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*.

The catalog section of the Cologne Database for Molecular Spectroscopy, CDMS,[abc] contains experimental and calculated transition frequencies of molecules and atoms observable by radioastronomical means with information on uncertainties, intensities and quantum numbers. Initially constructed as ascii tables, its inclusion into a database environment within the framework of the European Framework Programme 7 project Virtual Atomic and Molecular Data Centre (VAMDC)[d] has begun in June 2008. The conversion required time because of the extensive content of the CDMS, the desire to maintain the existing functionality, the additional requisites as part of the VAMDC framework, and the sustained development of the VAMDC infrastructure. The new CDMS is scheduled to be available publicly prior to this conference; the old CDMS will be accessible for a transitional period.

We will present some of the new CDMS features, provide some overview on new or updated entries from our last account three years ago[e] as well as activities in other sections of the CDMS.

---

[a] Internet address: http://www.astro.uni-koeln.de/cdms/

[b] H. S. P. Müller, F. Schlöder, J. Stutzki, and G. Winnewisser, *J. Mol. Struct.* **742**, 215−227 (2005)

[c] H. S. P. Müller, S. Thorwirth, D. A. Roth, and G. Winnewisser, *Astron. Astrophys.* **370**, L49−L52 (2001)

[d] Internet address: http://www.vamdc.org/

[e] H. S. P. Müller, J. Stutzki, S. Schlemmer, contribution WH07, presented at the 64th International Symposium on Molecular Spectroscopy, Columbus, OH, USA, 2009

RC03 **15 min 9:04**

OBSERVING MOLECULES IN THE INTERSTELLAR MEDIA: THEORETICAL AND EXPERIMENTAL STUDIES OF ENERGY TRANSFER.

LAURENT WIESENFELD, ALEXANDRE FAURE, *UJF-Grenoble 1/CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, France*; FRANÇOIS LIQUE, *LOMC – CNRS, Le Havre University, 76058 Le Havre France*; and NICOLE FEAUTRIER, *LERMA and UMR 8112 of CNRS, Observatoire de Paris-Meudon, 92195 Meudon Cedex, France*.

In order to retrieve actual molecular abundances from molecular spectral lines astrophysical observations, knowledge of the molecular rotational levels excitation schemes is essential. Actual excitation results of a trade-off between photon excitation and collisional excitation by the main constituents of the interstellar gas, molecular hydrogen, and, to a lesser extent, atomic hydrogen and helium. These rates are almost always obtained from theoretical investigations, by computing classical or quantum dynamics of the interaction of the observed molecule with electrons, He, H or H2.

Our laboratories have recently calculated a set of collision coefficients characterizing the efficiency of energy transfer between helium and/or hydrogen and a large variety of interstellar molecules. We have been dealing with molecules ranging from light hydrides, observed by the Herschel Space Telescope in the sub-mm (THz) range, to medium size molecules, observed at wavelengths in the mm range (80-400 GHz) to heavy complex organic molecules, observed also in the cm range.

We shall present a review of recent theoretical results obtained in our laboratories, for various kind of commonly observed molecules.

In order to validate the theoretical computations, comparison with experimental measures is essential. We present here such comparisons mainly for water, on total and differential cross section.

RC04 **15 min 9:21**

COMPUTATION OF COLLISION-INDUCED ABSORPTION BY SIMPLE MOLECULAR COMPLEXES, FOR ASTROPHYSICAL APPLICATIONS

MARTIN ABEL, LOTHAR FROMMHOLD, *Department of Physics, The University of Texas at Austin, Austin, TX 78712*; XIAOPING LI, KATHARINE L. C. HUNT, *Department of Chemistry, Michigan State University, East Lansing, MI 48824*.

The interaction-induced absorption by collisional pairs of H_2 molecules is an important opacity source in the atmospheres of various types of planets and cool stars, such as late stars, low-mass stars, brown dwarfs, cool white dwarf stars, the ambers of the smaller, burnt out main sequence stars, exoplanets, etc., and therefore of special astronomical interest [a]. The emission spectra of cool white dwarf stars differ significantly in the infrared from the expected blackbody spectra of their cores, which is largely due to absorption by collisional H_2–H_2, H_2–He, and H_2–H complexes in the stellar atmospheres. Using quantum-chemical methods we compute the atmospheric absorption from hundreds to thousands of kelvin [b]. Laboratory measurements of interaction-induced absorption spectra by H_2 pairs exist only at room temperature and below. We show that our results reproduce these measurements closely [c], so that our computational data permit reliable modeling of stellar atmosphere opacities even for the higher temperatures [d]. First results for H_2–He complexes [e] have already been applied to astrophysical models [f] and have shown great improvements in these models.

---

[a] L. Frommhold, Collision-Induced Absorption in Gases, Cambridge University Press, Cambridge, New York, 1993 and 2006

[b] X. Li, K. L. C. Hunt, F. Wang, M. Abel, and L. Frommhold, Collision-Induced Infrared Absorption by Molecular Hydrogen Pairs at Thousands of Kelvin, Int. J. of Spect., vol. 2010, Article ID 371201, 11 pages, 2010. doi: 10.1155/2010/371201

[c] M. Abel, L. Frommhold, X. Li, and K. L. C. Hunt, Collision-induced absorption by H_2 pairs: From hundreds to thousands of Kelvin, J. Phys. Chem. A, 115, 6805-6812, 2011

[d] L. Frommhold, M. Abel, F. Wang, M. Gustafsson, X. Li, and K. L. C. Hunt, "Infrared atmospheric emission and absorption by simple molecular complexes, from first principles", Mol. Phys. 108, 2265, 2010

[e] M. Abel, L. Frommhold, X. Li, and K. L. C. Hunt, Infrared absorption by collisional H_2–He complexes at temperatures up to 9000 K and frequencies from 0 to 20000 cm^{-1}, J. Chem. Phys., 136, 044319, 2012âĂÍ

[f] D. Saumon, M. S. Marley, M. Abel, L. Frommhold, and R. S. Freedman, New H_2 collision-induced absorption and NH_3 opacity and the spectra of the coolest brown dwarfs, Astrophysical Journal, 2012

RC05 **15 min 9:38**

METHANOL PHOTODISSOCIATION STUDIES USING MILLIMETER AND SUBMILLIMETER SPECTROSCOPY

JACOB C. LAAS and SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

Many complex organic molecules (COMs) of prebiotic interest have been detected in interstellar environments, and new astronomical observatories such as ALMA and SOFIA are likely to extend our knowledge of the chemical composition of the universe. Astrochemical models suggest the formation of interstellar COMs is dominated by combination reactions between radicals on grain surfaces. These radicals are primarily produced from UV and cosmic-ray induced photodissociation. The various competing photodissociation pathways greatly contribute to the complexity of the reaction products, but in many cases the photodissociation branching ratios are not well-known. This is a particular challenge in ice photolysis studies, where the products are formed in a complex mixture in the condensed phase. Gas-phase spectroscopic studies offer a means to investigating photodissociation mechanisms in an environment where each product can be directly and separately monitored. To this end, we are developing a laboratory technique utilizing millimeter and submillimeter spectroscopy to directly observe photodissociation products and to quantify their branching ratios. We are focusing our first studies on methanol, which is predicted by astrochemical models to provide much of the starting material for COM chemistry in interstellar clouds. Here we will present our progress toward obtaining a quantitative description of the gas-phase methanol photodissociation mechanism.

Intermission

RC06 **15 min 10:10**

TIME-SLICE VELOCITY-MAP ION IMAGING STUDIES OF THE PHOTODISSOCIATION OF ASTROPHYSIC IMPORTANT SMALL MOLECULES IN THE VACUUM ULTRAVIOLET REGION BY RESONANT SUM/DIFFERENCE FOUR-WAVE MIXING

HONG GAO, YU SONG, LEI YANG, JINGANG ZHOU, C. Y. NG, WILLIAM M. JACKSON, *Department of Chemistry, University of California, Davis, Davis, CA 95616, USA*; YANG PAN, *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China.*

We have recently built an apparatus that combines two tunable vacuum ultraviolet (VUV) radiation laser systems and a time-slice velocity-map ion imaging (TSVMI) detection system to study the photodissociation dynamics of astrophysical important small molecules. The two tunable VUV lasers are both generated in rare gases jets by resonant four-wave sum and difference-frequency mixing (FWSDFM) in the energy range from 8.0 eV to 15.4 eV and used respectively for state-selected photodissociation and state-selected photoionization. Preliminary experimental results on state-selected photodissociation of CO will be presented. In this experiment, the CO molecule is excited to one of its ro-vibronic states by absorbing one VUV photon, and it undergoes predissociation to produce C($^3\mathrm{P}_{0,1,2}$ or $^1\mathrm{D}_2$) and O ($^3\mathrm{P}_{0,1,2}$ or $^1\mathrm{D}_2$) atoms. The C atom in one of the $^3\mathrm{P}_0$, $^3\mathrm{P}_1$ and $^3\mathrm{P}_2$ states is selectively ionized by using the second VUV beam and detected with the time-slice velocity-map ion imaging (TSVMI) system. From the images, we can obtain the branching ratio between each of the spin orbit states of carbon atoms with an oxygen atom in the ^3P state or the ^1D state. The results indicate that the ratio is strongly dependant on which sub-level of the C(^3P) is being probed. It is also strongly dependant on which state of CO is excited. We are going to use this method to study the photodissociation dynamics of other astrophysical important small molecules, like N_2, NO, C_2, CO_2 and H_2O, in the VUV region by state-selected detection of the C, O and N atoms.

Acknowledgements: a) H. Gao, Y. Song, Y. Pan, and W. M. Jackson were supported by NSF under grant # CHE-0957872. b) H. Gao, L. Yang, and C. Y. Ng were supported by AFOSR under Grant # FA9550-06-1-0073, NASA under Grant No. 07-PATM07-0012, DOE on Contract # DEFG02-02ER15306 and NSF on Grant # CHE 0910488.

RC07 **15 min 10:27**

OSCILLATOR STRENGTHS AND PREDISSOCIATION RATES FOR RYDBERG COMPLEXES IN $^{12}C^{16}O$ BETWEEN 92.9 AND 93.4 NM

M. EIDELSBERG, J. L. LEMAIRE, *Observatoire de Paris, Paris, France*; S. R. FEDERMAN, *Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606*; G. STARK, A. N. HEAYS, *Department of Physics, Wellesley College, Wellesley, MA 02481*; L. GAVILAN, *Observatoire de Paris, Paris, France*; J. H. FILLION, *Université PVI UMPC, Paris, France*; F. ROSTAS, *Observatoire de Paris, Paris, France*; J. R. LYONS, *IGPP, University of Califormia, Los Angeles, CA 90095*; P. L. SMITH, *Department of Physics, Wellesley College, Wellesley, MA 02481*; N. DE OLIVEIRA, D. JOYEUX, M. ROUDJANE, L. NAHON, *Synchrotron SOLEIL, Saint Aubin, France*.

We are conducting experiments on the DESIRS beam-line at the SOLEIL Synchrotron to acquire the necessary data on oscillator strengths and predissociation rates for modeling CO photochemistry in astronomical environments. A VUV Fourier Transform Spectrometer provides a resolving power of about 350,000, allowing us to discern individual lines in electronic transitions. Here we focus on results for six overlapping bands seen in spectra of $^{12}C^{16}O$ and compare them with earlier determinations. Absorption from the ground electronic level, $X\ ^1\Sigma^+\ v'' = 0$, to the upper levels 4pπ(2), II $^1\Pi$, 4pσ(2), 5pπ(0), 5pσ(0), and I $^1\Pi$ was analyzed. Our results are the first to provide data on each band. The spectra also reveal a continuum feature that was modeled, but its identification is not known at the present time.

RC08 **15 min 10:44**

THE ANALYSIS OF ASTROPHYSICAL 'WEEDS' USING 3-D SUBMILLIMETER SPECTROSCOPY

SARAH M. FORTMAN, JAMES P. MCMILLAN, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, *Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210, USA*.

We have previously reported on an experimental spectroscopic approach that makes possible the calculation of lower state, energy levels and transition strengths without the need for spectral assignment. We produce results both in the standard catalog format (frequency, line strength and lower state energy) as well as a point by point fit which allows the user to predict the complete spectrum at an arbitrary temperature. We report our continued analysis of several weeds in the 210-270 and 560-650 GHz regions as well as improvements in our analysis strategies.

RC09 **15 min 11:01**

COMPUTATIONAL STUDY AND LABORATORY SPECTROSCOPY OF PREBIOTIC MOLECULES PRODUCED BY O(^{1}D) INSERTION REACTIONS

BRIAN M. HAYS, BRIDGET A. DEPRINCE, SUSANNA L. WIDICUS WEAVER, *Emory University, Department of Chemistry, Atlanta, GA 30322*.

Methanediol ($HOCH_2OH$), methoxymethanol (CH_3OCH_2OH), and aminomethanol ($HOCH_2NH_2$) are unstable organic reaction intermediates that are predicted by astrochemical models to be present in detectable quantities in the interstellar medium. Their astronomical investigation has been precluded by a lack of gas-phase spectroscopic information. In order to obtain such spectra, on-the-fly O(^{1}D) insertion reactions in a supersonic expansion have been proposed as an efficient synthetic route to form these molecules. *Ab initio* calculations have been performed to determine the spectroscopic constants of these species so that the rotational spectra can be predicted as a guide for laboratory studies. Additionally, a multipass millimeter and submillimeter spectrometer has been coupled with a photolysis fast-mixing source to enable spectroscopic studies of the target molecules. We will report on the results of the computational studies, the instrument and source design, and experimental progress toward obtaining the rotational spectra of methanediol, methoxymethanol, and aminomethanol.

RC10 15 min 11:18

HIGH RESOLUTION SPECTROSCOPY OF HEXAMETHYLENETETRAMINE (HMT) $C_6N_4H_{12}$

V. BOUDON, *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne, 9. Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*; O. PIRALI[a], *Ligne AILES – Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France.*

Hexamethylenetetramine, or HMT ($C_6N_4H_{12}$) is a N-substituted derivative of adamantane $C_{10}H_{16}$ which is the smallest sample of the diamondoid molecules family. Thanks to their high stability, diamond-like molecules have long been suspected to be present in space[b] (note that diamond nanocrystals are extracted from Murchinson meteorites[c]), and HMT is known to be an abundant residue of UV irradiated ice analogs[d] and might be present in Titan's atmosphere. Using the Bruker IFS 125 coupled to a multipass cell (absorption path length of 150 m) of the AILES beamline at SOLEIL, we recorded the IR spectrum of gas phase HMT in the 300–3000 cm^{-1} spectral region with an unapodized resolution 0.001 cm^{-1}. HMT is a solid powder with about 0.008 mbar vapour pressure at room temperature, it is a T_d molecule (as adamantane) and has 25 vibrational modes from which only 9 are infrared active. Over the 9 IR active modes, we were able to rotationlly resolved the spectra of 6 of them.

The analysis of all the resolved bands has been performed thanks to the XTDS and SPVIEW softwares developed in Dijon for such molecules[e]. Each band can be considered as isolated and we get very good fits of line positions, with a root mean square deviation better than 5×10^{-4} cm^{-1} for J values up to 80 or more in each case. As for our recent study concerning adamantane[f], the resulting synthetic spectra will permit an active search of this very stable specie in different sources of the interstellar medium.

---

[a] Also at: Institut des Sciences Moléculaires d'Orsay, UMR8214 CNRS-Université Paris-Sud, Bat.210, 91405 Orsay cedex, France.

[b] W. C. Saslaw and J. E. Gaustad, Nature, **221**, 160 (1969)

[c] R. S. Lewis et al., Nature, **326**, 160 (1987)

[d] M. P. Bernstein et al., ApJ, **454**, 327 (1995)

[e] Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov and J.-P. Champion, *J. Mol. Spectrosc.*, **251** 102–113 (2008).

[f] O. Pirali, V. Boudon, J. Oomens, M. Vervloet, J. Chem. Phys., **136**, 024310 (2012)

RC11 15 min 11:35

NUCLEAR SPIN OF H_3^+ AND H_2 IN DENSE MOLECULAR CLOUDS

KYLE N. CRABTREE, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy, and Physics, University of Illinois, Urbana, IL 61801.*

The ortho:para ratio of H_2 is a critical parameter for deuterium fractionation in cold, dense quiescent cores. The dominant reservoir for interstellar deuterium is in the inert molecule HD, but the exothermic reaction $H_3^+ + HD \rightarrow H_2D^+ + H_2 + 220$ K (and H_2D^+ + HD, etc.) can yield highly reactive species capable of distributing deuterium to other molecules. The barrier to the reverse reaction, however, can be overcome even at temperatures below 10 K when ortho-H_2 (o-H_2) reacts with H_2D^+ (or D_2H^+, D_3^+), as ortho-H_2 possesses $\sim$170 K of internal rotational energy in its ground state. Recent modeling work has demonstrated the importance of o-H_2 in cold, dense, highly depleted cores using a chemical network that includes all nuclear spin modifications of H_3^+, H_2, and their isotopologues, but the initial o-H_2 fraction is taken as a parameter in the model. Observationally or computationally constraining this quantity would aid in understanding deuterium fractionation in dense cores.

To learn about the initial o-H_2 fraction in a cold core, we have modeled the chemistry of non-depleted dense interstellar clouds from which cold cores are thought to form. A simplified gas-phase chemical network consisting of 28 species and $\sim$170 reactions is combined with a physical model of a dense cloud, including time-dependent physical conditions. Included in the network are the nuclear spin modifications of H_2, H_2^+, and H_3^+, as well as nuclear spin dependent rate coefficients for the thermalization reactions $H_2 + H^+$ and $H_3^+ + H_2$. By modeling the time-dependent chemistry, we find that the ortho:para ratio of H_2 requires 10^7-10^8 years to reach steady state under "standard" dense cloud conditions, which is at least on the order of the cloud lifetime. The timescale depends on the ionization rate, the rate coefficients of the various $H_3^+ + H_2$ reactions, and the relative abundances of H_3^+ and H^+, but is largely insensitive to the total density and temperature. Even at steady state, the o-H_2 fraction is calculated to be $>$0.5% at 10 K, which is several orders of magnitude above its value at thermodynamic equilibrium. The prospects for using observations of the ortho:para ratio of H_3^+ as a probe of the H_2 ortho:para ratio will be discussed.

RC12 **15 min 11:52**

GAS-GRAIN MODELING OF O_2 IN INTERSTELLAR CLOUDS

DONGHUI QUAN, *Department of Chemistry, Eastern Kentucky University, Richmond, KY 40475*; ERIC HERBST, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904*.

The lack of detection of interstellar gas phase O_2 in cold dense interstellar clouds has been a problem to modelers of the chemistry of these regions. This non-detection disagrees with steady-state models which predict overly high concentrations compared with observed upper limits of this molecule obtained with SWAS and Odin observatories. Recently, gas phase O_2 was detected in an unusual region in Orion by the Herschel Space Observatory. In this work, we continue the study of Quan et al. 2008. Apart from the gas phase chemistry discussed in detail in Quan et al. 2008, the role of dust grains in interstellar chemistry is included. Here we present the results from a series of gas-grain models in which physical conditions were varied to simulate several interstellar hot and cold regions. The role of the dust grains can explain the low abundances of gaseous O_2 in the cold regions, and the possible places where this molecule may have observable abundances are suggested.

RD. MINI-SYMPOSIUM: COLD QUANTUM SYSTEMS

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 1015 MCPHERSON LAB

Chair: GARY DOUBERLY, University of Georgia, Athens, Georgia

RD01 *INVITED TALK* **30 min 8:30**

PROBING MOLECULES WITH LASER-COOLED ATOMIC IONS

KENNETH R. BROWN, *Schools of Chemistry and Biochemistry; Computational Science and Engineering; and Physics*
Georgia Institute of Technology, Atlanta, GA 30332-0400.

Trapped, laser-cooled atomic ions can be controlled with unprecedented precision and accuracy as demonstrated by both atomic ion clocks and prototype quantum computing devices. By trapping a mixture of laser-cooled atomic and molecular ions, the molecular ions will be sympathetically cooled to millikelvin temperatures. The reaction dynamics and spectroscopy of the molecular ion can then be observed without the thermal distribution of ion motion. Furthermore, the bright fluorescence of the atomic ion can be used as a signal for obtaining information about the molecular ion via the Coulombic interaction. In this talk, I will present our work towards performing single molecular ion spectroscopy on an atomic ion - molecular ion pair. I will discuss fundamental limits and applications of the technique for astrochemistry and the direct laser-cooling of molecular ions.

RD02 **15 min 9:05**

SPECTROSCOPIC APPLICATIONS OF STATE-SELECTED SYMPATHETICALLY-COOLED MOLECULAR IONS

XIN TONG, MATTHIAS GERMANN and STEFAN WILLITSCH, *Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.*

Cold molecular ions prepared by sympathetic cooling with laser-cooled ions in an ion trap[a] represent attractive systems for new spectroscopic experiments. The long trapping times (up to hours) and state lifetimes (up to minutes)[b] in an almost perturbation-free environment enable the long interaction times required for the study of forbidden spectroscopic transitions which have not been accessible before in molecular ions.

Here, we present a proof-of-principle experiment for the investigation of dipole-forbidden infrared transitions in cold N_2^+ ions using quantum-cascade-laser technology in combination with action spectroscopy. Because sympathetic-cooling experiments typically use small ensembles of tens to hundreds of ions, the confinement of their population into a single quantum state is essential to improve the sensitivity of our experiments. This is achieved by state-selective generation of the ions using threshold photoionization followed by sympathetic cooling[c].

Finally, we discuss the experimental requirements for performing highly sensitive spectroscopic measurements on trapped, cold molecular ions and present an outlook on current developments which employ quantum-logic methods for non-destructive spectroscopic studies on single sympathetically cold molecular ions.[d]

---

[a] S. Willitsch, M. Bell, A. Gingell and T. P. Softley *Phys. Chem. Chem. Phys.* **10**, 7200 2008.
[b] X. Tong, A. Winney and S. Willitsch *Phys. Rev. Lett.* **105**, 143002 2010.
[c] X. Tong, D. Wild and S. Willitsch *Phys. Rev. A* **83**, 023415 2011.
[d] J. Mur-Petit, J. J. Carcia-Ripoll and S. Willitsch *et al. Phys. Rev. A* **85**, 022308 2012.

RD03 **15 min 9:22**

DETECTING HYDROGEN ATOMS IN SOLID PARAHYDROGEN USING FTIR SPECTROSCOPY

DAVID T. ANDERSON and MAHMUT RUZI, *Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.*

Our group is currently studying the 193.3 nm photochemistry of a number of precursor molecules isolated in solid parahydrogen (pH_2) using high-resolution FTIR spectroscopy. In photochemical studies of formic acid[a] and ammonia, right after the photolysis laser is turned off, we observe metastable satellite peaks in close proximity to the strong rovibrational transition out of the ground state of the respective monomer photoproducts H_2O and NH_3. In both cases, there are two satellite peaks near the R(0) monomer transition. We have assigned these satellite features to H-H_2O and H-NH_3 radical clusters that form via reactions of the photoproduct with the pH_2 host. We will present IR spectroscopic studies of these two H-atom cluster systems that we hope to use in future photochemical studies to measure the concentration of H-atoms in our sample using FTIR spectroscopy.

---

[a] K. A. Kufeld, W. R. Wonderly, L. O. Paulson, S. C. Kettwich, and D. T. Anderson, *J. Phys. Chem. Lett.* **3**, 342-347 (2012).

RD04 **15 min 9:39**

PHOTOCHEMICAL STUDIES OF CH_3OH ISOLATED IN SOLID PARAHYDROGEN

DAVID T. ANDERSON, KYLIE A. KUFELD, DOMINIQUE SCHOECH, ROBERT B. SLIPP, AND FARAJ M. ALMARRI, *Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.*

Our group is studying the 193.3 nm photochemistry of methanol (CH_3OH) isolated in solid pH_2 using high-resolution FTIR spectroscopy to explore the low temperature reactions of H-atoms with CH_3OH. Gas phase studies have shown that the dominant photodissociation channel is CH_3OH + h$\nu \rightarrow CH_3$O + H,[a] and thus the *in situ* photochemistry is expected to produce methoxy and H-atom radicals. After photolysis the methoxy radicals are immobilized at these temperatures, but the H-atoms can still readily move through solid pH_2. For short time 193.3 nm exposures, greater than 90% of the CH_3OH remains intact and therefore repeated FTIR spectra immediately after photolysis can be used to record the kinetics of reactions of H-atoms with CH_3OH. We observe exponential growth in the intensities of a number of peaks that can be assigned to the hydroxymethyl CH_2OH radical. Further, the growth is bi-exponential and we believe there are two processes that lead to the formation of CH_2OH: (1) fast growth by interconversion of CH_3O to CH_2OH and (2) slow growth due to hydrogen abstraction reactions of cold H-atoms with CH_3OH. We have not observed the methoxy radical. Currently we are performing photochemical experiments on fully deuterated methanol (CD_3OD) in solid pH_2 to test these kinetic interpretations, and the most recent results and analysis will be presented.

---

[a] Y. Wen, J. Segall, M. Dulligan, and C. Wittig, *J. Chem. Phys.* **101**, 5665 (1994).

RD05 **15 min 9:56**

FTIR STUDIES OF AMMONIA PHOTOCHEMISTRY IN SOLID PARAHYDROGEN

MAHMUT RUZI and DAVID T. ANDERSON, *Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.*

It is believed that producing and trapping high concentrations of reactive species in solid molecular hydrogen will ultimately lead to the development of new high performance rocket fuels.[a] We think the NH radical could be a viable candidate and try to produce it by photolyzing ammonia (NH_3) at low temperature in solid parahydrogen. Upon 193.3 nm photolysis of NH_3, we observe both NH_2 and NH radical photoproducts. No significant changes in the NH radical concentration have been detected during a period of 3 hours at 1.8 K, even though the reaction NH + $H_2 \rightarrow NH_3$ is highly exothermic and can occur by quantum mechanical tunneling even at these low temperatures. In contrast, the NH_2 radical is only observed in FTIR scans recorded during photolysis and rapidly decays once the 193.3 nm laser is turned off. We will discuss the possible fates of NH_2 and how conditions can be optimized to produce high concentrations of NH radicals.

---

[a] M. E. Fajardo, S. Tam, T. L. Thompson, and M. E. Cordonnier, *Chem. Phys.* **189**, 351-365 (1994).

RD06 **15 min 10:13**

DECELERATING MOLECULES WITH MICROWAVE FIELDS

MELANIE SCHNELL, *Center for Free-Electron Laser Science, Hamburg, Germany*; SIMON MERZ, NICOLAS VANHAECKE, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*; WOLFGANG JÄGER, *University of Alberta, Edmonton, Canada*; GERARD MEIJER, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*.

An important remaining issue in the field of cold molecules is a general technique to manipulate the motion of polar molecules in high-field-seeking states, which is crucial for the investigation of molecules in their ground states and of all large and more complex molecules. Complementary to the already demonstrated and experimentally rather challenging alternating gradient methods, we exploit the interaction of polar molecules with electromagnetic radiation in a microwave cavity.

Based on the concept of our microwave lens [a] we have developed a decelerator for polar molecules that allows motion control in three dimensions. It consists of a cylindrically symmetric microwave resonator, which is cooled to liquid nitrogen temperature. For our deceleration experiments, we are using the $TE_{1,1,12}$ mode, i.e., the decelerator consists of 12 stages. We will present a detailed characterization of the microwave deceleration process and discuss prospects for future experiments, which are opening the door for novel control experiments of larger molecules.

---

[a] H. Odashima et al., Microwave Lens for Polar Molecules, *Phys. Rev. Lett.*, 104, 253001, 2010

Intermission

RD07 **15 min 10:45**

HOW CHLORINE ATOM REACTS WITH H_2 IN IR-IRRADIATED SOLID PARA-HYDROGEN

JEN-YU WU, MOHAMMED BAHOU, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*; AND YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*

The use of solid para-hydrogen (p-H_2) as a matrix host has generated considerable interest in recent years. Solid p-H_2 is considered as a quantum solid; hence it is ąÂğsofterąÂÍ than noble gas matrices and has several unique properties such as narrow bandwidths, feasibility of molecular and internal rotation, and a diminished cage effect, which is particularly relevant to the formation of atoms and radicals in a matrix using photolysis $insitu$. Raston and Anderson employed laser emission at 355 nm to photodissociate Cl_2 trapped in solid p-H_2 at 2 K and produced isolated Cl atoms.[a] Excitation of the solid p-H_2 with IR light in the range 4000-5000 cm^{-1} from a globar source induces reactions of Cl atoms with p-H_2 to form HCl.[b] We investigated the reaction of Cl with solid p-H_2 with a tunable IR laser and a FTIR spectrometer. The Cl atoms were produced on irradiation of a Cl_2/p-H_2 (1/1000-1/4000) matrix with light at 365 nm from a light-emitting diode. By monitoring continuously the formation of HCl while tuning the wavelength of the IR laser, we obtained the relative yield of HCl as a function of excitation wavelength. We found that absorption of the Cl-H_2 complex and solid H_2, but not the Cl_2-H_2 complex, induced the reaction Cl + H_2. In separate experiments we irradiated a selective area of the matrix with UV light and compared the yields of HCl in this area when we irradiated IR light at various locations. When the IR laser light irradiated outside the UV-irradiated area, excitation of p-H_2 near 4229 cm^{-1}, but not the Cl-H_2 complex at 4148.5 cm^{-1}, still produced HCl. In contrast, when the IR light irradiated inside the UV-irradiated region, more HCl was produced at 4148.5 cm^{-1}. This indicates that the excited H_2 can move around and react with Cl located far away from the originally excited area, whereas the IR excited Cl-H_2 complex reacts directly to form HCl. We also found that irradiation of H_2 produced some dimers of HCl, whereas irradiation at the Cl-H_2 complex produced only HCl monomer.

---

[a] P. L. Raston and D. T. Anderson, *J. Chem. Phys.* **126**, 021106 (2007).

[b] P. L. Raston and D. T. Anderson, *Phys. Chem. Chem. Phys.* **8**, 3124 (2006).

