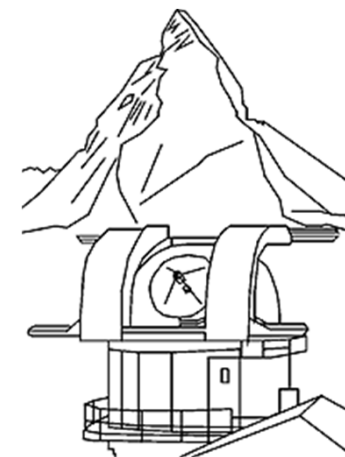


Light Induced Reactions In Cold Traps

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Sandra Brünken

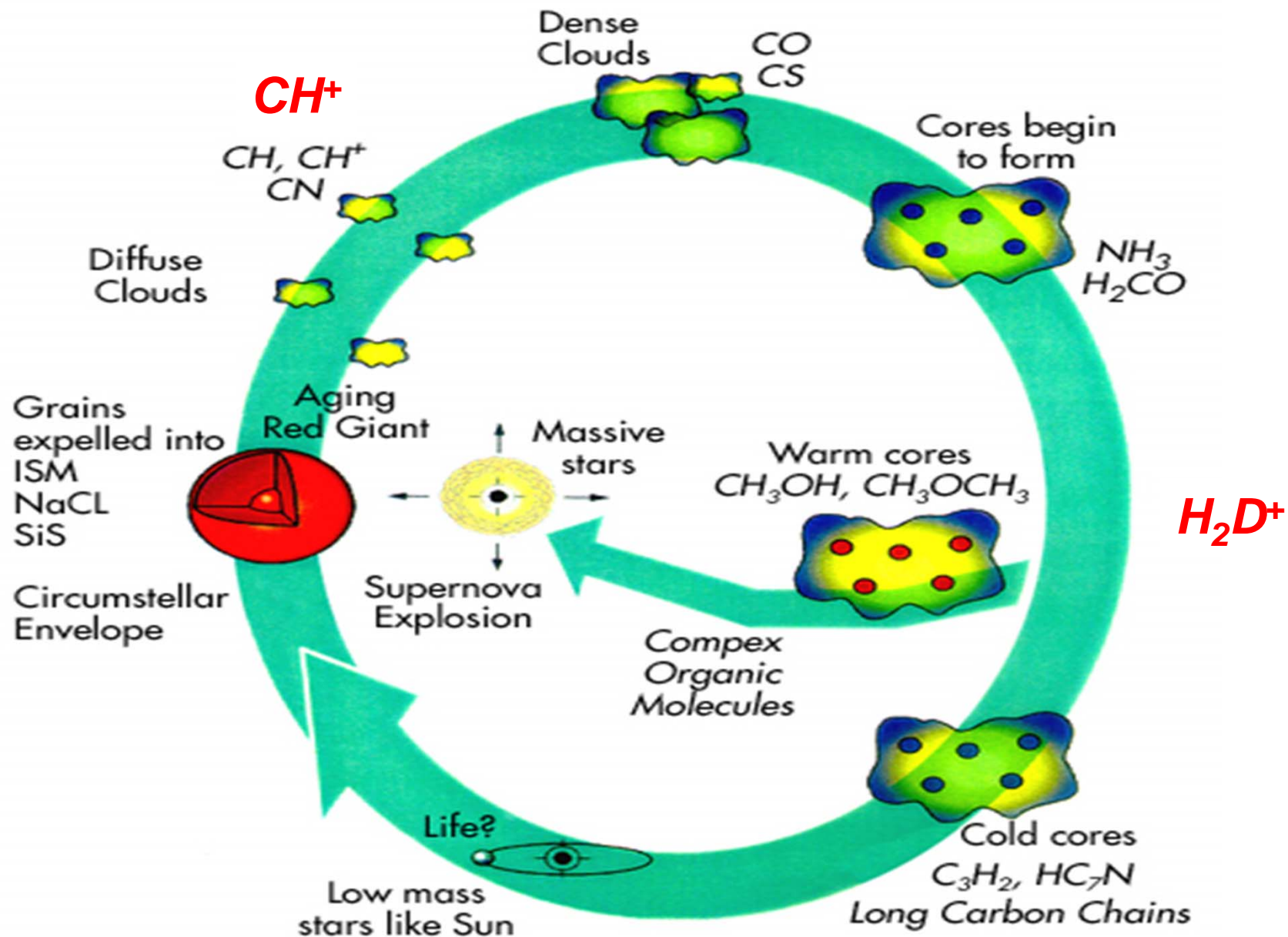


Oskar Asvany

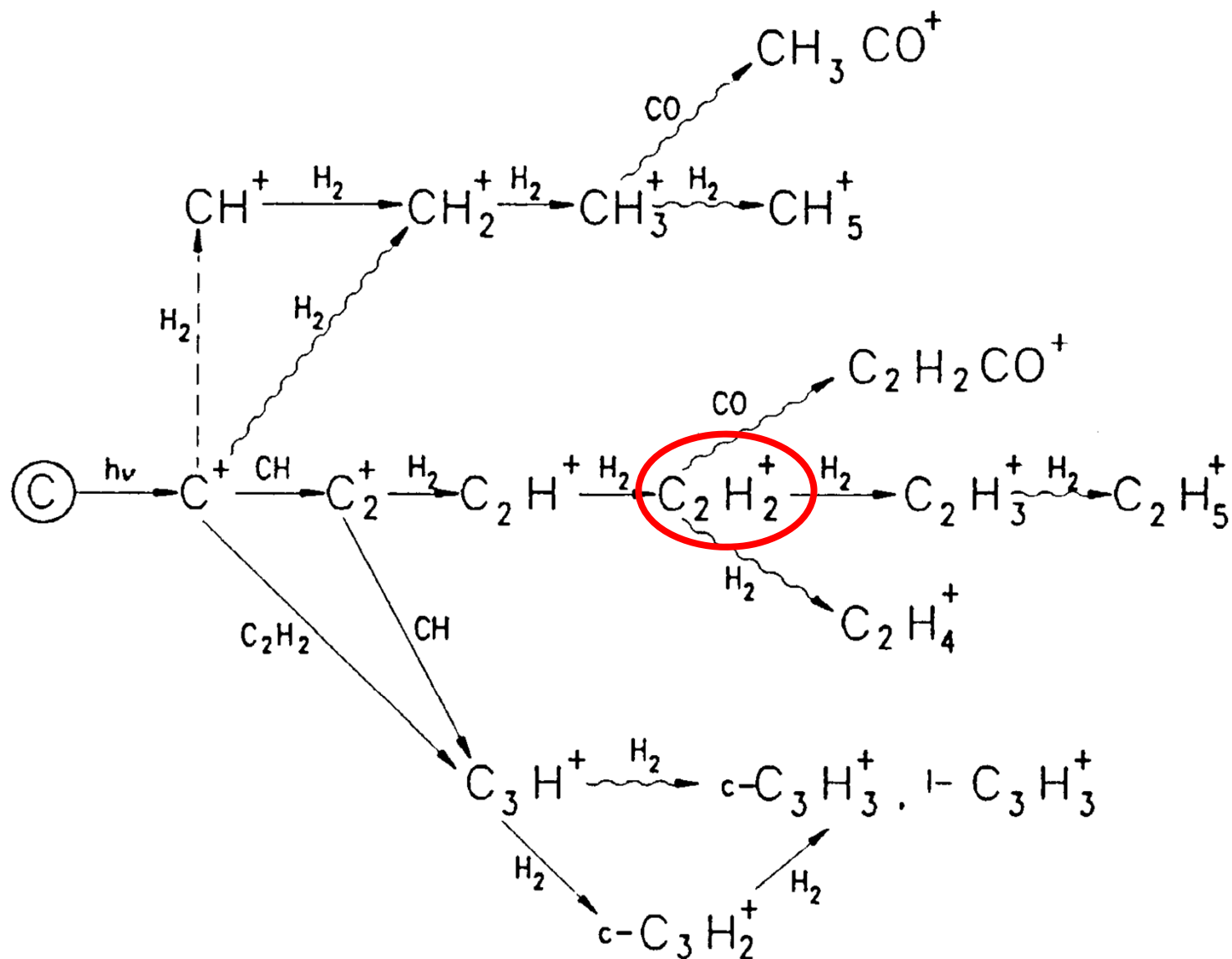


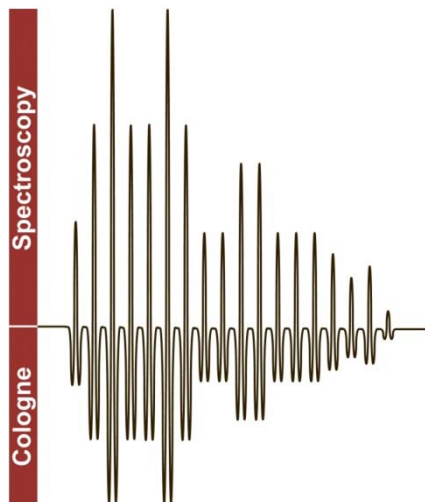
Dieter Gerlich

Life cycle of Stars



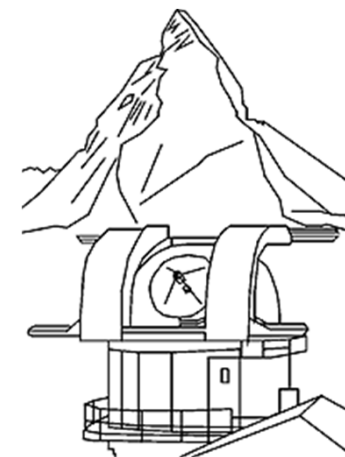
Formation of Small Hydrocarbons under Interstellar Conditions





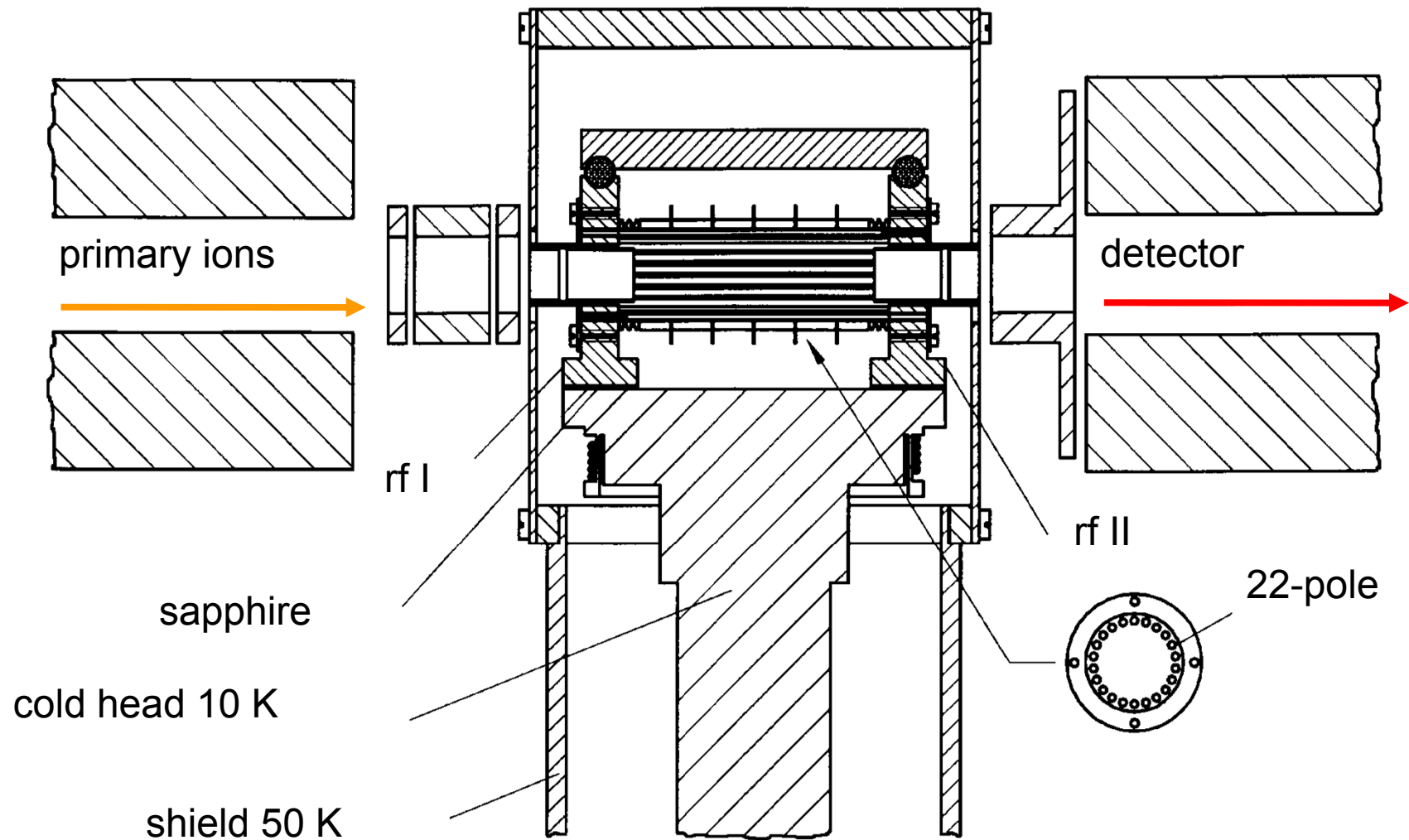
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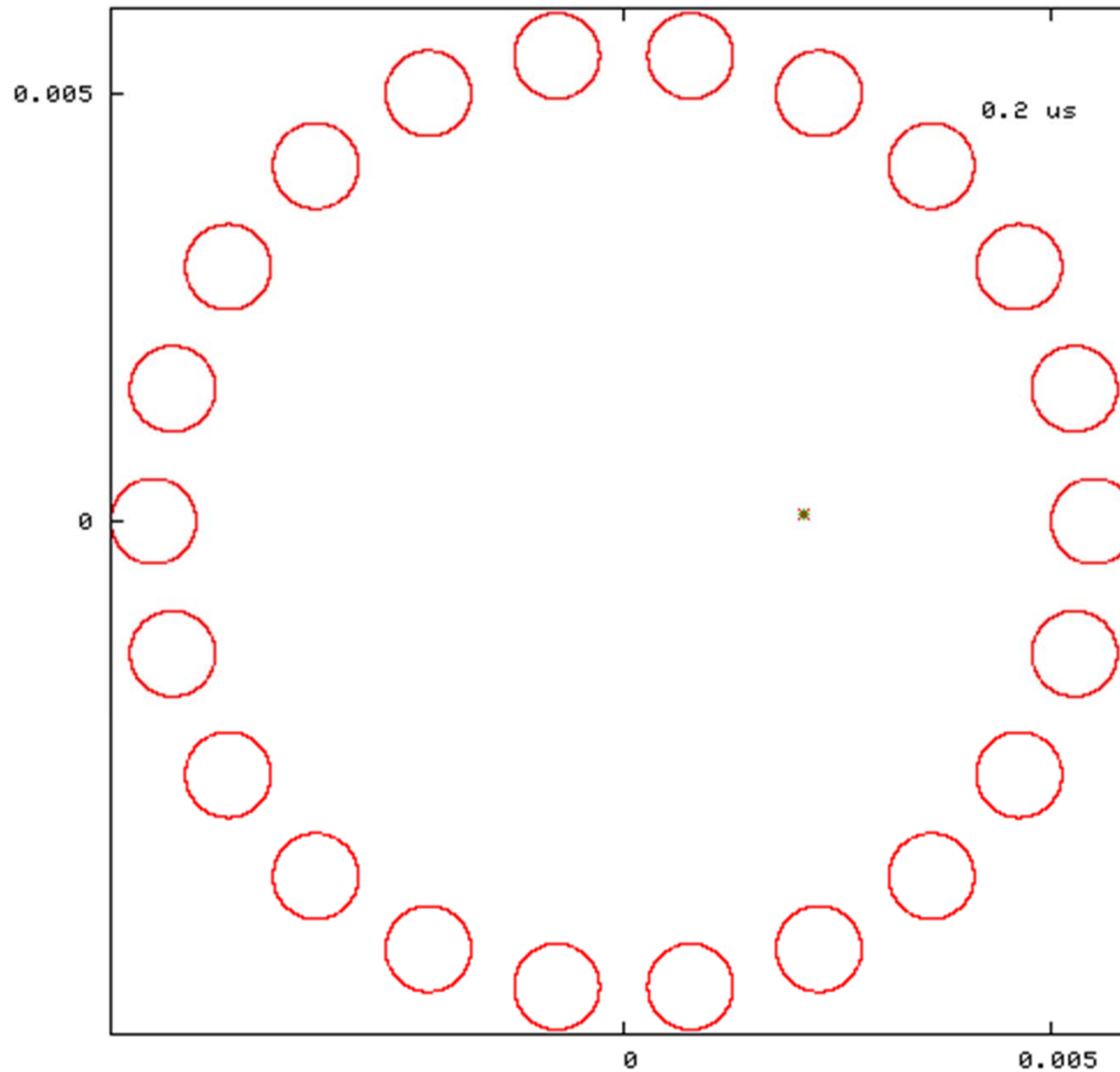


- The Astrophysical Picture: Cold Ions in Space and Laboratory
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22-Pole Low Temperature Ion Trap