RD08 **15 min 11:02**

THEORETICAL SPIN-ORBIT SPECTROSCOPY OF Cl DOPANTS IN SOLID PARAHYDROGEN

ROBERT HINDE, *Department of Chemistry, University of Tennessee, Knoxville, TN 37996 USA.*

Solid parahydrogen (pH_2) matrices containing open-shell (^2P) Cl and Br atoms as substitutional impurities exhibit several infrared (IR) absorption features associated with intermolecular interactions between the halogen atom and nearby pH_2 molecules.[a] These dopant-induced IR absorption features are associated with (i) spin-orbit (SO) excitation of the halogen atom, and (ii) cooperative excitations in which a single IR photon both triggers SO excitation of the halogen atom and excites the H-H stretching coordinate of a nearby pH_2 molecule. The IR spectral features thus contain detailed information about the interaction between the open-shell halogen atom and the surrounding pH_2 molecules, and in particular tell us about the coupling between the atom's electronic degrees of freedom and the nuclear motion of its H_2 neighbors.

Here we present recent progress towards understanding these features in Cl-doped solid pH_2. This system represents an arena for testing theoretical approaches that generate many-body, non-pairwise-additive potential energy functions for the dopant–matrix interaction by combining multiple low-lying Cl–H_2 pair potential energy functions. Our analysis must account for the fact that the individual pH_2 molecules in the doped solid undergo large amplitude zero-point motions;[b] we use quantum Monte Carlo simulations[c] to model these zero-point motions. We interpret our findings in terms of a reduced dimensionality model that provides a qualitative understanding of the role that matrix zero-point motions play in the observed spectra.

---

[a] P. L. Raston and D. T. Anderson, J. Chem. Phys. **126**, 021106 (2007); S. C. Kettwich, L. O. Paulson, P. L. Raston and D. T. Anderson, J. Phys. Chem. A **112**, 11153 (2008).

[b] I .F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[c] R. J. Hinde, Comput. Phys. Commun. **182**, 2339 (2011).

RD09 **15 min 11:19**

INFRARED SPECTROSCOPY OF 1-CHOLOROMETHYLALLYL AND 1-METHYLALLYL RADICALS PRODUCED IN A SOLID PARA-HYDROGEN MATRIX.

MOHAMMED BAHOU, JEN-YU WU, KEIICHI TANAKA, *Dept of Applied Chemistry, National Chiao Tung University, Hsinchu, 30010, TAIWAN* ; YUAN-PERN LEE, *Dept of Applied Chemistry, National Chiao Tung University, and Institute of Atomic & Molecular Sciences, Academia Sinica, Taipei 10617, TAIWAN.*

The reaction of chlorine atoms with trans-1,3-butadiene in solid para-hydrogen (p-H_2) matrix has been studied using Fourier transform infrared spectroscopy. When a mixture of Cl_2, trans-1,3-butadiene and p-H_2 was deposited onto a cold target at 3 K and irradiated by UV light at 365 nm, new intense lines at 809.0, 962.1, 1240.6 cm^{-1} and several weaker ones appeared. The carrier of this spectrum was assigned to the 1-chloromethylallyl radical, •(CH_2CHCH)CH_2Cl, based on the anharmonic vibrational frequencies calculated with the DFT method, indicating that the addition of the Cl atom to trans-1,3-butadiene occurs primarily at the terminal carbon atom. This is in sharp contrast to the reaction of chlorine atoms with propene in a solid p-H_2 matrix[a] in which the addition of Cl to the central carbon atom to produce selectively the 2-chloropropyl is favored due to the steric effects. The energy diagram calculated with B3PW91 method supports this selective reaction process because 1) the channel from trans-1,3-butadiene to 1-chloro-methylallyl is almost barrierless (0.4 kcal/mol), and 2) isomereization from 1-chloromethylally to the 2-chloro-3-buten-1-yl radical, $CH_2CHCHClCH_2$•, by migration of Cl atom from the terminal to the central C atom, hardly occur in the p-H_2 matrix because of the isomerization barrier height (18.8 kcal/mol). We also observed a second set of lines with intense ones at 781.6, 957.93, 1433.6 cm^{-1} and several weaker ones when the UV-irradiated Cl_2/trans-1,3-butadiene/p-H_2 matrix was further irradiated with infrared light from a globar source. These lines are assigned to the 1-methylallyl radical, •(CH_2CHCH)CH_3, produced from reaction of 1,3-butadiene with an H atom that was produced from the reaction of Cl atoms with IR-irradiated p-H_2, $Cl + H_2^* \rightarrow H + HCl$. The energy diagram calculated at the G3//B3LYP level[b] similarly supports the reaction process to form selectively 1-methylallyl in the p-H_2 matrix.

---

[a] J. C. Amicangelo and Y. P. Lee, *J. Phys. Chem. Lett.* **1**, 1956 (2010).

[b] J. L. Millerngelo, *J. Phys. Chem. A* **108**, 2268 (2004).

RD10 15 min 11:36

IR-IR DOUBLE RESONANCE EXPERIMENT OF $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$ CLUSTERS IN SOLID $para$-$\mathrm{H_2}$

Y. MIYAMOTO, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530 JAPAN*; A. MIZOGUCHI, and H. KANAMORI, *Department of Physics, Tokyo Institute of Technology, Tokyo, 152-8551 JAPAN.*

FTIR absorption spectrum of the ν_3 vibrational band of $\mathrm{CH_3F}$ in solid $para$-$\mathrm{H_2}$ shows a series of lines at regular intervals, which could be assigned to clusters forming $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$, with n = 0 to 12[a]. However, such a distinct feature appears only in the ν_3 mode but is not observed in the other vibrational modes. In order to solve this problem, we applied IR-IR double resonance spectroscopy using 3 μm OPO laser and 9 μm QC laser to the vibrational bands of $\mathrm{CH_3F}$ in solid $para$-$\mathrm{H_2}$. Because, very recently, high resolution cw-QC laser spectroscopy demonstrated a perfect bleaching effect on a spectral peak in ν_3 mode[b]. By bleaching the n=1 component of the ν_3 band at 9 μm, we can see a corresponding depletion in the broad spectral feature of the ν_1 band at 3 μm. This simultaneous disappearance of the spectral peaks is a proof of the $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$ cluster model, and it suggests that all the vibrational bands should be explained by the same model.

---

[a] K. Yoshioka and D. T. Anderson, *J. Chem. Phys.* 119, 4731(2003)

[b] A. R. W. McKellar, A. Mizoguchi, and H. Kanamori, *Phys. Chem. Chem. Phys.*, 13, 11587 (2011)

RD11 15 min 11:53

LINESHAPE ANALYSIS OF $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$ ABSORPTION SPECTRA IN 3000 $\mathrm{cm^{-1}}$ REGION IN SOLID $para$-$\mathrm{H_2}$

Y. MIYAMOTO, *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka Okayama 700-8530, Japan*; T. MOMOSE, *Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada*; H. KANAMORI, *Department of Physics, Tokyo Institute of Technology, Ohokayama 2-12-1, Tokyo 152-8551, Japan.*

FTIR absorption spectra of $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$ clusters in solid $para$-$\mathrm{H_2}$ were studied in the C-H stretching region ($\sim$3000 $\mathrm{cm^{-1}}$). As shown previously[a], the ν_3 C-F stretching band at 1040 $\mathrm{cm^{-1}}$ of the $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$ (n = 0$\sim$12) gives a distinct regular series of absorption lines in solid $para$-$\mathrm{H_2}$, which correspond to each n-th component of the cluster. On the other hand, broaden single lines were observed in the 3000 $\mathrm{cm^{-1}}$ region, which were assigned to the ν_1 and ν_4 modes with axial rotation[b]. We found that their lineshape varied depending on $ortho$-$\mathrm{H_2}$ concentration in crystals and could be represented as superposition of the cluster components. Least square fitting based on the $\mathrm{CH_3F}$-$(ortho\text{-}\mathrm{H_2})_n$ cluster model worked very well to resolve the broaden bands and provided us the linewidth and line shift of resolved lines. The large difference of the linewidth and line shift between the vibrational modes shows the distinct nature of each mode in cold quantum solids.

---

[a] K. Yoshioka and D. T. Anderson *J. Chem. Phys.* **119**, 4731 (2003).

[b] Y. -P. Lee, Y. -J. Wu and J. T. Hougen *J. Chem. Phys.* **129**, 104502 (2008).

RE. DYNAMICS

THURSDAY, JUNE 21, 2012 – 8:30 AM

Room: 2015 MCPHERSON LAB

Chair: GEOFFREY DUXBURY, University of Strathclyde, Glasgow, United Kingdom

RE01 15 min 8:30

GAIN AND LASING OF OPTICALLY PUMPED METASTABLE RARE GAS ATOMS

JIANDE HAN and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

In recent years there have been concerted efforts to develop high energy diode-pumped alkali vapor lasers (DPAL). These hybrid gas phase / solid state laser systems offer possibilities for constructing high-powered lasers that have high beam quality. DPAL's utilize excitation of the alkali metal $^2P_{3/2} \leftarrow {}^2S_{1/2}$ transition, followed by collisional relaxation and lasing on the $^2P_{1/2} \rightarrow {}^2S_{1/2}$ line. Considerable progress has been made, but there are technical challenges associated with the reactivity of the metal atoms.

Rare gas atoms (Rg) excited to the np^5(n+1)s $^3P_2$ configuration are metastable and have spectral properties that are closely similar to those of the alkali metals. In principle, optically pumped lasers could be constructed using excitation of the np^5(n+1)p $\leftarrow$ np^5(n+1)s transitions. We have recently demonstrated gain and lasing for optically pumped Ar*, Kr* and Xe*. Three-level lasing schemes were used, with He as the collisional energy transfer agent that established the population inversion. These laser systems have the advantage using inert reagents that are gases at room temperature.

RE02 15 min 8:47

COOPERATIVE EFFECTS IN A RYDBERG GAS

YAN ZHOU, DAVID GRIMES, ANTHONY COLOMBO, and ROBERT FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02319.*

Rydberg-Rydberg transitions of Ca atoms are directly detected by chirped-pulse millimeter-wave spectroscopy with broadband, high-resolution spectra with accurate relative intensities. At moderate high number density, the radiation of a Rydberg gas behaves as strong cooperative effects. Compared to a rotational transition, Rydberg-Rydberg transitions have enormous electric dipole transition moments and polarizabilities, which are sensitive to external and self-induced electric fields. In a dense Rydberg gas, a large group of molecules can share an electric field, and absorb and radiate cooperatively. A model with semiclassical method describes several significant cooperative effects in the time-domain and frequency-domain in two-level systems and Λ-type three-level systems. Several experimental evidences which partly support this model will be discussed and a new experiment with buffer gas cooling technique will be proposed.

RE03 15 min 9:04

USING A HIGH RESOLUTION MID-IR OPO FOR CHEMICAL DYNAMICS STUDIES OF HIGHLY EXCITED MOLECULES

GERALDINE O. ECHEBIRI, MATTHEW D. SMARTE, WENDELL W. WALTERS and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

Quantum state-resolved energy flow dynamics are investigated for inelastic collisions of highly vibrationally excited molecules with HCl and DCl using high resolution transient IR absorption spectroscopy with a mid-IR OPO. Pyrazine molecules are optically pumped into high vibrational states with E_{vib} = 37,900 cm^{-1} using the quadrupled output Nd:YAG laser at λ = 266 nm. The state-resolved outcome of collisions is probed by measuring transient IR absorption for individual quantum states of HCl and DCl. The nascent energy partitioning among the rotational and translational degrees of freedom of the scattered HCl and DCl molecules is used to reveal how isotopic shifts in rotational energy states affect collisional energy transfer.

RE04 **10 min 9:21**

OPTICAL PROBING OF OCS IN EXTREME ROTATIONAL STATES

QINGNAN LIU, CARLOS TORO and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

We have used an optical centrifuge to drive OCS into extreme rotational states and interrogated the outcome using high resolution transient IR absorption spectroscopy. The extreme rotational states are not accessible with traditional optical methods. OCS is of interest in optical centrifuge studies because it has molecular features that lead to efficient centrifugation, namely a large polarizability anisotropy and a small moment of inertia. In these studies we explore how molecular rotation can be controlled by varying the nature of the trapping optical field and how molecular dissociation competes with the preparation of high rotational states.

RE05 **15 min 9:33**

POLARIZATION DEPENDENT DYNAMICS OF CO_2 TRAPPED IN AN OPTICAL CENTRIFUGE

CARLOS TORO, GERALDINE ECHEBIRI, QINGNAN LIU and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

An optical centrifuge (Yuan *et al.* *PNAS* 2011, 108, 6872) has been employed to prepare carbon dioxide molecules in very high rotational states (“hot” rotors, $J \sim 220$) in order to investigate how collisions relax ensembles of molecules with an overall angular momentum that is spatially oriented. We have performed polarization-dependent high resolution transient IR absorption measurements to study the spatial dependence of the relaxation dynamics. Our results show that the net angular momentum of the initially centrifuged molecules persists for at least 10 gas kinetic collisions and that the translational energy distributions are dependent on the probe orientation and polarization. These studies indicate that the centrifuged molecules tend to maintain the orientation of their initial angular momentum for the first set of collisions and that relatively large changes in J are involved in the first collisions.

RE06 **15 min 9:50**

IR/THZ DOUBLE RESONANCE SPECTROSCOPY OF METHYL FLUORIDE AND COLLISION PARTNERS SELF, N_2, Ar, He, CO_2, AND AIR

DANE J. PHILLIPS, *Kratos Defense and Security Solutions Digital Fusion, 4904 Research Dr., Huntsville, Al, 35805*; FRANK C. DE LUCIA, *Department of Physics, 191 Woodruff Ave. Ohio State University, Columbus, OH 43210*; HENRY O. EVERITT, *Army Aviation and Missile RD&E Center, Weapon Sciences Directorate, Redstone Arsenal, AL, 35898.*

Time resolved IR/THz double resonance (DR) spectroscopy has been performed with a Q-switched CO_2 laser and heterodyne detection. The effect of various collision partners; self, N_2, Ar, He, CO_2, and air on the temporal response of the strength of multiple rotational lines is analyzed. A rate equation model is implemented to solve for the rates of population exiting the directly pumped states. These collision partner dependent rates are then utilized to ascertain the potential for IR/THz DR spectroscopy for chemical detection at atmospheric pressures. Preliminary results indicate pumped state relaxation occurs at rates approximating gas kinetic collisions for collisions between CH_3F and N_2 , Ar, and He, while rates of collisions between CH_3F and CO_2 are faster. Additionally the rates between CH_3F and Air appear to follow those of N_2 as expected.

Intermission

RE07 15 min 10:20

ULTRAVIOLET PHOTODISSOCIATION DYNAMICS OF THE 1-PROPENYL RADICAL

MICHAEL LUCAS, *Department of Chemistry, University of California at Riverside, Riverside, CA 92521*; YU SONG, *Department of Chemistry, University of California at Davis, Davis, CA 95616*; JINGSONG ZHANG [a], *Department of Chemistry, University of California at Riverside, Riverside, CA 92521*; CHRISTOPHER BRAZIER, *Department of Chemistry and Biochemistry, California State University, Long Beach, Long Beach, CA 90840.*

Ultraviolet (UV) photodissociation dynamics of jet-cooled 1-propenyl radical (C_3H_5) were studied in the photolysis wavelength region of 224 to 248 nm using high-n Rydberg atom time-of-flight (HRTOF) and resonance enhanced multiphoton ionization (REMPI) techniques. The 1-propenyl radical were produced from 193-nm photolysis of 1-chloropropene and 1-bromopropene precursors. The H-atom photofragment yield (PFY) spectra have a broad peak centered around 230 nm. The H + C_3H_4 product translational energy distributions, $P(E_T)$'s, peak near $\sim$ 10 kcal/mol, and the fraction of average translational energy in the total excess energy, $\langle f_T \rangle$, is nearly a constant of $\sim$ 0.14 from 224 to 248 nm. The $P(E_T)$'s along with recent theoretical calculations indicate that H + propyne dissociation is the predominant H-atom product channel. The H-atom product angular distribution is isotropic, with the anisotropy parameter $\beta \sim 0$. The dissociation mechanism is consistent with unimolecular dissociation of hot 1-propenyl radical after internal conversion from the electronically excited state.

---

[a] Corresponding author.

RE08 15 min 10:37

OBSERVATION OF VIBRATIONALLY HOT CH_2CHO IN THE 351NM PHOTODISSOCIATION OF XCH_2CH_2ONO (X=F,Cl,Br,OH)

RABI CHHANTYAL-PUN, MING-WEI CHEN[a] and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

Alkyl nitrites have been used in the past as precursors for producing alkoxy radicals which are important intermediates in combustion and atmospheric chemistry. Substituted alkoxies, particularly hydroxy substituted alkoxy radicals, are important intermediates in the atmospheric chemistry of alkenes. In this talk we will present results obtained from the 351nm photodissociation of XCH_2CH_2ONO (X=F,Cl,Br,OH). The resulting photo-fragments were probed by laser induced fluorescence (LIF) technique downstream of a free-jet expansion. We were not able to observe any transitions resulting from the corresponding XCH_2CH_2O radicals except for FCH_2CH_2ONO. We were able to observe HCHO and also vibrationally hot CH_2CHO from all the different precursors. In CH_2CHO, there is a significant excitation in the CC torsion and CCO bend vibrations. There is also some excitation in CC stretching and CH_2 rock vibrations. HCHO is produced due to dissociation of XCH_2CH_2O in the ground state as the CC scission energy is less than the available photon energy.

---

[a] Present address: School of Chemical Science, University of Illinois at Urbana Champaign,106 Noyes Lab, 505 S. Mathews, Urbana, IL 61801

RE09 **15 min 10:54**

PRODUCT STATE AND SPEED DISTRIBUTIONS IN PHOTOCHEMICAL TRIPLE FRAGMENTATIONS

M.S. QUINN, G. DE WIT, B.R. HEAZLEWOOD, K. NAUTA, S.H. KABLE, and M.J.T. JORDAN, *School of Chemistry, University of Sydney, Sydney, NSW, 2006, Australia*; S.A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI, 53233, USA*; A.T. MACCARONE, *Department of Chemistry, University of Wollongong, Wollongong, NSW, 2522, Australia.*

The clearest dynamical signature of a roaming reaction is a very cold distribution of energy into the rotational and translational degrees of freedom of the roaming donor fragment (e.g. CO) and an exceptionally hot vibrational distribution in the roaming acceptor fragment (e.g. H_2, CH_4). These signatures were initially identified in joint experimental/theoretical investigations of roaming in H_2CO and CH_3CHO and are now being used to infer the presence of roaming mechanisms in other photodissociating molecules. In this seminar we present a phase space theory (PST) model of triple fragmentation (3F) and show that the dynamical signature of triple fragmentation is very similar to that of the roaming donor fragment.

The 3F-PST model assumes that the initial two-body fragmentation (2F) step occurs via a barrierless bond cleavage process (which is true for many many closed shell systems), and calculates the 2F-PST distribution of energy in each fragment. The 2F-PST model is benchmarked against $H_2CO \rightarrow H + HCO$, $CH_3CHO \rightarrow HCO + CH_3$, $CH_3CHO \rightarrow H + CH_3CO$, and $CH_3OCHO \rightarrow H + CH_3OCO$ and shown to provide a good representation of the available experimental data. Every fragment with sufficient internal energy to undergo subsequent spontaneous dissociation is allowed to dissociate and the 3F-PST distribution of energy into secondary products is calculated.

Using $CH_3CHO \rightarrow HCO + CH_3 \rightarrow H + CO + CH_3$ as an example, we calculate that the energy disposal into the product rotational and translational degrees of freedom of the secondary fragments is very low. In the case of the CO fragment this is similar to the dynamical signature for production of CO via a roaming mechanism. We compare the 3F-PST model with published experimental data for photodissociation of several molecules at energies above the 3F threshold, and demonstrate that, in some cases, 3F provides an alternative explanation for the observed product state distribution.

RE10 **15 min 11:11**

HYDROGEN ABSTRACTION FROM CH_3D BY CHLORINE RADICALS WITH VARYING KINECTIC ENERGY DISTRIBUTIONS

ANDREW E. BERKE, ETHAN H. VOLPA, F. FLEMING CRIM, *Chemistry Department, University of Wisconsin - Madison, Madison, Wisconsin 53706.*

Vibrationally driven hydrogen abstraction from methane and its isotopologues has become nearly ubiquitous as a standard in gas phase reaction dynamics studies. To obtain a more complete view of the reaction dynamics of the hydrogen abstraction reaction of CH_3D with Chlorine radicals, we have studied how a dramatic change in the kinetic energy distribution of the Cl radicals affects the abstraction dynamics of our system. To this end, we have performed pump-probe experiments, exciting the $2\nu_4$ CH_3D antisymmetric C-H stretch overtone, photolyzing Cl_2 with laser pulses of 309 nm, 355 nm, and 416 nm, then probing the products with (2+1) REMPI. We find both similarities and marked differences in the abstraction dynamics at the three different photolysis energies.

RE11 **15 min 11:28**

VIBRATIONALLY DRIVEN HYDROGEN ABSTRACTION BY THE BROMINE ATOM FROM CYCLOHEXANE

THOMAS J. PRESTON, MICHAEL A. SHALOSKI, and F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

Using ultrafast pump-probe spectroscopy, we study vibrationally driven bimolecular chemistry in the condensed phase. Our current focus is on the abstraction of hydrogen by the bromine atom from cyclohexane. This reaction has a barrier close in energy to that of a C-H stretch and also avoids isomer and complex complications seen in other systems. We produce bromine atoms using 400 nm photolysis of Br_2 and explore the influence of C-H excitation on the abstraction reaction in solution. We present here preliminary results of experiments probing the production of HBr and loss of bromine atoms through the use of infrared probing of the HBr fundamental and visible probing of the charge transfer transition of the cyclohexane and bromine atom complex.

RE12 **15 min 11:45**

THE MARRIAGE OF SPECTROSCOPY AND DYNAMICS: CHIRPED-PULSE FOURIER-TRANSFORM MM-WAVE (CP-FT-MMW) SPECTROSCOPY IN PULSED UNIFORM SUPERSONIC FLOWS

CHAMARA ABEYSEKERA, JAMES M. OLDHAM, ARTHUR G. SUITS, *Department of Chemsitry, Wayne State University, Detroit, MI 48202*; G. BARRATT PARK, ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*.

A new experimental scheme is presented that combines two powerful emerging technologies: chirped-pulse Fourier-transform mm-Wave spectroscopy and pulsed uniform supersonic flows. It promises a nearly universal detection method that can deliver quantitative isomer, conformer, and vibrational level specific detection, characterization of unstable reaction products and intermediates, and perform unique spectroscopic, kinetics, and dynamics measurements.

Chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy, pioneered by Pate and coworkers, allows rapid acquisition of broadband microwave spectrum through advancements in waveform generation and oscilloscope technology. This revolutionary approach has successfully been adapted to higher frequencies by the Field group at MIT.

Our new apparatus will exploit amplified chirped pulses in the range of 26-40 GHz, in combination with a pulsed uniform supersonic flow from a Laval nozzle. This nozzle source, pioneered by Rowe, Sims, and Smith for low temperature kinetics studies, produces thermalized reactants at high densities and low temperatures perfectly suitable for reaction dynamics experiments studied using the CP-mmW approach. This combination of techniques shall enhance the thousand-fold improvement in data acquisition rate achieved in the CP method by a further 2-3 orders of magnitude. A pulsed flow alleviates the challenges of continuous uniform flow, e.g. large gas loads and reactant consumption rates. In contrast to other pulsed Laval systems currently in use, we will use a fast piezo valve and small chambers to achieve the desired pressures while minimizing the gas load, so that a 10 Hz repetition rate can be achieved with one turbomolecular pump.

The proposed technique will be suitable for many diverse fields, including fundamental studies in spectroscopy and reaction dynamics, reaction kinetics, combustion, atmospheric chemistry, and astrochemistry. We expect a significant advancement in the ability to detect absolute populations of complex reaction products under near-nascent conditions, providing the powerful method of reaction dynamics with a universal spectroscopic probe capable of capturing the details of complex chemistry for specific product isomers and conformers.

RF. ASTRONOMICAL SPECIES AND PROCESSES

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 160 MATH ANNEX

Chair: NICHOLAS INDRIOLO, Johns Hopkins University, Baltimore, Maryland

RF01 **15 min 1:30**

THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

R. D. GEHRZ, *Department of Astronomy, University of Minnesota, 116 Church Street, S. E., Minneapolis, MN 55455*; E. E. BECKLIN, *Universities Space Research Association, NASA Ames Research Center, MS 211-3, Moffett Field, CA 94035.*

The joint U.S. and German Stratospheric Observatory for Infrared Astronomy (SOFIA) is a 2.5- meter infrared airborne telescope in a Boeing 747-SP. SOFIA can conduct photometric, spectroscopic, and imaging observations at wavelengths from 0.3 microns to 1.6 millimeters. At SOFIA's maximum service ceiling of 45,000 feet, the average transmission at these wavelengths is greater than 80 percent. SOFIA flys out of the NASA Dryden Flight Research Center aircraft operations facility at Palmdale, CA and the SOFIA Science Mission Operations (SMO) Center is located at NASA Ames Research Center, Moffett Field, CA. SOFIA's first-generation instrument complement includes broadband imagers and spectrographs that can resolve spectral features due to dust and large molecules, and high resolution spectrometers facilitating kinematic studies of molecular and atomic gas lines at km/s resolution. More than 30 science flights of 10 hours length (take-off to landing) were conducted in the past year. About 100 eight to ten hour flights per year are planned by 2014, and the observatory will operate until the mid-2030ÂŠs.

RF02 **15 min 1:47**

INFRARED SPECTROSCOPIC STUDIES WITH THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

R. D. GEHRZ, *Minnesota Institute for Astrophysics, University of Minnesota, 116 Church Street, S. E., Minneapolis, MN 55455*; E. E. BECKLIN, *Universities Space Research Association, NASA Ames Research Center, MS 211-3, Moffett Field, CA 94035.*

The joint U.S. and German Stratospheric Observatory for Infrared Astronomy (SOFIA) will be a premier facility for studying the physics and chemistry of the interstellar medium and the stellar evolution process for many decades. SOFIA's first-generation instrument complement includes broadband imagers and moderate resolution spectrographs capable of resolving spectral features due to dust and large molecules, and high resolution spectrometers suitable for kinematic studies of molecular and atomic gas lines at km/s resolution. SOFIA spectroscopic science results from the first flight sequences will be reviewed. We will present plans for future spectroscopic studies.

RF03 **15 min 2:04**

ROTATIONAL SPECTRA OF VIBRATIONALLY EXCITED HCL

BRIAN J. DROUIN, HARSHAL GUPTA, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

Survey spectra of a cold, inductively coupled discharge through He and HCl revealed a series of vibrationally excited transitions. The temperature dependence of these states was similar to that observed for the HCl cation and suggests a link in the formation or destruction mechanisms. Unlike the cation, the vibrational excitation was unaffected by larger concentrations of HCl and both were relatively insensitive to the pressure of the Helium buffer gas. Predictions based on band parameters from rotational spectra up to $v = 2$ and infrared overtone studies allowed rapid collection of spectra from $v = 0$ through $v = 8$ for both chlorine isotopologues. The new data set has been combined with existing rotational and infrared data in an isotope-independent Dunham model and fitted. We will compare this refined model to previous isotope-independent models of HCl.

RF04 **15 min 2:21**

THE ROTATIONAL SPECTRA OF OH DOUBLET PI ISOTOPOLOGUES

BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

Two new sources of THz radiation have enabled in depth studies of the rest frequencies for rarer isotopologues of the hydroxyl radical (OH). These sources operate from 1.4-2.0 THz and 2.47-2.75 THz, and span the fundamental transitions for OH $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ and its rare oxygen isotopologues. Transitions for OD and several v = 1 states are also accessible. The new measurements add significantly to the wealth of high-resolution measurements for the OH radical. Analyses using combined data sets are underway, with the goal of providing a full isotope-independent Dunham analysis. Measurements include the rare ^{17}OH and ^{17}OD isotopologues, we will present the magnetic and electric quadrupole hyperfine parameters for ^{17}O and compare these to values determined via LMR, EPR and theory.

RF05 **15 min 2:38**

MICROWAVE STUDY OF METHYL FORMATE IN THE NEW VIBRATIONAL EXCITED STATES

YUSUKE SAKAI, KAORI KOBAYASHI, *Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan*; MASAHIRO TSUKAMOTO, MASAHARU FUJITAKE, and NOBUKIMI OHASHI, *Kanazawa University, Japan.*

The methyl formate molecule is a typical example of the molecule with high spectral density found in interstellar space. We have recently identified methyl formate in its second torsional excited state in Orion KL [a]. The observed intensity suggests the possible detection of the transitions of this molecule in the higher vibrational states, which prompted us to conduct this study. The accumulated microwave spectral data taken at the University of Toyama was used to search for the excited state with the aid of the computer program developed at Kanazawa University. We have assigned series of lines in the two new vibrational excited states. There seems to exist perturbation between these two states. The results of the fit and the origin of these two states will be presented.

---

[a] S. Takano *et al.*, *Accepted to Publications of the Astronomical Society of Japan*

RF06 **15 min 2:55**

LABORATORY STUDY OF THE ROTATIONAL SPECTRUM OF 2-BUTANONE

JAY A. KROLL and SUSANNA L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; STEVEN T. SHIPMAN, *Division of Natural Sciences, New College of Florida, Sarasota, FL 34243..*

Our recent observations of the Orion-KL region in the λ = 1.3 mm window reveal that $\sim$55% of the observed transitions cannot be assigned to previously identified molecules. In addition, the strongest unidentified transitions have peak intensities on the order of 7 K. This provides strong evidence that new molecules of astrochemical interest need to be studied in the laboratory in order to compare to interstellar spectra. A starting point for this work is to target complex organic molecules that are structurally-similar to molecules that have already been detected in interstellar environments. We have therefore collected the microwave, millimeter, and submillimeter spectra of 2-butanone [also known as methyl ethyl ketone (MEK), $CH_3COCH_2CH_3$]. MEK is a likely candidate for detection in the ISM because it contains similar functional groups to known and highly abundant interstellar molecules such as ethanol, acetaldehyde, and acetone. The microwave spectrum of MEK was acquired with the chirped-pulse waveguide Fourier Transform Microwave (CP-FTMW) spectrometer at New College of Florida; and the millimeter and submillimeter spectrum was acquired with the direct absorption flow cell spectrometer at Emory University. We have collected the spectrum of MEK from 8 GHz to 1 THz and assigned the ground vibrational state spectrum of MEK from 8 GHz to 500 GHz using the ERHAM program. We will report here on the laboratory characterization and assignment of the MEK spectrum. We will also report on the analysis of observational lines surveys in the context of the identification of new, complex organic molecules such as MEK.

Intermission

RF07 **15 min 3:30**

USING HOT EMISSION SPECTRA IN GENERATING LINE LISTS OF MOLECULES (NH_3, CH_4) FOR ASTROPHYSICAL APPLICATIONS

R.J. HARGREAVES, L. MICHAUX, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; G. LI, *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, MS#50, 60 Garden St., Cambridge, MA, 02138,USA*; C. BEALE, *Department of Chemistry & Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, VA, 23529-0126, USA*; M. IRFAN, *School of Physics and Astronomy, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK*; and P.F. BERNATH, *Department of Chemistry & Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, VA, 23529-0126, USA; and University of York, Dept. of Chemistry, Heslington, York, YO10 5DD, UK.*

Spectra of cool stars, brown dwarfs and extrasolar planets (exoplanets) contain a dense forest of lines from hot molecules. Examples include CH_4 and NH_3 in brown dwarfs and CH_4 in 'hot Jupiter' exoplanets. These observations present challenges to astronomers, who typically use databases such as HITRAN intended for room-temperature applications, to model the spectral energy distributions. We have used a novel technique to combine 'hot' emission spectra recorded for a range of sample temperatures (300 – 1400°C) in order to deduce empirical lower state energies of the emitted lines. We have applied this method to NH_3 in the 740 – 2100 cm^{-1} range[a] which includes the ν_2 and the ν_4 fundamental modes and in the 1650 – 4000 cm^{-1} range[b] which includes the ν_1 and ν_3 fundamental modes. We have estimated empirical lower state energies and our values have been incorporated into the line lists along with line positions and calibrated line intensities. This method is currently being extended to CH_4. Our results can be used directly for the simulation of astronomical spectra.

---

[a] Hargreaves, R. J., Li, G., and Bernath, P. F. *Astrophys. J.* **735** (2011) 111.

[b] Hargreaves, R. J., Li, G., and Bernath, P. F. *J. Quant. Spectrosc. Radiat. Transfer*, (2012) in press.

RF08 **15 min 3:47**

BROADBAND SCREENING FOR INTERSTELLAR SPECIES: ADDITIONAL LABORATORY MEASUREMENTS AND INTERSTELLAR DETECTION OF ETHANIMINE (CH_3CHNH) IN SGR B2(N)

RYAN A. LOOMIS, DANIEL P. ZALESKI, AMANDA L. STEBER, JUSTIN L. NEILL, MATT T. MUCKLE, NATHAN A. SEIFERT, and BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904*; VALERIO LATTANZI, OSCAR MARTINEZ, JR., and MICHAEL C. MCCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138*; ANTHONY J. REMIJAN, *National Radio Astronomy Observatory, 520 Edgemont Rd., Charlottesville, VA 22904.*

As the availability of publicly accessible spectral line surveys from radio astronomy increases, new approaches to the identification of molecules in the interstellar medium are possible. We have performed reaction product screening measurements using broadband rotational spectroscopy to identify potential matches in the laboratory and radio astronomy spectra. A broadband spectrum of an electrical discharge of CH_3CN and H_2S contained several matches to unidentified features in the GBT PRIMOS Survey[a] of Sgr B2(N) that did not have molecular assignments in the radio astronomy spectral catalogs. These transitions have been assigned to the E- and Z-isomers of ethanimine (CH_3CHNH). The rotational spectrum of the E and Z isomers of CH_3CHNH have been reported at mm-wave frequencies in 1980 by Lovas et al.[b] and then in 1981 by Brown et al.[c] The analysis of the rotational spectra of these two isomers has been extended to the microwave frequency region to verify the assignments from the GBT PRIMOS Survey. Combined fits over the range of 8 to 130GHz consisting of data from Lovas et al., broadband CP-FTMW measurements, and cavity double resonance measurements are presented for both isomers. Evidence for the detection of both isomers in Sgr B2(N) is shown along with a discussion of the method of their detection and a brief analysis of possible formation routes.

---

[a] GBT PRIMOS Survey, http://www.cv.nrao.edu/ aremijan/PRIMOS

[b] F. J. Lovas, R. D. Suenram, D. R. Johnson, F. O. Clark, E. Tiemann, *J. Chem. Phys.*, **72**, 4964-4972, (1980).

[c] R. D. Brown, P. D. Godfrey, D. A. Winkler, *Chem. Phys.*, **59**, 243-247, (1981).

RF09 **10 min 4:04**

UNRAVELING THE COMPLEX NEAR-UV SPECTRUM OF Si_2C

N. J. REILLY and M. C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138*; D. L. KOKKIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*; R. C. FORTENBERRY, and T. D. CRAWFORD, *Department of Chemistry, Virginia Tech, Blacksburg, VA 24061.*

Though it has yet to be detected in space, there is good reason to believe that the disilicon carbide molecule, Si_2C, is an abundant constituent of circumstellar shells such as IRC+10216, in which the isovalent ionic ring SiC_2 is highly conspicuous. Si_2C exhibits a surprisingly complicated R2C2PI spectrum, which EOM-CCSD calculations indicate arises from a bent-to-linear transition involving several interacting electronic states in the region of vertical excitation. Some of the observed spectral features show well-resolved emission spectra when probed by LIF/DF, yielding vibrational frequencies in excellent agreement with *ab initio* and matrix IR studies of the ground electronic state. Partially resolved rotational structure for these bands, which appear to be dominated by a vibronically allowed transition to a dark A_2 state, suggests a ground state bond angle significantly larger than predicted by theory. Owing to the presence of overlapping, unresolved bands, in addition to spectral contamination from Si_2 and SiC, further experimental characterization would appear ideally suited to a two-dimensional fluorescence approach.

RF10 **15 min 4:16**

LABORATORY DETECTIONS OF CYANOTHIOFORMALDEHYDE (HCSCN) AND MERCAPTOACETONITRILE ($HSCH_2CN$) BY CP-FTMW SPECTROSCOPY

DANIEL P. ZALESKI, JUSTIN L. NEILL, MATT T. MUCKLE, NATHAN A. SEIFERT, AMANDA A. STEBER, BRENT J. HARRIS, AND BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904*; VALERIO LATTANZI AND MICHAEL MCCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.*; ANTHONY J. REMIJAN, *National Radio Astronomy Observatory, 520 Edgemont Rd., Charlottesville, VA 22904..*

We have previously reported results for reaction product screening of potential interstellar molecules using broadband rotational spectroscopy. This approach was applied to the reaction products created in an electrical discharge of CH_3CN and H_2S [a]. By screening the product mixture with molecular rotational spectroscopy it is possible to directly compare laboratory and observatory surveys to identify overlapping transitions. Also, as the product molecules are identified, it becomes possible to propose the formation mechanism in the experiment and use this chemical insight to propose new candidate products. For the electrical discharge chemistry of CH_3CN and H_2S radical-radical recombination reactions followed by elimination of molecular hydrogen were inferred to be important and has led to the laboratory identification of additional products âĂŞ HCSCN and $HSCH_2CN$. A previous mm-wave study of HCSCN motivated by its possibility as an interstellar species reported a pure rotational spectrum different form the one we obtain [b]. A Kraitchman substitution structure confirms the assignment of our spectrum to HCSCN. Possible causes for the discrepancy in microwave and mm-wave rotational spectroscopy results will be discussed. The $HSCH_2CN$ rotational spectrum shows two low-lying torsional levels that can interact through proton tunneling as is observed in the structurally similar propargyl alcohol. The design of a 40-60 GHz CP-FTMW, used to aid in the laboratory analysis of HCSCN, is also briefly presented.

---

[a] D.P. Zaleski *et al.* 66th OSU ISMS: WF01.

[b] M. Bogey *et al.* *JACS*, 111, (1989), 7399.

RF11 **10 min 4:33**

HIGH RESOLUTION SPECTRUM OF THE $^{13}C^{12}C^{12}C$ LOWEST BENDING MODE

C. P. ENDRES, V. LUTTER, J. KÖTTING, J. KRIEG, S. THORWIRTH, S. SCHLEMMER, T. F. GIESEN, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; M. E. HARDING, *Karlsruher Institut für Technologie, Institut für Nanotechnologie, 76021 Karlsruhe, Germany*; J. VÁZQUEZ, *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA.*

Linear C_3 is a floppy molecule which possesses an extremely low lying bending mode, ν_2, at roughly 60 cm^{-1} or 1.9 THz. Based on highly accurate laboratory data[a,b,c] C_3 has been detected in various astronomical sources[d,e] most recently with the HIFI instrument aboard the Herschel satellite[f]. Although C_3 turns out to be quite abundant in interstellar environments which makes a search for ^{13}C substituted isotopologs feasible, other isotopologs could not be detected so far, because no accurate transition frequencies have been available for these species in this frequency range. Relative abundance ratios of C_3 isotopologs might give important hints on its building mechanism and further constraints for chemical networks.

In this work, the spectrum of the ν_2 lowest bending mode of ^{13}CCC has been investigated. We used laser ablation of ^{13}C enriched carbon samples to record absorption spectra in a supersonic jet expansion. The radiation in our setup is generated by a synthesizer referenced to a Rubidium standard in combination with a frequency multiplier chain and detected by a liquid Helium cooled InSb bolometer. The laboratory search has been supported by high-level coupled-cluster calculations, which turns out to compare very favorably with obtained experimental molecular parameters.

---

[a] Schmuttenmaer, C. A., Cohen, R. C., Pugliano, N., Heath, *et al.*, *Sience* **249**, 897−900 (1990)

[b] Giesen, T. F., van Orden, A. O., Cruzan, J. D., and Provencal, R. A., *et al.*, *Astrophys. J.* **551**, L181−L184 (2001)

[c] Gendriesch, R. and Pehl, K. and Giesen, T. and Winnewisser, G. and Lewen, F., *Z. Naturforsch.* **58a**, 129−138 (2003)

[d] Van Orden, A., Cruzan, J. D., Provencal, R. A., *et al. in Proc. Airborne Astronomy Symp., ASP Conf. Ser.* **73**, 67 (1995)

[e] Cernicharo, J. and Goicoechea, J. R. and Caux, E., *Astrophys. J. Lett.* **534**, L199−L202 (2000)

[f] Mookerjea, B., Giesen, T., Stutzki, J., Cernicharo, J., *et al.*, *Astron. Astrophys.* **521**, L13 (2010)

RF12 **15 min 4:45**

ASSIGNMENTS, PERTURBATIONS, PATHOLOGIES AND A ROTATIONAL ANALYSIS OF THE SPECTRUM OF CH_2DOH

JOHN C. PEARSON, SHANSHAN YU, BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109.*

Theory and analysis of three-fold internal rotors is a well established science allowing for a wide variety of molecules to be successfully analyzed to experimental accuracy. However, once the three-fold symmetry is broken with the substitution of a single deuterium, the problem becomes much less well described either theoretically or experimentally. CH_2DOH is rapidly formed on grains in the interstellar medium at low temperatures where it is energetically favorable for atomic deuterium to replace hydrogen in the methyl rotor of methanol. Additionally, the three equivalent ways to substitute in the methyl rotor suggest that CH_2DOH will be at least three times as abundant as CH_3OD. The observational evidence does not always support this assertion potentially because the intensities of CH_2DOH are poorly understood. An analysis of over 8000 transitions in the three torsional substates of the ground torsional state of CH_2DOH will be presented. Analysis of the data set shows a number of pathologies both in the energy level structure as well as with the labeling of transitions for this class of molecules. The analysis shows some surprising deviations from available theory. A number of assignments and pathologies in the excited torsional states will be presented as well.

RF13 **15 min 5:02**

THZ AND LONG PATH FOURIER TRANSFORM SPECTROSCOPY OF METHANOL; TORSIONALLY COUPLED HIGH-K LEVELS

JOHN C. PEARSON, SHANSHAN YU, BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109*; RONALD M. LEES, LI-HONG XU, *Centre for Laser, Atomic and Molecular Sciences (CLAMS) Physics Department University of New Brunswick, 100 Tucker Park Road, Saint John, NB, Canada E2L 4L5*; BRANT E. BILLINGHURST, *Canadian Light Source Inc, University of Saskatchewan, 100 Perimeter Drive, Saskatchewan, SK, Canada S7N 0X4.*

Methanol is nearly ubiquitous in the interstellar gas. The presence of both $a-$type and $b-$type dipole moments, asymmetry, and internal rotation assure that any small astronomical observation window will contain multiple methanol transitions. This often allows a great deal about the local physical conditions to be deduced, but only insofar as the spectra are characterized. The Herschel Space Observatory has detected numerous, clearly beam diluted, methanol transitions with quanta surpassing J = 35 in many regions. Unfortunately, observations of methanol often display strong non-thermal behavior whose modeling requires many additional levels to be included in a radiative transfer analysis. Additionally, the intensities of many more highly excited transitions are strongly dependent on the accuracy of the wave functions used in the calculation. We report a combined Fourier Transform Infrared and THz study targeting the high J and K transitions in the ground torsional manifold. Microwave accuracy energy levels have been derived to $J > 40$ and K as high as 20. These levels illuminate a number of strongly resonant torsional interactions that dominate the high K spectrum of the molecule. Comparison with levels calculated from the rho-axis method Hamiltonian suggest that the rho-axis method should be able to model $\mathrm{v}_t = 0$, 1 and probably $\mathrm{v}_t = 2$ to experimental accuracy. The challenges in determining methanol wave functions to experimental accuracy will be discussed.

RF14 **15 min 5:19**

ON THE ELECTRONIC SPECTROSCOPY OF CLOSED SHELL CATIONS DERIVED FROM RESONANCE STABILIZED RADICALS: INSIGHTS FROM THEORY AND FRANCK-CONDON ANALYSIS

TYLER P. TROY, SCOTT H. KABLE, TIMOTHY W. SCHMIDT, *School of Chemistry, The University of Sydney, NSW 2006, Australia*; SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

Recent attention has been directed on closed shell aromatic cations as potential carriers of the diffuse interstellar bands. The spectra of mass-selected, matrix-isolated benzylium and tropylium cations were recently reported [Nagy, A., Fulara, J., Garkusha, I. and Maier, J. P. (2011), *Angew. Chem. Int. Ed.*, 50: 3022-3025]. The benzylium spectrum shows an extended progression in a low frequency (510 cm^{-1}) ring distortion mode. Modeling of the benzylium spectrum using (TD)DFT and MCSCF-PT2 methods in concert with multidimensional Franck-Condon (FC) analysis is found to yield excellent agreement with the experimental spectrum. We extended this analysis to larger (2 and 3 ring) PAH cations derived from resonance stabilized radicals, which are predicted to show strong $S_0 \rightarrow S_n$ transitions in the visible region. The FC progression is significantly quenched in the larger species, and our results for 1-napthylmethylium are in excellent agreement with very recent experiments [Nagy, A., Fulara, J., and Maier, J. P. (2011), *J. Am. Chem. Soc.*, 133, 19796]. Since carriers of the DIBs should exhibit spectra dominated by a single vibronic transition, our results demonstrate that closed-shell cations may present spectra with the required properties. Furthermore, the calculated ionization energies of a range of CSCs were found to be in the 13-14 eV range, consistent with variations in behaviour of the DIB carriers with respect to various astrophysical environments.

RG. ELECTRONIC

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 170 MATH ANNEX

Chair: YEN-CHU HSU, Academia Senica, Taipei, Taiwan

RG01 **10 min 1:30**

DIRECT POTENTIAL FITTING FOR THE $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ STATES OF Br_2

TOKIO YUKIYA, NOBUO NISHIMIYA, MASAO SUZUKI, *Department of Electronics and Information Technology, Tokyo Polytechnic University, Iiyama 1583, Atsugi City, Kanagawa 243-0297, Japan*; ROBERT J. LE ROY, *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.*

Bromine dimer has been studied by many researchers in various wavelength regions. The $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ states have been well observed using magnetic rotation spectroscopy,[a] by laser-induced fluorescence,[b,c] by laser absorption,[d] by Fourier transform absorption,[e] and by UV emission.[f] This yields a data set consisting of 16916 transitions in which the observed vibrational levels for the $X\,^1\Sigma_g^+$ and $A\,^3\Pi_{1u}$ states span 83% and 99% of the potential well depths, respectively, with the highest observed vibrational level of the $A\,^3\Pi_{1u}$ state lying only 2 cm^{-1} below the dissociation limit.[a] In order to provide the most compact and comprehensive description of these data, and the ability to make reliable predictions outside their range, we have chosen to perform a "direct potential fit" (DPF), rather than a conventional Dunham-expansion analysis. In particular, accurate analytic potential energy functions for the $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ states are determined from a combined-isotopologue DPF analysis that also yields the electronic isotope shift, the Ω-doubling radial strength function, and an experimental value for the long-range inverse-power C_5 constant of the $A\,^3\Pi_{1u}$ state, as well as centrifugal Born-Oppenheimer Breakdown (BOB) functions for both states. To reveal characteristics of the $A\,^3\Pi_{1u}$ state, band constants calculated from these potentials are compared with those determined from a conventional parameter-fitting analysis reported by Coxon.[g]

---

[a] C. D. Boone, PhD Thesis, University of British Columbia (1999).

[b] C. Focsa *et al.*, J. Mol. Spectrosc. 200, 104 (2000).

[c] D. J. Postell *et al.*, to be published.

[d] N. Nishimiya *el al.*, Columbus Meeting, paper WH02 (2005).

[e] S. Gerstenkorn *et al.*, J. Physique, 48, 1685 (1987).

[f] P. Venkateswarlu *et al.*, J. Mol. Spectrosc. 96, 247 (1982).

[g] J. A. Coxon, J. Mol. Spectrosc. 41, 548 (1972).

RG02 **15 min 1:42**

ANALYSIS OF THE VISIBLE ABSORPTION SPECTRUM OF I_2 IN INERT SOLVENTS USING A PHYSICAL MODEL

J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235.*

Absorption spectra of I_2 dissolved in n-heptane and CCl_4 are analyzed with a quantum gas-phase model, in which spectra at four temperatures between 15C and 50C are least-squares fitted by bound-free spectral simulations to obtain estimates of the excited-state potential energy curves and transition moment functions for the three component bands: $A - X$, $B - X$, and $C - X$. Compared with a phenomenological band-fitting model used previously on these spectra, the physical model (1) is better statistically, and (2) yields component bands with less variability. The results support the earlier tentative conclusion that most of the 20 percent gain in intensity in solution is attributable to the $C - X$ transition. The T-dependent changes in the spectrum are accounted for by potential energy shifts that are linear in T and negative (giving red shifts in the spectra) and about twice as large for CCl_4 as for heptane. The derived upper potentials resemble those in the gas phase, with one major exception: In the statistically best convergence mode, the A potential is much lower and steeper, with a strongly varying transition moment function. This observation leads to the realization that two markedly different potential curves can give nearly identical absorption spectra.

RG03 5 min 1:59

WAVELENGTH ANOMALIES IN UV-Vis SPECTROPHOTOMETRY

J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235.*

Commercial spectrophotometers are great tools for recording absorption spectra of low-to-moderate resolution and high photometic quality. However, in the case of at least one such instrument, the Shimadzu UV-2101PC (and by assumption, similar Shimadzu models), the wavelength accuracy may not match the photometric accuracy. In fact the wavelength varies with slit width, spectral sampling interval, and even the specified range, with a smoothing algorithm invoked any time the spectrum includes more than 65 sampled wavelengths. This behavior appears not to be documented anywhere, but it has been present for at least 20 years and persists even in the latest software available to run the instrument. The wavelength shifts can be as large as 1 nm, so for applications where wavelength accuracy better than this is important, wavelength calibration must be done with care to ensure that the results are valid for the parameters used to record the target spectra.

RG04 15 min 2:06

DEPERTURBATION STUDIES OF AlO : INTERACTIONS IN THE $A^2\Pi \sim X^2\Sigma^+$ STATES

K. SUNANDA, M. D.SAKSENA, and B. N. JAGATAP, *Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085,India*; M. N. DEO, *High Pressure Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*; N. MHASKE and S. H. BEHERE, *Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India.*

The rotational structure of $D^2\Sigma^+$ - $A^2\Pi$ band system of AlO molecule, at moderate high resolution, was photographed by Singh et. al[a]. They carried out the rotational analyses of seven bands of this system, involving vibrational levels v′= 0 - 5 and v″= 0 - 4 for both the sub-transitions $D^2\Sigma^+$ - $A^2\Pi_{1/2}$ and $D^2\Sigma^+$ - $A^2\Pi_{3/2}$ and reported several rotational perturbations in the $A^2\Pi_i$ state. In this work, we present a deperturbation analysis which yields deperturbed molecular constants of the $X^2\Sigma^+$, $A^2\Pi_i$, and $D^2\Sigma^+$ states. The revised molecular parameters for the $X^2\Sigma^+$ and $D^2\Sigma^+$ states are first obtained from a simultaneous fit performed using previous high resolution data of the $D^2\Sigma^+$ - $X^2\Sigma^+$ system [b] involving v′=0 - 6 and v″= 0 - 4 vibrational levels and $B^2\Sigma^+$ - $X^2\Sigma^+$, system [c] involving v′= 0 - 11 and v″= 0 - 7 vibrational levels. PGOPHER program is used to simulate and fit the observed spectra[d] . The branch frequencies involving the $D^2\Sigma^+$ - $A^2\Pi_i$ transitions from our earlier studies have been incorporated into a single Hamiltonian to obtain improved molecular constants together with the L- doubling and spin splitting coefficients for these states. Further, invoking perturbing state ($X^2\Sigma^+$) molecular parameters in this fit, deperturbation of the vibrational levels within the $A^2\Pi_i$ state of AlO up to v″ = 4 is obtained. A global least squares fit to all the data allows determination of $A^2\Pi_i$ state molecular constants with much improved precision. The results of this study will be presented.

---

[a] M. Singh and M. D. Saksena, Can. J. Phys. 63, 1162 (1985).

[b] M. Singh and M. D. Saksena, Proc. Indian Acad. Sci. 77, 139 (1973).

[c] M. D. Saksena, M. N. Deo, K. Sunanda, S. H. Behere and C. T. Londhe, 247, 47(2008).

[d] PGOPHER, a Program for Simulating Rotational Structure, C. M.Western, University of Bristol.

RG05 15 min 2:23

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $A^2\Pi$–$X^2\Sigma^+$ (RED) SYSTEM OF $^{13}C^{14}N$.

R.S. RAM, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA*; and P.F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 USA; Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.*

High resolution emission spectra of the $A^2\Pi$–$X^2\Sigma^+$ transition of $^{13}C^{14}N$ have been measured in the 15000–24000 cm^{-1} region. Molecules were produced by the reaction of $^{13}CH_4$ and $^{14}N_2$ in an active nitrogen afterglow discharge. The spectra were recorded using the Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory. A rotational analysis of 27 bands involving the excited state vibrational levels v′ = 9–22 and the ground state vibrational levels up to v″ = 12 has been obtained. A much improved set of spectroscopic constants have been determined for the v = 0–22 vibrational levels of the $A^2\Pi$ state by combining the present measurements with those reported previously for the v = 0–8 vibrational levels of the $A^2\Pi$ state[a] and existing infrared and millimeter-wave measurements of $^{13}C^{14}N$. The 6–3, 7–4, 8–5 and 9–6 bands of the $B^2\Sigma^+$–$A^2\Pi$ transition were also identified in the 23300–24000 cm^{-1} region and were included in the final analysis. An experimental line list and calculated term values are provided.

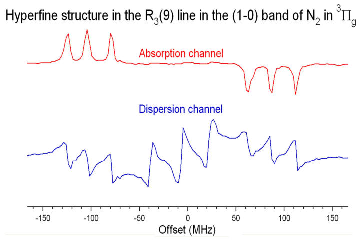
---

[a] Ram et al., Astrophys. J. Suppl. Ser., 188, (2010), 500.

RG06 **15 min 2:40**

HYPERFINE-RESOLVED SATURATION SPECTROSCOPY OF METASTABLE N_2 IN THE (1-0) BAND OF THE $\tilde{B}^3\Pi_g - \tilde{A}^3\Sigma_u^+$ ELECTRONIC TRANSITION

D. FORTHOMME, C. MCRAVEN, G. E. HALL, T. J. SEARS, *Chemistry Department, Brookhaven National Laboratory, Bldg. 555A, P.O. Box 5000, Upton, NY 11973, USA.*



A spectrometer for measuring sub-Doppler saturation spectra in a discharge flow cell has been built and tested on the (1-0) band of the $\tilde{B}^3\Pi_g - \tilde{A}^3\Sigma_u^+$ electronic transition of $^{14}N_2$ near 11250 cm^{-1}. A cw Ti:sapphire laser is stabilized relative to a single frequency HeNe laser and offset scanned with a RF synthesizer. An amplitude-modulated bleach beam is counter-propagated with a phase-modulated probe beam through the discharge cell. Absorption and dispersion phase signals are demodulated in a probe beam receiver, then demodulated at the lower bleach modulation frequency and finally averaged with lock-in detection at the audio frequency of the AC-discharge. Isolated hyperfine lines are observed with a FWHM of about 7 MHz and the splittings can be recorded with a precision of a few hundred kHz. Comparisons will be made with more extensive prior work by Giesen et al.[ab]

---

[a] H. Geisen, D. Neuschäfer and Ch. Ottinger, Z. Phys. D. 4 (1987) 263-290

[b] H. Geisen, D. Neuschäfer and Ch. Ottinger, Z. Phys. D. 17 (1990) 137-144

RG07 **15 min 2:57**

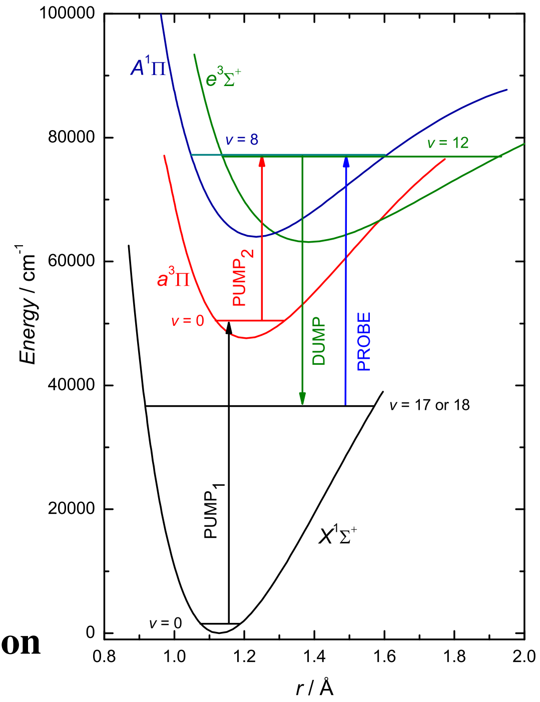
PRODUCTION OF A BEAM OF HIGHLY VIBRATIONALLY EXCITED CO USING PERTURBATIONS

N. BARTELS, T. SCHÄFER, J. HÜHNERT, A. M. WODTKE, *Georg August Universität Göttingen, Institut für Physikalische Chemie, Tammanstrasse 6, 37075 Göttingen, Germany*; and R. W. FIELD, *Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA.*

For many experimentalists (especially those, who are not spectroscopists), molecular pertubations are a curse, as they make assignments and analysis of spectral data more difficult. Nevertheless, they can also be a boon!

In this talk we will show how a molecular beam of CO in high vibrational states ($v = 17, 18$) can be prepared by an optical pumping scheme that we call PUMP-PUMP-PERTURB and DUMP (P^3D). P^3D exploits the loaning, via spin-orbit perturbations, of the large oscillator strength of the 4th positive system, $A^1\Pi \leftarrow X^1\Sigma^+$, to the triplet manifold. This allows some nominally spin-forbidden transitions to be exploited in multistep optical pumping schemes.

The ability to *state-selectively* prepare CO in high vibrational states opens up new opportunities for molecular beam scattering experiments.



Intermission

RG08 **15 min 3:30**

IS THE EQUILIBRIUM STRUCTURE OF BeOH LINEAR OR BENT?

KYLE J. MASCARITOLO, JEREMY M. MERRITT, and MICHAEL C. HEAVEN,
Department of Chemistry, Emory University, Atlanta, GA 30322.

The hydroxides of Ca, Sr, and Ba are known to be linear molecules, while MgOH is quasilinear. High-level ab initio calculations for BeOH predict a bent equilibrium structure with a bond angle of 140.9°, indicating a significant contribution of covalency to the bonding. However, experimental confirmation of the bent structure is lacking. IR and ESR spectra for matrix-isolated BeOH have been interpreted under the assumption of a linear equilibrium structure. Low resolution electronic spectra have been reported for gas phase BeOH and BeOD[a] but they have not been analyzed. In the present study we have used resonantly enhanced multiphoton ionization, with mass resolved ion detection, to observe the near UV electronic band systems of BeOH and $Be^{18}OH$. Rotationally resolved data have been obtained, which yield preliminary rotational constants. However, the resolution was not sufficient to show the asymmetry splttings that would be expected for a bent geometry. Experiments are now in progress to examine the rotational structure of BeOD, which should provide better constraints on the bond angle in both the ground and excited states. Results for both BeOH and BeOD will be reported.

---

[a] A. Antic-Jovanonvic, V. Bojovic, and D. Pesic *Spectrosc. Lett.* **21**(8),757-765 1988.

RG09 **15 min 3:47**

AN EXPERIMENTAL AND QUANTUM CHEMICAL STUDY OF THE ELECTRONIC SPECTRUM OF THE HBCl FREE RADICAL

MOHAMMED A. GHARAIBEH, RAMYA NAGARAJAN and DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*; RICARDO TARRONI, *Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy.*

The chloroborane (HBCl) free radical has a complex electronic spectrum in the visible that involves a transition from a bent ground state to a linear excited state, both of which are the Renner-Teller components of what would be a $^2\Pi$ state at linearity. We have used the synchronous-scan LIF and single vibronic level emission techniques to untangle the many overlapping vibronic bands and assign upper state K quantum numbers for jet-cooled HBCl and DBCl. The radicals were produced in a pulsed electric discharge jet using a precursor mixture of boron trichloride (BCl_3) and hydrogen or deuterium in high-pressure argon. As an important aid to understanding the data, the ground and excited state high level *ab initio* potential energy surfaces (PES) have been calculated and the vibrational levels obtained variationally. The calculated ground state levels are in excellent agreement with the emission data validating the quality of the PES. Aside from an approximately 100 cm^{-1} shift in the upper state electronic term value, the calculated excited state vibrational energy levels and isotope shifts match the LIF data very well, allowing the observed bands to be assigned with confidence.