Trajectories of ions in 22-pole trap



$$\Omega = 17 \text{ MHz}$$

$$V_0 = 20 \text{ V}$$

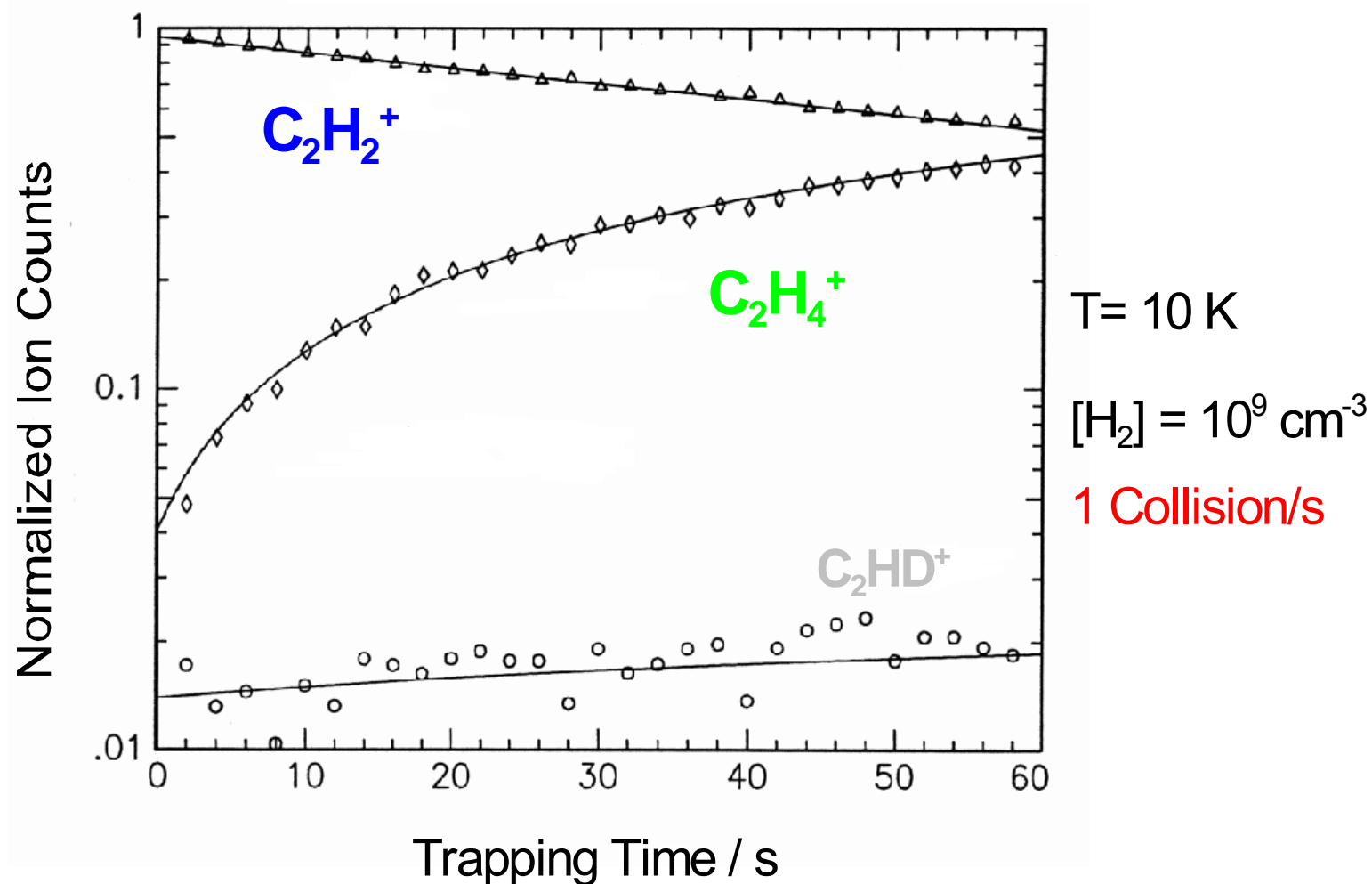
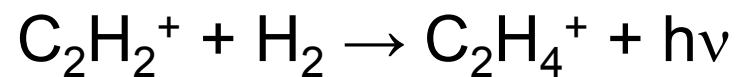
$$+ \quad m=20u$$

$$\times \quad m=2u$$

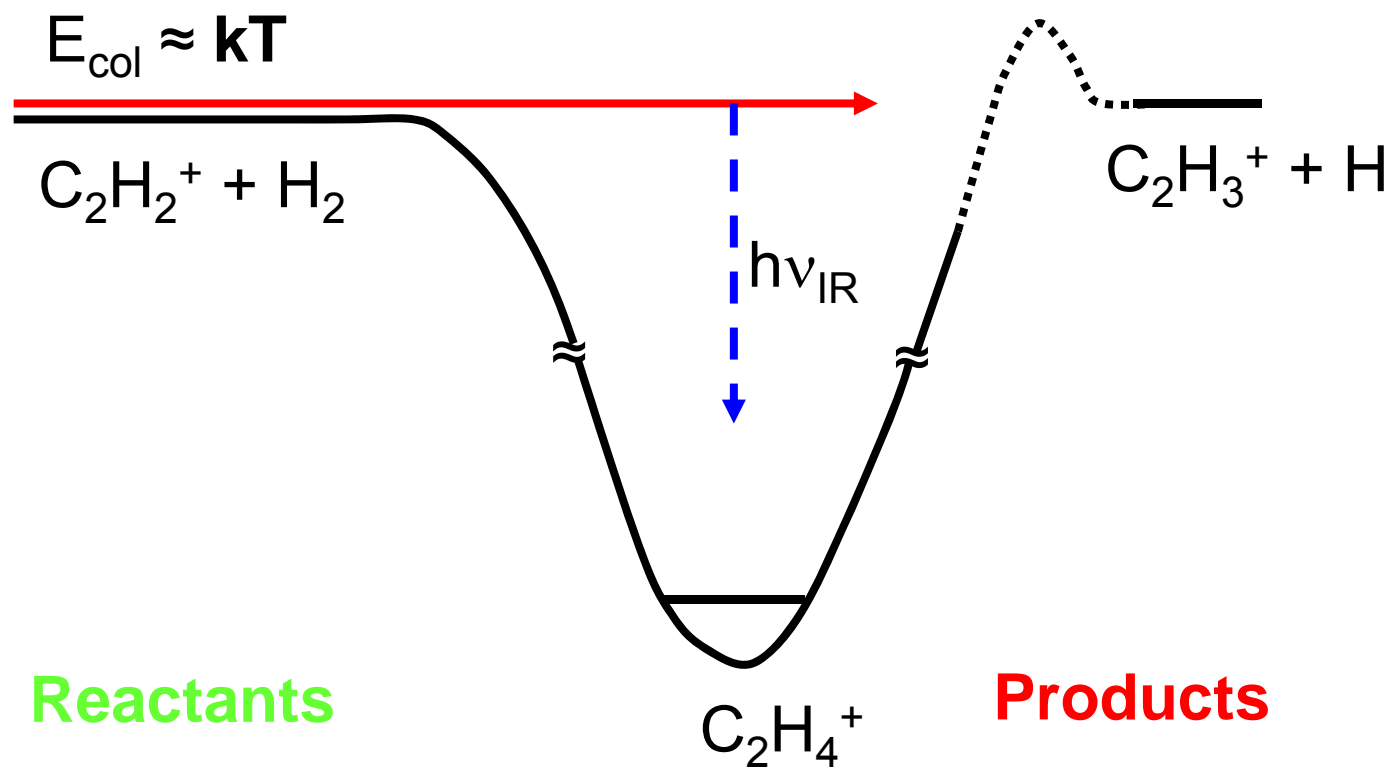
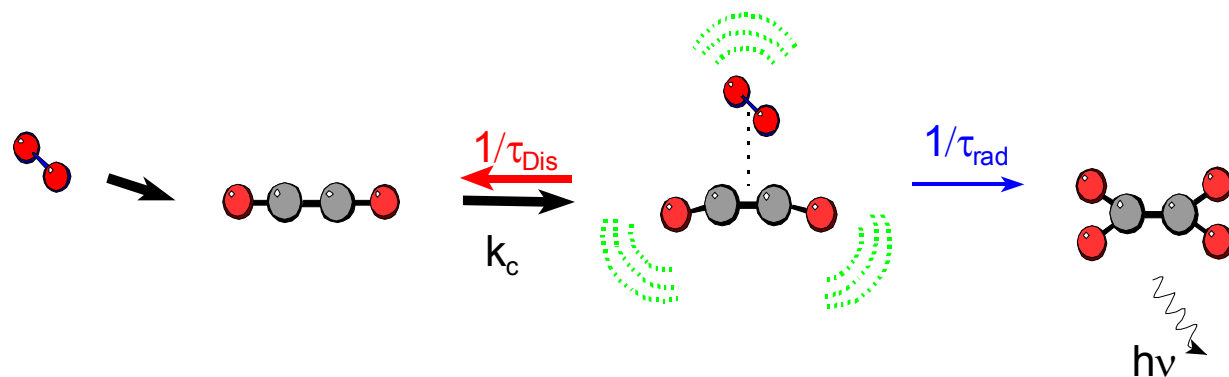