RG10 **15 min 4:04**

GAS PHASE SPECTROSCOPIC INVESTIGATION OF CHROMATE-ESTERS

SYDNEY H. KAUFMAN and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

Chromate and dichromate ions are frequently used in the oxidation of alcohols. Chromate esters containing a Cr–O–C bridge are thought to be important intermediates in such reactions. We report the photofragment action spectra of two chromate ester complexes in the UV and visible regions, both of which primarily undergo cleavage of the chromate ester bond resulting in reduction of the chromate from Cr(VI) to Cr(V). Comparison to the UV/Vis absorption spectrum of a methanolic dichromate solution suggests the electronic transitions are the same ligand-to-metal charge transfer transitions in both environments. Comparing the spectral features for different fragment channels leads to insight into the energetics and fragmentation mechanism of these species.

RG11 15 min 4:21

ELECTRONIC SPECTROSCOPY OF THE NO-X (X = RARE GAS, ALKANE) COMPLEXES

ADRIAN M. GARDNER, VICTOR TAMÉ-REYES, JOE HARRIS, JODIE McDANIEL and TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

The Rydberg states of the complexes of nitric oxide with rare gases and small alkane molecules have been investigated using (1 + 1) and (2 + 1) Resonance Enhanced Multiphoton Ionization, REMPI, spectroscopy. Trends in dissociation energies within the ligand groups, along with trends in increasing principal quantum number of the Rydberg states will be discussed. Rationalization is aided through the implementation of high level *ab initio* calculations.

RG12 15 min 4:38

GAS PHASE ELECTRONIC PHOTODISSOCIATION SPECTRA OF COPPER NITRATE CLUSTER IONS

SYDNEY H. KAUFMAN, CASEY R. CHRISTOPHER and J. MATHIAS WEBER, *JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.*

We report UV photodissociation action spectra of copper nitrate cluster anions $Cu(NO_3)_3^-$. The parent ion decays upon electronic excitation by loss of neutral NO_3 fragment. THe gas phase spectrum is similar to but slightly more structured than UV absorption spectra of solutions of the parent salt $Cu(NO_3)_2$. We discuss our experimental results in the framework of quantum chemical calculations.

RG13 15 min 4:55

THE OPTICAL SPECTRUM OF THE SILICON TERMINATED CARBON CHAINS SiCnH

D. L. KOKKIN, *IRAP; Université de Toulouse, UPS; CNRS; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France and Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138*; N. J. REILLY, and M. C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138*; R. C. FORTENBERRY, and T. D. CRAWFORD, *Department of Chemistry, Virginia Tech, Blacksburg, VA 24061.*

The gas phase optical spectra of the silicon terminated carbon chains, SiC_nH (n=3-5) formed in a silane acetylene discharge, have been investigated by R2C2PI and LIF/DF and will be reported here for the first time. Complementary to the experimental work, a theoretical investigation was undertaken with coupled cluster methods to garner a comprehensive understanding of the molecular structures and electronic properties of these systems. For the linear chains where there is an odd number of carbon atoms (SiC_3H and SiC_5H), the observed transitions are primarily from a $^2\Pi$ ground state to a $^2\Sigma$ state, but as in the case of isovalent carbon chains there are some Herzberg-Teller active modes from an excited $^2\Pi$ state. While a strong $\Pi - \Pi$ transition is predicted for SiC_4H, the spectrum is dominated by relatively dark sigma state which is vibronically coupled to the bright $^2\Pi$ state. In contrast to the odd carbon chains, which exhibit relatively sharp spectral features and lifetimes in the 10-100 ns regime, SiC_4H shows broadened spectral features consistent with a ca. 10 ps lifetime, and a subsequent long-lived decay ($>$ 30 microseconds) which we tentatively interpret in terms of mixing with a nearby quartet state arising from the same electronic configuration, a process unavailable for the odd chains.

RG14 15 min 5:12

LASER INDUCED FLUORESCENCE SPECTROSCOPY SiCN : ROTATIONAL ANALYSIS OF THE $\tilde{A}\,^2\Delta$ – $\tilde{X}\,^2\Pi$ TRANSITION

MASARU FUKUSHIMA and TAKASHI ISHIWATA, *Faculty of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.*

We have generated SiCN in supersonic free jet expansions, and observed the laser induced fluorescence (LIF) of the $\tilde{A}\,^2\Delta$ – $\tilde{X}\,^2\Pi$ transition. We have measured rotationally resolved LIF excitation spectra of the three vibronic bands. Combining with rotational reported transitions[a], the rovibronic transitions of the three vibronic bands were analyzed simultaneously, and the spin-orbit constant of the $\tilde{X}\,^2\Pi$ state has been determined with precision of the rotational spectroscopy.

---

[a] A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, Astrophys. J. 536, L55 (2000).

RH. MICROWAVE

THURSDAY, JUNE 20, 2012 – 1:30 PM

Room: 1000 MCPHERSON LAB

Chair: JENNIFER VAN WIJNGAARDEN, University of Manitoba, Winnipeg, MB, Canada

RH01 **15 min 1:30**

THE ROTATIONAL SPECTRUM OF $D_2{}^{17}O$: ACCURATE SPECTROSCOPIC AND HYPERFINE PARAMETERS

CRISTINA PUZZARINI, GABRIELE CAZZOLI, *Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy*; JUANA VÁZQUEZ, *Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, USA*; MICHAEL E. HARDING, *Karlsruher Institut für Technologie, Institut für Nanotechnologie, 76021, Karlsruhe, Germany*; JÜRGEN GAUSS, *Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany*.

The Lamb-dip technique was employed to resolve the hyperfine structure of the rotational lines of $D_2{}^{17}O$. The high resolution of such a technique allowed us to obtain the hyperfine parameters (quadrupole coupling of ^{17}O and D, spin-rotation constants as well as ^{17}O-D and D-D direct spin-spin interaction constants) with high accuracy. The experimental determination was strongly supported by highly accurate quantum-chemical calculations of the hyperfine parameters involved. The experimental spin-rotation constants of ^{17}O were used to evaluate the paramagnetic contribution to the magnetic shielding constants, whereas the diamagnetic contribution was accurately determined by means of CCSD(T) calculations. These steps are part of a well-tested procedure, which also involves the determination of vibrational and temperature corrections. The present study is part of a wider project which aims at establishing an alternative experimental absolute NMR scale for oxygen and that has been started with an analogous investigation on $H_2{}^{17}O$.[a]

Due to the lack of information on spectroscopic parameters, the rotational spectrum of $D_2{}^{17}O$ was also investigated at a Doppler-limited resolution, spanning a large frequency range: from the millimeter-wave region up to the THz frequency domain. The recorded transitions allowed to determine rotational and centrifugal-distortion constants to a good accuracy.

---

[a] C. Puzzarini, G. Cazzoli, M. E. Harding, J. Vázquez and J. Gauss *J. Chem. Phys.* **131**, 234304 (2009).

RH02 **15 min 1:47**

IDENTIFICATION OF THE CAGE, PRISM, AND BOOK ISOMERS OF WATER HEXAMER AND THE PREDICTED LOWEST ENERGY HEPTAMER AND NONAMER CLUSTERS BY BROADBAND ROTATIONAL SPECTROSCOPY

CRISTOBAL PEREZ, MATT T. MUCKLE, DANIEL P. ZALESKI, NATHAN SEIFERT, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904*; ZBIGNIEW KISIEL, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; BERHANE TEMELSO, GEORGE C. SHIELDS, *Dean's Office, College of Arts and Sciences, and Department of Chemistry, Bucknell University, Lewisburg, PA 17837.*

The water hexamer is predicted to be the smallest water cluster with a three-dimensional hydrogen bonding network as its minimum energy structure. Calculations indicate that there are several possible low-energy isomers, with different levels of theory identifying different isomers as the global minimum. Previous experimental work has provided evidence for the cage, book, and cyclic isomers but no experiment has identified multiple coexisting structures. Using broadband rotational spectroscopy in pulsed supersonic expansion these three isomers have now been unambiguously identified and their oxygen framework structures determined by means of $H_2^{18}O$ substitution. Relative isomer populations at different expansion conditions establish that the cage isomer is the minimum energy structure. The comparison of experimental and theoretical rotational constants shows that significant improvement in the agreement is achieved when vibrationally averaged (0 K) theoretical structures are used. For the water hexamer isomers, only the prism shows effects from tunneling associated with the rearrangement of the H-bond network. This tunneling is quenched upon the incorporation of a single $H_2{}^{18}O$ monomer into the prism cluster. Rotational spectra consistent with predictions for the lowest energy heptamer and nonamer structures have also been identified and the structure of the heptamer oxygen atom framework has also been determined using $H_2{}^{18}O$ substitution.

RH03 **15 min 2:04**

WATER CLUSTERS OBSERVED BY CHIRPED-PULSE ROTATIONAL SPECTROSCOPY: STRUCTURES AND HYDROGEN BONDING

ZBIGNIEW KISIEL, *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*; CRISTOBAL PEREZ, MATT T. MUCKLE, DANIEL P. ZALESKI, NATHAN SEIFERT, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319*; BERHANE TEMELSO, GEORGE C. SHIELDS, *Dean's Office, College of Arts and Sciences, and Department of Chemistry, Bucknell University, Lewisburg, PA 17837.*

The chirped-pulse rotational spectra of the hexamer, heptamer, and nonamer water clusters have been assigned and analysed as described in the preceding talk. The observation of all singly substituted ^{18}O isotopologues for several clusters allowed direct determination of the r_s geometries of their oxygen atom frameworks. The r_s analysis was then complemented by least-squares determination of the r_0 geometries, which circumvented the problems with some imaginary substitution coordinates and allowed direct comparisons with computations. For the cage, prism and the book water hexamer clusters the agreement in $O\cdots O$ distances between experiment and vibrationally averaged computed geometries is typically at the 0.01Å level. This is a previously unanticipated level of agreement between experiment and theory, which facilitates more confident discussion of the internal properties of these clusters. The hexamer and larger water clusters begin to display the diversity of hydrogen bonding that is characteristic of condensed water and various aspects of this behaviour are discussed.

RH04 **15 min 2:21**

FTMW SPECTROSCOPY OF SILYL MERCAPTAN, H_3SiSH

S. THORWIRTH, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*; V. LATTANZI, OSCAR MARTINEZ, JR., MICHAEL C. MCCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, U.S.A. and School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, U.S.A.*; LI-HONG XU, *Department of Physics, Centre for Laser, Atomic and Molecular Studies (CLAMS) University of New Brunswick, Saint John, New Brunswick, Canada E2L 4L5.*

By means of Fourier transform microwave spectroscopy of a supersonic jet, the pure rotational spectrum of silyl mercaptan, H_3SiSH, has been observed for the first time in a low-current dc discharge through a mixture of silane and hydrogen sulfide heavily diluted in neon. The spectroscopic identification was based on predictions from high-level quantum-chemical calculations at the CCSD(T) level of theory in combination with large basis sets performed using the CFOUR suite of programs[a]. In addition to the parent isotopic species, rotation lines of the rare isotopologs $H_3^{29}SiSH$, $H_3^{30}SiSH$, $H_3Si^{34}SH$, and D_3SiSD have also been observed.

---

[a] CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay et al., for the current version, see http://www.cfour.de.

RH05 **15 min 2:38**

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF SCS ($X^2\Sigma$), YS ($X^2\Sigma$) AND VS ($X^4\Sigma$)

L. M. ZIURYS, G. R. ADANDE, D. T. HALFEN, *Department of Chemistry and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

Pure rotational spectra of three transition-metal monosulfides, ScS, YS, and VS, have been recorded using Fourier transform microwave spectroscopy (FTWM) in the range 10-40 GHz. These molecules are all free radicals and have been synthesized in a mixture of H_2S gas with metal vapor, obtained by laser ablation of a metal rod. In the case of ScS and VS, a discharge was necessary to successfully produce the molecules. For YS, the $N=1\longrightarrow0$, $2\longrightarrow1$, $3\longrightarrow2$ and $4\longrightarrow3$ rotational transitions have been recorded. For ScS and VS, the $N=1\longrightarrow0$, $N=2\longrightarrow1$ and $N=3\longrightarrow2$ have been obtained. Vanadium, scandium and yttrium hyperfine structures were resolved for these species. Rotational, fine structure and hyperfine coupling constants have been determined for all three radicals. This works completes the high-resolution pure rotational measurements of 3d transition-metal monosulfides, and provides the most accurate values of the hyperfine parameters for these molecules to date. Bond lengths and spectroscopic parameters will be presented.

RH06 **15 min 2:55**

THE CCN ($\tilde{X}^2\Pi_{1/2}$) RADICAL REVISITED: NEW FOURIER TRANSFORM MICROWAVE MEASUREMENTS

J. K. ANDERSON, D. T. HALFEN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

The CCN ($\tilde{X}^2\Pi_{1/2}$) radical was first studied by Ohshima & Endo in 1995, who measured the lowest rotational transition, J = 3/2 → 1/2, in the Ω = 1/2 ladder near 35 GHz. No subsequent work has been performed for this species to date. Here we present measurements of the J = 5/2 → 3/2 rotational transition of CCN (Ω = 1/2) near 59 GHz, recorded using Fourier transform microwave (FTMW) spectroscopy. CCN was synthesized in a supersonic expansion from a dilute mixture of $(CN)_2$ and CH_4 in argon, in the presence of a DC discharge. Both lambda-doublets were recorded, each consisting of three hyperfine components. These measurements, combined with past data, have been analyzed and refined spectroscopic constants have been established. Studies of additional rotational transitions are currently being conducted.

RH07 **15 min 3:12**

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF ALKALI METAL HYDROSULFIDES: DETECTION OF KSH

P. M. SHERIDAN, M. K. L. BINNS, J. P. YOUNG, *Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY 14208*; M. P. BUCCHINO, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

Fourier transform microwave (FTMW) techniques have been used to record pure rotational spectra of potassium hydrosulfide and its deuterium isotopologue in their ground electronic states. This study represents the first gas phase spectroscopic observation of KSH. FTMW spectra of NaSH were also recorded. The metal hydrosulfides were produced by discharge assisted laser ablation of the solid alkali metal in the presence of hydrogen sulfide or deuterated hydrogen sulfide. Rotational transitions in the 5 ï£¡ 20 GHz range were measured and hyperfine splittings due to the alkali metals and deuterium were resolved. Rotational as well as metal and deuterium quadrupole coupling constants have been determined from the data. The hyperfine parameters will be interpreted in terms of metal-ligand bonding character. Geometric parameters of the alkali metal hydrosulfides will be compared.

Intermission

RH08 **15 min 3:45**

MICROWAVE SPECTRUM OF HEXAFLUOROISOPROPANOL

ABHISHEK SHAHI, DEVENDRA MANI and E. ARUNAN, *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India.*

Hexafluoroisopropanol (HFIP) is an important organic solvent and probably the only solvent which can dissolve polythene. IR studies, on this molecule confirm the existence of antiperiplanar (**ap**) and synclinical (**sc**) conformers[a]. We have observed pure rotational spectrum of this molecule and the fitted rotational constants (A= 2105.1208(11) MHz, B= 1053.9942(3) MHz, C= 932.3398(3) MHz) confirm the presence of **ap** conformer. There are many other observed lines which most probably corresponds to **sc** structure and due to the large amplitude motion of H-atom, some of these transitions show tunneling splitting. Work is in progress for the deuterated (OD) and C-13 isotopologues of the monomer. HFIP is expected to exhibit interesting hydrogen bonding properties and we are planning to investigate them by studying its complex with water. The results will be presented in this talk.

---

[a] H. Schaal, T. Höber, and M. A. Suhm, J. Phys. Chem. A 104, 265 (2000).

RH09 **15 min 4:02**

MILLIMETER-WAVE SPECTROSCOPY OF ETHYLMERCURY HYDRIDE

M. GOUBET, R. A. MOTIYENKO, L. MARGULÈS, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS - ENSCR, 35708 Rennes Cedex 7, France*.

The first millimeter-wave rotational spectrum of an organomercury compound, ethylmercury hydride (CH_3CH_2HgH), has been recorded using the Lille fast-scan spectrometer[a] in the frequency range 120 – 180 GHz. The spectroscopic study is complemented by quantum chemical calculations taking into account relativistic effects on the mercury atom. The very good agreement between theoretical and experimental molecular parameters validates the chosen ab initio method, in particular its capability to predict the accurate values of the quartic centrifugal distortion constants related to this type of compound. Estimations of the nuclear quadrupole coupling constants are not as predictive as the structural parameters but good enough to satisfy the spectroscopic needs. In addition, the orientation of the H–Hg–C bonds axis deduced from the experimental nuclear quadrupole coupling constants compares well with the corresponding ab initio value. From the good agreement between experimental and theoretical results, together with the observation of the six most abundant isotopes of mercury, ethylmercury hydride is unambiguously identified and its calculated equilibrium geometry is confirmed.

---

[a] Alekseev, E.A. et al. *Radio Physics and Radio Astronomy* **3** (2012) 78.

RH10 **15 min 4:19**

CHIRPED-PULSE AND CAVITY BASED FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF THE METHYL LACTATE-AMMONIA ADDUCT

JAVIX THOMAS, OLEKSANDR SUKHORUKOV, WOLFGANG JAEGER and YUNJIE XU, *Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada*.

The hydrogen bonded complex of ammonia with methyl lactate, a chiral alpha-hydroxyester, has been studied using rotational spectroscopy and high level ab initio calculations. Previous studies showed that methyl lactate can exist in a number of conformers. However, only the most stable one which has an intramolecular hydrogen bonded ring formed with its alcoholic hydroxyl and its carbonyl oxygen atom was detected experimentally An extensive ab initio search has been performed to locate all possible low energy conformers of the methyl lactate-ammonia contact pair. Five lowest energy conformers have been identified at the MP2/6-311++G(d,p) level. The lowest energy conformer favors an insertion arrangement, where ammonia is inserted into the existing intramolecular hydrogen bonded ring in the most stable methyl lactate conformer. Broadband scans for the rotational spectra of possible binary conformers have been carried out using a chirped-pulse Fourier transform microwave (FTMW) instrument. The most stable binary adduct was identified and assigned. The final frequency measurements have been done with a cavity based FTMW instrument. The spectrum observed shows complicated fine and hyperfine splitting patterns, likely due to the internal rotations of the methyl groups of methyl lactate and that of ammonia, as well as the 14N quadrupolar nucleus. The binary adduct with 15NH3 has also been studied to simplify the splitting pattern and to aid the assignments of the extensive splittings. The isotopic data and the fine and hyperfine structures will be discussed in terms of internal rotation dynamics and geometry of the hydrogen bonded adduct.

RH11 **15 min 4:36**

HALOGEN BOND AND INTERNAL MOTIONS: THE LOW-BARRIER CASE OF CF_3Cl-DIMETHYLETHER

LUCA EVANGELISTI, GANG FENG, QIAN GOU and WALTHER CAMINATI, *Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy*; JENS-UWE GRABOW, *Lehrgebiet Physikalische Chemie A, Institut für Physikalische Chemie und Elektrochemie, Universtät Hannover, Callinstr. 3A, D-30167 Hannover, Germany*.

If halogen containing molecules form complexes and several non-convalent interactions are possible, subtle effects can determine the globally most stable conformation. While, intuitively, one might assume that hydrogen bonds are the dominating interactions, halogen haloge bonds can be competitive or even most important. Most investigations of halogen bonds come from X-ray diffraction in solid state or sometimes vibrational spectroscopy in (cryo)-solutions. However, the structural results obtained in condensed phase might be biased by lattice, matrix or solvent effects.

Perhalogenated hydrocarbons are found to prefer halogen rather then hydrogen bonds in complexes with other species, even when the partner molecule is water. In the case of F_3CCl-H_2O [a] the water molecule undergoes an almost free rotation with respect to the Cl...O connection, making the complex an effective symmetric top.

What will happen to the complex when water is substituted with a heavier, but still C_{2v} symmetric molecule? Formed in the supersonic-jet expansion we measured the Fourier transform microwave spectra of two isotopologs of the 1:1 adduct of CF_3Cl with dimethylether (DME) to determine its native global minimum shape and dynamics.

The structural and dynamical information encoded in the rotational spectra is consitent with a global minimum conformation that forms a F_3C-Cl...O halogen bond, and an almost free rotation of the -CF3 group. Besides the rotational constants and information on the internal dynamics, the quadrupole coupling constants of the chlorine atom have been determined.

---

[a] L. Evangelisti, G. Feng, P. ÃĽcija, E. J. Cocinero, F. CastaÃÂśo, W. Caminati, Angew. Chem. Int. Ed. 50, 7807-7810 (2011).

RH12 **15 min 4:53**

THE COMMON CHLORINE NUCLEAR ELECTRIC QUADRUPOLE COUPLING TENSOR FOR ACYL CHLORIDES

R. A. POWOSKI, *Glori Energy, Inc., 4315 South Dr, Houston, Texas 77053*; S. A. COOKE, *School of Natural and Social Sciences, Purchase College SUNY, 735 Anderson Hill Road, Purchase, NY 10577*.

We have determined the complete ^{35}Cl and ^{37}Cl nuclear electric quadrupole coupling tensors for two conformers of valeroyl chloride, CH_3-$(CH_2)_3$-COCl, using pure rotational spectroscopy. These tensors have been diagonalized into the principal axes and compared with chlorine principal quadrupole coupling tensors for a number of simple acyl chlorides. In general the components of the chlorine principal quadrupole coupling tensor, and in particular χ_{zz}, are invariant to the organic group attached to the acyl chloride. It is evident, and not surprising, that the carbonyl of the acyl chloride functional group dominates the electric field gradient at the chlorine nucleus. We have found a common, acyl chloride functional group, ^{35}Cl χ_{zz} value of -59 ± 1 MHz. These findings will be discussed along with other work on tabulating common principal nuclear electric quadrupole coupling constants for relevant nuclei in simple organic functional groups[a].

---

[a] This work supported by IUPAC, Project No. 2010-048-3-100.

RH13 **15 min 5:10**

THE MILLIMETER WAVE SPECTRUM OF ESTRAGOLE AND VERBENONE

COREY J EVANS, STEPHANIE M ALLPRESS, *Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom*; PETER D GODFREY, DON MCNAUGHTON, *School of Chemistry, Monash University, 3800, Victoria, Australia*.

The rotational spectra of estragole and verbenone have been recorded in the millimeter wave region (48-72 GHz). This is the first ever investigation of the rotational spectroscopy of both estragole and verbenone. For estragole, lines from two conformers have been identified and assigned. Surprisingly, lines from a possible third low-lying conformer were unobserved. Precise rotational and centrifugal distortion constants for both conformers have been determined. For verbenone, lines have been assigned to the global minimum structure and precise rotational and centrifugal distortion constants have been determined.

RI. MINI-SYMPOSIUM: COLD QUANTUM SYSTEMS

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 1015 MCPHERSON LAB

Chair: TAKAMASA MOMOSE, The University of British Columbia, Vancouver, BC, Canada

RI01 *INVITED TALK* **30 min 1:30**

SPECTRA OF COLD MOLECULAR IONS FROM HOT HELIUM NANODROPLETS

MARCEL DRABBELS, *Laboratoire de Chimie Physique Moléculaire, Ecole polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.*

The function of a molecule is intimately related to its structure. Accordingly, in the quest for a better understanding of molecular function, the development of spectroscopic methods to elucidate molecular structures increasingly takes central stage. The amount of detail that can be derived from spectra depends on the experimental conditions, most notably on the temperature of the sample and the intermolecular interactions a molecule experiences. Helium nanodroplets provide in this respect an almost ideal matrix [1, 2]. For neutral molecules, helium nanodroplet spectroscopy thus has led to important discoveries related to the structure of key molecular systems and has provided insight into the mechanisms underlying chemical reactions.

Compared to the level of sophistication that has been reached for neutrals, the spectroscopic exploration of ions is still in its infancy. The use of helium droplets as a cryogenic matrix could potentially solve many of the technical challenges associated with recording high-resolution spectra of cold molecular ions. Here, we will present a method to record spectra of ion containing helium nanodroplets that finds its roots in the nonthermal cooling dynamics of excited molecular ions. In addition, spectra of several molecular ions will be present and the influence of the helium environment on these spectra will be discussed.

[1] G. Scoles, and K. K. Lehmann, Science 287, 2429 (2000).
[2] J. P. Toennies, and A. F. Vilesov, Angew. Chem. Int. Ed. 43, 2622 (2004).

RI02 **15 min 2:05**

HOT MOLECULES IN HELIUM NANODROPLETS: A NEW ROUTE TO OPTICAL SPECTRA

BENJAMIN SHEPPERSON, ADRIAN BOATWRIGHT, CHENG FENG, DANIEL SPENCE, SHENGFU YANG, and ANDREW M. ELLIS, *Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK.*

A new mechanism is described for recording optical spectra of molecules in helium nanodroplets. This “hot molecule" technique is applicable when optical excitation leads to a long-lived metastable excited state inside a helium droplet, which in turn changes the electron impact ionization cross section of specific ion product channels. This is illustrated by electronic excitation of toluene to its S1 state, which undergoes intersystem crossing into a long-lived triplet state with high quantum yield. By monitoring different ions, spectra in both depletion and enhancement modes have been obtained. The technique has potential for applications whenever optical excitation delivers a relatively long-lived (ms or longer) excited state and therefore complements existing depletion techniques, which require fast dissipation of energy into the helium matrix.

RI03 **15 min 2:22**

HELIUM NANODROPLET ISOLATION SPECTROSCOPY OF NO_2 AND VAN DER WAALS COMPLEXES

ROBERT R. FEHNEL, KEVIN K. LEHMANN, *Department of Chemistry, University of Virginia, Charlottesville VA, 22904-4319.*

We will report the infrared laser spectra of NO_2, NO_2-N_2, NO_2 - H_2O and NO_2 - O_2 complexes using Helium Nanodroplet Isolation (HENDI) Spectroscopy. These molecules were excited using an ARGOS cw PPLN OPO (Aculight) in the 3.2 - 3.9 μm spectral window and we excited the $\nu_1 + \nu_3$ transition of NO_2.

RI04 **15 min 2:39**

SATURATION OF THE NO_2 $\nu_1 + \nu_3$ AND THE CH_4 ν_3 TRANSITIONS IN HELIUM NANODROPLETS

ROBERT R. FEHNEL, KEVIN K. LEHMANN, *Department of Chemistry, University of Virginia, Charlottesville VA, 22904-4319.*

We will report our findings of quantitative study of saturation of IR transition in Helium nanodroplets. The excitation source is an Argos cw PPLN OPO (Aculight) that is focused to a spot of 27 μm, producing a pear power of 87 kW/cm^2.
We have also used a "Perry Cell" multi pass cell to study of the effect of extending the interaction time. We will present results for a study of the 2905.566 cm^{-1} R(0) transition of NO_2 and the 3029.07 cm^{-1} R(0) transition of CH_4.

RI05 **15 min 2:56**

INFRARED SPECTROSCOPY OF OH AND OH-C_2H_2 EMBEDDED IN HELIUM NANODROPLETS

PAUL RASTON, TAO LIANG, STEVEN D. FLYNN, ALEXANDER M. MORRISON, AND GARY E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, GA 30602-2556.*

The hydroxyl radical and its complex with acetylene have been characterized in superfluid helium nanodroplets by infrared depletion spectroscopy. For OH, two sharp Q(3/2) lines were observed, with a separation that is consistent with a fivefold increase in the parity (lambda type) doubling of the $^2\Pi_{3/2}$ state in helium droplets relative to the gas phase. This increase is rationalized in terms of the differences in the potential energy surfaces for He-OH(A$'$) and He-OH(A$''$), which are most pronounced at around 90°. Switching to the T-shaped OH-C_2H_2 complex, depletion signals corresponding to OH and CH stretching transitions were observed. The spectra reveal that the electronic angular momentum of OH in the complex is only partially quenched, and to a similar degree as observed in the gas phase[a,b]. This indicates that the helium droplet environment does not significantly affect the electronic intermolecular interactions in OH-C_2H_2.

---

[a] J. B. Davey, M. E. Greenslade, M. D. Marshall, M. I. Lester, and M. D. Wheeler *J. Chem. Phys.*, **121**, 3009 (2004).
[b] M. D. Marshall, J. B. Davey, M. E. Greenslade, and M. I. Lester *J. Chem. Phys.*, **121**, 5845 (2004).

Intermission

RI06 ***INVITED TALK*** **30 min 3:30**

DOPANT ROTATION IN MOLECULAR SUPERFLUID CLUSTERS

PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.*

Liquid Helium becomes superfluid and frictionless at very low temperature. We are interested in the superfluid properties of helium and hydrogen clusters doped with molecular impurities. Molecular hydrogen has been suggested as a potential candidate but this substance crystallizes before reaching a temperature low enough for superfluidity to appear. We will show theoretical and experimental results that demonstrate the possibility of obtaining a molecular superfluid response at the nanoscale via the formation of doped hydrogen clusters. The theoretical results are based on the path integral description of quantum statistical mechanics. We will discuss the advantages of this approach for the quantum simulation of complex molecular systems. Properties such as density distributions and spectral features can be extracted from the simulations. We will present new results for the case of asymmetric top molecules embedded in superfluid para-hydrogen clusters.

RI07 **10 min 4:05**

OBSERVATION OF VORTICES IN SUPERFLUID He DROPLETS

LUIS F. GOMEZ, EVGENY LOGINOV, ANDREY F. VILESOV, *Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.*

A continuous beam of superfluid He droplets has been used to assemble Ag clusters consisting of up to 10^6 atoms. The obtained clusters have been characterized by imaging after being surface-deposited via the droplet beam. The average sizes of the deposited clusters are in good agreement with an estimate based on the energy conservation of Ag cluster growth in He droplets. Whereas the deposited clusters obtained in droplets of less than 100 nm in diameter are round, those obtained in droplets larger than about 300 nm are elongated and track-shaped. The prevalence of the tracks shows that quantum vortices are present in such large droplets and that their lifetime exceeds a few milliseconds. We also discuss the possible formation mechanisms and the stability of the vortices.

RI08 **15 min 4:17**

PYRIDINE AGGREGATION IN HELIUM NANODROPLETS

PABLO NIETO, TORSTEN POERSCHKE, DANIEL HABIG, GERHARD SCHWAAB and MARTINA HAVENITH, *Department of Physical Chemistry II, Ruhr-Universität Bochum, Germany.*

Pyridine crystals show the unusual property of isotopic polymorphism. Experimentally it has been observed that deuterated pyridine crystals exist in two phases while non-deuterated pyridine does not show a phase transition[a]. Therefore, although isotopic substitution is the smallest possible modification of a molecule it greatly affects the stability of pyridine crystals. A possible experimental approach in order to understand this striking effect might be the study of pyridine aggregation for small clusters. By embedding the clusters in helium nanodroplets the aggregates can be stabilized and studied by means of Infrared Depletion Spectroscopy.