$$2 r_0 = 10 \text{ mm}$$

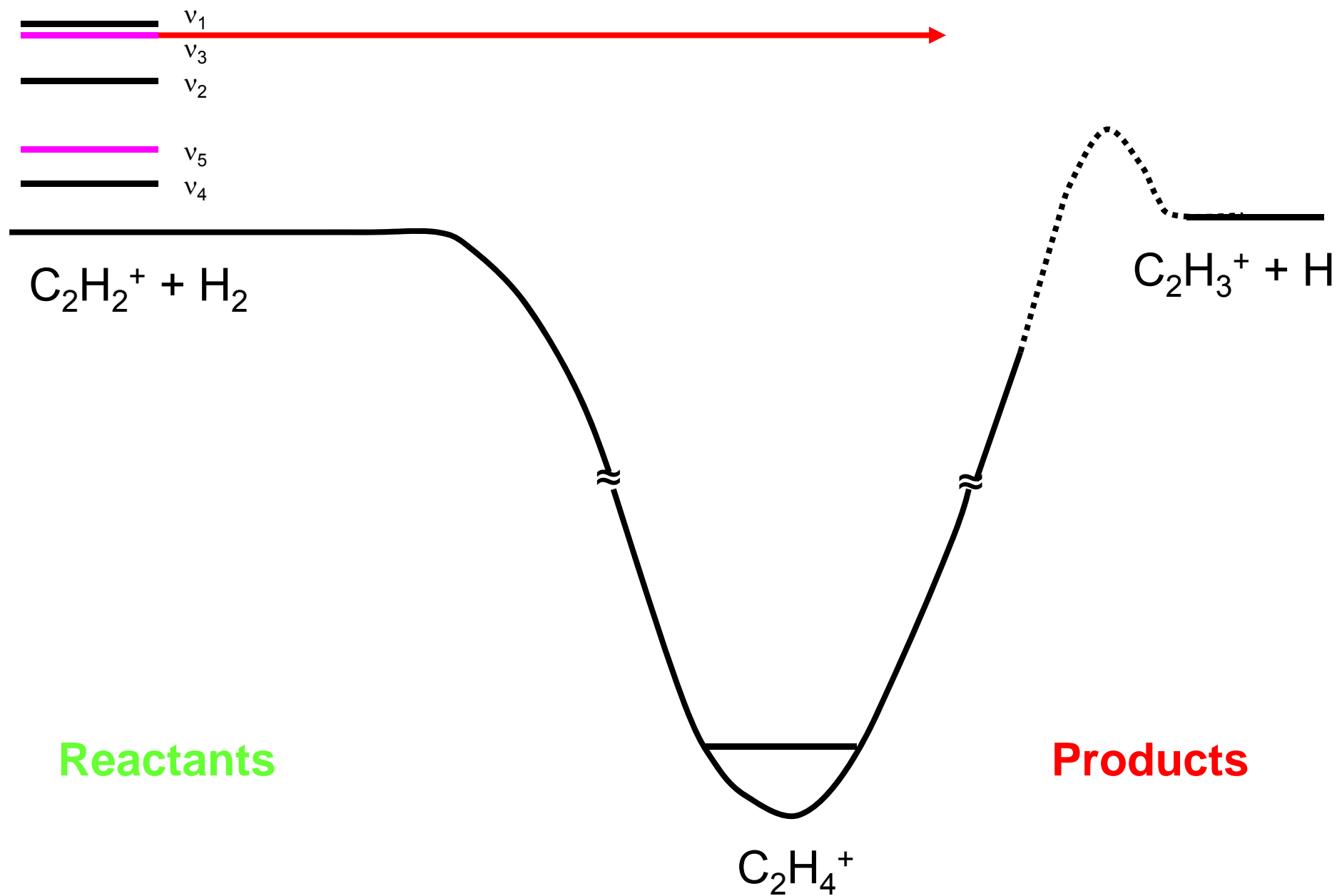
Radiative Association



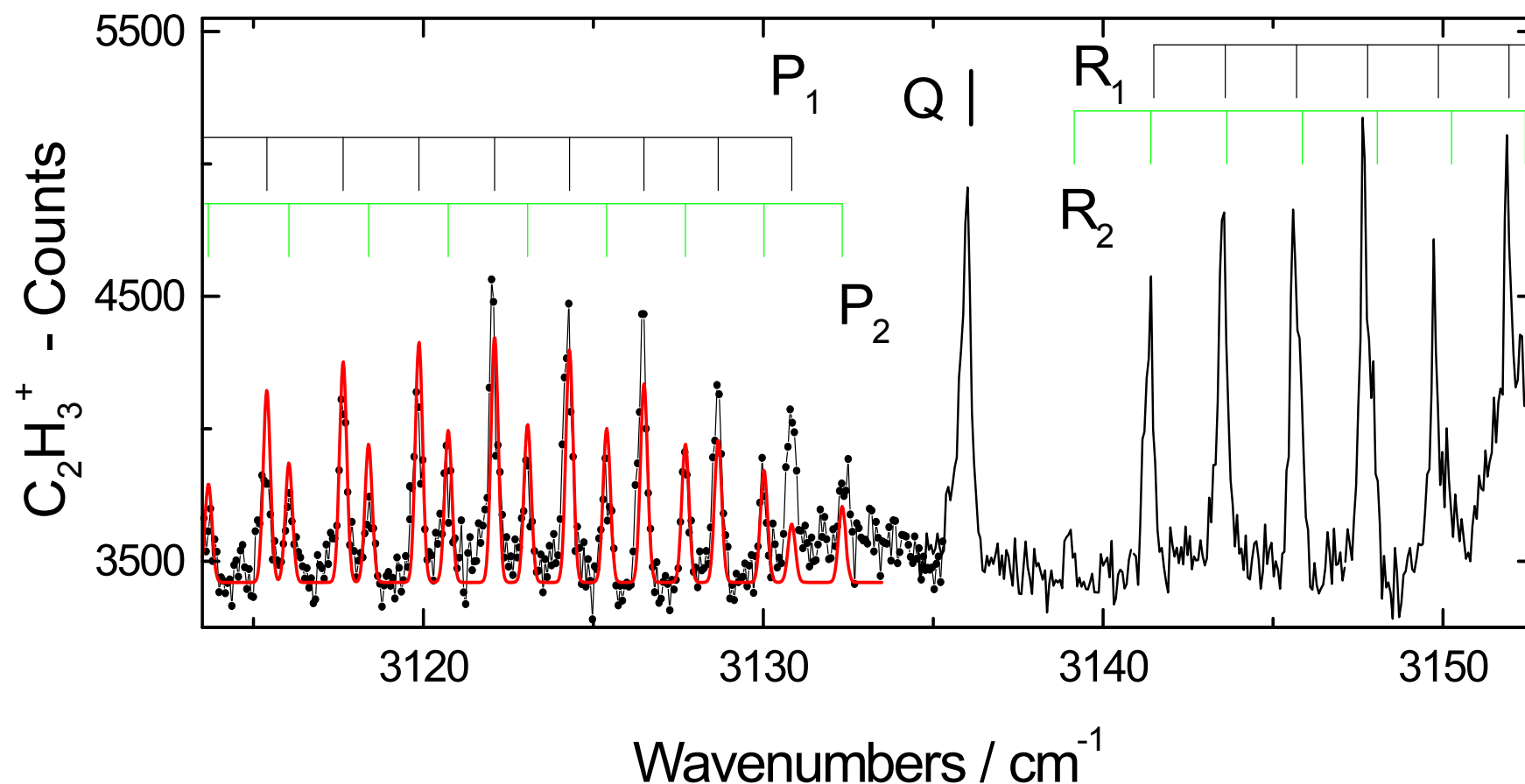
Radiative Association



Light Induced Reactions

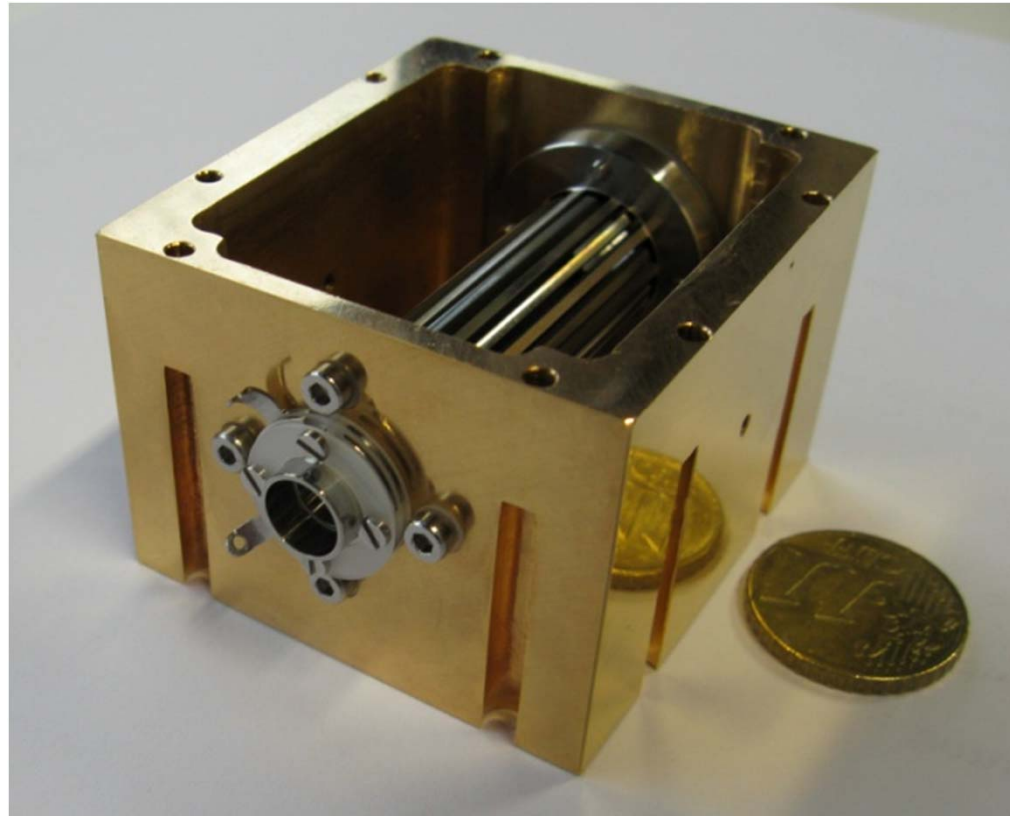


Asymmetric Stretching Mode of $C_2H_2^+$



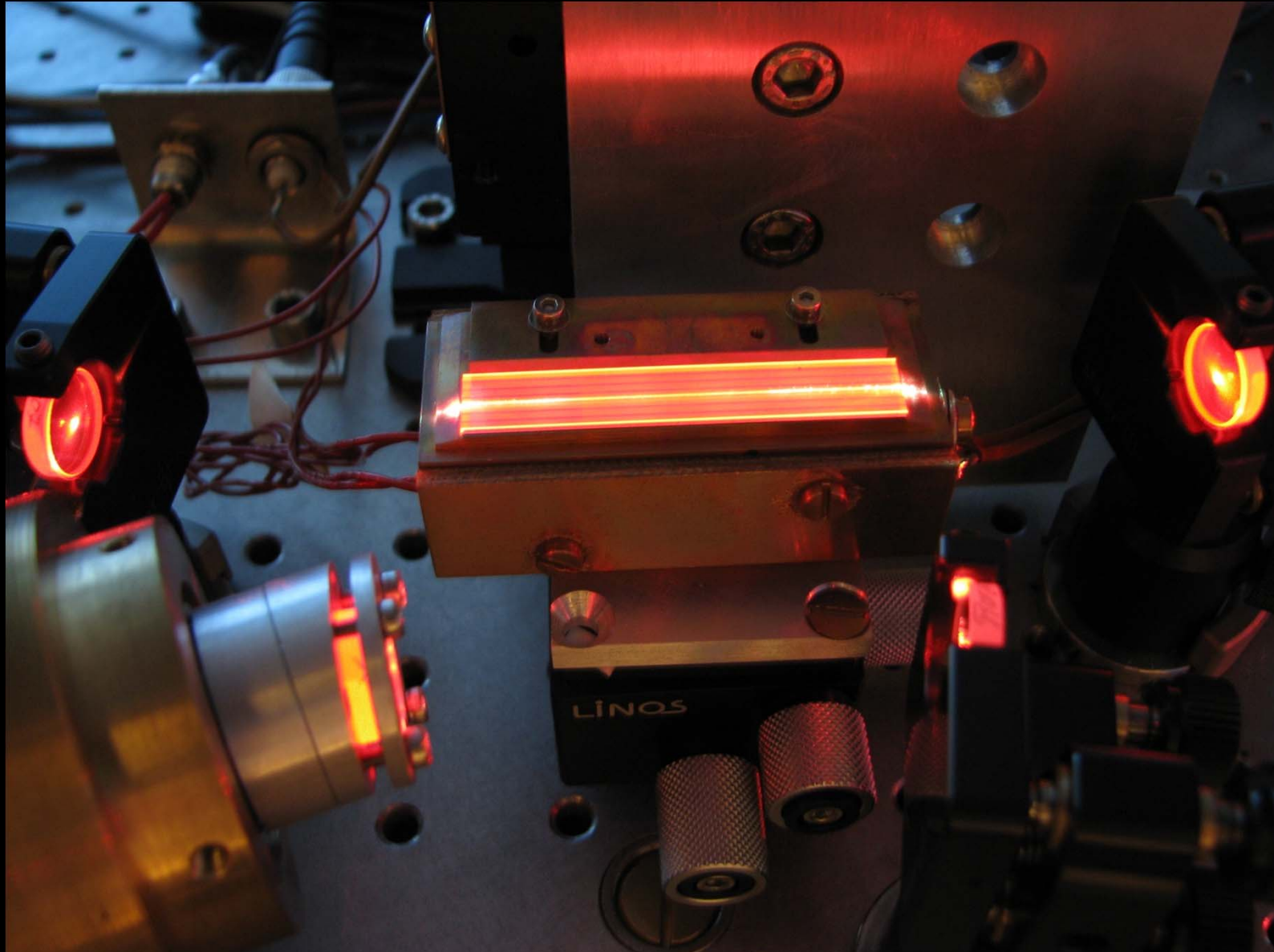
„High Resolution“ $\sim 0.2\text{ cm}^{-1}$

Ion Spectroscopy in Traps

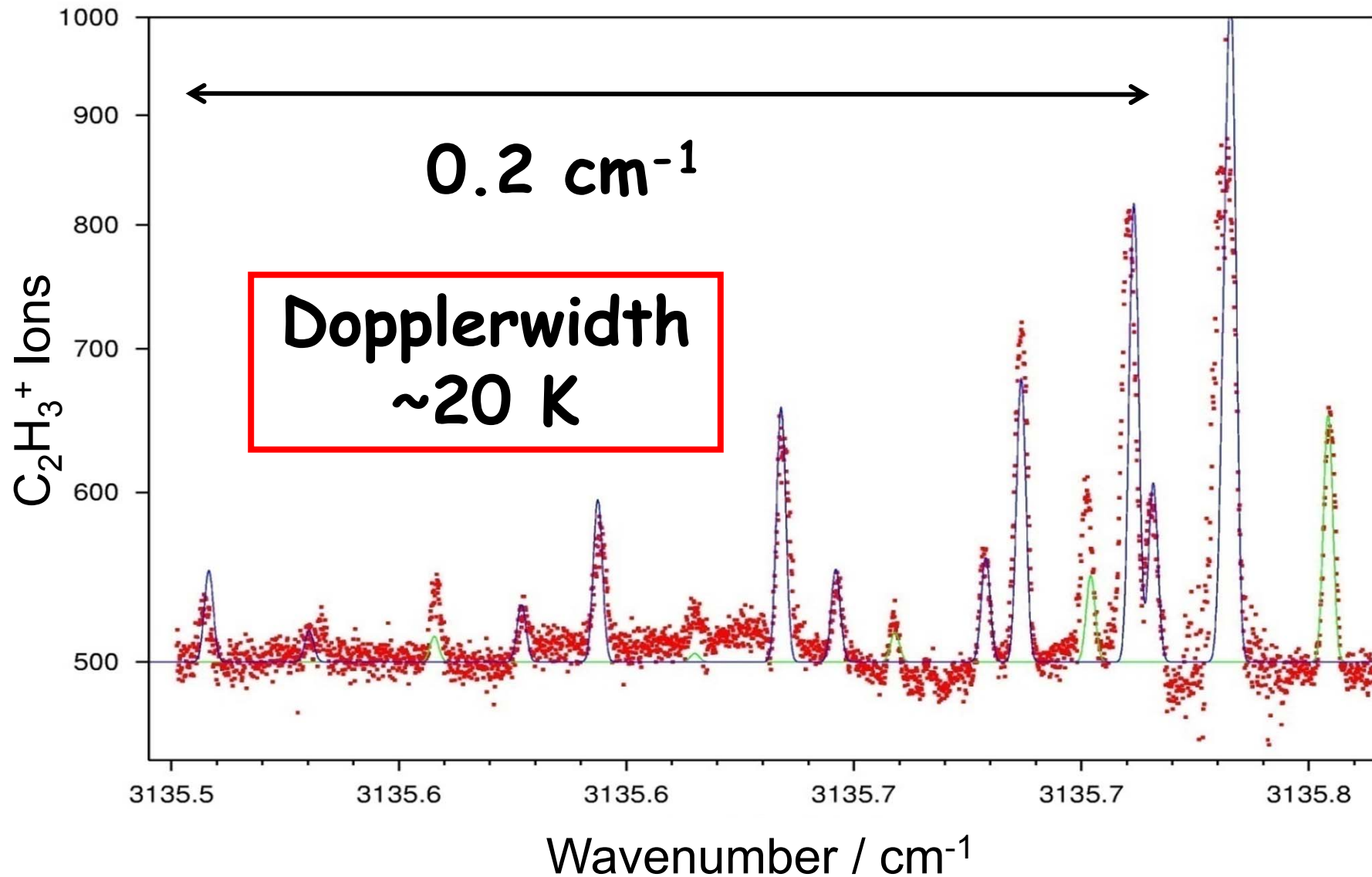


- Mass Selection
- Sensitivity: $[\text{Ions}] \approx 100 - 10000 \text{ cm}^{-3}$
- Near Background free
- Low Temperatures - Density of States

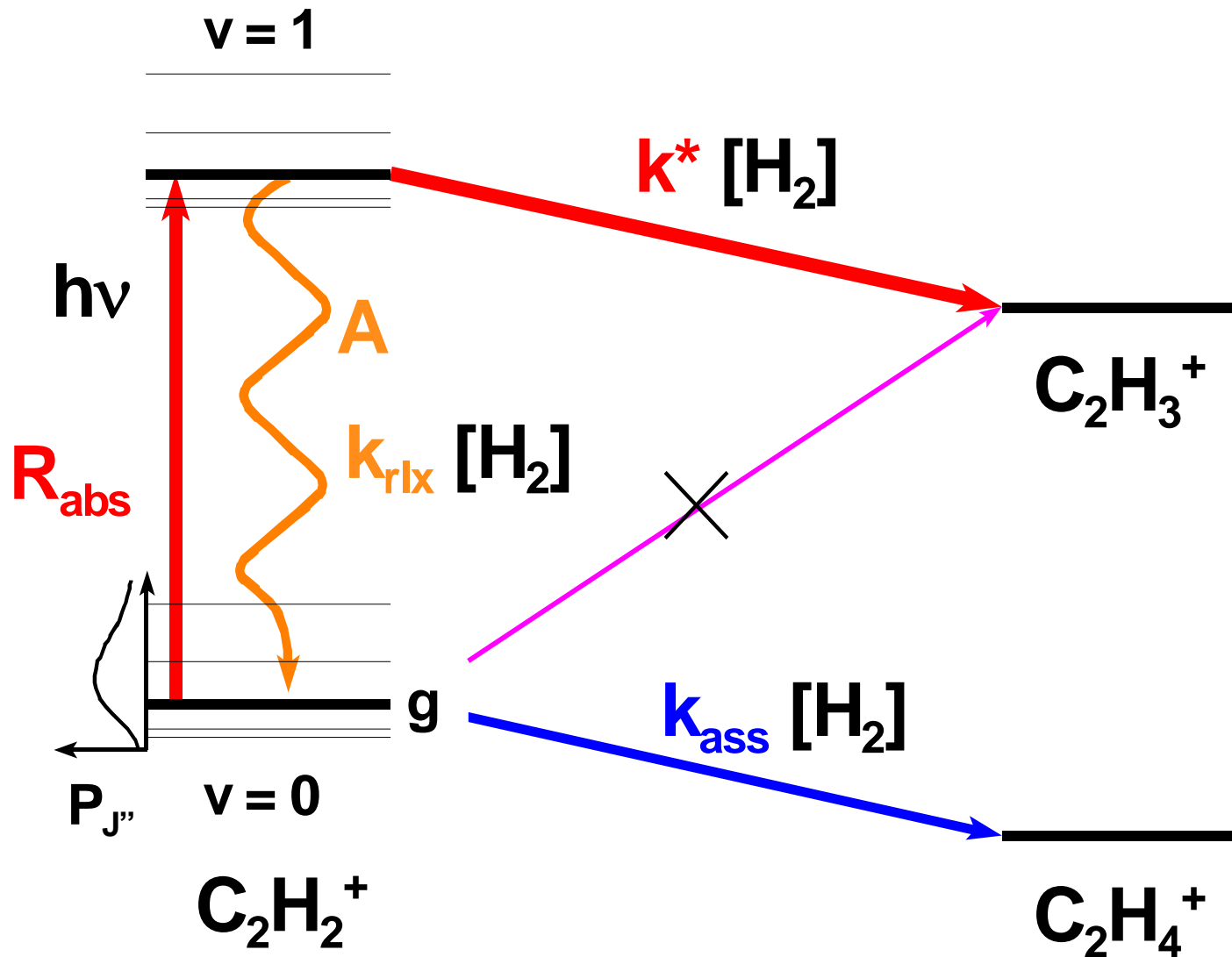
Cologne CW IR OPO Laser



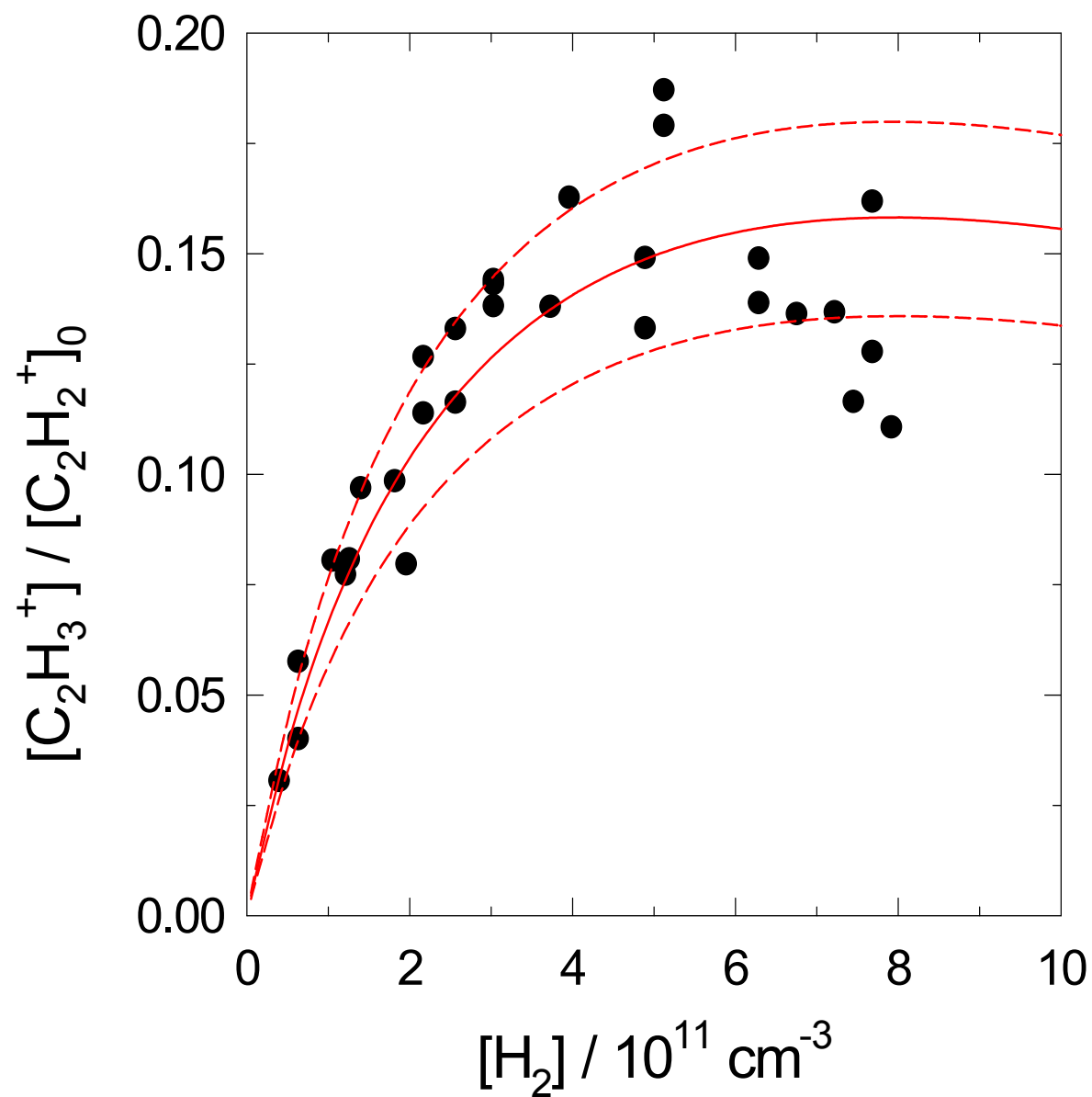
Q-branch transitions of $C_2H_2^+$



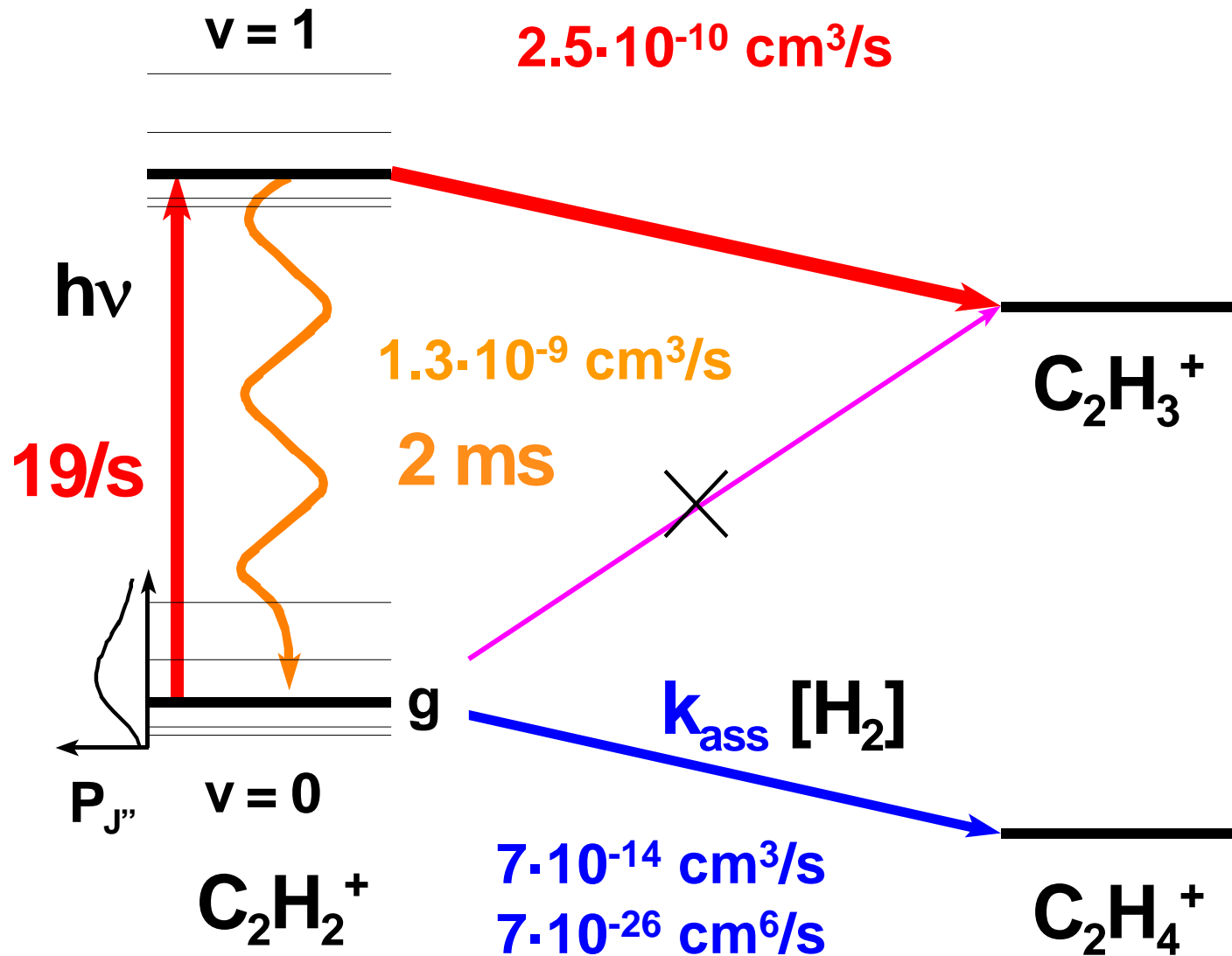
Simplified Reaction Kinetics



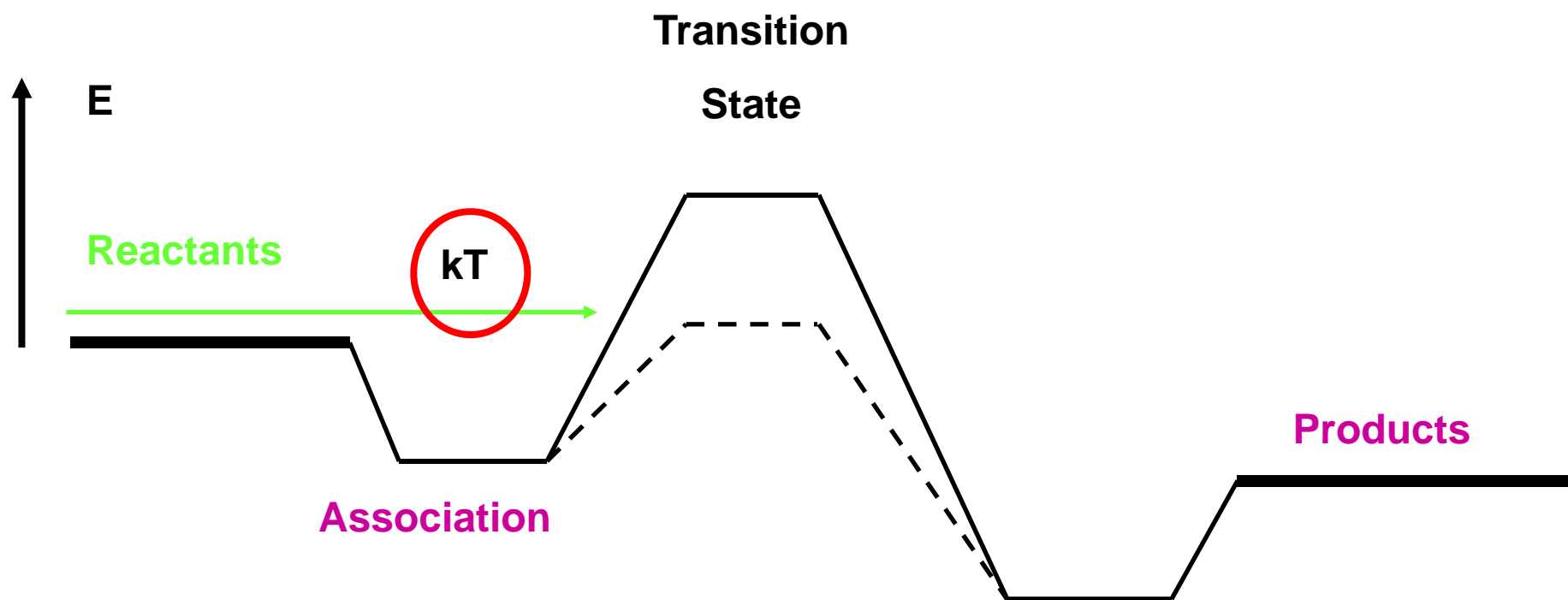
H₂ - Density Dependence of the LIR-Signal