Pyridine oligomers were investigated in the C-H asymmetric vibration region (2980-3100 cm^{-1}) using this experimental technique. The number of molecules for the clusters responsibles for each band were determined by means of pick-up curves as well as mass sensitive depletion spectra. Furthermore, the intensity dependence of the different bands on applying a dc electric field was studied. The assignment of the different structures for pyridine clusters on the basis of these measurements were also carried out.

---

[a] S. Crawford *et al.*, Angew. Chem. Int. Ed., 48, 755 (2009).

RI09 **15 min 4:34**

PROBING TRANS-HOOO/DOOO AND HOOO-$(O_2)_n$ CLUSTERS: A HENDI APPROACH

T. LIANG, P. RASTON, and G. E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556.*

Trans-HOOO and HOOO-$(O_2)_n$ clusters have been assembled in helium nanodroplets and probed with a tunable narrow linewidth PPLN-OPO laser system in the O-H stretching region. We observed the ν_1 band at 3569.45 cm^{-1}, which consists of rotationally resolved a- and b-type components, in addition to the broad c-type ν_1+ν_6 band at 3699.06 cm^{-1}. The band origins for ν_1 and ν_1+ν_6 are shifted to the blue by only 0.15 cm^{-1} and 1.03 cm^{-1}, respectively, compared to the gas phase values by Lester and co-workers.[a,b] Neither of the two other predicted stable isomers, namely cis-HOOO and the hydrogen-bound OH-O_2 species,[c] were found within a broad survey scan. The HOOO-$(O_2)_n$ clusters grow in to the red of the ν_1 band of trans-HOOO as the O_2 pick-up pressure is increased. Cluster signals are resolved for up to $n = 4$, while signals for clusters with $n > 4$ pile up to form a broad feature. High level *ab initio* multireference calculations are needed to help understand the geometries for these multiple O_2 clusters. The O-D stretch of trans-DOOO was measured at 2635.02 cm^{-1}, which is extremely close to the gas phase value at 2635.06 cm^{-1}.[d] The linewidths of the transitions within this band are narrower than those within the O-H stretching band of trans-HOOO, which suggests that the lifetime of the excited vibrational state is longer for trans-DOOO than trans-HOOO.

---

[a] E. L. Derro, C. Murray, T. D. Sechler, and M. I. Lester, J. Phys. Chem. A. **111**, 11592, (2007).

[b] E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, J. Chem. Phys. **128**, 244313, (2008).

[c] B. J. Braams and H. G. Yu, Phys. Chem. Chem. Phys. **10**, 3150, (2008).

[d] E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, J. Phys. Chem. A. **112**, 9269, (2008).

RI10 **15 min 4:51**

ON THE OUTCOME OF THE REACTIONS BETWEEN HYDROCARBON RADICALS AND O_2 IN HELIUM NANODROPLETS

A. M. MORRISON and G. E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556.*

Helium nanodroplet isolation and infrared laser spectroscopy are used to investigate the CH_3 + O_2 and C_3H_3 (propargyl) + O_2 reactions. The hydrocarbon radicals are generated in an effusive pyrolysis source located upstream from a differentially pumped O_2 gas pick-up cell. In this experimental configuration, the reaction occurs between sequentially picked-up and presumably cold fragments. The CH_3 + O_2 reaction leads barrierlessly to the methyl-peroxy radical, and despite having to dissipate an energy of approximately 30 kcal/mol, the infrared spectra reveal a large abundance of droplets containing the cold CH_3O_2 radical. Theoretical studies have predicted an approximately 2-4 kcal/mol barrier in the entrance channel of the C_3H_3 + O_2 reaction. Therefore, we initially expected to see a weakly bound âĂIJentrance channelâĂİ C_3H_3–O_2 van-der-Waals complex, given the rapid cooling provided by the dissipative helium environment. However, only the trans-acetylenic isomer of the propargyl-peroxy radical is observed. The dipole moment of this species is measured with infrared laser Stark spectroscopy.

RI11 **15 min 5:08**

INFRARED SPECTROSCOPY OF HOCl EMBEDDED IN HELIUM NANODROPLETS

PAUL RASTON, DONALD KELLOWAY, AND WOLFGANG JÄGER, *Department of Chemistry, University of Alberta, Edmonton, Alberta T6G-2G2, Canada.*

The infrared depletion spectrum of hypochlorous acid (HOCl) embedded in superfluid helium nanodroplets has been measured in the region near 2.8 μm. The spectrum consists of baseline resolved *a*-type lines and a broad convoluted *b*-type feature. The *a*-type lines are asymmetrically skewed in the direction of the band origin, and an analysis of their line shapes based on the chirped damped oscillator function introduced by van Staveren and Apkarian[a] yields a response time of the helium solvent of 1 ns. The *b*-type lines are much broader due to the greater number of droplet states available for relaxation of the excited rotational states.

---

[a] M. N. van Staveren, and V. A. Apkarian *J. Chem. Phys.*, **133**, 054506 (2010).

RI12 **15 min 5:25**

ASYMMETRIC TOP ROTORS IN SUPERFLUID *PARA*-HYDROGEN NANO-CLUSTERS

TAO ZENG, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1*; HUI LI, *Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, 2519 Jiefang Road, Changchun 130023, People's Republic of China*; and PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1.*

We present the first simulation study of bosonic clusters doped with an asymmetric top molecule. A variation of the path-integral Monte Carlo method is developed to study a *para*-water (pH_2O) impurity in *para*-hydrogen (pH_2) clusters. The growth pattern of the doped clusters is similar in nature to that of the pure clusters. The pH_2O molecule appears to rotate freely in the cluster due to its large rotational constants and the lack of adiabatic following. The presence of pH_2O substantially quenches the superfluid response of pH_2 with respect to the space fixed frame. We also study the behaviour of a sulphur dioxide ($^{32}S^{16}O_2$) dopant in the pH_2 clusters. For such a heavy rotor, the adiabatic following of the pH_2 molecules is established and the superfluid renormalization of the rotational constants is observed. The rotational structure of the SO_2-$p(H_2)_N$ clusters' ro-vibrational spectra is predicted. The connection between the superfluid response respect to the external boundary rotation and the dopant rotation is discussed.

RI13 **15 min 5:42**

MOLECULAR DYNAMICS SIMULATIONS ON VARIOUS WEAKLY BOUND WATER-PARAHYDROGEN SYSTEMS AT ULTRACOLD TEMPERATURE

MATTHEW SCHMIDT, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1*; CHRISTOPHER ING, *Department of Biochemistry, University of Toronto, 27 King's College Circle, Toronto, Ontario, Canada M5S 1A1*; STEPHEN CONSTABLE, TAO ZENG, JING YANG, MICHAEL NYMAN and PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1.*

We report path integral molecular dynamics (PIMD) studies on the low temperature properties of weakly bound clusters. We use a new version of the molecular modeling toolkit (MMTK) with an implementation of the Path Integral Langevin Equation (PILE) thermostat. We focus on the low temperature dynamics of parahydrogen clusters with a non-rotating water dopant molecule. We also extend our study to the reverse case where hydrogen is doped in a water cluster. The low temperature properties of parahydrogen clusters within water clathrates are explored. These systems are of great interest in the context of hydrogen storage. We compare our PIMD results to those of more traditional path integral Monte Carlo (PIMC) methods. We also report on an extension of the PIMD approach to zero temperature using the so-called Path Integral Ground State (PIGS) approach. The technique is analogous to diffusion Monte Carlo (DMC) but with important differences that will be presented. We discuss the merits of various trial functions and the PIGS results are benchmarked using exact calculations for small clusters.

RJ. THEORY

THURSDAY, JUNE 21, 2012 – 1:30 PM

Room: 2015 MCPHERSON LAB

Chair: PETER BOTSCHWINA, University of Goettingen, Goettingen, Germany

RJ01 *INVITED TALK* **30 min 1:30**

INTENSITIES OF FUNDAMENTAL AND OVERTONE VIBRATIONAL TRANSITIONS

HENRIK G. KJAERGAARD, *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark.*

We have measured and calculated vibrational XH-stretching overtone spectra (where X is C,N,O,S,..) for a range of molecules and hydrated complexes (e.g. water dimer). Spectroscopic studies of such systems are difficult because: vibrational overtone transitions have low intensities, species that exhibit intramolecular hydrogen bonding typically have low vapor pressures and hydrated complexes have small equilibrium constants. The use of coupled cluster theory including perturbative triples, CCSD(T) or CCSD(T)-F12, as well as a large augmented basis, aug-cc-pVTZ or VDZ-F12, is necessary to obtain calculated vibrational spectra of near experimental accuracy.

We explain the interesting intensity patterns in terms of an anharmonic oscillator local mode model. The intensity ratio of the fundamental to first XH-stretching overtone covers a wide range. In the past decade, we have used this local mode model to explain observed spectra of both molecules and complexes. I will show recent results for amines and complexes with amines and will illustrate how the ratio of calculated to measured intensity can provide the room temperature equilibrium constant for formation of the binary complex, a quantity that is difficult to calculate accurately.

RJ02 **15 min 2:05**

HIGH-ACCURACY POTENTIALS FOR VAN DER WAALS SYSTEMS

RICHARD DAWES, *Missouri University of Science and Technology, Rolla, MO 65409, USA*; XIAO-GANG Wang, JAMES BROWN, TUCKER CARRINGTON, JR., *Queen's University, Kingston, Ontario, K7L 3N6 Canada.*

Recent experimental studies of vdWs systems including those by Moazzen-Ahmadi and McKellar,1,2 as well as microwave studies by Minei and Novick3,4 have observed previously unknown stable polar isomers for systems such as (NNO)2 and (OCS)2. The multi-welled floppy nature of the PESs and the small barriers between minima place stringent requirements on the PES for a successful theoretical description of these states. An automated method of generating accurate PESs for vdW systems has been developed and is demonstrated here.5,6 A limited number of ab initio data at the explicitly correlated CCSD(T)-F12b level are interpolated into analytic PESs with negligible fitting error. High-accuracy PESs were developed for a number of systems including (NNO)2, (OCS)2, (CO)2, CO2:CS2 and (NH3)2.

Using the PESs, the rovibrational SchrÃÂűdinger equation is solved with a symmetry-adapted Lanczos algorithm and an uncoupled product basis set. All inter-monomer coordinates are included in the calculations. Calculated transition frequencies are in very close agreement with experiment.

References (1) M. Dehghani, M. Afshari, Z. Abusara, N. Moazzen-Ahmadi, A. R. W. McKellar, J. Chem. Phys. 126, 164310 (2007). (2) M. Dehghani, M. Afshari, Z. Abusara, N. Moazzen-Ahmadi, A. R. W. McKellar, J. Chem. Phys. 126, 071102 (2007). (3) N. R. Walker, R. Nicholas, A. J. Minei, S. E. Novick, A. C. Legon, J. Mol. Spec. 251, 153 (2008). (4) A. J. Minei and S. E. Novick, J. Chem. Phys. 126, 101101 (2007). (5) R. Dawes, X.-G. Wang, A. W. Jasper, T. Carrington Jr., J. Chem. Phys. 133, 134304 (2010). (6) X.-G. Wang, T. Carrington Jr., R. Dawes and A. W. Jasper, J. Mol. Spec. 268, 53 (2011).

RJ03 **15 min 2:22**

THE AMMONIA DIMER REVISITED

RICHARD DAWES, *Missouri University of Science and Technology, Rolla, MO 65409-0010*; AD VAN DER AVOIRD, *Radboud University, 6525 AJ Nijmegen, The Netherlands.*

The conclusion from microwave spectra by Nelson, Fraser, and Klemperer [a] that the ammonia dimer has a nearly cyclic structure led to much debate about the issue of whether $(NH_3)_2$ is hydrogen bonded. This structure was surprising because most *ab initio* calculations led to a classical, nearly linear, hydrogen-bonded structure. An obvious explanation of the discrepancy between the outcome of these calculations and the microwave data which led Nelson *et al.* to their "surprising structure" might be the effect of vibrational averaging: the electronic structure calculations focus on finding the minimum of the intermolecular potential, the experiment gives a vibrationally averaged structure. Isotope substitution studies seemed to indicate, however, that the complex is nearly rigid. Additional data became available from high-resolution molecular beam far-infrared spectroscopy in the Saykally group [b]. These spectra, displaying large tunneling splittings, indicate that the complex is very floppy. The seemingly contradictory experimental data were explained when it became possible [c] to calculate the vibration-rotation-tunneling (VRT) states of the complex on a six-dimensional intermolecular potential surface. The potential used was a simple model potential, with parameters fitted to the far-infrared data. Now, for the first time, a six-dimensional potential was computed by high level *ab initio* methods and this potential will be used in calculations of the VRT states of $(NH_3)_2$ and $(ND_3)_2$. So, we will finally be able to answer the question whether the conclusions from the model calculations are indeed a valid explanation of the experimental data.

---

[a] D. Nelson, G. T. Fraser, and W. Klemperer *J. Chem. Phys.* **83** 6201 (1985)

[b] J. G. Loeser, C. A. Schmuttenmaer, R. C. Cohen, M. J. Elrod, D. W. Steyert, R. J. Saykally, R. E. Bumgarner, and G. A. Blake *J. Chem. Phys.* **97** 4727 (1992)

[c] E. H. T. Olthof, A. van der Avoird, and P. E. S. Wormer *J. Chem. Phys.* **101** 8430 (1994); E. H. T. Olthof, A. van der Avoird, P. E. S. Wormer, J. G. Loeser, and R. J. Saykally *J. Chem. Phys.* **101** 8443 (1994)

RJ04 **15 min 2:39**

RESONANCE AND REVIVALS I. QUANTUM ROTOR AND INFINITE-WELL DYNAMICS

WILLIAM G. HARTER, *Department of Physics, University of Arkansas, Fayetteville, AR 72701*; ALVASON ZHENHUA LI, *Microelectronics-Photonics, University of Arkansas, Fayetteville, AR 72701.*

Space-time structure of exploding quantum wave packets exhibit a resonate beating phenomena. Such "super-beats" were called "revivals" by J. H. Eberly in connection with numerical studies of Jaynes-Cummings models of atom-in-cavity quantum electrodynamics. The term revival refers to the ability of an initial localized wave packet to dramatically "un-explode" after a period of decoherent quiescence and then more-or-less repeat the process.

Analogous revival dynamics can be seen most clearly in a simple 1D rotor or Bohr-ring atomic model, and this provides what is perhaps the clearest understanding so far of the underlying wave mechanics. In this model the main revival and its multitude of sub-revivals repeat perfectly. For this model it is possible predict the space-time location of each revival peak and rank its coherence using a Farey-sum formula so named after a geologist who studied tidal resonance in the early 1800's. Moreover, it is possible to calculate the phases of individual revival peaks using overlapping Cyclic (Cn) group character tables.

The resulting interference patterns clearly exhibit all factors of each integer n below a certain Farey-threshold determined by spatial width of the initial packet.

A subsequent talk will discuss the revivals observed in Morse oscillator vibrational potential models.

RJ05 **15 min 2:56**

RESONANCE AND REVIVALS II. MORSE OSCILLATOR AND DOUBLE MORSE WELL DYNAMICS

ALVASON ZHENHUA LI, *Microelectronics-Photonics Program, University of Arkansas, Fayetteville, AR 72701*; WILLIAM G. HARTER , *Department of Physics, University of Arkansas, Fayetteville, AR 72701.*

Analytical solutions for the Morse oscillator are applied to investigate the quantum resonance and revivals that occur in position and momentum spaces. The anharmonicity of this oscillator appears to cause interesting space-time phenomena that includes relatively simple Farey-sum revival structure. Furthermore, a simple sum of two Morse oscillators leads to a double Morse well whose geometric symmetry provides a quasi-analytical solution. The resonant beats and revivals of wavepacket propagation involve quantum tunneling between the double Morse wells and mode dynamics local to each well. Such quantum dynamic systems may have applications for quantum information processing and quantum computing.

Intermission

RJ06 **15 min 3:30**

MULTI-VALUED VERSUS SINGLE-VALUED LARGE-AMPLITUDE BENDING-TORSIONAL-ROTATIONAL COORDINATE SYSTEMS FOR SIMULTANEOUSLY TREATING TRANS-BENT AND CIS-BENT ACETYLENE IN ITS S_1 EXCITED ELECTRONIC STATE

JON T. HOUGEN, *Sensor Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA.*

There are now a large number of papers in the spectroscopic literature which make use of multiple-valued (frequently double-valued) coordinate systems and multiple-groups of the permutation-inversion group to deal with the symmetry properties of large-amplitude motions in molecules of high symmetry. The use of multiple-valued coordinate systems, and the resultant appearance of more minima on the potential surface than would be found on the surface for a single-valued coordinate system, can lead to conceptual discomfort and questions of mathematical legitimacy. In the present talk we show that treatments using multiple-valued coordinate systems simply represent one scheme for applying the appropriate quantum mechanical boundary conditions to Schrödinger's equation defined in a single-valued coordinate system. The demonstration is not general, but rather focusses on the specific example of a non-linear electronic state of C_2H_2 and on the two-fold and eight-fold extended permutation-inversion groups recently introduced to treat simultaneously symmetry questions in trans-bent and cis-bent acetylene. Some discussion of the mathematical convenience lost by insisting on using a single-valued coordinate system will also be presented.

RJ07 **15 min 3:47**

USING FIXED-NODE DIFFUSION MONTE CARLO TO PROBE ROTATION-VIBRATION COUPLING IN HIGHLY FLUXIONAL ASYMMETRIC TOP MOLECULES

ANDREW S. PETIT, BETHANY A. WELLEN, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

Our group has developed a fixed-node Diffusion Monte Carlo (DMC) methodology that can be used to describe rotationally excited states of highly fluxional symmetric top molecules.[a] This technique has been thoroughly benchmarked using rotationally excited states of H_3^+, H_3O^+, and NH_3 with $J \leq 12$.[b] Here, we report a recently developed extension of this methodology to asymmetric top molecules which undergo large amplitude, zero-point vibrational motion. The nodal surfaces used in the fixed-node DMC calculations are obtained from rigid-rotor wave functions calculated using the system's ground state vibrationally averaged rotational constants. The algorithms used to evaluate node crossing and re-crossing are generalized to account for the pronounced curvature exhibited by the nodal surfaces of asymmetric top molecules with $\kappa \approx 0$ due to the strong mixing of two or more symmetric top basis functions. Finally, the insight that can be obtained from these calculations into the nature and strength of the vibration-rotation coupling present in highly fluxional asymmetric top molecules will be briefly discussed and further elaborated on in the following talk.

---

[a] A. S. Petit and A. B. McCoy, J. Phys. Chem. A 113, 12706 (2009).

[b] A. S. Petit, B. A. Wellen, and A. B. McCoy, J. Chem. Phys. 136, 074101 (2012).

RJ08 **15 min 4:04**

EXTENSIONS OF FIXED-NODE DIFFUSION MONTE CARLO TO THE STUDY OF THE ROTATIONALLY EXCITED STATES OF H_2D^+

BETHANY A. WELLEN, ANDREW S. PETIT, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

Diffusion Monte Carlo (DMC) has been shown to be a highly successful technique for treating quantum zero-point effects of very floppy molecules and clusters. Our group has developed a fixed-node DMC methodology that allows us to expand the application of the approach to studies of rotationally excited states of such systems. We recently applied this approach to the study of H_3^+.[a] We chose this system because of the availability of a global potential energy surface of spectroscopic accuracy, and the results of converged variational calculations have been reported that can be used to assess the accuracy of the DMC calculations. As a symmetric top molecule, the nodal structures of the rotationally excited states of H_3^+ are well known and can be used in fixed-node DMC calculations. We have recently extended this methodology to asymmetric top molecules, using H_2D^+ as a test system for these types of molecules as it has a κ value near zero. Here, we describe these extensions and present the results of DMC calculations of representative rotationally excited states of H_2D^+.

---

[a] A. S. Petit, B. A. Wellen, and A. B. McCoy, J. Chem. Phys. 136, 074101 (2012).

RJ09 **15 min 4:21**

EXPLORING ROTATION-VIBRATION COUPLING IN HIGHLY FLUXIONAL MOLECULES USING SURFACE HOPPING DIFFUSION MONTE CARLO

ANDREW S. PETIT, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

Diffusion Monte Carlo (DMC) has widely been shown to be a powerful technique for studying ro-vibrational states of highly fluxional molecules and clusters. An extension of DMC to multiple potential energy surfaces (PESs) based on the Tully surface hopping approach[a] has previously been developed by our group.[b] Here, we report an application of this approach to the calculation of rotationally excited states of systems with pronounced rotation-vibration coupling and large-amplitude, zero-point vibrational motion. More specifically, for a chosen value of J, each walker in the DMC ensemble is expanded in a symmetric top basis. The expansion coefficients are updated each time-step based on the action of the rigid-rotor asymmetric top Hamiltonian. This Hamiltonian is constructed using the inverse moment of inertia tensor evaluated in the Eckart frame at the walker's position in configuration space. Each walker is then localized onto a single, K-dependent effective PES, and the effective potential energy associated with the walker's position on that surface determines the evolution of its weight in the DMC ensemble. Preliminary results of the application of this methodology to model systems such as H_3^+ and H_2D^+ will be discussed as well as its prospect for accurately evaluating ro-vibrational states of systems like CH_5^+. Finally, a comparison of this technique with our previously developed fixed-node DMC approach for the evaluation of ro-vibrational energies and wave functions will be presented.[c]

---

[a] J. C. Tully, J. Chem. Phys. 93, 1061 (1990).

[b] A.B. McCoy, Chem. Phys. Lett. 321, 71 (2000).

[c] A. S. Petit, B. A. Wellen, and A. B. McCoy, J. Chem. Phys. 136, 074101 (2012).

RJ10 **10 min 4:38**

BOUND AND SCATTERING STATE SOLUTIONS OF SCHRODINGER EQUATION FOR ASYMMETRIC WOODS SAXON POTENTIAL

N. CANDEMIR, *Physics Department, Science Faculty, Anadolu University, Eskişehir, 26470, Turkey.*

The one-dimensional time-independent Schrödinger equation is solved for asymmetric Woods-Saxon potential. The reflection and transmission coefficients and bound state solutions are obtained in terms of hypergeometric functions. Some useful figures are plotted to show the accuracy of the obtained results.

FA. ASTRONOMICAL SPECIES AND PROCESSES

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 160 MATH ANNEX

Chair: JOHN C. PEARSON, Jet Propulsion Laboratory, Pasadena, California

FA01 **15 min 8:30**

THEORETICAL AND EXPERIMENTAL WATER COLLISIONS WITH NORMAL AND PARAHYDROGEN

BRIAN J. DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099*; LAURENT WIESENFELD, *UJF-Grenoble 1/CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France*.

The experimental data set of water-hydrogen collisions has been expanded and added to previously reported data[1]. In all, three rotational transitions of water; $1_{11} \leftarrow 0_{00}$, $2_{02} \leftarrow 1_{11}$ and $1_{10} \leftarrow 1_{01}$, have been studied in the 20-250 K range via lineshape measurements in a collisional cooling system with buffer gas of both normal and parahydrogen. Unlike previous studies with the same apparatus, these measurements have a verified, stable, ortho-parahydrogen ratio and qualitatively follow trends previously predicted from collision theory. However, the agreement with theory was not uniform, and measurements of pressure-shifts were not following the predicted trends. Since these measurements provide a valuable probe of the H_2O-H_2 potential energy surface (PES), we decided to repeat the theoretical calculations with the most current PES. To improve precision of the collisional energy calculations, several more time consuming steps were applied (1) Tighter convergence of inelastic scattering was forced through a summation in partial waves up to J = 10; (2) Even tighter convergence of elastic scattering was forced through a summation up to J^{Total} = 55 (3) the parahydrogen basis sets always included the j = 2 level of H_2. Finally, the detailed resonances observed (especially in parahydrogen) required a fine energy grid for conversion of the collisional energy cross sections into temperature dependent cross-sections. The resulting data-sets are compared for each rotational transition and found to be in tight agreement ($<$ 30%) for two of the three transitions. Comparisons of the other transition, the fundamental transition of water ($1_{11} \leftarrow 0_{00}$), disagree up to 80%. We will discuss these results and their pertinence to models of cold interstellar material.

[1] B.J. Drouin, J.C. Pearson, L. Wiesenfeld and A. Faure - TF13, International Symposium on Molecular Spectroscopy, Ohio State University, 2011.

FA02 **15 min 8:47**

ROTATIONAL SPECTROSCOPY OF ISOCYANIC MOLECULES: ALLYL ISOCYANIDE AND DIISOCYANOMETHANE

R. A. MOTIYENKO, L. MARGULES, I. HAYKAL, T. R. HUET, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; E. J. COCINERO, P. ECIJA, J. A. FERNANDEZ, F. CASTANO, *Dpto. Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Barrio Sarriena s/n, 48940, Leioa, Spain*; A. LESARRI, *Dpto. Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena s/n, 47005, Valladolid, Spain*; J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS - ENSCR, 35708 Rennes Cedex 7, France*.

Isocyanides are less stable isomers of nitriles and some of them have already been observed in the interstellar medium (HNC, CH_3NC, HCCNC). But still there exists a lack of experimental spectroscopic data on simple isocyanic molecules that can represent potential astrophysical interest. In this view we have performed high resolution studies of rotational spectra of allyl isocyanide (CH_2=CH–CH_2–NC) and diisocyanomethane (CN–CH_2–NC). The rotational spectra of allyl isocyanide have been measured in the frequency range 6 – 18 GHz by means of FTMW spectrometer in Bilbao and in the frequency range 150 – 945 GHz by means of classic absorption spectroscopy in Lille. Two stable confomers of allyl isocyanide have been observed in both series of measurements. In addition, all ^{13}C-monosubstituted isotopologues and ^{15}N isotopologues were detected in natural abundance. Due to much lower kinetic stability the rotational spectrum of diisocyanomethane has been measured only in absorption using the Lille spectrometer. The spectral assignments have been supported by high-level quantum chemical calculations. For both molecules accurate sets of rotational and centrifugal distortion constants (up to the octics) have been produced. As a result, reliable predictions of transitions frequencies suitable for astrophysical detection have been obtained for both molecules. Finally, the effective and substitution structures were determined for the two conformers of allyl isocyanide, comparing the result with ab initio data.

This work is supported by Centre Nationale d'Etudes Spatiales (CNES), Action sur Projet Physico-Chimie du Milieu Interstellaire (PCMI-CNRS) and by the contract ANR-08-BLAN-0054. Spanish part acknowledges funding from the MICINN and the MINECO.

FA03 **15 min 9:04**

TERAHERTZ SPECROSCOPY OF METHYLAMINE

R. A. MOTIYENKO, L. MARGULÈS, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; V. V. ILYUSHIN, E. A. ALEKSEEV, *Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine*; B. DROUIN, S. YU, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA*; J. CERNICHARO, B. TERCERO, *Centro de Astrobiología (CSIC-INTA). Laboratory of Molecular Astrophysics. Department of Astrophysics. Ctra de Ajalvir, Km 4, 28850 Torrejòn de Ardoz, Madrid, Spain.*

Methylamine (CH_3NH_2) is a light molecule with an intense rotational spectrum that extends far beyond 1 THz even at temperatures characteristic for interstellar medium. This fact makes methylamine an interesting object of studies for THz radio telescopes like Herschel and SOFIA. In this context we present recent advances in global fitting of the rotational spectrum of parent isotopic species of CH_3NH_2 up to 2.6 THz. The Hamiltonian used in the analysis is based on the group-theoretical formalism developed by Ohashi and Hougen[a]. It has been successfully applied for the analysis of mm-wave and far-IR spectrum of methylamine[b] as well as for the analysis of sub-THz spectra of its ^{13}C isotopologue[c]. We will also present the latest results on searches for interstellar $^{13}CH_3NH_2$ as well as the results on the analysis of deuterated species of methylamine which is in progress now.

This work is supported by Centre Nationale d'Etudes Spatiales (CNES), Action sur Projet Physico-Chimie du Milieu Interstellaire (PCMI-CNRS) and by the contract ANR-08-BLAN-0054.

---

[a] Ohashi, N. and Hougen, J. T. *J. Mol. Spec.* **121** (1987) 474.

[b] Ilyushin, V.V. et al. *J. Mol. Spec.* **229** (2005) 170.

[c] R.A. Motiyenko et al. FA08, 66th International Symposium on Molecular Spectroscopy (2011).

FA04 **15 min 9:21**

THZ SPECTROSCOPY OF ACETALDEHYDE AND SEARCH OF ^{13}C SPECIES IN ORION

L. MARGULÈS, R. A. MOTIYENKO, *Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; V. V. ILYUSHIN, *Institute of Radio Astronomy of NASU, Chervonopraporna Str., 4, 61002 Kharkov, Ukraine*; B. TERCERO, J. CERNICHARO, *Centro de Astrobiología (CSIC-INTA). Laboratory of Molecular Astrophysics. Department of Astrophysics. Ctra de Ajalvir,Km 4, 28850 Torrejón de Ardoz, Madrid, Spain*; and J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France*.

Acetaldehyde (CH_3CHO) is one of the high priority complex organic molecules for the astrophysical community. There is a lack of data concerning the ^{13}C species since the measurements are limited to 40 GHz[a] up to date. This molecule displays a large amplitude motion: the hindered rotation of the methyl group with respect to the rest of the molecule. The analysis is performed with RAM36 code[b] which used the Rho Axis Method. Last year we presented the analysis of the millimeterwave spectra of the $^{13}CH_3CHO$ species[c]. We extended the analysis to the THz range of the vibrational ground state for both species. We are also analyzing the first torsional state ($\approx$140 cm^{-1}) for two reasons: first, this permits to remove correlation between parameters. Second, this state contribute to the partition function even at ISM temperature (100–150 K) since there is an influence on the column density determined in case of detection. The searches of these isotopomers are in progress in ORION.

This work was supported by the CNES and the Action sur Projets de l'INSU, PCMI. This work was also done under the ANR-08-BLAN-0054.

---

[a] Kilb, R.W.; Lin, C.C.; and Wilson, E.B.*J. Chem. Phys.* **26**, (1957) 1695

[b] Ilyushin, V.V. et al;*J. Mol. Spectrosc.* **259**, (2010) 26

[c] Margulès, L. et al; **FA07**, *66th International Symposium on Molecular Spectroscopy (2011)*

FA05 **15 min 9:38**

SPECTROSCOPY OF A MAJOR COMPLEX ORGANIC MOLECULE: MONO-DEUTERATED DIMETHYL ETHER

C. RICHARD, L. MARGULÈS, R. A. MOTIYENKO, *Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d'Ascq Cedex, France*; P. GRONER, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499*; L. H. COUDERT, *LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France*; J.-C. GUILLEMIN, *Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France*.