Kinetics Model Results

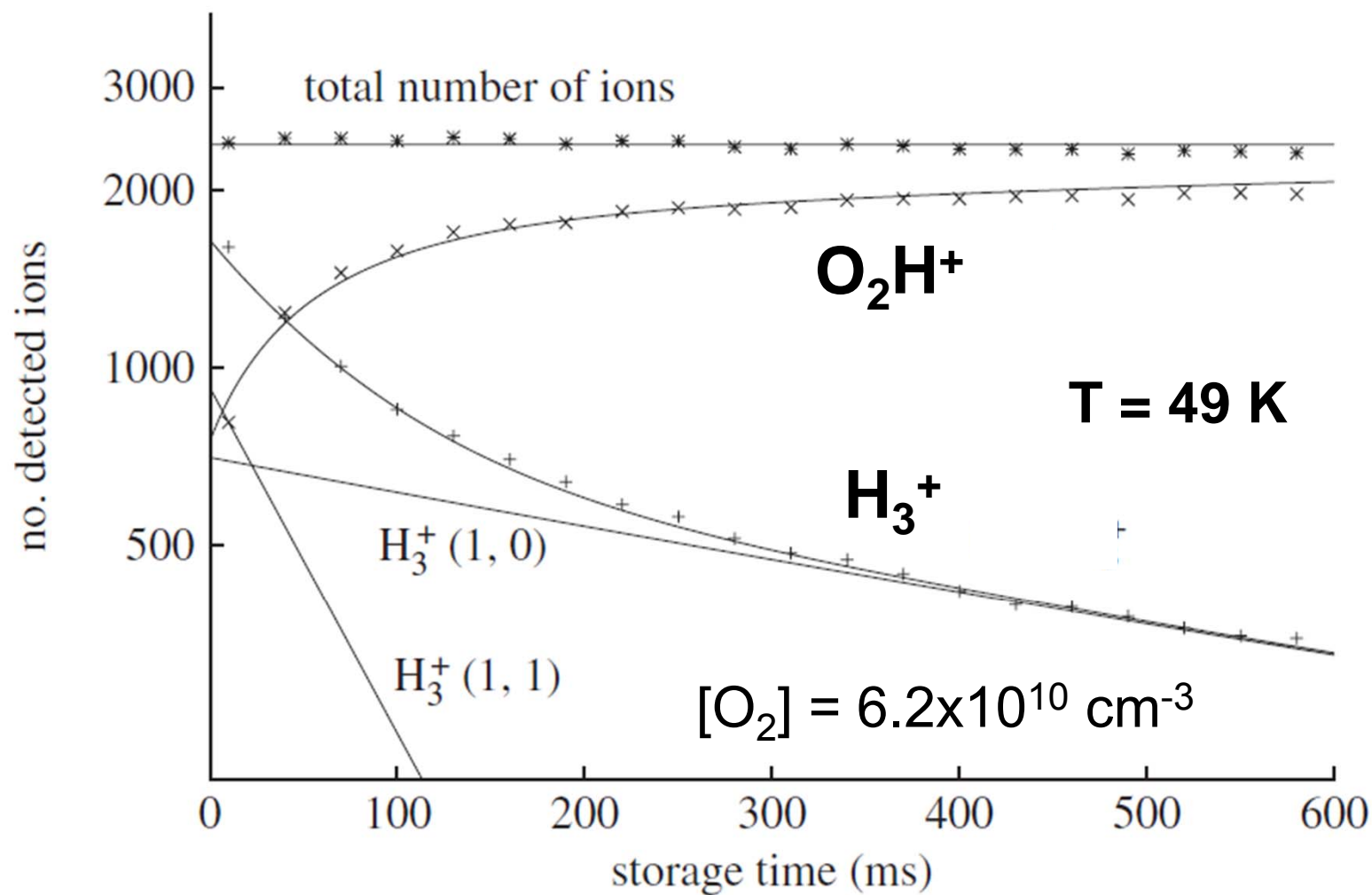


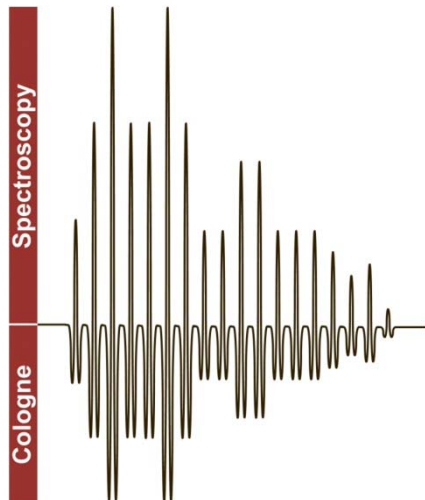
Details of Potential Energy Surface



Rotational Energy, Zero Point Energy and Fine Structure Energy

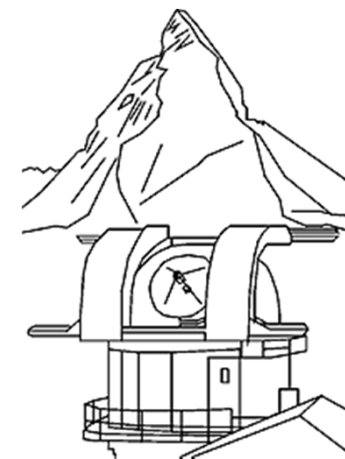
Towards State Specific Chemistry





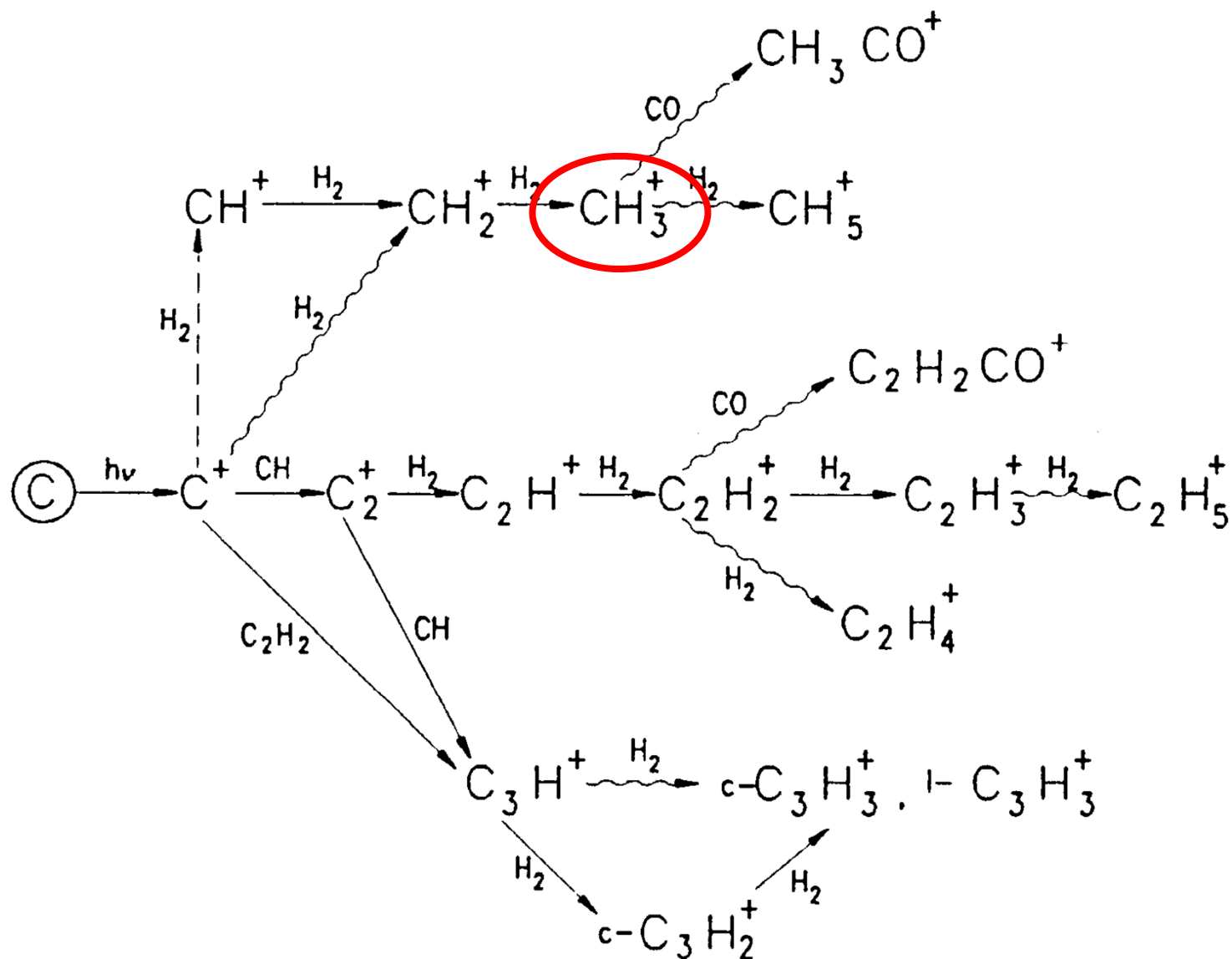
Light Induced Reactions In Cold Traps

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Universität zu Köln

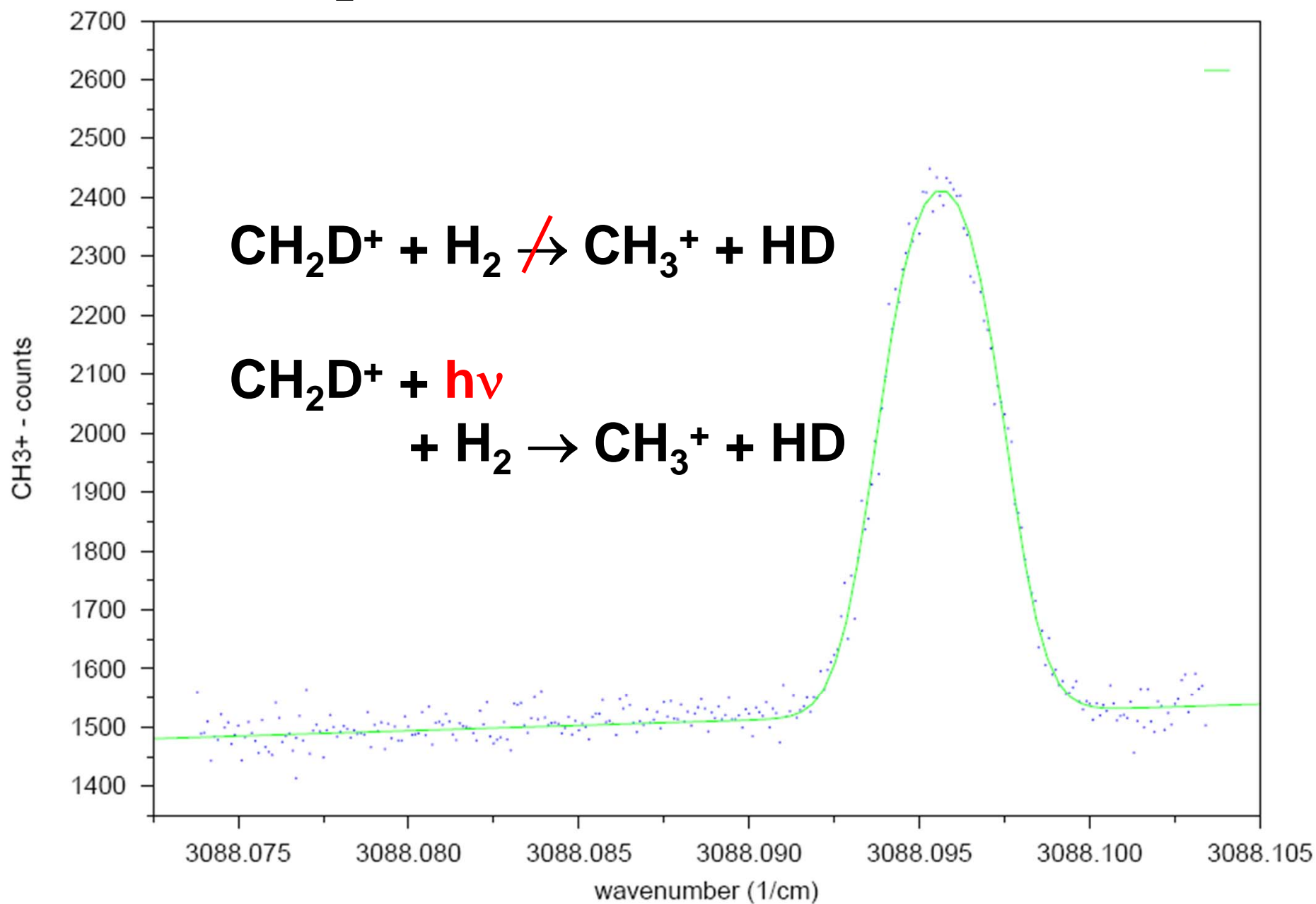


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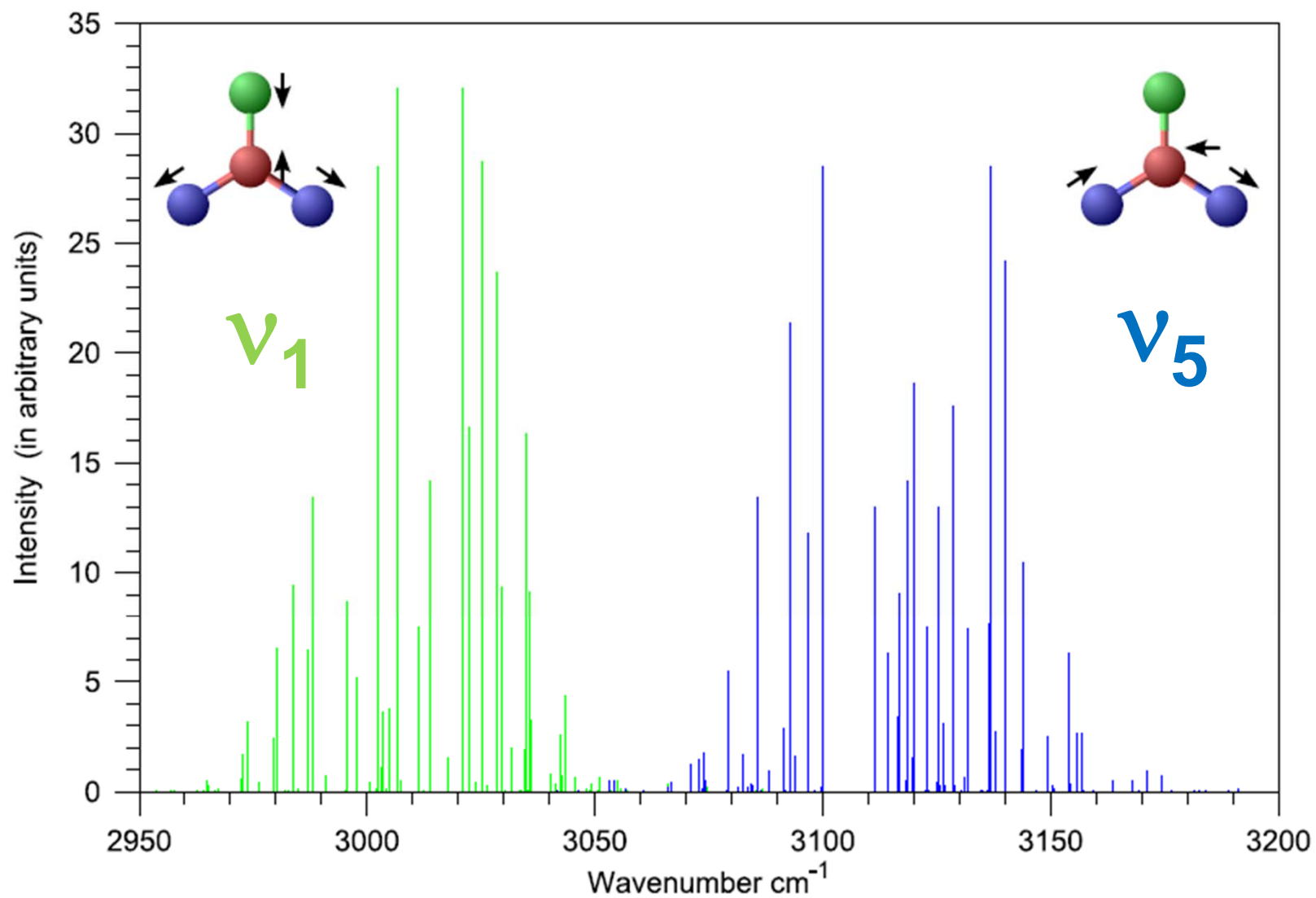
Formation of Small Hydrocarbons under Interstellar Conditions