Dimethyl ether is one of the most abundant molecule in star-forming regions. Like other complex organic molecules, its formation process is not yet clearly established. The study of deuteration may provide crucial hints.[a]

The mono-deuterated species (CH_2DOCH3) is still a relatively light molecule; its spectrum is the most intense in the THz domain even at ISM temperatures (100–150 K). Therefore, it is is necessary to measure and assign its transitions in this range in order to be able to compute accurate predictions which should allow us to detect it with ALMA, expected to be a powerful tool to observe such isotopic species. In this context, spectra between 50 and 950 GHz were recorded in Lille with a solid-state submillimeter-wave spectrometer.

The starting point of the analysis was the centimeter-wave measurements carried out in 2003 for almost all isotopic species.[b] Results concerning the symmetric conformer of the mono-deuterated species will be presented in the paper. The fits performed with the ERHAM code[c] will be discussed. Theoretical development are in progress in order to treat the case of the asymmetric conformer.

This work is supported by the CNES and the Action sur Projets de l'INSU, PCMI. This work is also funded by the ANR-08-BLAN-0054 and ANR-08-BLAN-0225 contracts.

---

[a] Ceccarelli, Caselli, Herbst, *et al.,* (eds.), University of Arizona Press, Tucson, **951** (2007) 47

[b] Niide *et al., J. Mol. Spectrosc.* **220** (2003) 65

[c] Groner, *J. Chem. Phys.* **107** (1997) 4483

Intermission

FA06 **15 min 10:10**

TOWARDS AN ACCURATE INFRARED LINELIST FOR SO_2

XINCHUAN HUANG, *SETI Institute, 189 Bernardo Ave, Suite #100, Mountain View, CA, 94043*; DAVID W. SCHWENKE, *MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035*; TIMOTHY J. LEE, *MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035.*

The "Best Theory + High-resolution Expt Data" strategy now extends from NH_3, CO_2 to SO_2 which is considered a "weed" in ÂÂăhigh resolution astronomical data analysis (such as for Herschel, SOFIA, and JWST).ÂÂă Refining a high quality ab initio potential energy surface (PES) with selected HITRAN data, we have made significant progress toward an accurate IR line list for SO_2. Similar to the situation for CO_2, we have achieved 0.01-0.02 cm^{-1} accuracy for reliable line positions. Outliers in existing HITRAN models have been identified. Compared to CO_2, the SO_2 rovibrational energy levels are more difficult to converge. A pure, experimentally measured dataset (instead of HITRAN models) would greatly enhance the reliabilty of higher J/K and higher energy levels computed on the refined PES. An initial IR line list has been generated to test an ab initio dipole moment surface (DMS). Limitations, deficiencies, and future developments for both line positions and IR intensities will be discussed.

FA07 **15 min 10:27**

THEORETICAL NH_3 SPECTRA IN 5800-7000 CM^{-1} REGION AND CO_2 IR INTENSITY: UPDATES

XINCHUAN HUANG, *SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, CA, 94043*; DAVID W. SCHWENKE, *MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035*; TIMOTHY J. LEE, *MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035*; KEEYOON SUNG, LINDA R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109*; and SERGEY A. TASHKUN, *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 634055, Tomsk, Russia.*

Recently we have successfully applied the "Best Theory + High-resolution Experimental Data" strategy to NH_3 [a] and CO_2. [b] The essential strategy is to refine a high quality, purely ab initio potential energy surface (PES) with reliable high resolution experimental data, so the IR line lists computed on the refined PES and dipole moment surface (DMS) can go beyond simple data reproduction. The goal is to make reliable predictions for higher J/K/energy rovibrational transitions with similar accuracies, i.e. 0.01-0.03 cm^{-1}. The reliability and accuracy of data included in the refinement largely determines the quality of predictions and the ultimate merit of our work. With recent $^{14}NH_3$ experiments in 5800 - 7000 cm^{-1}, the effective coverage (with 0.01-0.03 cm^{-1} accuracy) of our NH_3 PES has extended to this complex spectral region. Excellent agreement between current experiment analysis and our primitive HSL-3 PES refinement will be presented, and source of discrepancies will be discussed. The synergy between the experiments and theory is of great value. For CO_2, we have updated the theoretical IR intensity of the $^{12}C^{16}O_2$ line list with a more reliable DMS, then carried out very detailed comparisons with both pure experimental data and HITRAN/CDSD models. Results suggest that our line lists should be useful for the astronomical or earth-based detection of CO_2 isotopologues.

---

[a] X. Huang, D.W. Schwenke, and T.J. Lee, *J. Chem. Phys.* 129, 214304 (2008); *J. Chem. Phys.* 134, 044320/044321 (2011).

[b] X. Huang, D.W. Schwenke, S.A. Tashkun, and T.J. Lee *J. Chem. Phys.* 136, ,submitted (2012).

FA08 15 min 10:44

LINE PARAMETERS OF THE PH_3 PENTAD IN THE $4 - 5\mu$m REGION

V. MALATHY DEVI, D. CHRIS BENNER, *The College of William and Mary, Williamsburg, VA 23187*; I. KLEINER, *Laboratoire Interuniversitaire des Systemes Atmospheriques (LISA), UMR 7583 CNRS/IPSL-Universites Paris-ESt and Diderot, 94010 Creteil Cedex, France*; R. L. SAMS, T. A. BLAKE, *Pacific Northwest National Laboratory, Richland, WA 99352*; LINDA R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; L. N. FLETCHER, *Department of Physics, University of Oxford, Clarendon Laboratory, Oxford, OX1 3PU, UK.*

Line positions, intensities and line shape parameters are reported for four bands of phosphine between 2150 and 2400 cm^{-1} in order to improve the spectroscopic database for remote sensing of the giant planets. Knowledge of PH_3 in this spectral region is important for Cassini/VIMS exploration of dynamics and chemistry on Saturn, as well as for interpreting the near-IR data from Juno and ESA's proposed Jupiter mission. For this study, five high-resolution (0.0023 cm^{-1}), high signal-to-noise (>2000) spectra of pure PH_3 were recorded at room temperature (298.2 K) with the Bruker IFS 125HR Fourier transform spectrometer at Pacific Northwest National Laboratory. Individual line parameters were retrieved by multispectrum fitting[a] of all five spectra simultaneously. Positions and intensities were measured for over 3100 transitions. The rotational quantum numbers of measured lines go as high as $J'' = 16$ and $K'' = 15$ in the ν_3 and ν_1 bands; some lines of the weaker bands $2\nu_4$ and $\nu_2 + \nu_4$ are also reported. The measured positions and intensities are compared to new theoretical calculations of the pentad. Lorentz self-broadened width and pressure-induced shift coefficients of many transitions were also obtained, along with speed dependence parameters. Line mixing coefficients were determined for several A^+A^- pairs of transitions for $K'' = 3, 6,$ and 9. [b]

---

[a] D. C. Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. A. Atkins, *JQSRT* **53** (1995) 705-721.

[b] Research described in this paper was performed at the College of William and Mary and the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration. L. Fletcher acknowledges support from a Glasstone Science Fellowship.

FA09 15 min 11:01

LINE BY LINE SPECTRAL PARAMETERS IN THE $4\nu_3$ SPECTRAL REGION OF METHANE

D. CHRIS BENNER, V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*; J. J. O'BRIEN, S. SHAJI, *Department of Chemistry, University of Missouri - St. Louis, St. Louis, MO 63121-4400*; P. T. SPICKLER, C. P. HOUCK, J. A. COAKLEY, J. DOLPH, K. RANKIN, *Department of Physics, Bridgewater College, Bridgewater, VA 22812.*

The near infrared bands of methane were first observed in the outer planets and Titan where atmospheric ray paths are long. The spectrum is complex, and long absorption paths in the laboratory are difficult to cool to outer solar system temperatures. At room temperature, many significant spectral lines appear per Doppler width. The band models generally used in the 890 nm spectral region of methane do not provide transmissions that are multiplicative, so scattering and inhomogeneous atmospheres cannot be properly treated using this approach.

The intracavity laser spectrometer at the University of Missouri-St. Louis was used to obtain low temperature (99-161K), low pressure (0.12-7.13 Torr), long path (3.14-5.65 km) and high resolution (0.01 cm^{-1} HWHM) spectra of methane covering the entire 890nm feature (10925-11500 cm^{-1}), the deepest band in the CCD spectral region. At these temperatures the Doppler width is 0.01 cm^{-1} and the spectral lines originating from levels higher than J"=11 and excited vibrational states are not visible. The result is a dense, but manageable spectrum from which over 11,200 line positions, intensities and lower state energies are derived on a line by line basis by the College of William and Mary multispectrum nonlinear least squares fitting program[a]. Simulations of the methane spectrum for outer planet atmospheres using our positions, intensities and lower state energies reveal a surprising amount of spectral structure at high resolution. This structure carries a great deal of atmospheric information[b].

---

[a] D. Chris Benner, C. P. Rinsland, V. M. Devi, M. A. H. Smith, and D. A. Atkins, JQSRT 1995;53:705-21.

[b] Support for the work at William and Mary was provided by NASA through grant NNX08AF06G. Support for the work at UM-St. Louis provided by NASA through grant NAG5-12013, from NSF through grant CHE-0213356 and by the University of Missouri Research Board. Partial support at Bridgewater College was provided by its Martin Science Research Institute and from an AAS Small Research Grant.

FA10 **15 min 11:18**

A GLOBAL FREQUENCY ANALYSIS OF ^{13}CH$_3$CH$_3$ INCLUDING DATA FROM THE LOWEST FOUR VIBATIONAL STATES

N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada*; V.-H. HORNEMAN, *Department of Physical Sciences, University of Oulu, PO Box 3000, Fin-90014, Oulu, Finland.*

Accuracy of the retrieved abundances for ethane from planetary atmospheres is directly linked to the quality of the spectroscopic parameters which are obtained from laboratory studies. For this reason, we have made several detailed studies of the lowest four vibrational states of ethane. We have previously reported global fits including data from the torsional bands in the ground vibrational state, the ν_9 and ν_3 fundamentals, the $\nu_9 - \nu_4 - \nu_4$ hot band, and the $\nu_{12} - \nu_9$ difference band.

Because measurements of ^{12}C/^{13}C and other isotope ratios are used to study the fractionation processes and to make inferences regarding the evolution of the planetary atmospheres, it is desirable to also have high quality spectroscopic parameters for the lowest four vibrational states of ^{13}CH$_3$CH$_3$. We have already reported a global fit which included data from the torsional bands, and the ν_{12} and ν_5 fundamentals.[a] In this work we describe a global fit which also includes data from $\nu_{12} + \nu_6 - \nu_6$ and $\nu_{11} - \nu_{12}$ bands.

---

[a] N. Moazzen-Ahmadi, R.Z. Martinez, and D. Bermejo, J. Mol. Phys. 269 (2011) 151.

FA11 ***Post-deadline Abstract*** **15 min 11:35**

DIRECT FREQUENCY COMB SPECTROSCOPY FOR THE STUDY OF MOLECULAR DYNAMICS IN THE INFRARED FINGERPRINT REGION.[a]

ADAM J. FLEISHER, BRYCE BJORK, KEVIN C. COSSEL, JUN YE, *JILA, National Institute of Standards and Technology and University of Colorado, Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA*; LORA NUGENT-GLANDORF, FLORIAN ADLER, TYLER NEELY, and SCOTT DIDDAMS, *National Institute of Standards and Technology, Boulder, Colorado 80305-3337, USA.*

The simultaneous identification of multiple chemical compounds requires spectroscopic techniques with inherently broad spectral bandwidth and high frequency resolution. This combination has been realized in the mid-infrared (MIR) molecular fingerprint region using direct frequency comb spectroscopy (DFCS) with an achieved spectral resolution on the order of 100 MHz over the entire comb bandwidth of several 100 cm^{-1}. When coupled to a high-finesse enhancement cavity or a multipass absorption cell, DFCS becomes an ultrasensitive tool for the detection of trace molecules in gas samples of biological, industrial, and atmospheric importance. Recently, the addition of a massively parallel detection scheme based on a MIR virtually imaged phased array (VIPA) disperser provides millisecond (ms) or better temporal resolution simultaneously over thousands of individual frequency channels making possible the study of transient chemical phenomena within the 2000-3500 cm^{-1} spectral window.

---

[a] This research is supported by AFOSR, DTRA, NSF, NRC, and NIST

FA12 ***Post-deadline Abstract*** **15 min 11:52**

MILLIMETRE-WAVE SPECTRUM OF ANTI-$^{13}C_1$ AND $^{13}C_2$ ISOTOPOLOGUES OF ETHANOL AND APPLICATIONS TO RADIO ASTRONOMY

AURELIA BOUCHEZ, ADAM WALTERS, SANDRINE BOTTINELLI, *IRAP, Université de Toulouse, UPS-OMP, CNRS; 9 Av. colonel Roche, BP 44346, 31028 Toulouse Cedex 4, France*; HOLGER S. P. MÜLLER, MATTHIAS H. ORDU, FRANK LEWEN, MONICA KOERBER, CHRISTIAN P. ENDRES, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany*.

The rotational spectra of the two monosubstituted ^{13}C isotopologues of the anti conformer of ethanol have been measured between 80 and 800 GHz using three different spectrometers at the Cologne Laboratory Astrophysics group. The data set was constrained for fitting with a standard Watson-S reduction Hamiltonian by rejecting transitions from high-lying states showing significant perturbation with the gauche states and by averaging some small methyl torsional splits.

This treatment is compatible with the needs for a first astrophysical search in several hot cores where the parent molecule has been already identified[abc]. Observations we carried out towards G34.3+0.15 to specifically search for ^{13}C-ethanol with the IRAM-30m single-dish telescope are presently being analyzed. I will present the preliminary results as well as upper limits obtained from spectral surveys of other hot cores. Further observations with higher-sensitivity interferometers are envisaged.

---

[a] Zuckerman B, Turner BE, Johnson DR, Clark FO, Lovas FJ, Fourikis N, et al. *Astrophys J* 1975; 196: L99−L102.

[b] Millar TJ, Olofsson H, Hjalmarson A, Brown PD. *Astron. Astrophys* 1988; 205: L5−7.

[c] Millar TJ, MacDonald GH, Habing RJ *Mon Not R Astron Soc* 1995; 273: 25-9.

FA13 ***Post-deadline Abstract*** **10 min 12:09**

INFRARED SPECTRAL STUDIES OF THE THERMALLY-DRIVEN CHEMISTRY PRESENT ON ICY SATELLITES

MARK J. LOEFFLER, REGGIE L. HUDSON, *NASA Goddard Space Flight Center, Astrochemistry Laboratory, Mail Code 691.1, Greenbelt, Md 20771.*

Remote sensing of JupiterÂŠs icy satellites has revealed that even though their surfaces are composed mostly of water ice, molecules such as SO_2, CO_2, H_2O_2, O_2, and O_3 also are present. On Europa, a high radiation flux is believed to play a role in the formation of many of the minor species detected, and numerous laboratory studies have been devoted to explore this hypothesis. In this presentation we will discuss some of our recent research on another alteration pathway, thermally-driven chemical reactions, which are also important for understanding the chemical evolution of Europa's surface and sub-surface ices. We will focus on the infrared spectra of and reactions between H_2O, SO_2, and H_2O_2 at 80 - 130 K.

FB. INFRARED/RAMAN

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 170 MATH ANNEX

Chair: SVEN THORWIRTH, University of Cologne, Koeln, Germany

FB01 **15 min 8:30**

HIGH RESOLUTION EMISSION SPECTROSCOPY OF THE VIBRATION-ROTATION BANDS OF HBO AND HBS.

G. LI[a], R.S. RAM, R.J. HARGREAVES, *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; P.F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 USA; Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*; and H. LI, *State Key Lab of Theoretical and Computational Chemistry, Jilin University, Changchun City, China, 130023.*

The vibration-rotation spectra of HBO and HBS have been investigated at high resolution using a Fourier transform spectrometer. The HBO molecules were produced in a high temperature furnace from the reaction of H_2O vapor with boron by heating a mixture of crystalline boron and boron oxide (B_2O_3) at a temperature $\sim$1350°C. The spectra were recorded in the 1100–2200 cm^{-1} and 1700–4000 cm^{-1} wavenumber regions covering the ν_3 and ν_1 fundamentals, respectively. In total 24 vibrational bands involving 30 vibrational levels of $H^{11}BO$ and 12 bands involving 18 levels of $H^{10}BO$ have been rotationally analyzed. After combining the existing microwave and infrared measurements, the absolute term values have been determined for a number of vibrationally-excited states of $H^{11}BO$ and $H^{10}BO$.

The HBS molecules were formed by the reaction of CS_2 and water vapor with crystalline boron at a temperature $\sim$1300°C. The spectra were recorded in the 850–1500 cm^{-1} and 1750–4000 cm^{-1} wavenumber regions covering the ν_3 and ν_1 frequency regions. In total 29 vibrational bands involving 33 vibrationally-excited levels of $H^{11}BS$ and 9 bands involving 12 vibrational levels of $H^{10}BS$ have been analyzed. The fitted spectroscopic parameters agree very well with the results of our *ab initio* calculations. *L*-resonance interactions observed between the 02^00 (Σ) and 02^20 (Δ) levels of HBO and HBS were analyzed using a 2×2 matrix to yield deperturbed constants.

---

[a] Current address: Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, MS#50, 60 Garden St., Cambridge, MA, 02138, USA.

FB02 **15 min 8:47**

FIRST INFRARED SPECTRA OF NITROUS OXIDE PENTAMER

M. REZAEI, J. NOROOZ OLIAEE, N. MOAZZEN-AHMADI, *Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N 1N4, Canada*; A.R.W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.*

High resolution spectra have previously been studied for N_2O dimers (two isomers), trimers (one isomer), and tetramers (two isomers). Here, we assign two new bands to the N_2O pentamer. The bands are observed in the region of the N_2O ν_1 fundamental using a tunable laser to probe a pulsed supersonic slit jet expansion. They are centered at 2233.9 and 2236.4 cm^{-1} for $^{14}N_2O$, and at 2164.4 and 2166.8 cm^{-1} for $^{15}N_2O$. Attribution to the pentamer is based on comparison of the observed rotational constants with theoretical ones from calculated cluster structures based on two rather different N_2O pair potentials. The first potential function is from a recent high level *ab initio* study.[a] The second potential is a relatively simple empirical one, based partly on fitting to bulk properties.[b] The likely pentamer structure is a completely unsymmetric one. It can be visualized starting with a highly symmetric oblate tetramer[c] which is attacked by a fifth monomer, locating itself at a favorable distance and breaking the symmetry. Interestingly, analysis of the two bands yields very similar but not quite identical ground state parameters. We believe that they are due to distinct isomers having this same basic structure but differing in the orientation direction of one N_2O monomer.

---

[a] R. Dawes, X.-G. Wang, A.W. Jasper, and T. Carrington, Jr., *J. Chem. Phys.* **133**, 134304 (2010).

[b] B. Kutcha, R.D. Etters, and R. LeSar, *J. Chem. Phys.* **97**, 5662 (1992).

[c] J.N. Oliaee, M. Dehghany, N. Moazzen-Ahmadi, and A.R.W. McKellar, *J. Chem. Phys.* **134**, 074310 (2011).

FB03 **15 min 9:04**

“PROTON SPONGES": A RIGID ORGANIC SCAFFOLD TO REVEAL THE QUANTUM STRUCTURE OF THE INTRAMOLECULAR PROTON BOND

ANDREW F. DEBLASE, MARK A. JOHNSON, *Yale University, P. O. Box 208107, New Haven, CT, 06520*; MICHAEL T. SCERBA, STEVEN BLOOM, AND THOMAS LECTKA, *Johns Hopkins University, 3400 North Charles Street, Baltimore, MD, 21218*; TRAVIS DUDDING, *Brock University, St. Catherines, ON, Canada L2S 3A1.*

Spectroscopic analysis of systems containing charged hydrogen bonds (e.g. the Zundel ion, $\mathrm{H_5O_2^+}$) in a vibrationally cold regime is useful in decongesting numerous anharmonic features common to room temperature measurements.[Roscioli, J. R.; et. al. Science 2007] This approach has been extended to conjugate acids of the “Proton Sponge" family of organic compounds, which contain strong intramolecular hydrogen bonds between proton donor (D) and acceptor (A) groups at the 1- and 8-positions. By performing $\mathrm{H_2/D_2}$ vibrational predissociation spectroscopy on cryogenically cooled ions, we explore how the proximity and spatial orientation of D and A moieties relates to the spectroscopic signature of the shared proton. In the cases studied $(\mathrm{D = Me_2N - H^+; A = OH, O(C = O)Ph})$, we observe strong anharmonic couplings between the shared proton and dark states that persist at these cryogenic temperatures. This leads to intense NH stretching features throughout the nominal CH stretching region $(2800 - 3000\mathrm{cm}^{-1})$. Isotopic substitution has verified that the oscillator strength of these broad features is driven by NH stretching. Furthermore, the study of A = O(C=O)Ph has provided a spectroscopic snapshot of the shared proton at work as an active catalytic moiety fostering ester hydrolysis by first order acylium fission $(\mathrm{A_{AC}1})$. This is apparent by the high frequency carbonyl stretch at $1792\ \mathrm{cm}^{-1}$, which is a consequence of the strong hydrogen bond to the ether-ester oxygen atom. Thus, these “Proton Sponges" are useful model systems that unearth the quantum structure and reactivity of shared proton interactions in organic compounds.

FB04 **15 min 9:21**

OBSERVATION OF SINGLE AND DOUBLE IONIC H-BONDS IN PROTONATED DIPEPTIDE IONS USING IR-IR DOUBLE RESONANCE SPECTROSCOPY

CHRISTOPHER M. LEAVITT, ARRON B. WOLK, JOSEPH A. FOURNIER, MICHAEL Z. KAMRATH, ETIENNE GARAND and MARK A. JOHNSON , *Sterling Chemistry Laboratory, Yale University, PO Box 208107, New Haven, CT 06520*; MICHAEL J. VAN STIPDONK, *Department of Chemistry, Wichita State University, 1845 Fairmont Ave, Wichita, KS 67208.*

Isomer-specific vibrational predissociation spectra are reported for the gas-phase GlySarH$^+$ and SarSarH$^+$ [gly=glycine; sar=sarcosine] ions prepared by electrospray ionization and tagged with weakly bound $\mathrm{D_2}$ adducts using a cryogenic ion trap. The contributions of individual isomers to the overlapping vibrational band patterns are isolated using a pump-probe photochemical hole-burning scheme involving two tunable infrared lasers. These patterns are then assigned by comparison with harmonic (MP2/6-311+G(d,p)) spectra for various possible conformers. In the case of GlySarH$^+$, a 9 cm^{-1} splitting of the OâĂŞH stretches associated with the C-terminal acid group is traced to cis- and trans-isomers with respect to rotation about the amide bond. The SarSarH$^+$ ion displayed three distinct band patterns, two of which are assigned to variations of the analogous cis-conformer while the third arises from a trans-configuration. Two distinct types of hydrogen bonding are observed: one involving the usual single intramolecular hydrogen bond (IHB) between the protonated amine and the nearby amide oxygen and another, only displayed in the cis-configuration, which features two amino NâĂŞHs acting as IHB donors. The latter results in formation of 5- and 8-membered intramolecular cycles, tethered by H-bonds to the amide oxygen and to the acid carbonyl, respectively. When the N-H bonds to the acid group, red-shifts are clearly recovered for both the H-bond donor (NH) and acceptor (C=O) groups involved in the linkage.

FB05 **15 min 9:38**

VIBRATIONAL COOLING OF LARGE MOLECULES IN SUPERSONIC EXPANSIONS: THE CASE OF C_{60} AND PYRENE

JACOB T. STEWART, BRIAN E. BRUMFIELD,[a] BRADLEY M. GIBSON, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; BENJAMIN J. McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

Supersonic expansions are a useful tool for cooling molecules in the gas phase. While translational and rotational degrees of freedom can generally be cooled to low temperatures ($<$30 K) using this technique, there has been conflicting evidence concerning the cooling of vibrational degrees of freedom. This cooling is particularly important for gas-phase absorption spectroscopy of large molecules with many vibrational degrees of freedom, such as buckminsterfullerene (C_{60}). We have attempted gas-phase infrared spectroscopy of C_{60} by producing C_{60} vapor in a hot ($\sim$900 K) oven and seeding the vapor in an argon supersonic expansion, but have been unable to observe any absorption signal. We attribute this to insufficient cooling of vibrational degrees of freedom in the expansion. In contrast, we have performed a similar experiment with pyrene ($C_{16}H_{10}$) heated to $\sim$430 K, which yielded rotationally-resolved spectra and an estimated vibrational temperature of 25-90 K. We will discuss these results and possible methods to obtain gas-phase absorption spectra of C_{60}.

---

[a] Present Address: Department of Electrical Engineering, Princeton University, Princeton, NJ 08544

Intermission

FB06 **15 min 10:10**

SUB-TERRAHERTZ SPECTROSCOPY OF E.COLI DNA: EXPERIMENT, STATISTICAL MODEL, AND MD SIMULATIONS

I. SIZOV, T. DOROFEEVA, T. KHROMOVA, B. GELMONT, and T. GLOBUS, *Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, VA 22904.*

We will present result of combined experimental and computational study of sub-THz absorption spectra from *Escherichia coli* (*E.coli*) DNA. Measurements were conducted using a Bruker FTIR spectrometer with a liquid helium cooled bolometer and a recently developed frequency domain sensor operating at room temperature, with spectral resolution of 0.25 cm^{-1} and 0.03 cm^{-1}, correspondingly. We have earlier demonstrated that molecular dynamics (MD) simulation can be effectively applied for characterizing relatively small biological molecules, such as transfer RNA or small protein thioredoxin from *E. coli* , and help to understand and predict their absorption spectra. Large size of DNA macromolecules (5 million base pairs for *E. coli* DNA) prevents, however, direct application of MD simulation at the current level of computational capabilities. Therefore, by applying a second order Markov chain approach and Monte-Carlo technique, we have developed a new statistical model to construct DNA sequences from biological cells. These short representative sequences (20-60 base pairs) are built upon the most frequently repeated fragments (2-10 base pairs) in the original DNA. Using this new approach, we constructed DNA sequences for several non-pathogenic strains of *E.coli*, including a well-known strain BL21, uro-pathogenic strain, CFT073, and deadly EDL933 strain (O157:H7), and used MD simulations to calculate vibrational absorption spectra of these strains. Significant differences are clearly present in spectra of strains in averaged spectra and in all components for particular orientations. The mechanism of interaction of THz radiation with a biological molecule is studied by analyzing dynamics of atoms and correlation of local vibrations in the modeled molecule. Simulated THz vibrational spectra of DNA are compared with experimental results. With the spectral resolution of 0.1 cm^{-1} or better, which is now available in experiments, the very easy discrimination between different strains of the same bacteria becomes possible.

FB07 **15 min 10:27**

ISOMER-SPECIFIC INFRARED SPECTROSCOPY AS A DIAGNOSTIC TOOL FOR REACTIVE INTERMEDIATES TOWARDS NAPHTHALENE

NATHANAEL M. KIDWELL, DEEPALI N. MEHTA, JOSEPH A. KORN, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*; JOSHUA A. SEBREE, *NASA Goddard Space Flight Center, Greenbelt, MD 20771.*

In the context of combustion, both the formation and destruction of fused-ring aromatics are important to understand in some detail. Determining the principal pathways from benzene to naphthalene and on to larger polyaromatic hydrocarbons is imperative, but with increased chemical complexity is likely to involve free radicals as intermediates which are themselves structurally complex, necessitating more detailed spectroscopic characterization for their identification. Our group has recently studied the vibronic spectroscopy of a series of $C_{10}H_9$ and $C_{10}H_{11}$ hydronaphthyl radicals, in which their thermochemical properties were evaluated with isomer specificity.[a] Here, we extend this characterization to include infrared spectra in the alkyl CH stretch region, and explore the spectroscopic consequences of electronic excitation on these CH stretch absorptions. Utilizing resonant ion-dip infrared spectroscopy (RIDIRS), we report the infrared spectra of 2,3,4-Trihydronaphthyl ($C_{10}H_{11}$) and Inden-2-ylmethyl ($C_{10}H_9$) radicals taken in the alkyl and aromatic CH stretch regions. The latter radical was misidentified in earlier studies by our group[a] as 2-Hydronaphthyl radical, appearing in a discharge of 1,2-Dihydronaphthalene in close proximity to 1-Hydronaphthyl radical. The alkyl CH stretch IR spectrum positively identifies the radical as Inden-2-ylmethyl radical, as recently reported by Schmidt and co-workers.[b] RIDIR spectra in the D_1 excited state will also be reported. These spectra show significant changes that reflect the response of the CH stretch absorptions to electronic excitation. The implications of such measurements for future studies of free radicals will be discussed.

---

[a] J. A. Sebree, V. V. Kislov, A. M. Mebel, and T. S. Zwier *J. Phys. Chem. A* **114** (6255-6262), 2010.

[b] T. P. Troy, N. Chalyavi, A. S. Menon, G. D. O'Connor, B. Fückel, K. Nauta, L. Radom, and T. W. Schmidt *Chem. Sci.* **2** (1755-1765), 2011.

FB08 **15 min 10:44**

SINGLE CONFORMATION SPECTROSCOPY OF SUBEROYLANILIDE HYDROXAMIC ACID: A MOLECULE BITES ITS TAIL

DI ZHANG, JACOB DEAN and TIMOTHY S. ZWIER, *Department of chemistry, Purdue University, West Lafayette, IN 47906..*

Suberoylanilide hydroxamic acid ($C_6H_5NHCO(CH_2)_6CONHOH$, SAHA) is a histone deacetylase inhibitor approved by the FDA for the treatment of cutaneous T-cell lymphoma. With one hydrogen bonding group adjacent to ring and the other at the end of a long C_6 hydrocarbon tail, SAHA possesses an interesting potential energy landscape to be probed by single-conformation methods. A large number of extended structures favored by entropy are offset by a few structures in which head-to-tail or tail-to-head H-bonds close a large loop between the two groups separated by the C_6 chain. We use laser desorption to bring SAHA into the gas phase and cool it in a supersonic expansion before interrogation with resonant two-photon ionization. Single-conformation UV spectra in the S_0-S_1 region and infrared spectra in the hydride stretch region were recorded using IR-UV hole-burning and resonant ion-dip infrared (RIDIR) spectroscopies, respectively. Four different conformers were observed and spectroscopically characterized. Comparison of the experimental IR spectra with density functional theory (DFT) calculations leads to assignments for two of the major conformers, which adopt head-to-tail and tail-to-head binding patterns. The implication of the observed structures for the folding landscape and configuration preference of SAHA will be discussed.