CH₂D⁺ High Resolution Spectra



CH_2D^+ Ro-vibrational Spectra



CH₂D⁺ Analysis: Molecular Parameters

Parameter	Ground State	v5	v1
ν / cm-1	0.0	3105.8406293(857)	3004.768903(602)
A	9.3685161(371)	9.2703345(471)	9.209521(102)
B	5.7713301(385)	5.7324587(357)	5.7568062(1698)
C	3.5252807(326)	3.5029457(338)	3.4945443(2690)
D _K	2.6689(185)e-4	2.9833(258)e-4	---
D _{JK}	3.54562(5451)e-4	3.50161(7162)e-4	3.6386(1543)e-4
D _J	1.22468(1580)e-4	1.21888(1912)e-4	1.18494(3170)e-4
d _K	4.2489(721)e-4	3.8877(840)e-4	3.7480(2115)e-4
d _J	4.6020(1056)e-5	4.5780(476)e-5	---
H _{JK}	-3.424(1237)e-7	3.626(1772)e-7	---
H _J	9.102(3255)e-8	-1.501(4352)e-8	---
ϕ_{JK}	9.94(243)e-7	-4.47(318)e-7	---
ϕ_K	-4.89(196)e-8	---	---

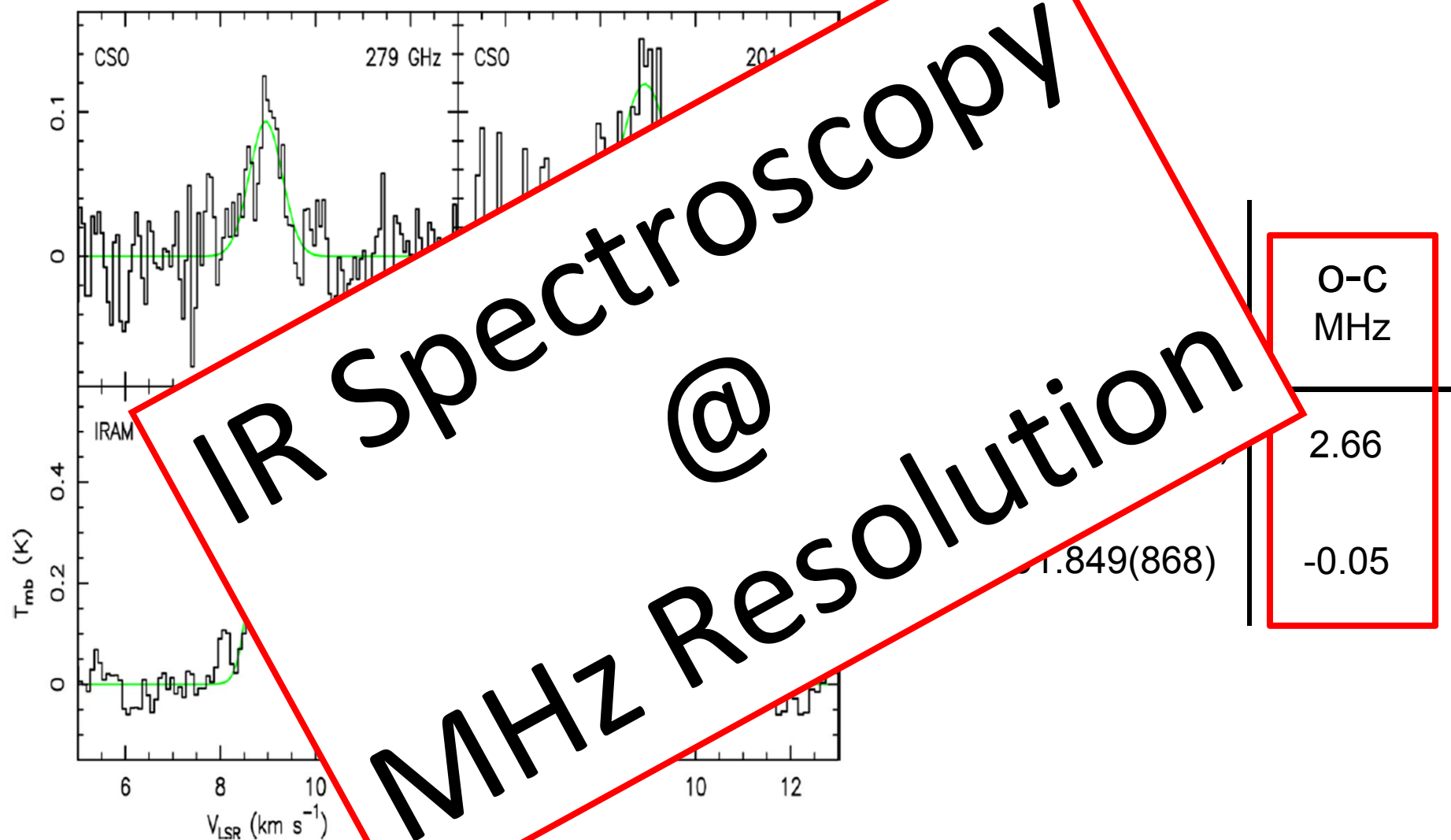
T. Amano,

S. Gärtner, J. Krieg, A. Klemann, O. Asvany & St. S.,

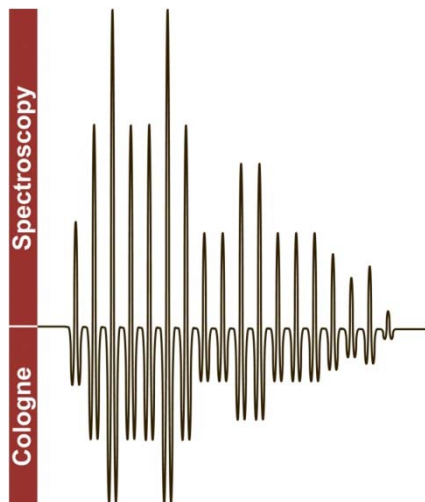
Astron. Astrophys., 516 (2010) L4

Astron. Astrophys., 516 (2010) L3

CH₂D⁺ in Space and Laboratory

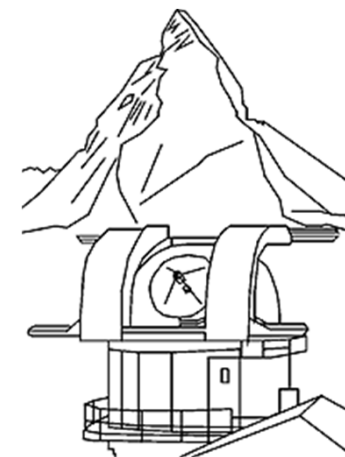


E. Roueff, M. Gerin, D. Lis, A. Wootten, N. Marcelino, J. Cernicharo
& B. Tercero, J. Phys. Chem. A, in press



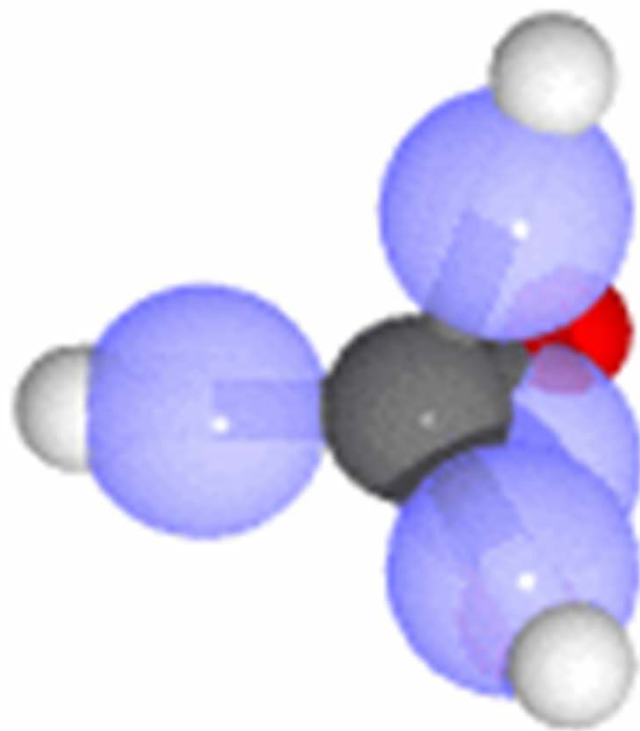
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FELIX Spectroscopy of CH_5^+

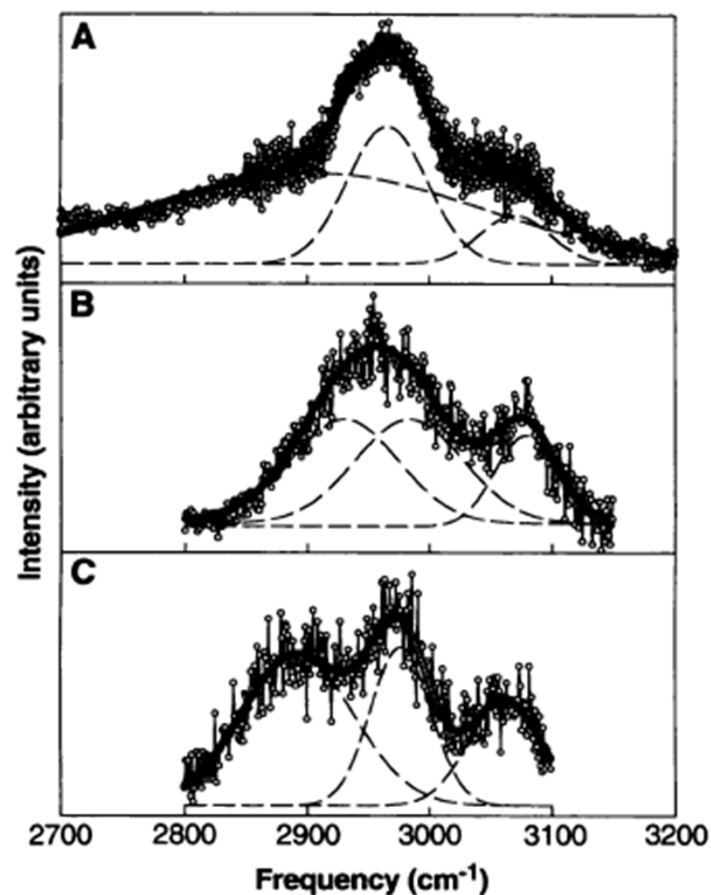


Animation: Dominik Marx/Bochum

Dynamics of Carbonium Ions Solvated by Molecular Hydrogen: $\text{CH}_5^+(\text{H}_2)_n$ ($n = 1, 2, 3$)

D. W. Boo, Z. F. Liu, A. G. Suits, J. S. Tse,* Y. T. Lee*

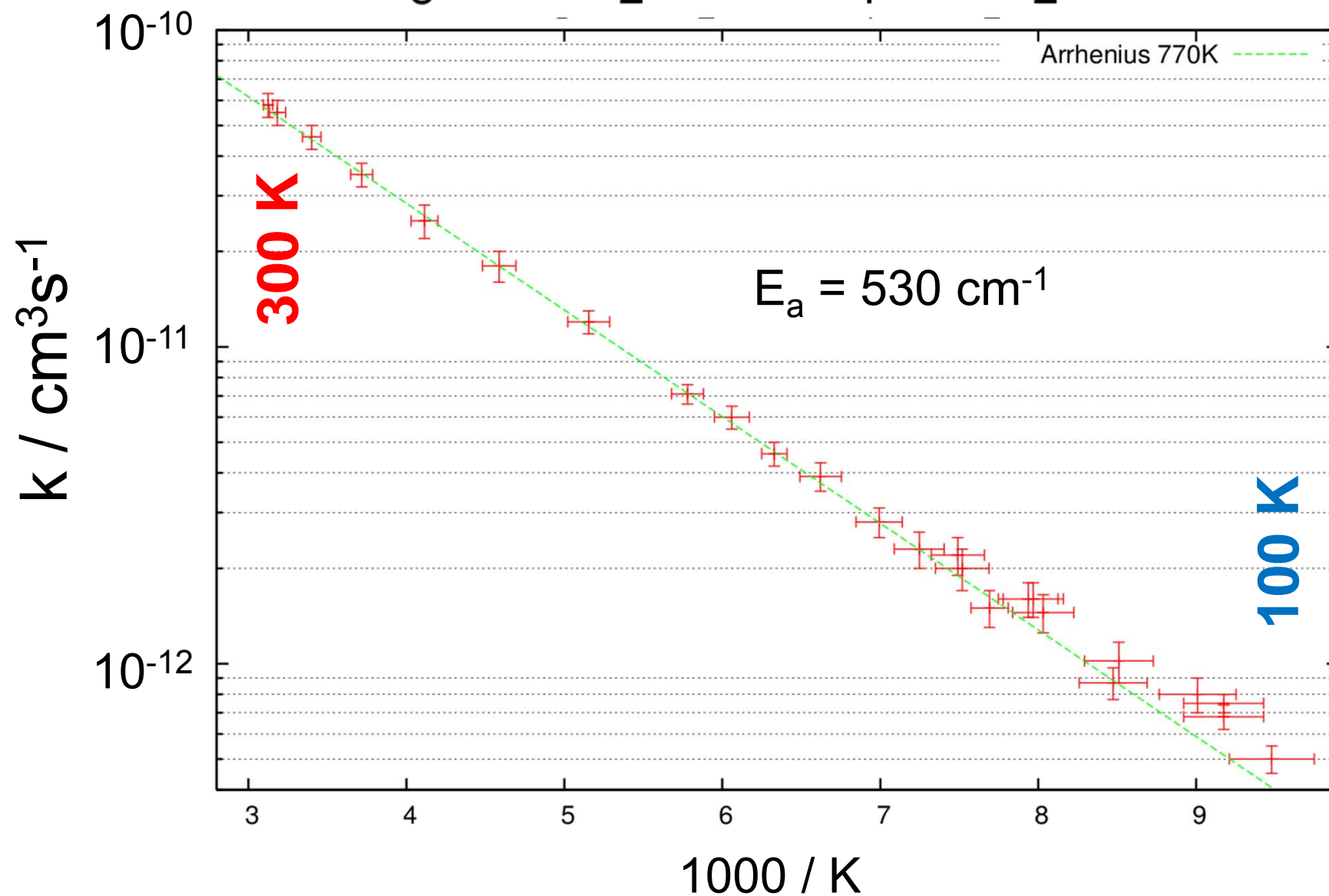
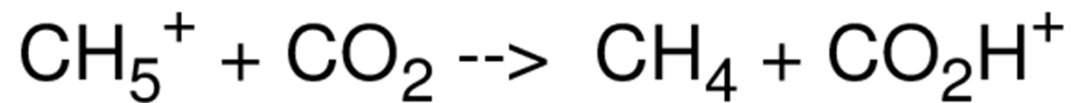
SCIENCE, vol. 269 (1995) 57



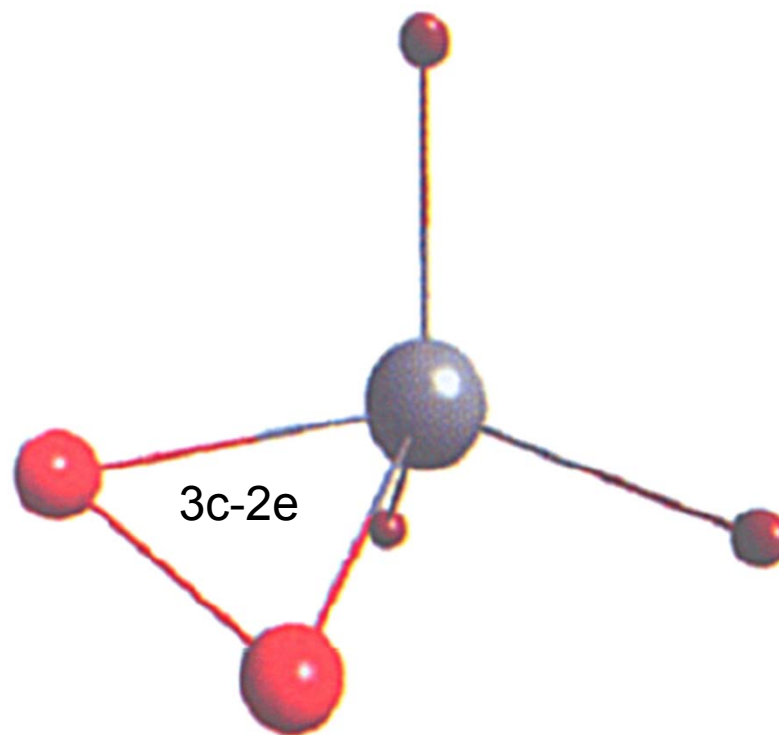
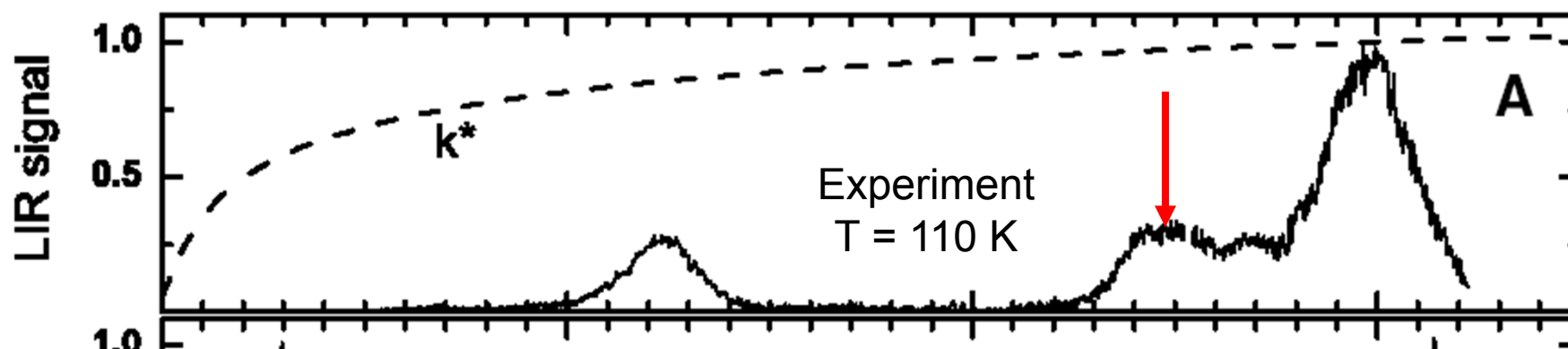
„Ion trap vibrational
predissociation spectroscopy“