FB09 **10 min 11:01**

DFT STUDY OF SOLVENT EFFECTS ON CONFORMATIONAL EQUILIBRIA AND VIBRATIONAL SPECTRA OF 4-(1-PYRROLIDINYL)PIPERAZINE

O. BAGLAYAN, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*; G. KESAN, *Faculty of Science, University of South Bohemia, Czech Republic*; C. PARLAK, *Department of Physics, Dumlupýnar University, Kutahya, 43100, Turkey*; and M. SENYEL, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey.*

The optimized structural parameters (bond lengths, bond and dihedral angles), conformational equilibria and normal mode frequencies and corresponding vibrational assignments of 4-(1-Pyrrolidinyl)piperazine (4-pypp) have been examined by means of B3LYP hybrid density functional theory (DFT) method with 6-31++G(d,p) basis set. Furthermore, reliable vibrational assignments have made on the basis of potential energy distribution (PED) calculated and the thermodynamics functions, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of 4-pypp ($C_8H_{17}N_3$) have been predicted. Calculations are employed for different conformations of 4-pypp both in gas phase and in solution. Solvent effects are investigated using chloroform and dimethylsulfoxide. Results from the theoretical values are showed that the structural parameters, mole fractions of stable conformers, vibrational frequencies, IR intensities and Raman activities of 4-pypp are solvent dependent.

Keywords: 4-(1-Pyrrolidinyl)piperazine, vibrational spectra, solvent effect, DFT.

FB10 **10 min 11:13**

DFT, FT-RAMAN AND FT-IR INVESTIGATIONS OF 1-CYCLOPENTYLPIPERAZINE

O. BAGLAYAN, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*; M. FATIH KAYA, *Department of Physics, Dumlupýnar University, Kutahya, 43100, Turkey*; C. PARLAK, *Department of Physics, Dumlupýnar University, Kutahya, 43100, Turkey*; O. ALVER, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey*; M. SENYEL, *Physics Department, Science Faculty, Anadolu University, Eskisehir, 26470, Turkey.*

FT-IR and FT-Raman spectra of 1-cyclopentylpiperazine (1cppp) have been experimentally reported in the region of 4000-50 cm^{-1}. The optimized geometric parameters (bond lengths, bond and dihedral angles), conformational analysis, normal mode frequencies and corresponding vibrational assignments of 1cppp ($C_9H_{18}N_2$) are theoretically examined by means of B3LYP hybrid density functional theory (DFT) method together with $6-31++$G(d,p) basis set. Furthermore, reliable vibrational assignments have been made on the basis of potential energy distribution (PED) and the thermodynamics functions, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of 1cppp have been predicted. Calculations are employed for four different conformations of 1cppp both in gas phase and in solution. Solvent effects are investigated using chloroform and dimethylsulfoxide. All results indicates that B3LYP method is able to provide satisfactory results for predicting vibrational frequencies and the structural parameters, mole fractions of stable conformers, vibrational frequencies and assignments, IR and Raman intensities of 1cppp are solvent dependent.

Keywords: 1-cyclopentylpiperazine; Vibrational spectra; Solvent effect; PED; DFT; B3LYP

FB11 **15 min 11:25**

FEMTOSECOND TIME-RESOLVED INFRARED SPECTRA OF ORGANOMETALLIC COMPLEXES BOUND TO A DINUCLEAR METAL CENTER

SAMANTHA E. BROWN-XU and CHRISTOPHER B. DURR, *The Ohio State University, Department of Chemistry and Biochemistry, Columbus, Ohio 43210.*

Compounds of the form $M_2L_2L'_2$, where M_2 is a quadruply bonded metal center (M = Mo or W) and L and L' are conjugated organic ligands, are known to show interesting photophysical properties and exhibit intense metal-to-ligand charge transfer (MLCT) transitions throughout the visible spectrum. Recently, we have modified one of the ligands to incorporate a transition metal carbonyl complex bound to an organic moiety. Following excitation into the MLCT band, the vibrational modes of the organometallic ligand can be observed by fs time-resolved infrared (TRIR) spectroscopy. This allows for a visualization of where the electron density resides in the excited states, which provides useful information for designing new materials that could later be incorporated into solar devices.

FB12 *Post-deadline Abstract* **10 min 11:42**

ANALYSIS OF HIGH RESOLUTION INFRARED SPECTRA OF 1,1-DICHLOROETHYLENE IN THE $500 - 1000\ \mathrm{cm}^{-1}$ RANGE

REBECCA A. PEEBLES, SEAN A. PEEBLES, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920*; DANIEL A. OBENCHAIN, *Department of Chemistry, Wesleyan University, 52 Lawn Avenue, Middletown, CT 06459-0180.*

The far infrared beamline of the Canadian Light Source synchrotron facility has been used to record three rotationally resolved vibrational bands of 1,1-dichloroethylene in the $500 - 1000$ cm^{-1} range, at 0.00096 cm^{-1} resolution. These correspond, for the $H_2C{=}C^{35}Cl_2$ isotopologue, to an a-type band (CCl_2 antisymmetric stretch) at 796.0 cm^{-1}, a b-type band (CCl_2 symmetric stretch) at 603.0 cm^{-1}, and a c-type band (CH_2 wag) at 868.6 cm^{-1}. Anharmonic frequency calculations at the MP2/6-311++G(2d,2p) level, combined with rotational and centrifugal distortion constants from a millimeter wave study of the ground state[a], were an invaluable aid in facilitating the spectroscopic assignment for this asymmetric top ($\kappa = -0.58$). Analysis of the 796 cm^{-1} band is nearly complete, giving well determined excited state rotational and centrifugal distortion constants. Results of this analysis and progress with analysis of the other two bands will be presented.

---

[a] Z. Kisiel, L. Pszczółkowski, *Z. Naturforsch*, **50a**, (1995), 347-351.

FC. MICROWAVE

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 1000 MCPHERSON LAB

Chair: SUSANNA WIDICUS WEAVER, Emory University, Atlanta, Georgia

FC01 **15 min 8:30**

A NEW U-BAND (40 - 60 GHz) FOURIER TRANSFORM MICROWAVE SPECTROMETER

D. T. HALFEN, J. MIN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

A new U-band (40 - 60 GHz) system have been constructed for cavity Fourier transform microwave (FTMW) spectroscopy and used for molecular measurements. Cavity FTMW spectrometers typically operate between 0.5 and 40 GHz, relying on coaxial components and quarter-wave antennas to inject microwave radiation into the Fabry-Perot cavity. Above 40 GHz, these components become inefficient. The new system, implemented as a higher frequency band on the current Ziurys group spectrometer, utilizes waveguide for radiation propagation and commercial doublers to achieve continuous operation from 40 - 60 GHz. Also, the cavity has been modified for this range, and now consists of 170 mm diameter mirrors with a radius of curvature of 840 mm and a separation of 700 mm. The Q factor of the system is around 75,000. This spectrometer has been used for measurements of the N = 4 → 3 and 5 → 4 transitions of YC_2 near 46 and 57 GHz, and the N = 3 → 2 line of ScC_2 near 47 GHz.

FC02 **15 min 8:47**

FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE AlC_2 ($\tilde{X}^2A_1$) RADICAL

D. T. HALFEN, J. MIN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

The pure rotational spectrum of the AlC_2 ($\tilde{X}^2A_1$) radical in the range 4 - 60 GHz has been measured using Fourier transform microwave (FTMW) methods. The species was produced using the Discharge Assisted Laser Ablation Source (DALAS) technique in a supersonic jet expansion of aluminum vapor and CH_4, diluted in argon carrier gas. The N = 1 → 0 and 2 → 1 transitions have been measured near 22 and 44 GHz, each exhibiting fine structure and hyperfine splittings, arising from the nuclear spin of aluminum, $I(^{27}Al) = 5/2$. The higher frequency transition was recorded using a newly constructed U-band FTMW system operating at 40 - 60 GHz. The data have been analyzed with a case (b) asymmetric top Hamiltonian, and rotational, fine structure, and hyperfine constants have been determined. Measurements of the ^{13}C isotopologues are currently underway to establish a precise structure for AlC_2.

FC03 **15 min 9:04**

THE FOURIER TRANSFORM MICROWAVE SPECTRUM OF YOH AND YOD ($\tilde{X}^1\Sigma^+$)

D. T. HALFEN and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

The pure rotational spectra of YOH and YOD ($\tilde{X}^1\Sigma^+$) have been recorded in the 4 - 40 GHz range using Fourier transform microwave (FTMW) techniques. These species were created in a supersonic jet expansion of laser ablated yttrium vapor and either H_2O or D_2O vapor. The J = 1 → 0 and 2 → 1 rotational transitions have been measured for both YOH and YOD. The data have been analyzed, and rotational and centrifugal distortion constants have been determined. Metal hydroxides can possess either a linear or bent geometry. The structure of this species has been determined from these data to be linear, in agreement with previous electronic spectra. YOH is only the second 4d transition metal hydroxide, after AgOH - a bent species, to have its pure rotational spectrum measured.

FC04 **15 min 9:21**

DEVELOPMENT OF A SUBMILLIMETER MULTIPASS SPECTROMETER FOR THE STUDY OF MOLECULAR IONS

A. CARROLL, B. ROCHER, J. C. LAAS, B. A. DePRINCE, B. HAYS, S. L. WIDICUS WEAVER, *Department of Chemistry, Emory University, Atlanta, GA 30322*; S. LANG, *Department of Chemistry, New College of Florida, Sarasota, FL 34243.*

We have developed a multipass spectrometer for the submillimeter spectral region that is being used to study molecular ions through gas phase spectroscopy. The optical configuration is based on the design of Perry and coworkers that was implemented in the optical regime. To our knowledge, this is the first implementation of this optical configuration at long wavelengths. The setup involves two nearly concentric spherical mirrors that focus the multiple beam passes into a small area, or "waist", in the middle of the sample chamber. A supersonic molecular beam is coupled to the setup so that the molecular beam crosses the optical path at the waist. Initial studies have focused on neutral test molecules to probe the physical properties of the molecular beam under various arrangements of the molecular source relative to the optical path. Current studies focus on coupling a plasma discharge source to the setup to enable the study of molecular ions. Here we present the design of this instrument, compare the spectrometer capabilities to a traditional single pass spectrometer, and discuss the results of initial spectroscopic studies.

FC05 **15 min 9:38**

THE DEVELOPMENT AND IMPLEMENTATION OF CHIRPED-PULSE FREQUENCY COMBS AT MILLIMETER WAVELENGTHS

AMANDA L. STEBER, BRENT J. HARRIS, JUSTIN L. NEILL, KEVIN K. LEHMANN, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904.*

Technological advances in such areas as active multiplier chains and high-speed digital electronics are enabling the development of sensitive high-throughput spectroscopic instruments in the millimeter and submillimeter ranges. Recently there has been an effort to develop multiplexed direct absorption spectroscopy techniques that use frequency comb sources derived from phase-locked pulse trains (often created using ultrafast lasers). We have used a high-speed arbitrary waveform generator (AWG with 12 GHz sample rate) to create frequency combs at mm-wave wavelengths using a chirped pulse as the repeating waveform. This waveform has important advantages including 100% duty cycle for the light output and compatibility with the use of frequency multiplier chains that extend the bandwidth of the comb proportional to the frequency multiplication factor. A new spectrometer operating in the 260-290 GHz range using active multiplier chains has been constructed to test the capabilities of chirped-pulse frequency comb spectroscopy for molecular rotational spectroscopy. The spectral properties of the mm-wave combs generated following x24 frequency multiplication, methods for compressed bandwidth detection using a dual-comb approach, and frequency comb analogs of FM spectroscopy will be presented.

FC06 **10 min 9:55**

CHIRPED-PULSE FOURIER TRANSFORM MM-WAVE SPECTROSCOPY FROM 260-290 GHz

BRENT J.HARRIS, AMANDA L. STEBER, JUSTIN L. NEILL, KEVIN K. LEHMANN, BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904.*

A broadband chirped-pulse Fourier transform mm-wave spectrometer operating in the 260-290 GHz frequency range has been constructed. The spectrometer uses a dual channel arbitrary waveform generator to create both the chirped excitation pulse and local oscillator (LO) inputs to the mm-wave multiplier chains for excitation (x24) and detection in a sub-harmonic mixer. The excitation and LO pulses are derived from the same single frequency phase-locked microwave oscillator giving good phase stability to permit deep averages of the molecule free induction decay signals. The excitation chirp from 2 to 3.5 GHz is generated by a high-speed arbitrary waveform generator and provides direct access to the full bandwidth of the spectrometer. All frequency sources in the experiment are locked to a 10 MHz Rb-disciplined oscillator providing direct frequency calibration for molecular transitions in the Fourier transform frequency-domain spectrum. Benchmark measurements on methylamine, ethyl cyanide, acetonitrile, and acrylonitrile will be presented. The design advantages and disadvantages for full bandwidth and segmented measurements will be discussed with an emphasis on detection limits caused by the presence of spurious signals from either LO purity or intermodulation (IM) at the digitizer.

Intermission

FC07 15 min 10:30

BROADBAND MICROWAVE SPECTROSCOPY OF LARGE MOLECULES

V. ALVIN SHUBERT, DAVID SCHMITZ, THOMAS BETZ, and MELANIE SCHNELL, *Max-Planck Advanced Study Group at the Center for Free-Electron Science, Hamburg, Germany and Max-Planck-Institut für Kernphysik, Heidelberg, Germany.*

The rotational spectra of large molecules and their complexes have transitions that are dense and spread over a wide range of the microwave region of the electromagnetic spectrum, thus making their investigation with cavity-based rotational spectrometers very time-consuming and tedious. Recent developments now allow broadband microwave spectrometers to record wide portions of the rotational spectrum within a single, 100 μs measurement.[a] We have constructed a broadband rotational spectrometer covering the 2-8 GHz frequency region, a range particularly well suited to obtain the spectra of large and more complex molecules with large moments of inertia and thus small rotational constants. These spectra, aided by theory, offer detailed insights about the molecular geometry, conformational preferences, hyperfine structure, internal rotation, and, in combination with IR excitation, conformational isomerization reactions. Here we present the characterization and performance of our spectrometer and report the initial results of selected molecules.

---

[a] G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman, and B. H. Pate *Rev. Sci. Instr.* **79**(5), 053103 2008.

FC08 15 min 10:47

SENSITIVITY LIMITS OF DEEP AVERAGE BROADBAND MICROWAVE AND MM-WAVE SPECTRA

MATT T. MUCKLE, DANIEL P. ZALESKI, AMANDA STEBER, BRENT HARRIS, AND BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319.*

High-speed digitizers have enabled the field of broadband molecular rotational spectroscopy at microwave-to-THz frequencies. Improvements in data throughput from these digitizers makes it feasible to perform deep averages (often more than 1 million time-domain averages of the free induction decay) to increase the measurement sensitivity. The use of broadband signal detection introduces new issues that are key for determining the practical sensitivity limits of these spectrometers. The practical limit on spectrometer sensitivity is often set by the number of spurious signals that are generated by the molecular signals themselves. For example, in cases where the molecular signals are down converted prior to digitization, the spectral purity of the local oscillator is crucial with spurious frequencies introducing spectral images. It is also possible to generate new local oscillator frequencies within the broadband mixers typically used in the broadband down conversion. A second issue it the potential for a vast number of intermodulation (IM) spurious signals resulting from the beating of two strong molecular transitions. This beat frequency can subsequently modulate all other molecular signals adding sidebands to all transitions at the beat frequency of the transition pair. This talk will summarize our experience with the spurious signal levels coming from these effects and the strategies we have adopted to minimize spurious signals in spectra where high sensitivity is necessary.

FC09 10 min 11:04

PRECISE THZ MEASUREMENTS OF HCO^+, N_2H^+ AND CF^+

CRISTINA PUZZARINI, GABRIELE CAZZOLI, *Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy.*

Herschel Space Observatory, Stratospheric Observatory for Infrared Astronomy (SOFIA), and Atacama Large Millimeter Array (ALMA) opened up the submillimeter-wave region of the electromagnetic spectrum by making astronomical investigations of unprecedented high sensitivity and angular resolution possible. Observations with these tools require the knowledge of transition frequencies in the frequency regions mentioned above with accuracies preferably better than 100 kHz. In view of this need, we have extended the investigation of the rotational spectra of HCO^+, N_2H^+ and CF^+ up to the THz region, thus improving the predictive capabilities at higher frequencies of the determined spectroscopic parameters.

FC10 **15 min 11:16**

MOLECULAR SUPERFLUIDITY IN SMALL CLUSTERS OF (pH$_2$)$_N$-HCN STUDIED WITH ROTATIONAL SPECTROSCOPY

STEVE P. DEMPSTER and WOLFGANG JÄGER, *Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.*

In a recent experimental and theoretical study by Li *et al.*[a], direct evidence for molecular superfluidity in small clusters of *para*-hydrogen molecules (pH$_2$) seeded with CO$_2$ was discovered. The authors also found that the anisotropy of the CO$_2$–pH$_2$ interaction potential promotes localization of the pH$_2$ molecules at larger cluster sizes ($N \approx 17$ *para*-hydrogen molecules), with a simultaneous reduction of the superfluid pH$_2$ fraction. It has been suggested that light rotors with a more isotropic interaction potential, such as CO and HCN, are potentially more subtle probes of pH$_2$ superfluidity that would allow superfluidity to persist, especially at larger values of N. In the current study, the hyperfine structures of the end-over-end rotational transitions of (pH$_2$)$_N$-HCN clusters were measured using our chirped-pulse Fourier transform microwave spectrometer. Based on tentative assignments, the evolution of effective rotational constants, B_{eff}, as a function of N shows evidence for superfluid behaviour by a clear "turn-around" point at a low N value. The trend of B_{eff} vs. N and the results from the hyperfine structure analysis will be compared to the recent studies on He$_N$-HCN and (pH$_2$)$_N$-CO.

---

[a] H. Li, R. J. Le Roy, P.-N. Roy, and A. R. W. McKellar, *Phys. Rev. Lett.* **105**, 133401 (2010).

FC11 **15 min 11:33**

PUMP/PROBE MICROWAVE-OPTICAL DOUBLE RESONANCE (PPMODR) STUDY OF TUNGSTEN CARBIDE (WC) AND PLATINUM CARBIDE (PtC)

FANG WANG and TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry Arizona State University Tempe, Arizona 85287-1604 U.S.A.*

Gas-phase metal-containing molecules serve as ideal venues for testing computational methodologies being developed to predict chemical properties of simple molecules. The most accurate determination of molecular properties comes from the analysis of pure rotational spectra, which for metal containing molecules can be difficult to obtain. One powerful method for recording pure rotational spectrum is to use the PPMODR technique [a] which couples the sensitivity of optical detection with the precision of molecular beam microwave spectroscopy. Here we report on the application of PPMODR to the study of tungsten carbide, WC [b], and platinum carbide, PtC. The $J = 1 \rightarrow 2$ pure rotational transitions in the $X^3\Delta_1(v = 0)$ state of ^{186}W^{12}C and ^{184}W^{12}C reveal a small splitting, an analysis of which provides accurate determination of the rotational and Ω-doubling parameters for the $X^3\Delta_1(v = 0)$ state, which are critical to the proposed electron electric dipole moment experiments (eEDM) [c,d,e]. The implications for the proposed eEDM measurements will be presented. We also report on the $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ rotational transitions of PtC for the $X^1\Sigma^+(v = 0)$ state. The ^{195}Pt(I=1/2) nuclear spin-rotation interaction parameter, C$_I^{eff}$, was determined to be 0.138(6) MHz. A comparison with other Pt-containing molecules and a proposed molecular orbital correlation diagram is given.

---

[a] W. J. Childs, Physics Reports 211, No. 3 (1991).

[b] F. Wang and T. C. Steimle, J. Chem. Phys. 136, 044312 (2012).

[c] J. Lee, E. R. Meyer, R. Paudel, J. L. Bohn and A. E. Leanhardt, J. Mod. Opt. 56 2005, (2009).

[d] F. Wang and T. C. Steimle, J. Chem. Phys. 134, 201106 (2011).

[e] F. Wang and T. C. Steimle, J. Chem. Phys. 135, 104313 (2011).

FC12 **15 min 11:50**

LABORATORY DETECTION AND MICROWAVE SPECTRUM of ScC_2 RADICAL (X^2A_1)

JIE MIN, DEWAYNE T. HALFEN, LUCY. M. ZIURYS, *Department of Chemistry and Biochemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.*

The pure rotational spectrum of ScC_2 (X^2A_1) has been measured using Fourier transform microwave (FTMW) spectroscopy. This is the first study of ScC_2 by any spectroscopic technique. In the FTMW system, the molecule was synthesized using the discharge assisted laser ablation source (DALAS) from a mixture of 0.25 % methane in argon and the ablation of a scandium rod. Spectra of the main isotopologue, ScC_2, as well as $Sc^{13}C^{13}C$ and $Sc^{13}C^{12}C$, have been recorded in the frequency range of 4-60 GHz. Three rotational transitions have been measured, each exhibiting fine structure and hyperfine splittings due to scandium nuclear spin (I =7/2). The data have been analyzed with a $^2A_1$ Hamiltonian and rotational, spin-rotation constants and Sc and ^{13}C hyperfine parameters have been determined. The spectra are consistent with a triangular structure and a $^2A_1$ ground electronic state as predicted by theory. A precise structure will be presented.

FC13 ***Post-deadline Abstract*** **15 min 12:07**

SUB-MILLIMETER/TERAHERTZ SPECTROSCOPY OF FeH AND FeD ($X^4\Delta_i$)

M. P. BUCCHINO and L. M. ZIURYS, *Department of Chemistry and Biochemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, Arizona 85721.*

Direct measurements of the lowest pure rotational transitions of the Ω = 7/2, 5/2, and 3/2 ladders of FeD and of the Ω = 1/2 ladder of FeH in the $^4\Delta_i$ ground electronic states have been conducted using millimeter/sub-millimeter direct absorption techniques in the frequency range 530-810 GHz. Both species were created in an AC discharge from the reaction of $Fe(CO)_5$ with H_2 or D_2. In several of these transitions lambda-doubling and proton/deuterium hyperfine structure have been resolved. These data improve on the zero field frequencies predicted from previous LMR data by several MHz.[a] Accurate frequencies are crucial for sub-millimeter searches for FeH toward the interstellar medium. Searches for additional transitions are in progress.

[a] J.M. Brown, H. Korsgen, S.P. Beaton, & K.M. Evenson, J. Chem. Phys. 124, 234309 (2006)

FD. MINI-SYMPOSIUM: COLD QUANTUM SYSTEMS

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 1015 MCPHERSON LAB

Chair: DAVID ANDERSON, University of Wyoming, Laramie, Wyoming

FD01 ***INVITED TALK*** **30 min 8:30**

SPECTROSCOPY AND CHEMISTRY OF COLD MOLECULES

TAKAMASA MOMOSE, *Department of Chemistry, The University of British Columbia, Vancouver, CANADA.*

Molecules at low temperatures are expected to behave quite differently from those at high temperatures because pronounced quantum effects emerge from thermal averages. Even at 10 K, a significant enhancement of reaction cross section is expected due to tunneling and resonance effects. Chemistry at this temperature is very important in order to understand chemical reactions in interstellar molecular clouds. At temperatures lower than 1 K, collisions and intermolecular interactions become qualitatively different from those at high temperatures because of the large thermal de Broglie wavelength of molecules. Collisions at these temperatures must be treated as the interference of molecular matter waves, but not as hard sphere collisions. A Bose-Einstein condensate is a significant state of matter as a result of coherent matter wave interaction. Especially, dense para-H_2 molecules are predicted to become a condensate even around 1 K.

A convenient method to investigate molecules around 1 K is to dope molecules in cold matrices. Among various matrices, quantum hosts such as solid para-H_2 and superfluid He nano-droplets have been proven to be an excellent host for high-resolution spectroscopy. Rovibrational motion of molecules in these quantum hosts is well quantized on account of the weak interactions and the softness of quantum environment. The linewidths of infrared spectra of molecules in the quantum hosts are extremely narrow compared with those in other matrices. The sharp linewidths allow us to resolve fine spectral structures originated in subtle interactions between guest and host molecules. In this talk, I will describe how the splitting and lineshape of high-resolution spectra of molecules in quantum hosts give us new information on the static and dynamical interactions of molecules in quantum medium. The topics include dynamical response of superfluid environment upon rotational excitation, and possible superfluid phase of para-H_2 clusters. I will also describe our current efforts to make free cold molecules for the study of cold chemistry.

FD02 **15 min 9:05**

COLD ION-MOLECULE CHEMISTRY WITH A STARK DECELERATOR BEAMLINE

JAMES M. OLDHAM, MARTIN T. BELL, LEE D. HARPER, TIMOTHY P. SOFTLEY, *Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, United Kingdom OX1 3TA.*

We describe an experimental method for studying ion-molecule reactive collisions at very low energies. Building on our previous work using an electrostatic quadrupole guide as a source of cold neutral molecules, we discuss a proof of principle study of the charge-exchange reaction between cold xenon ions and Stark decelerated ammonia molecules.

Ammonia molecules from a pulsed supersonic expansion are produced at low velocities using the Stark deceleration technique of Meijer and co-workers. The decelerated molecules are focussed using pulsed electrostatic hexapoles into the centre of a radiofrequency ion trap where they collide with cold xenon ions. A fast-opening vacuum-compatible mechanical shutter installed in the beamline is used to prevent transmission of the undecelerated molecules and carrier gas into the ion trap chamber.

To prepare the target ions, the ion trap is loaded with calcium ions, which are Doppler laser cooled to form a low-temperature ordered “Coulomb crystal” phase. Xenon ions formed by resonant multiphoton ionisation are subsequently loaded and sympathetically cooled through their Coulomb interaction with the laser-cooled ions. The spatial distribution of fluorescence emitted by the laser-cooled ions in the multicomponent crystal is imaged; reactive collisions of Xe^+ with ND_3 are observed and quantified through changes in this distribution. By varying the high voltage switching sequence applied to the decelerator, the velocity of the ammonia molecules can be tuned from around 250 m/s to 35 m/s. For collisions with trapped xenon ions, this corresponds to collision energies (expressed in temperature units) from 65 K down to close to 1 K.

FD03 **15 min 9:22**

PROGRESS TOWARD SLOWING AND COOLING OF CaF WITH OPTICAL BICHROMATIC FORCES

EDWARD E. EYLER and MICHAEL A. CHIEDA, *Department of Physics, University of Connecticut, Storrs, CT 06269, USA*.

While rapid progress has been made on slowing and cooling of molecules by optical radiative forces,[a] there remain major obstacles because molecules do not have true two-level cyling transitions — eventually they are “lost" to radiative decay into a dark state. The optical bichromatic force (BCF) can multiply the available velocity change for a given number of radiative cycles, by employing alternating cycles of excitation and stimulated emission from opposing directions. We recently proposed methods for BCF deceleration of CaF molecules with about 12.4 times the acceleration of the usual radiative force,[b] and demonstrated the feasibility of the scheme with test experiments in metastable helium. Experiments on the CaF molecule are now getting underway, similar to the scheme in Ref. [*b*] except that we utilize the 531 nm $B\,^2\Sigma^+ \leftrightarrow X\,^2\Sigma^+$ transition rather than the $A \leftrightarrow X$ transition. Although our initial tests will emphasize transverse deflection, which is particularly easy to achieve, longitudinal deceleration by 150 m/s or more should eventually be possible. We also expect significant laser-induced cooling due to the non-adiabatic BCF velocity profile. This research is supported by the National Science Foundation.

---

[a] J. F. Barry, E. S. Shuman, E. B. Norrgard, and D. DeMille, *Phys. Rev. Lett.*, accepted (2012).

[b] M. A. Chieda and E. E. Eyler, *Phys. Rev. A* **84**, 063401 (2011).

FD04 **15 min 9:39**

SPECTROSCOPIC ANALYSIS OF THE A AND 3 $^1\Sigma^+$ STATES OF ^{39}K^{85}Rb

JIN-TAE KIM, *Department of Photonic Engineering, Chosun University, Gwangju, 501-759, Korea*; YONGHOON LEE, *Department of Chemistry, Mokpo National University, Jeonnam 534-729, Korea*; BONGSOO KIM, *Department of Chemistry, KAIST, Daejeon, 305-701, Korea*; DAJUN WANG, *Department of Physics,The Chinese University of Hong Kong, Shatin, Hong Kong*; PHILLIP L. GOULD, EDWARD E. EYLER, and WILLIAM C. STWALLEY, *Department of Physics, University of Connecticut, Storrs, CT 06269-3046, USA*.

The vibrational levels of the mutually strongly perturbed $1\,^1\Pi - 2\,^3\Sigma^+ - b\,^3\Pi$ states of ^{39}K^{85}Rb[a] were previously assigned by using a combination of molecular beam and ultracold molecule (UM) excitation spectra, the latter generated from levels of the $a\,^3\Sigma^+$ state formed following photoassociation to a level of the 3(0^-) state. In a follow-on study using the same techniques, we have now successfully assigned high vibrational levels of the A and 3 $^1\Sigma^+$ states from the excitation spectra of UMs formed by PA to both 3(0^+) and 3(0^-) levels. The $^1\Sigma^+$ states are absent in the UM spectra for levels formed by the 3(0^-) PA level. This absence has been explained by considering Hund’s case (c) selection rules and the transition dipole moment calculations by Kotochigova *et al.*[b] between the upper excited $A\,^1\Sigma^+(2(0^+))$ state and the three Ω components at the ground state dissociation limit. This work is supported by NRF in Korea (Grant 2009-0085319 at Chosun and Grants 2011-0001335 and 2011-0020419 at KAIST) and by NSF (Grant PHY-0855613) and AFOSR (Grant MURI FA9550-09-1-588) in the US.

---

[a] J. T. Kim, Y. Lee, B. Kim, D. Wang, W. C. Stwalley, P. L. Gould, and E. E. Eyler, Phys. Chem. Chem. Phys. **13**, 18755 (2011).

[b] S. Kotochigova, E. Tiesinga, and P. S. Julienne, Phys. Rev. A **68**, 022501 (2003).