IRMPD:
Infrared Multiple
Photon Dissociation

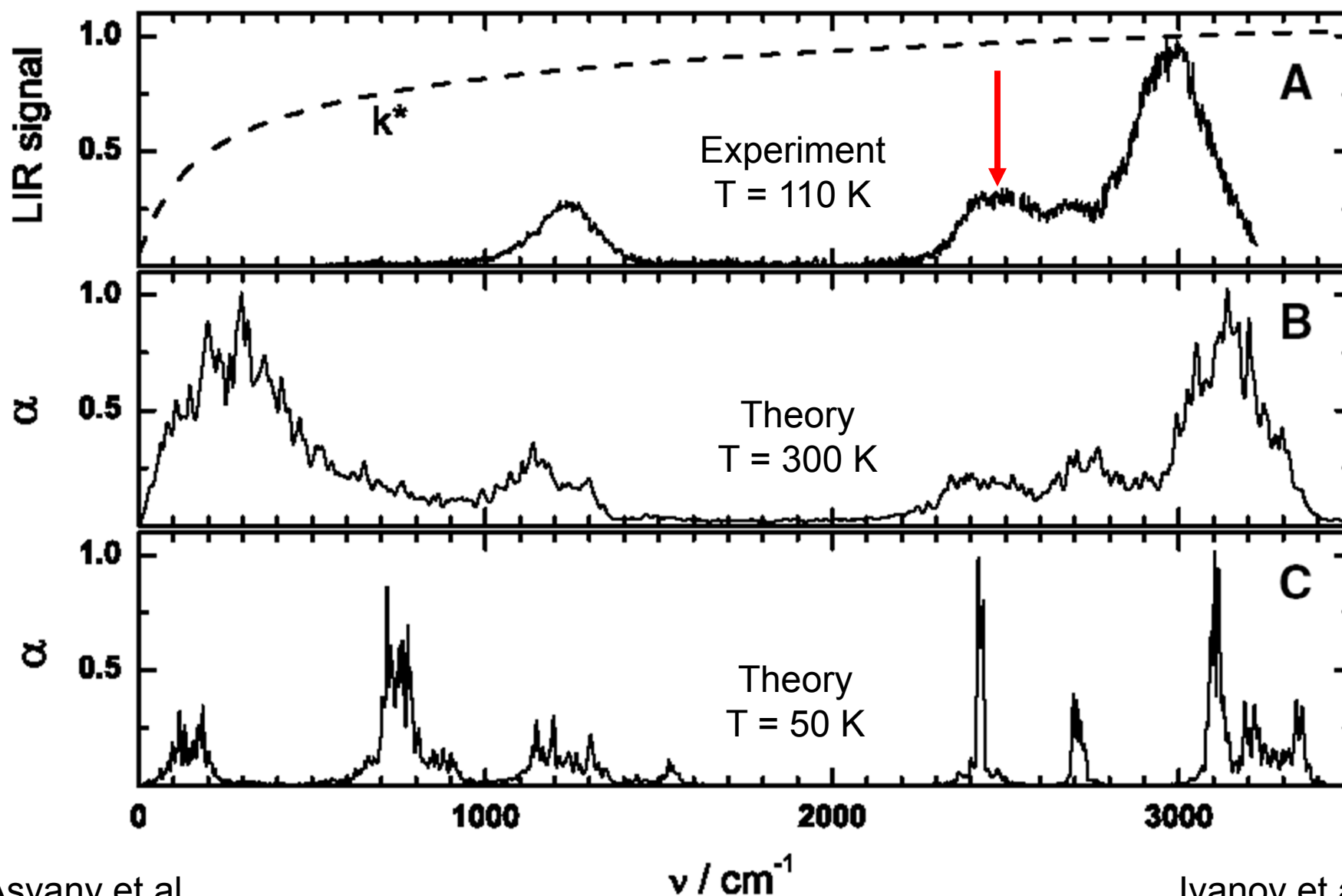
Endothermic Proton Transfer



CH_5^+ : LIR Spectrum and *Ab Initio* Simulations



CH_5^+ : LIR Spectrum and *Ab Initio* Simulations

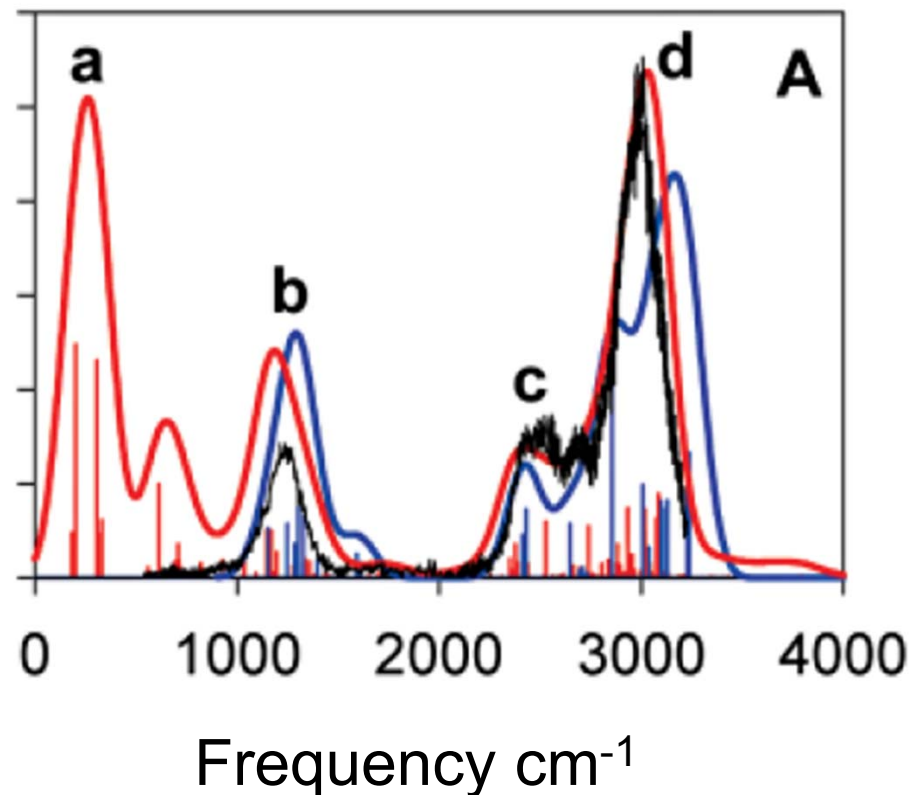


Asvany et al.,
Science, 309 (2005)

Ivanov et al.,
Nature Chem. **2**, 298 (2010)

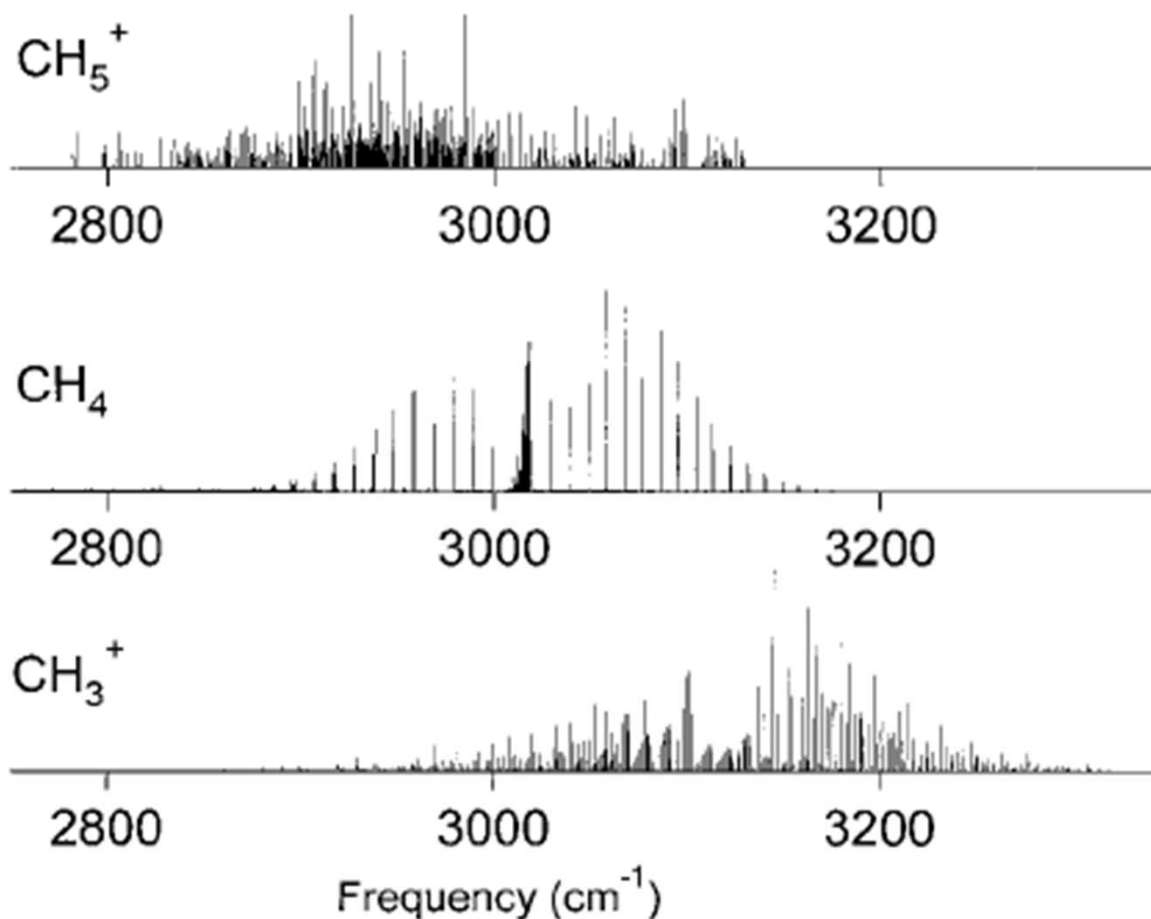
Quantum Deconstruction of the Infrared Spectrum of CH_5^+

X. Huang, A. McCoy, J. Bowman, L. Johnson, C. Savage, F. Dong, D. Nesbitt,
SCIENCE, vol. 311 (2006) 60



CH_5^+ : The Infrared Spectrum Observed

E. White, J. Tang & T. Oka, SCIENCE, vol. 284 (1999) 135



1000 lines, no assignment

„Experimentally the next step will be to observe the spectrum at low temperatures and to observe deuterated species“

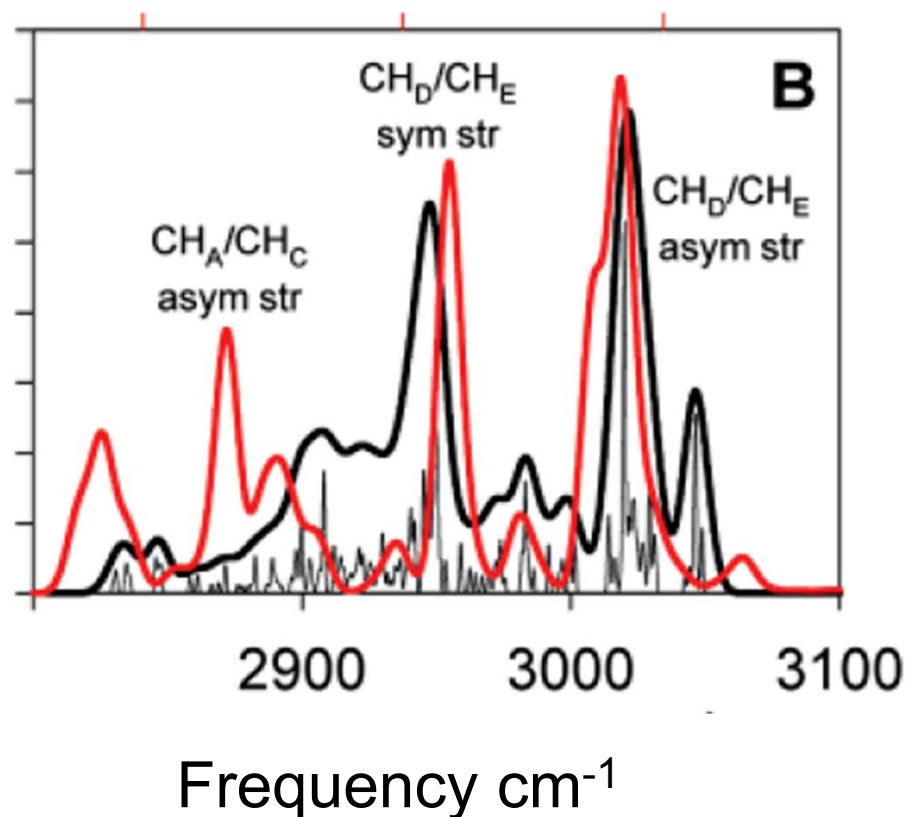
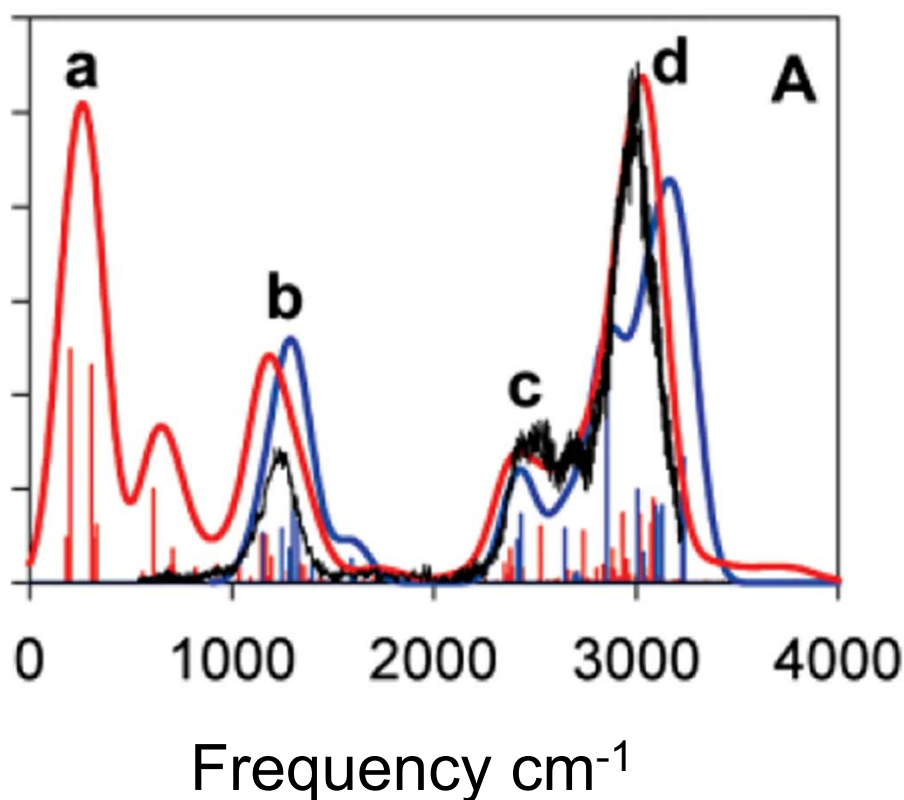


CH_5^+ : The Cheshire Cat Smiles

Marx & Parinello, SCIENCE, vol. 284 (1999) 59

Quantum Deconstruction of the Infrared Spectrum of CH_5^+

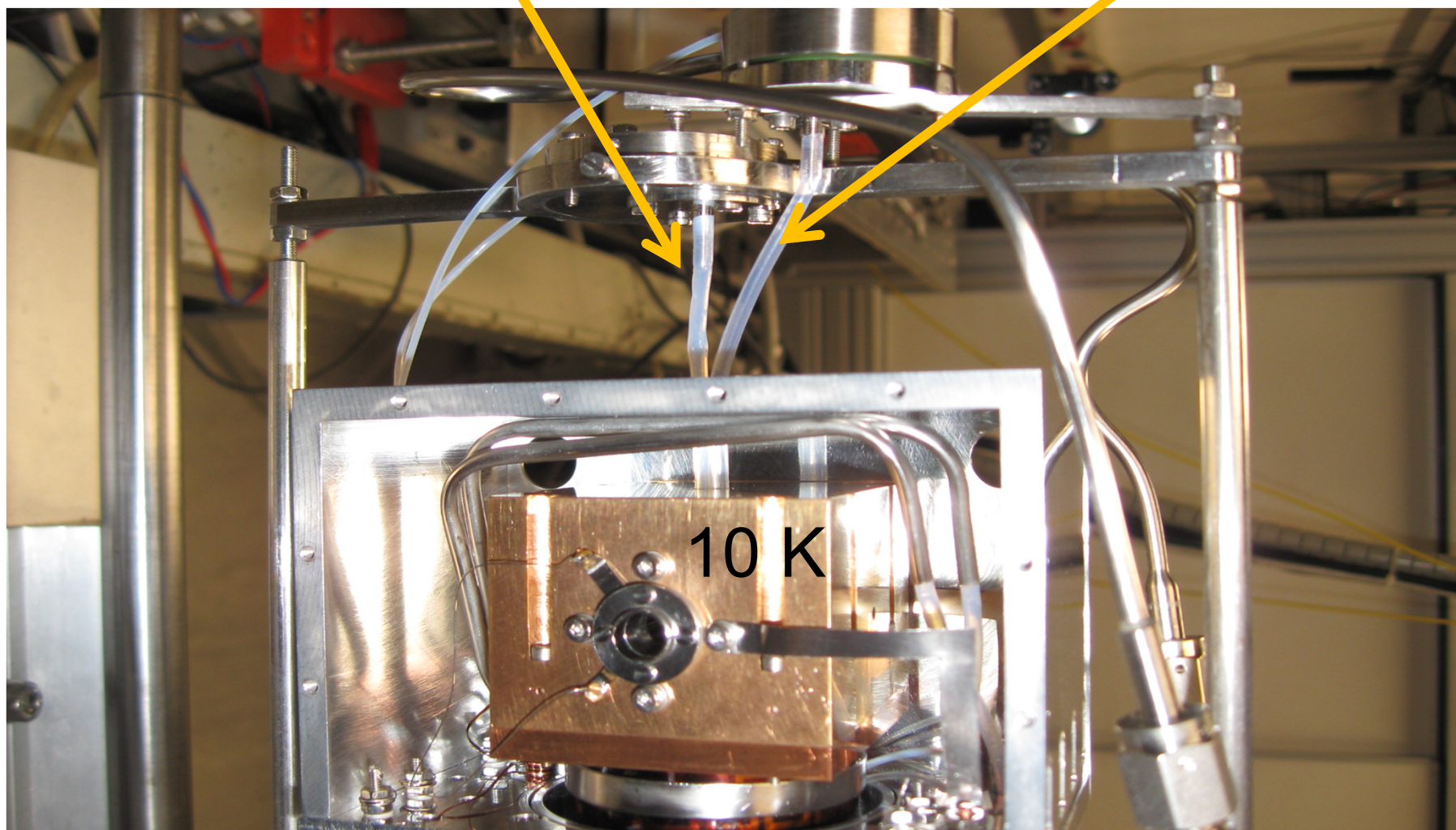
X. Huang, A. McCoy, J. Bowman, L. Johnson, C. Savage, F. Dong, D. Nesbitt,
SCIENCE, vol. 311 (2006) 60



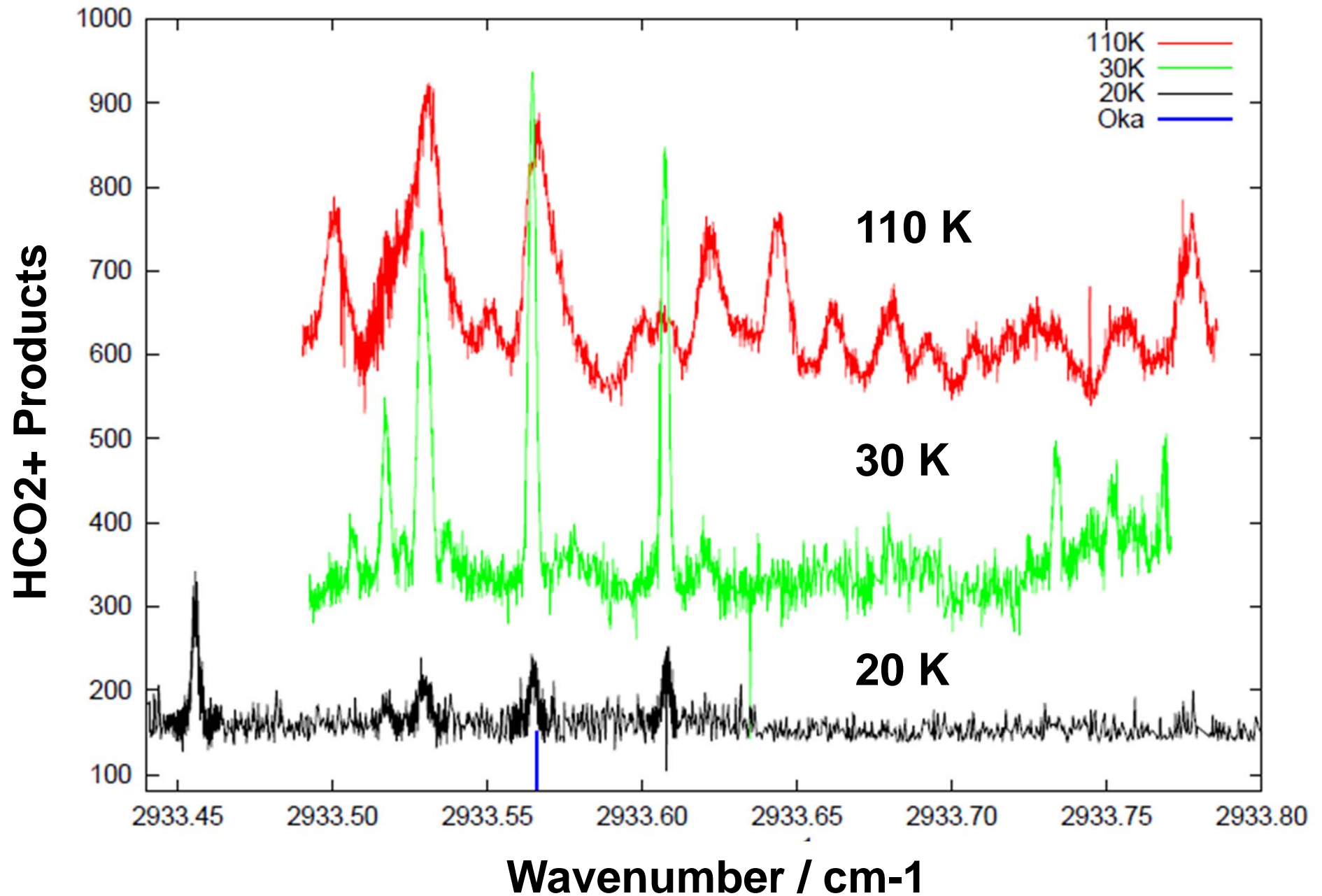
Low Temperature & High-Resolution?

Cooling: He

Reaction: CO₂

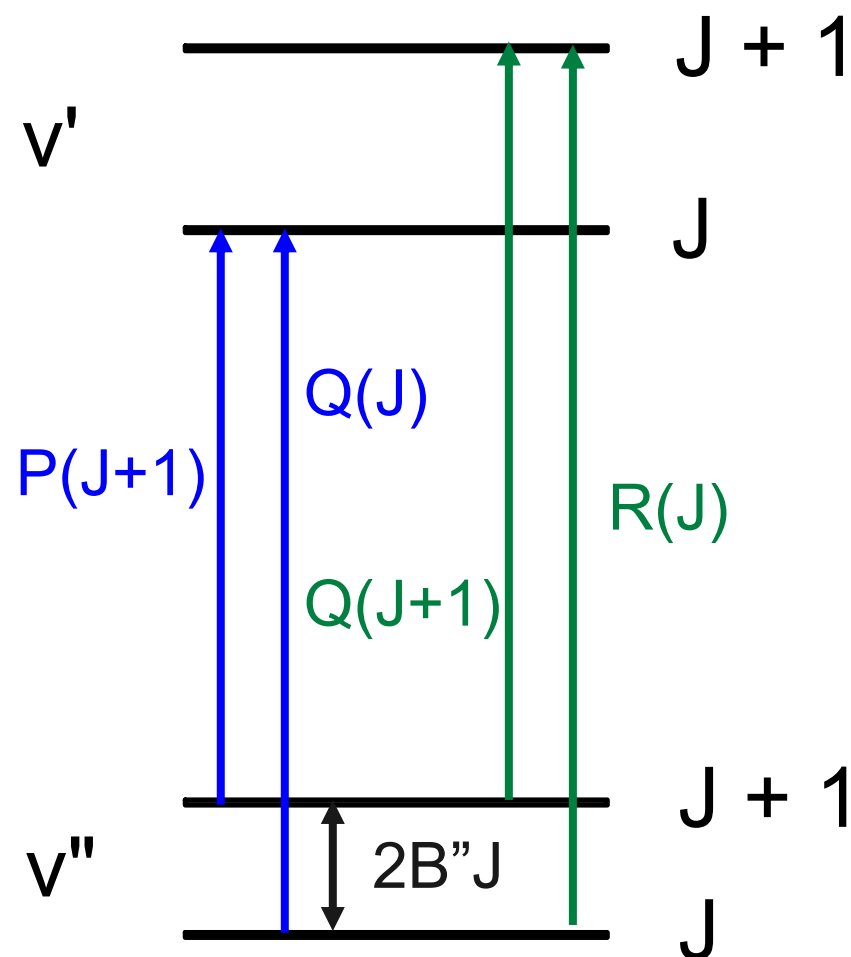


Low Temperature, High-Resolution Spectra !

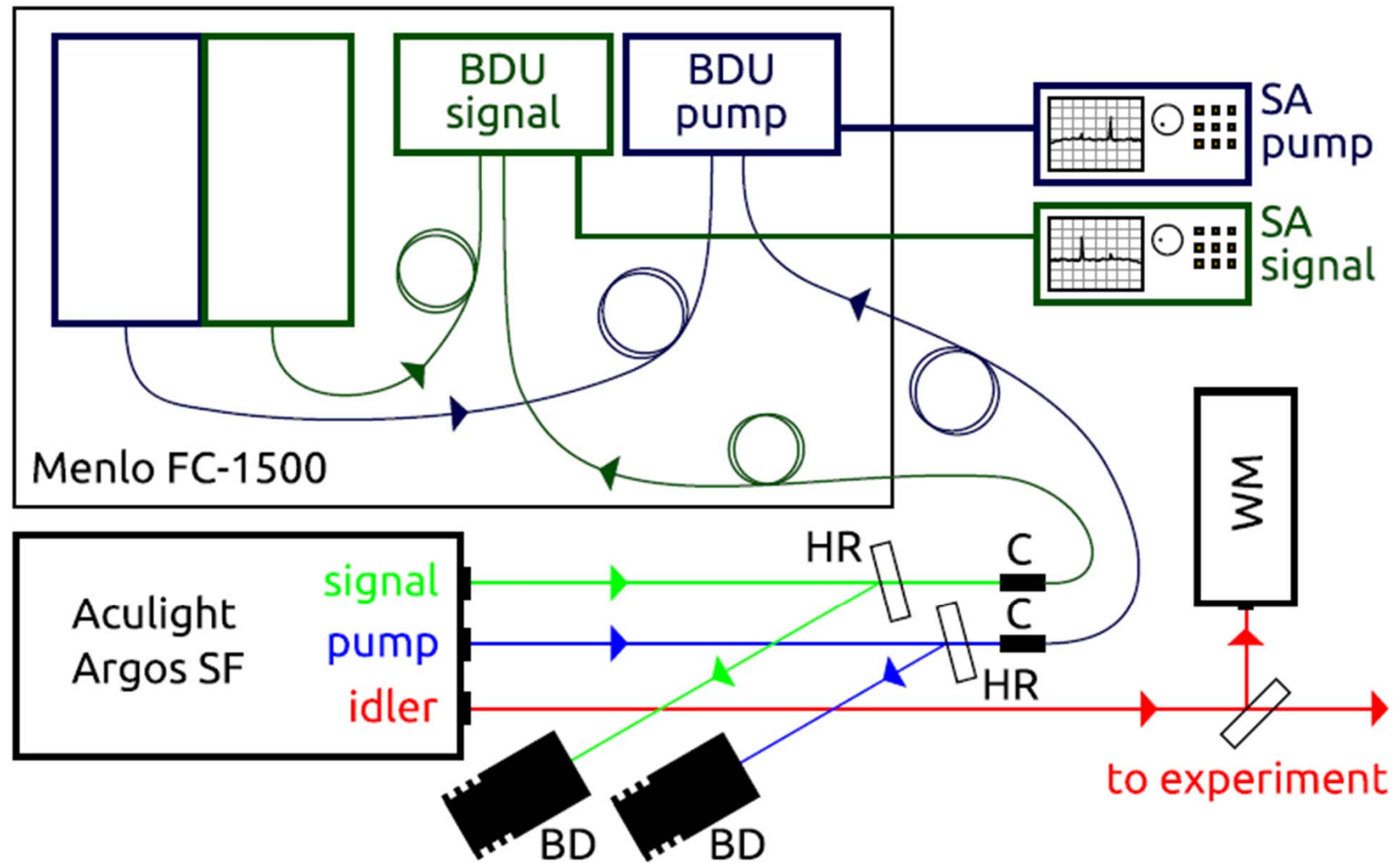


Rotational Structure of IR Spectra

Four Line Combination Differences (4LCD)

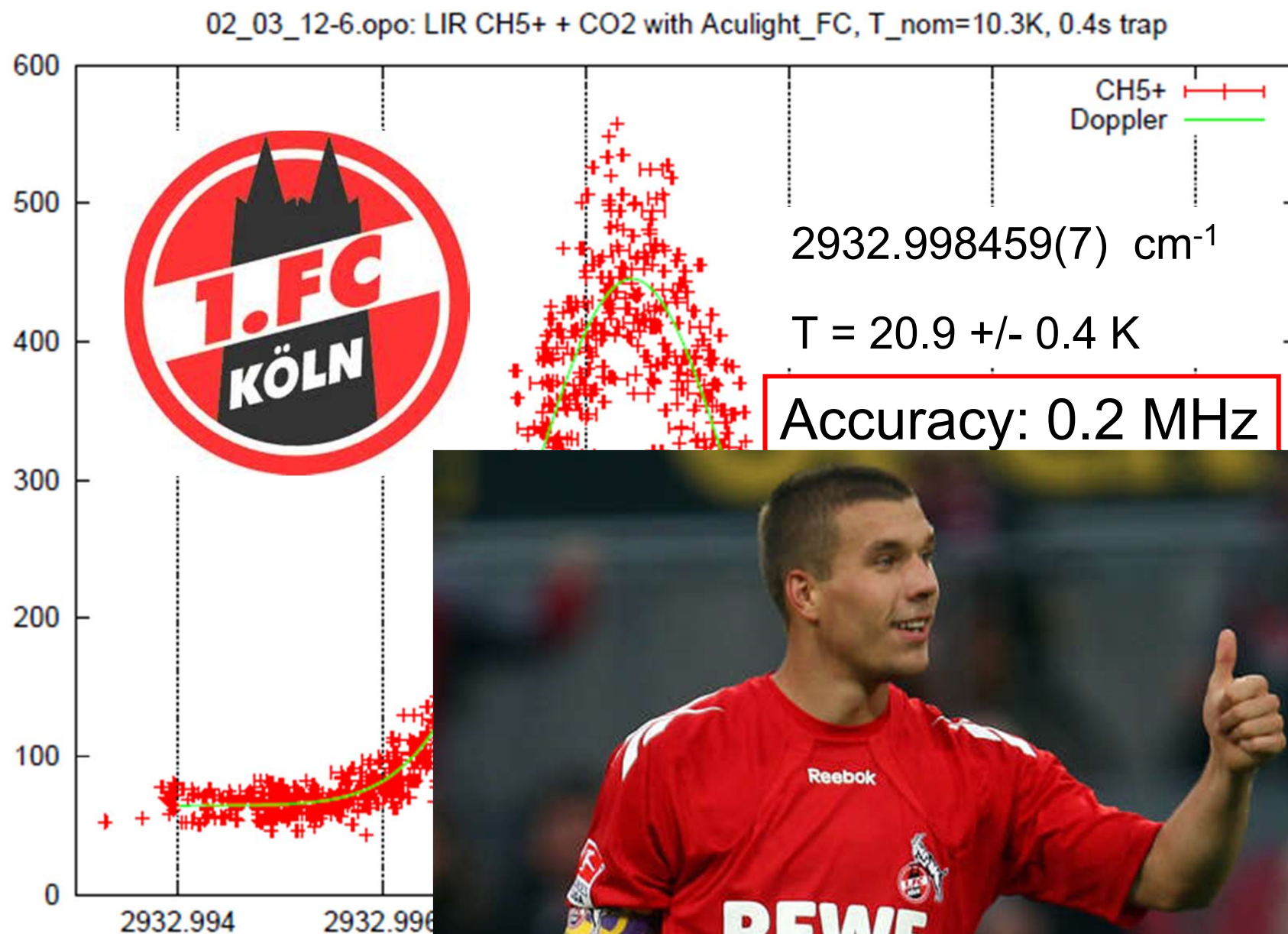


Calibration: Wavemeter & Frequency Comb



$$h \nu_{\text{idler}} = h \nu_{\text{pump}} - h \nu_{\text{signal}}$$

HCO₂⁺ Products



O. Asvany, J. Krieg, and S. Schlemmer, Rev. Sci. Instruments, **83** (2012), 076102

CH_5^+ : The Infrared Spectrum Observed

1999

~ 2900 lines, $T = 10$ K, 1 line / 2.4 GHz, MHz accuracy
Average gap of 4LCDs: ~ MHz
no clear assignment

2013

Experimentally the next step will be to observe the spectrum
at **lower temperatures** and in **higher resolution**.

MG07

15 min 3:12

HIGH PRECISION SPECTROSCOPY OF CH_5^+ USING NICE-OHVMS

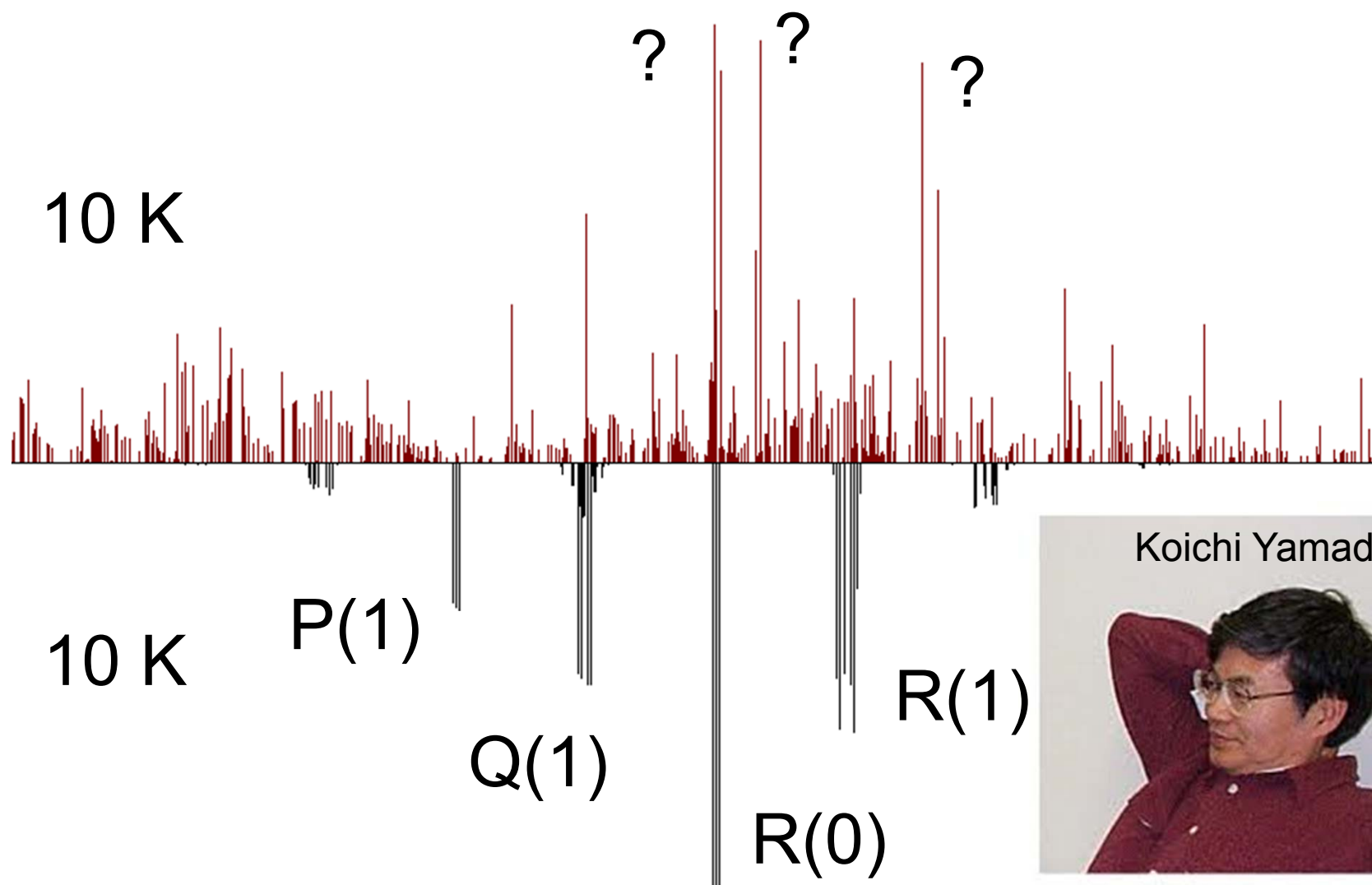
*JAMES N. HODGES, ADAM J. PERRY, Department of Chemistry, University of Illinois, Urbana, IL 61801;
BENJAMIN J. MCCALL, Departments of Chemistry, Astronomy, and Physics, University of Illinois, Urbana,
IL 61801.*

CH_5^+ : The never-ending story or the final word?