FD05 **15 min 9:56**

OBSERVATION OF BLUE-DETUNED PHOTOASSOCIATION TO THE 2 (0_g^+) STATE OF $^{85}\mathrm{Rb}_2$ VIA REMPI

M. A. BELLOS, R. CAROLLO, D. RAHMLOW, J. BANERJEE, M. BERMUDEZ, E. E. EYLER, P. L. GOULD, and W. C. STWALLEY, *Department of Physics, University of Connecticut, Storrs, CT 06269.*

We report photoassociation of ultracold atoms to vibrational levels blue of the $^{85}\mathrm{Rb}_2$ $5s + 5p_{1/2}$ asymptote, in the previously-unobserved 2 (0_g^+) Hund's case (c) state that corresponds to the 2 $^1\Sigma_g^+$ state in Hund's case (a). These excited-state ultracold molecules decay to the $a\,^3\Sigma_u^+$ state and are detected by pulsed REMPI through the 2 $^3\Sigma_g^+$ state. We also see an order of magnitude enhancement in the $v' = 111$, $J' = 5$ ro-vibrational level of the 2 (0_g^+) state and present evidence for resonant coupling between this level and the $v' = 155$ of the 2 (1_g) state, seen earlier in photoassociative trap loss[a]. Following photoassociation to the observed levels of the 2 (0_g^+) state, spontaneous decay populates vibrational levels approximately halfway up the $a\,^3\Sigma_u^+$ potential well, including levels $v'' = 18$ though $v'' = 24$. This pathway complements the blue-detuned photoassociation technique previously developed by this group[b], which accesses the bottom of the a state potential. This work is supported by the NSF and AFOSR.

---

[a] R. A. Cline, J. D. Miller, and D. J. Heinzen, Phys. Rev. Lett. **73**, 632 (1994)

[b] M. A. Bellos, *et. al.*, Phys. Chem. Chem. Phys. **13**, 18880 (2011)

Intermission

FD06 **15 min 10:30**

DEVELOPING CONTINUOUS-WAVE RAMAN LASERS USING SOLID PARA-HYDROGEN AND BARIUM NITRATE FOR MOLECULAR SPECTROSCOPY APPLICATIONS

WILLIAM R. EVANS, *Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801*; TAKAMASA MOMOSE, *Department of Chemistry, The University of British Columbia, Vancouver, BC Canada V6T 1Z1*; BENJAMIN J. McCALL, *Departments of Chemistry, Astronomy and Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

Many interesting molecular targets have vibrational transitions between 5 and 10 μm. However, widely tunable continuous-wave laser sources in this region are extremely rare. One possible solution to this situation is with continuous-wave Raman lasers. We will present our recent work toward the construction of two continuous-wave Raman lasers: one using solid *para*-hydrogen as the Raman shifting medium, and the other using barium nitrate. Solid *para*-hydrogen is a promising medium for a continuous-wave Raman laser because of its high Raman gain coefficient (18 cm/MW, almost 400 times higher than any room-temperature crystal), wide spectral transmission window (transparent from ~100 nm to ~30 μm), its nature as a "quantum crystal," and its large Raman shift (4150 cm^{-1} in the solid). We will also describe our more recent work designing and constructing a continuous-wave Raman laser in barium nitrate. Barium nitrate has the advantage of being the room-temperature crystal with the highest Raman gain coefficient, as well as being highly transparent from 350 to 1800 nm. Barium nitrate has been used as a continuous-wave Raman shifter for several years. Our recent work builds upon this foundation, combining lessons learned from our work with solid *para*-hydrogen. Our design is the first barium nitrate Raman laser using an actively-locked, doubly-resonant laser cavity. This holds the promise of requiring much lower threshold pump powers than previous setups. We will discuss some of the details in designing and building these lasers. Finally, we will report on the current state of our projects as well as anticipated future work.

FD07 15 min 10:47

IMPROVED ANALYTICAL POTENTIALS FOR THE $a\,^3\Sigma_u^+$ and $X\,^1\Sigma_g^+$ STATES OF Cs_2

JESSE BALDWIN, ROBERT J. LE ROY, *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.*

Recent studies of the collisional properties of ultracold Cs atoms have led to a renewed interest in the singlet and triplet ground-state potential energy functions of Cs_2. Coxon and Hajigeorgiou recently determined an analytic potential function for the $X\,^1\Sigma_g^+$ state that accurately reproduces a large body of spectroscopic data that spanned 99.45% of the potential well.[a] However, their potential explicitly incorporates only the three leading inverse-power terms in the long-range potential, and does not distinguish between the three asymptotes associated with the different Cs atom spin states. Similarly, Xie *et al.* have reported two versions of an analytic potential energy function for the $a\,^3\Sigma_u^+$ state that they determined from direct potential fits to emission data that spanned 93 % of its potential energy well.[b,c] However, the tail of their potential function model was not constrained to have the inverse-power-sum form required by theory. Moreover, a physically correct description of cold atom collision phenomena requires the long-range inverse-power tails of these two potentials to be identical, and they are not. Thus, these functions cannot be expected to describe cold atom collision properties correctly. The present paper describes our efforts to determine improved analytic potential energy functions for these states that have identical long-range tails, and fully represent all of the spectroscopic data used in the earlier work[a,b,c] as well as photoassociation data that was not considered there[d] and experimental values of the collisional scattering lengths for the two states.[e]

---

[a] J. A. Coxon and P. Hajigeorgiou, J. Chem. Phys. **132**, 09105 (2010).

[b] F. Xie *et al.* J. Chem. Phys. **130** 051102 (2009).

[c] F. Xie *et al.* J. Chem. Phys. **135**, 024303 (2011).

[d] J. G. Danzl *et al.*, Science, **321**, 1062 (2008).

[e] C. Chin, *et al.*, Phys. Rev. Lett. **85**, 2717 (2000); P. J. Leo, C. J. Williams, and P. S. Julienne, Phys. Rev. Lett. **85**, 2721 (2000).

FD08 15 min 11:04

RUBIDIUM ATOMS ON HELIUM DROPLETS: ANALYSIS OF AN EXOTIC RYDBERG COMPLEX

FLORIAN LACKNER, GÜNTER KROIS, MARKUS KOCH, and WOLFGANG E. ERNST, *Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.*

Rubidium atoms on the surface of superfluid helium droplets have been excited into Rydberg states. The excitation spectrum of the Rb-He_N system has been recorded from the 5^2D state manifold up to the ionization threshold[a] by resonant three-photon-ionization time-of-flight spectroscopy[b]. The observation of droplet size dependent shifts of excited states with respect to bare atom states is explained by a decreased quantum defect and a lowered ionization threshold. Within the scope of a Rydberg model[c] we demonstrate that quantum defects and ionization thresholds are constant for each specific Rydberg series, which confirms the Rydberg character of excited Rubidium states on helium droplets. A set of six Rydberg series could be identified. Individual Rydberg states are observed with effective principle quantum numbers up to $n^* \approx 19$ and $l \leq 3$, for which the expectation value of the electron orbital radius is about ten times larger than the droplet radius.

---

[a] M. Theisen, F. Lackner, G. Krois, and W.E. Ernst, J. Phys. Chem. Lett., 2, 2778-2782 (2011)

[b] F. Lackner, G. Krois, M. Theisen, M. Koch, and W.E. Ernst, Phys. Chem. Chem. Phys., 13, 18781-18788 (2011)

[c] J.E. Murphy, J.M. Berg, A.J. Merer, N.A. Harris, and R.W. Field, Phys. Rev. Lett. 65, 1861 (1990)

FD09 **10 min 11:21**

PHOTOABSORPTION OF Ag (N = 6 - 6000) CLUSTERS IN He DROPLETS: A TRANSITION FROM SINGLE- TO MULTI-CENTERED GROWTH

LUIS F. GOMEZ, EVGENY LOGINOV, RUSSELL SLITER, ANDREY F. VILESOV, *Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482*; AVIK HALDER, NAIHAO CHIANG, NICHOLAS GUGGEMOS, VITALY V. KRESIN, *Department of Physics, University of Southern California, Los Angeles, CA 90089-0484*.

Ag clusters with up to thousands of atoms were grown in large He droplets and studied by optical spectroscopy. For clusters smaller than about 10^3 the spectra are dominated by a surface plasmon resonance near 3.8 eV and a broad feature in the UV, consistent with the absorption of individual metallic particles. Larger Ag clusters reveal an unexpectedly strong, broad absorption extending to lower frequencies down to approximately 0.5 eV. This suggests a transition from single-center to multi-center formation, in agreement with estimates of the kinetics of Ag cluster growth in He droplets. Moreover, the spectra of large clusters develop a characteristic dispersion profile at 3.5âĂŞ4.5 eV, indicative of the coexistence of localized and delocalized electronic excitations in composite clusters, as predicted theoretically. We also report on the characterization of He droplet beams, obtained in the supercritical expansion regime, comprised of large droplets of up to 10^{11} atoms.

FD10 ***Post-deadline Abstract*** **15 min 11:33**

MOLECULAR ION SPECTROSCOPY OF BACL$^+$

STEVEN J. SCHOWALTER, KUANG CHEN, WADE G. RELLERGERT, SCOTT T. SULLIVAN, AND ERIC R. HUDSON, *Department of Physics and Astronomy, University of California, Los Angeles, California 90095, USA*.

We discuss our efforts to perform high-resolution spectroscopy of the BaCl$^+$ ion, an exciting candidate for ultracold molecular ion studies. This work details our search for a predicted predissociation channel between the first-excited $B^1\Sigma$ and $A^1\Pi$ states. It is expected that the rovibrational resolution afforded by predissociation spectroscopy will allow us to efficiently measure molecular-ion rovibrational temperatures. This is a crucial step in confirming our method to produce ultracold molecular ions via sympathetic collisions with a ^{40}Ca MOT. To observe the predissociation of trapped BaCl$^+$, we detect slight increases in fragment Ba$^+$ with a novel time-of-flight device using radial extraction from a linear quadrupole trap.

FE. THEORY

FRIDAY, JUNE 22, 2012 – 8:30 AM

Room: 2015 MCPHERSON LAB

Chair: RUSSELL PITZER, The Ohio State University, Columbus, Ohio

FE01 **10 min 8:30**

OBSERVATION OF SINGLET-TRIPLET TRANSITIONS IN CAPACITIVE PHOTOCURRENT SPECTROSCOPY OF ORGANIC SOLAR CELLS

HUI LIU, JINJUN LIU, *Department of Chemistry, University of Louisville, Louisville, KY 40292*; HEMANT M. SHAH, AND BRUCE W. ALPHENAAR, *Department of Electrical & Computer Engineering, University of Louisville, Louisville, KY 40292*.

Fullerene derivatives such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{60}BM$) and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$) are promising electron acceptors for use in efficient organic solar cells. Capacitive photocurrent spectra of both $PC_{60}BM$ and $PC_{70}BM$ in conjunction with indium tin oxide (ITO) reveal peaks with wavelengths longer than the $S_1 \leftarrow S_0$ transitions.[a] The energies of low-lying triplet states of both molecules calculated using the ZINDO/S method agree with the experimentally observed transition frequencies. An excitation mechanism that involves collisions between the photoinduced free electrons in ITO and the organic molecules on the interface is proposed to explain the experimental observation. Tests on other organic solar cells are in process. Possibilities of improving the conversion efficiency of organic solar cells utilizing this mechanism will be discussed.

---

[a] Hemant M. Shah and Bruce W. Alphenaar, unpublished result.

FE02 **15 min 8:42**

REMARKS ON THE PHASE CHANGE OF THE ELECTRONIC WAVE FUNCTION UPON GOING ONCE AROUND A JAHN-TELLER CONICAL INTERSECTION IN VIBRATIONAL COORDINATE SPACE

JON T. HOUGEN, *Sensor Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA*.

In this talk we revisit, with pedagogical emphasis for high-resolution spectroscopists, some presently existing discussions of phase factors for fixed-nuclei electronic wavefunctions in the Jahn-Teller problem. We give explicit examples, for a symmetric pyramidal NH_3-like molecular shape, of perfectly reasonable variants of such electronic wavefunctions that do not transform into their negatives upon going once around the conical intersection (i.e., that do not exhibit a Berry phase change of -1), as well as an example calculation for the pseudo-rotational energy levels and wavefunctions near the bottom of a deep Jahn-Teller moat that does not make use of half-integral quantum numbers and that does not require abandoning ordinary C_{3v} point group theory. Some cautionary remarks on drawing inappropriate conclusions from overly hasty Berry phase arguments will also be presented.

FE03 **15 min 8:59**

AN AB INITIO MODEL HAMILTONIAN FOR THE $e' \otimes e'$ and $e' \otimes e''$ SINGLET STATES OF Si_3

D. A. MATTHEWS, J. F. STANTON, *Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712*.

The recent[a] mass-selected REMPI spectrum of the silicon trimer in the 2.25-2.6 eV region has been partially assigned in terms of a triplet-triplet transition. However, several remaining features appear to be due to transitions from the ground singlet to one of two upper singlet states, both of these belonging to the same electron configuration. To aid in the assignment of these features, a model Hamiltonian has been developed for the $e' \otimes e'$ and $e' \otimes e''$ singlet states of Si_3 (7 states in total), including quadratic vibronic (Jahn-Teller and psuedo-Jahn-Teller) interactions and a quartic expansion of the diabatic potential. This Hamiltonian has been fit to *ab initio* single-point energies calculated using the full EOMDEA-CCSDT method and the Widmark-Roos ANO basis set.

---

[a] N. J. Reilly, D. L. Kokkin, J. F. Stanton and M. C. McCarthy, submitted.

FE04 15 min 9:16

DIFFUSION MONTE CARLO STUDIES OF THE GROUND-STATE STRUCTURE AND ENERGETICS OF H_5^+ AND ITS ISOTOLOGUES

ZHOU LIN and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

H_5^+ is an important intermediate in the proton transfer reaction between H_3^+ and H_2 in interstellar clouds. The highly fluxional nature of this simple molecular ion makes theoretical studies challenging. Diffusion Monte Carlo (DMC) is an excellent method to obtain accurate zero-point energies of such systems, given a potential energy surface (PES). In this work, the zero-point energies of H_5^+ and its deuterated isotopologues are calculated using DMC, with the full-dimensional PES's from the Roncero group[a] and the Bowman group.[b] The results are in good agreement with the previously reported values.[c] Using the descendant weighting method, projections of the probability amplitude onto various internal coordinates are investigated. Based on these projections, the ground-state expectation values of some microscopic properties, including the molecular geometries, rotational constants and dipole moments, are evaluated to aid in future high-resolution spectroscopic studies. Furthermore, the PES contains 120 equivalent minima, and the results of the DMC simulations are used to explore the extent to which the system is able to tunnel among these minima. The results show very low probabilities for exchanges between the center and outer hydrogen atoms at the ground vibrational state, due to the relatively high barriers that seperate these minima. Higher probabilities are predicted for the excited states.

---

[a] A. Aguado, P. BarragÃÂąn, R. Prosmiti, G. Delgado-Barrio, P. Villarreal, and O. Roncero, J. Chem. Phys. 133, 024306 (2010)

[b] Z. Xie, B. J. Braams, and J. M. Bowman, J. Chem. Phys. 122, 224307 (2005)

[c] P. H. Acioli, Z. Xie, B. J. Braams, and J. M. Bowman, J. Chem. Phys. 128, 104318 (2008)

FE05 15 min 9:33

MODELING SPIN-ORBIT COUPLING IN THE MONOHALOCARBENES

SILVER NYAMBO AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

The monohalocarbenes CHX (X = F, Cl, Br, I) are model systems for examining carbene singlet-triplet energy gaps and spin-orbit coupling. In a series of studies, our group and others have used Single Vibronic Level (SVL) emission spectroscopy and Stimulated Emission Pumping (SEP) spectroscopy to probe the ground vibrational level structure in these carbenes, which has provided a wealth of spectroscopic information and clearly demonstrated the presence of perturbations involving the low-lying triplet state for X = Cl, Br, and I. To model these interactions in more detail, we used the structures, harmonic frequencies, and normal mode displacements from *ab initio* and DFT calculations to calculate the vibrational overlaps of the singlet and triplet state levels, incorporating the full effects of Dushinsky mixing. These results were then incorporated with the purely electronic spin-orbit matrix element into a matrix diagonalization routine which calculated the term energies of the mixed singlet-triplet levels, which were iteratively fit to the extensive experimental results from SVL emission and SEP spectroscopy for the carbenes and their deuterated isotopomers. These calculations have allowed many new assignments to be made, particularly for CHI, and provided improved estimates of the spin-orbit coupling matrix elements and singlet-triplet gaps.

FE06 **15 min 9:50**

THEORETICAL INVESTIGATION OF THE M^+-RG_2 (M = ALKALINE EARTH METAL; RG = RARE GAS) COMPLEXES

ADRIAN M. GARDNER, RICHARD J. PLOWRIGHT, JACK GRANEEK, TIMOTHY G. WRIGHT, *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*; and W. H. BRECKENRIDGE, *Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112, USA.*

Metal cation rare gas complexes provide an expectedly simple system with which to investigate intermolecular interactions. Despite this, we have previously found the M^+-RG (M = alkaline earth metal) complexes to very complicated systems, with the complexes of the heavier rare gases displaying surprisingly large degrees of chemical character.[a,b,c] Here we extend these studies by examining the nature of these interactions with increasing degrees of solvation through investigating the M^+-RG_2 complexes using high level *ab initio* techniques. Intriguing trends in the geometries and dissociation energies of these complexes have been observed and are rationalized.

---

[a] A. M. Gardner, C. D. Withers, J. B. Graneek, T. G. Wright, L. A. Viehland and W. H. Breckenridge, *J. Phys. Chem. A*, **2000**, *114*, 7631.

[b] A. M. Gardner, C. D. Withers, T. G. Wright, K. I. Kaplan, C. Y. N. Chapman, L. A. Viehland, E. P. F. Lee and W. H. Breckenridge, *J. Chem. Phys.*, **2010**, *132*, 054302.

[c] M. F. McGuirk, L. A. Viehland, E. P. F. Lee, W. H. Breckenridge, C. D. Withers, A. M. Gardner, R. J. Plowright and T. G. Wright, *J. Chem. Phys.*, **2009**, *130*, 194305.

FE07 ***Post-deadline Abstract*** **15 min 10:07**

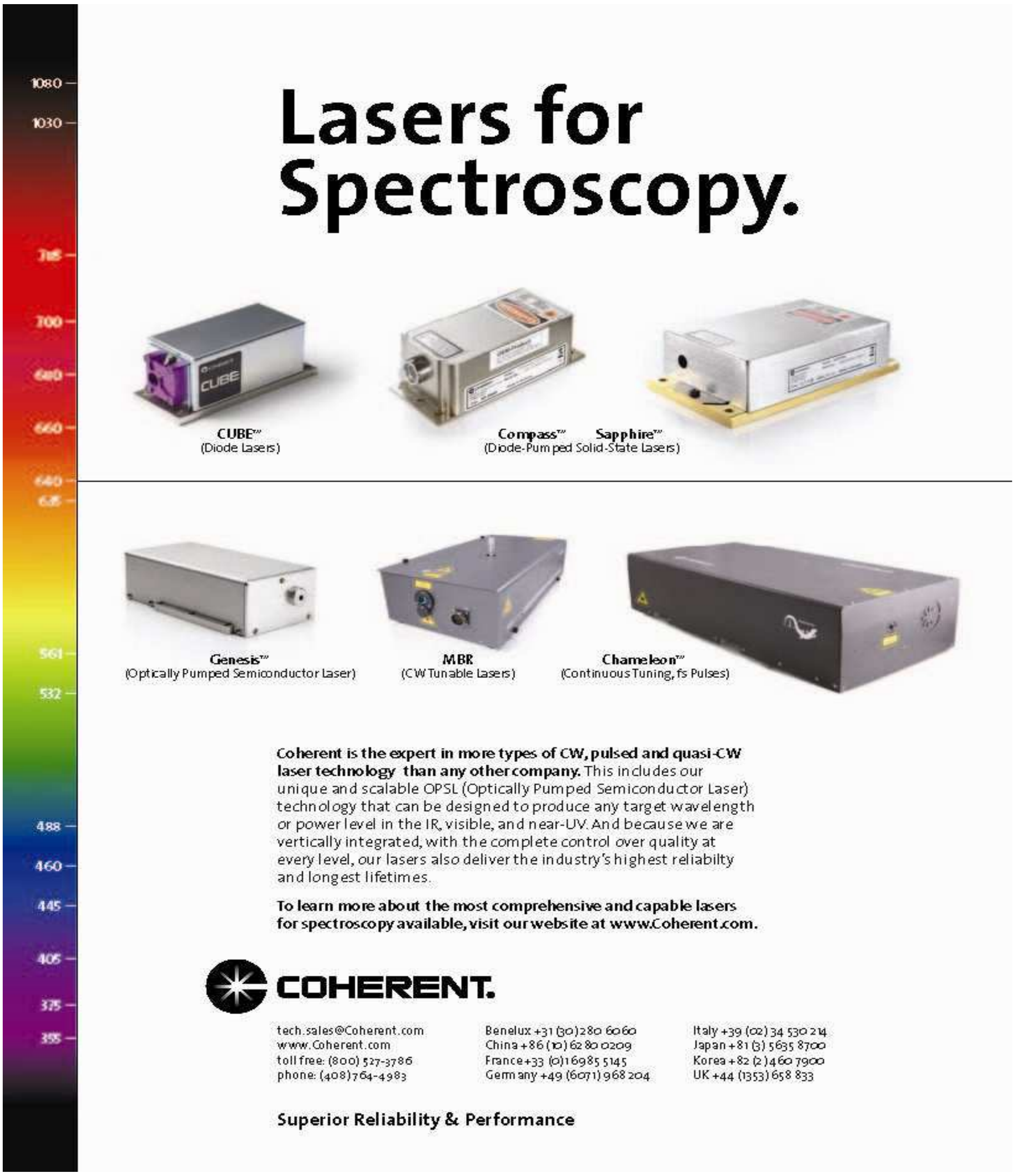
ELUCIDATION OF PROTON-ASSISTED FLUXIONALITY IN TRANSITION-METAL OXIDE CLUSTERS

RAGHUNATH O. RAMABHADRAN, NICHOLAS J. MAYHALL, EDWIN L. BECHER III, AREFIN CHOWDHURY, KRISHNAN RAGHAVACHARI(S), *Department of chemistry, Indiana University, Bloomington, IN-47405.*

The phenomenon of fluxionality in the reactions of transition-metal oxide clusters provides many opportunities in various industrial and catalytic processes. We present an electronic structure investigation of the fluxionality pathways when anionic W3O6âĂŞ and Mo3O6âĂŞ clusters react with three small molecules - water, ammonia and hydrogen sulfide. The presentation features a detailed understanding of (a) how the fluxionality pathway occurs and (b) the various factors that affect the fluxionality pathway - such as the metal, different spin-states and the nature of the non-metal in the reacting small molecule.

AUTHOR INDEX

The Symposium expresses its appreciation to
COHERENT
for Subsidizing the Cost of the Coffee



The Symposium expresses its appreciation to
Virginia Diodes
for Subsidizing the Cost of the Monday evening reception
for Distinguished Guests

Virginia Diodes Incorporated (VDI) is the leading supplier for solid-state based terahertz components and systems. VDI’s products include detectors, mixers, and frequency-multipliers as well as integrated transmitter and receiver sub-systems for reliable operation from 50 GHz to 2 THz. VDI integrated systems now include Vector Network Analyzer Extension systems and the PM4 Power Meter for test and measurement to THz frequencies. VDI components include in-house fabricated GaAs Schottky diodes and Microelectronic devices; visit www.vadiodes.com.

The Symposium Thanks *The Journal of Physical Chemistry A* for Subsidizing the Cost of the Picnic for the Students

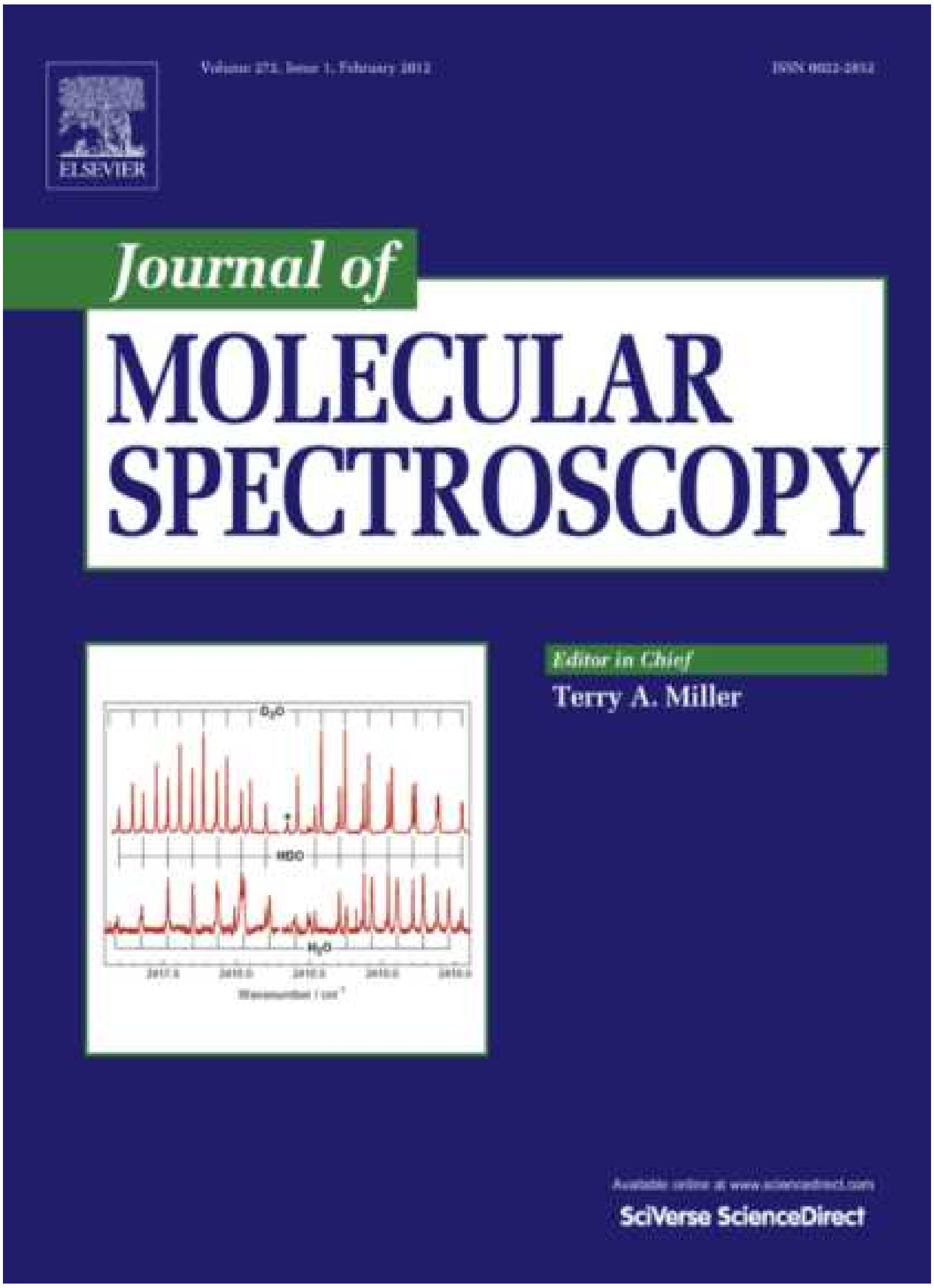
The Symposium Thanks **Quantel Laser**
for its Support of the Women's Lunch in Memory of Ralph Swaine

The Symposium expresses its appreciation to

Elsevier

for its support of the

Journal of Molecular Spectroscopy Special Lecture



Journal of
MOLECULAR
SPECTROSCOPY

Editor in Chief
Terry A. Miller

SciVerse ScienceDirect

The Coblentz Society – fostering understanding and application of vibrational spectroscopy

Call for Award Nominations

See http://www.coblentz.org/ for more information

ABB Bomem-Michelson Award: ABB sponsors the Bomem-Michelson Award to honor scientists whom have made theoretical and/or experimental contributions to vibrational, molecular, Raman, or electronic spectroscopy. The recipient must be actively working and at least 37 years of age. The nomination should include a resume of the candidate's career and a synopsis of research achievements that qualify the candidate for the ABB sponsored Bomem-Michelson Award. **Nominations for the 2013 award are open through June 30.**

Coblentz Award: The Coblentz Award is presented annually to a young molecular spectroscopist. The candidate must be under the age of 40 on January 1st of the year of the award. Nominations should include a detailed description of the nominee's accomplishments, a CV and as many supporting letters as possible. Annual updates to files of nominated candidates are encouraged. **Nominations for the Coblentz Award are open between January 3rd and July 15th each year.**

Craver Award: The Craver Award is presented annually to an outstanding molecular spectroscopist. The candidate must be under the age of 45 on January 1st of the year of the award. The work be in any aspect of applied analytical vibrational spectroscopy, including (near-, mid-, or far-infrared) IR, THz, or Raman spectroscopy. Nominees are welcome from academic, government, or industrial research. Nominations must include a detailed description of the nominee's accomplishments, CV or resume, and at least three supporting letters. **Nominations for the Craver Award are open between March 30th and August 30th each year.**

Ellis R. Lippincott Award: The Ellis R. Lippincott Award is presented annually in recognition of significant contributions and notable achievements in the field of vibrational spectroscopy. The medal is jointly sponsored by the Coblentz Society, the Optical Society of America and the Society for Applied Spectroscopy. Recipients must have made significant contributions to vibrational spectroscopy as judged by their influence on other scientists. Because innovation was a hallmark of the work of Ellis R. Lippincott, this quality in the contributions of candidates will be carefully appraised. **Nominations are open between January 1st and October 1st each year.**

Williams-Wright Award: The Williams-Wright Award is presented annually to an individual who has significantly contributed to vibrational spectroscopy while working in industry rather than academia or a national laboratory. The nomination should clearly state the significance of the candidate's contributions in IR and/or Raman spectroscopy, instrumental development, theory, and applications of vibrational spectroscopy. The nomination packet should additionally include a resume of the nominee's career including a publication list, and the Awardee must still be active in industry when the award is presented. **Nominations for the 2013 Williams-Wright award will be accepted through June 30.**

Honorary Membership: The Coblentz Society awards honorary memberships in the Society to people who have made outstanding contributions to the field of vibrational spectroscopy or any other field related to the purposes of the Society. Nominations close on **February 1st** each year, with awards announced at the Annual Members Meeting at Pittcon and presented at FACSS. Send your nomination for 2013 to Prof. Michael Myrick, Coblentz Society President at michael.myrick@coblentz.org.