1993

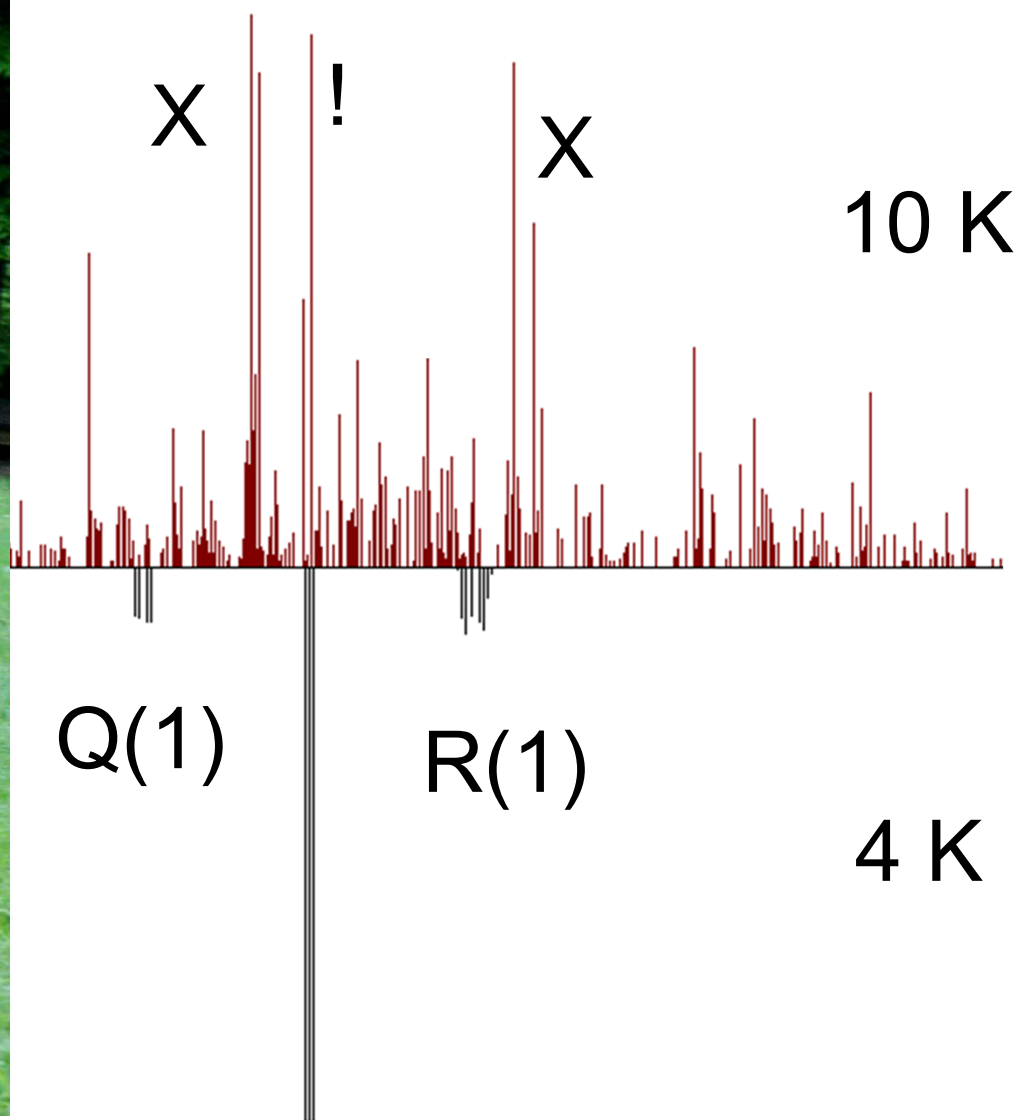
Peter R. Schreiner,^{a),b)} Seung-Joon Kim,^{a)} Henry F. Schaefer III,^{a),c)}
and Paul von Ragué Schleyer^{a),b)}

Rotational Structure of Vibrational Bands



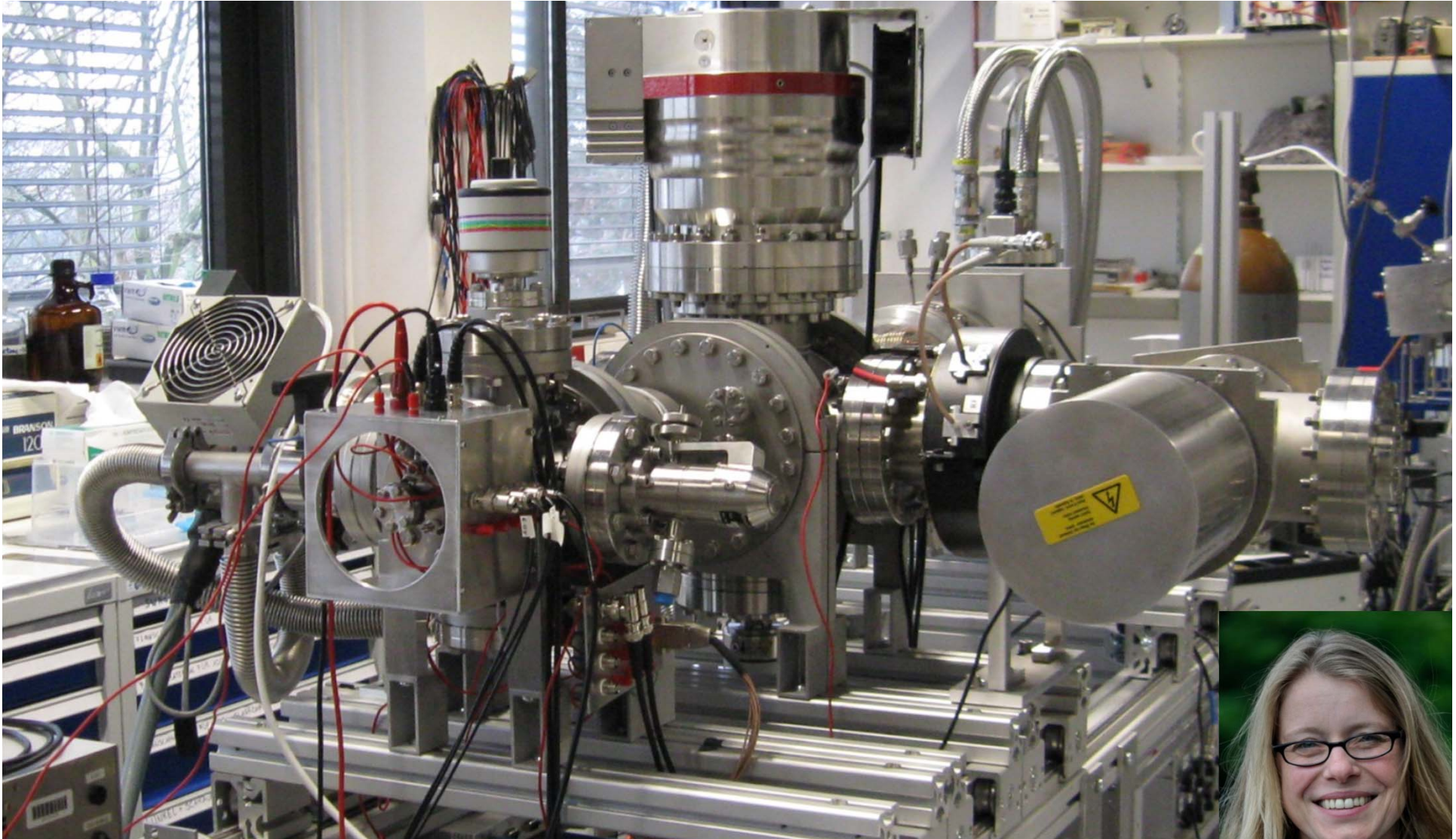
Band Origin, R(0) transition?

Lower Temperatures: Reduced Complexity



Band Origin, R(0) transition!

FELION: 4 K Trap for Spectroscopy



TJ13

15 min 4:57

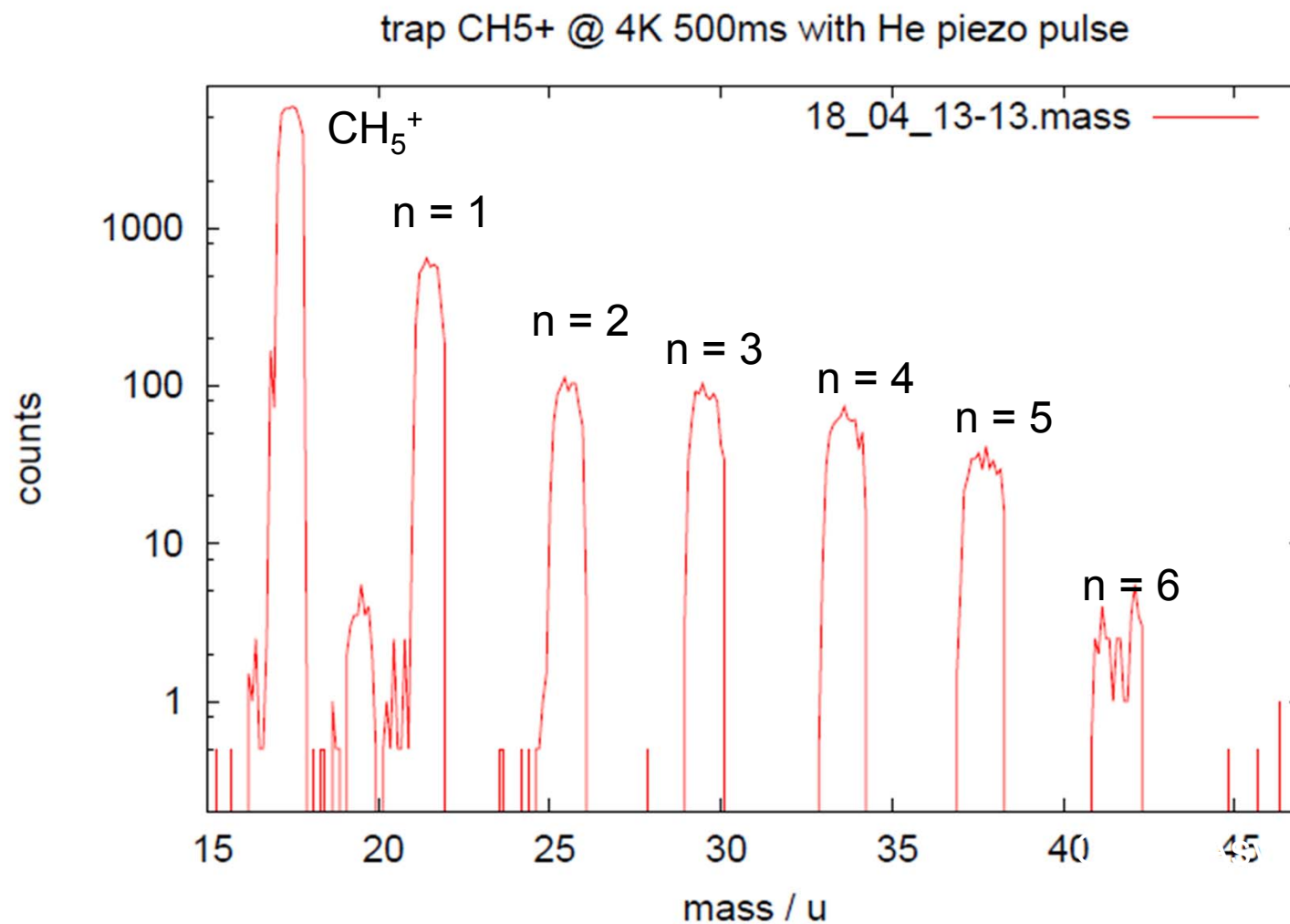
FELION: A CRYOGENIC ION TRAP APPARATUS FOR SPECTROSCOPIC STUDIES WITH FELIX

S. BRÜNKEN, L. KLUGE, S. FANGHÄNEL, A. POTAPOV, O. ASVANY, and S. SCHLEMMER,

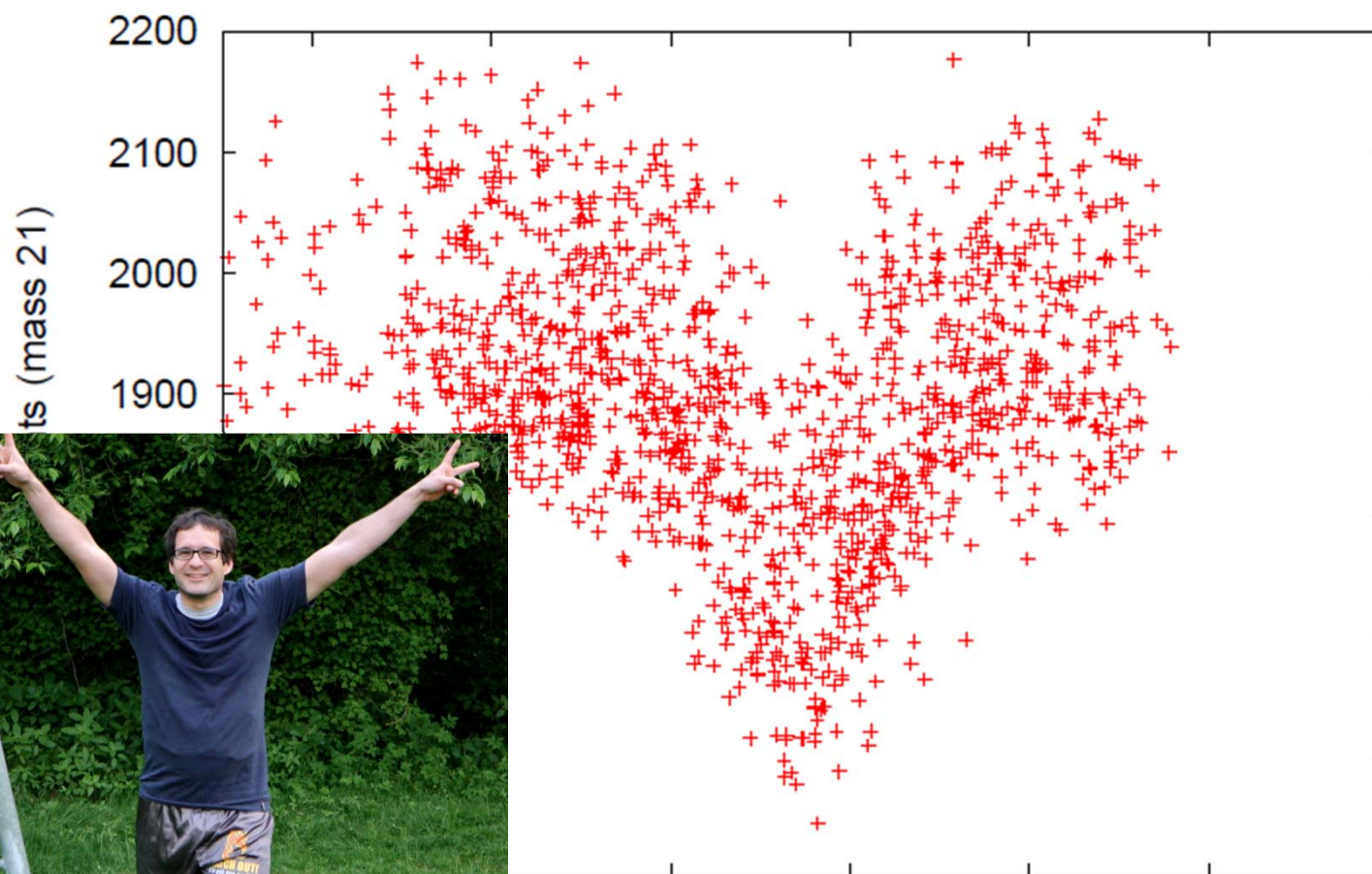


TJ13

Cluster Growth @ 4 K: $\text{CH}_5^+ \dots \text{He}_n$



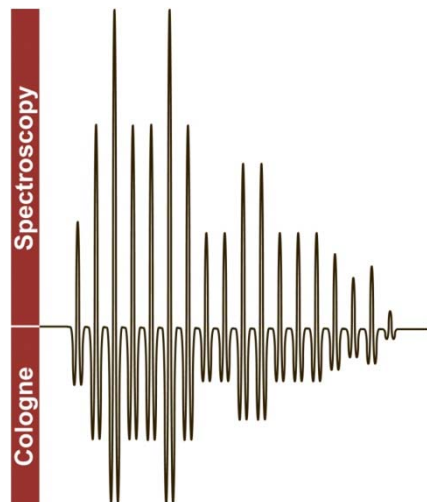
4 K Laser Inhibition of Cluster Growth (LIICG)



3044.3595 cm⁻¹



It's a CH₅⁺ Line

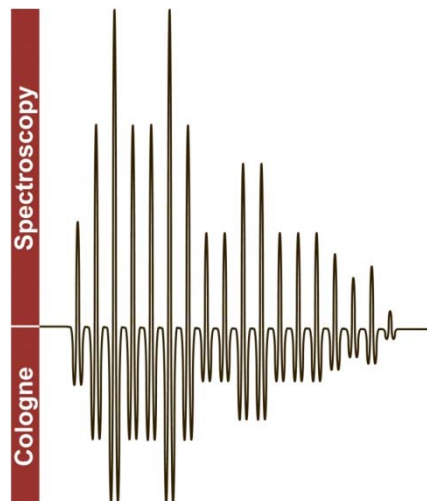


Light Induced Reactions In Cold Traps

Conclusions



- The Astrophysical Picture: **The Universe is molecular**
- $\text{C}_2\text{H}_2^+ + \text{H}_2$ Endothermic Reactions and Spectroscopy
- $\text{CH}_2\text{D}^+ + \text{H}_2$ IR Spectroscopy with MHz Resolution
- $\text{CH}_5^+ + \text{CO}_2 / \text{He}$ Structure of floppy Molecules
- $\text{H}_3^+ + \text{H}_2 / \text{O}_2$ Role of single Quantum States



Light Induced Reactions In Cold Traps

Perspectives



- Light Induced Reactions : Ion-Molecule **Collisions**
Bimolecular Process
- *Unimolecular Processes:* Messenger Method
IR-UV Dissociation,
- *Termolecular Processes:* Light Inhibited Association
- THz Spectroscopy: THz + IR Double Resonance
Sub-Doppler IR
- State-Specific Chemistry: Chemical Probing

Cologne Laboratory Astrophysics Group

