High Resolution Infrared and Microwave Spectra of HCCH-NH_3 and OCS-NH_3 Complexes

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66^{th} International Symposium on Molecular Spectroscopy

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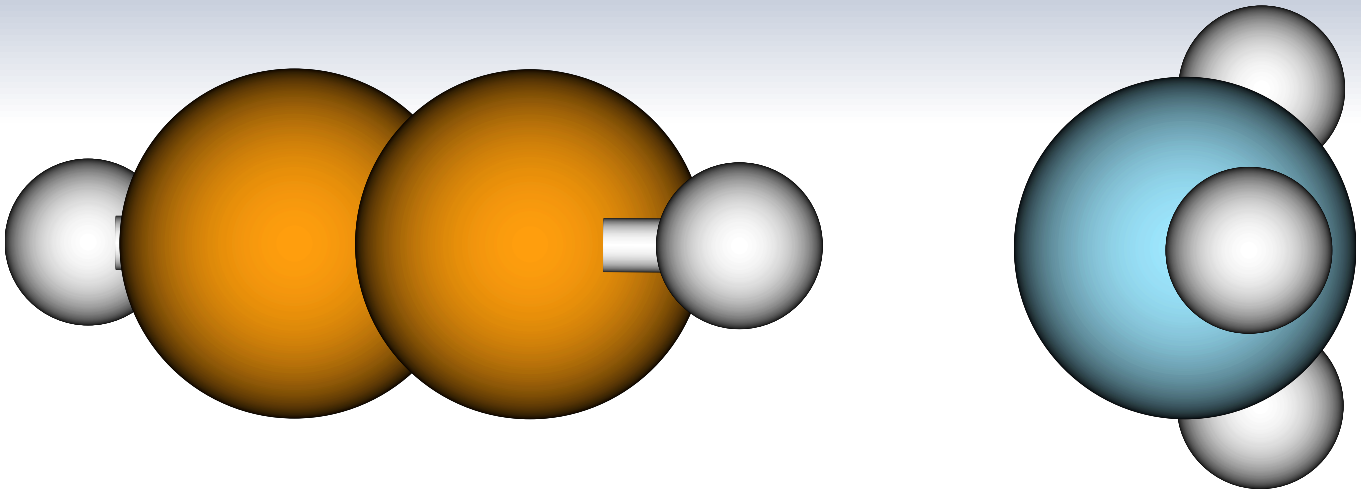
$HCCH\text{-}NH_3$



Prototype to Study C-H$\cdots$N Weak Hydrogen Bond

Previous Studies of HCCH-NH_3

- Microwave spectrum
  Fraser *et al., J. Chem. Phys*, 1984, **80**, 1423

The structure of NH_3–acetylene[a)]

G. T. Fraser, K. R. Leopold, and W. Klemperer

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
(Received 25 August 1983; accepted 9 November 1983)

- Perpendicular band of C-H stretching at 3 μm
  Hilpert *et al., J. Chem. Phys*, 1996, **105**, 6183

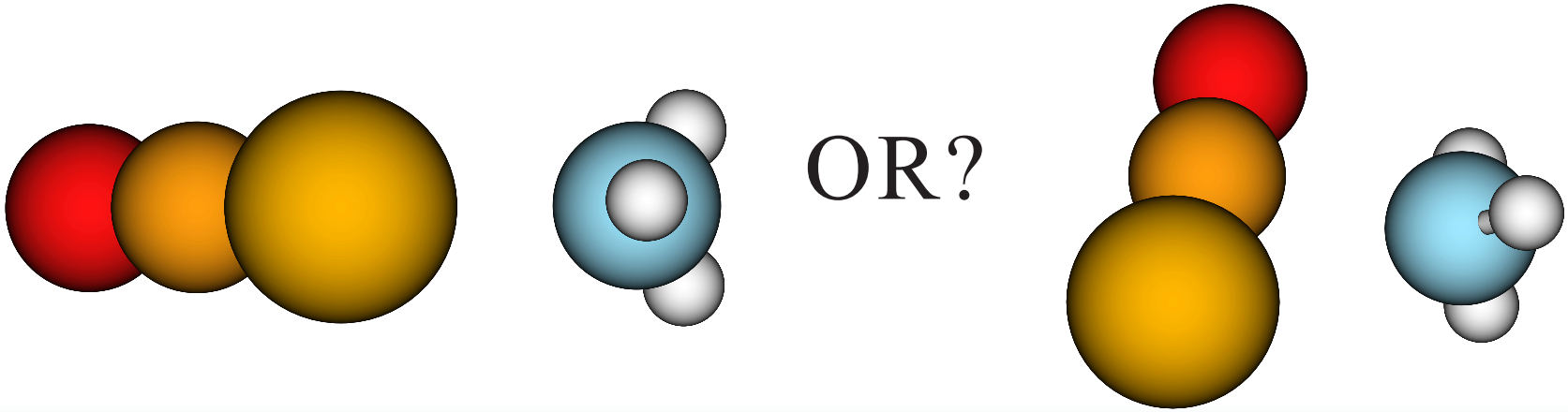
Vibrational couplings and energy flow in complexes of NH_3 with HCN, HCCH, and HCCCCH

G. Hilpert,[a),b)] G. T. Fraser, and A. S. Pine
Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-0001

(Received 29 March 1996; accepted 10 July 1996)

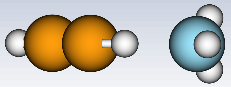
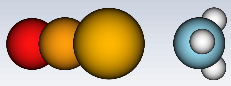
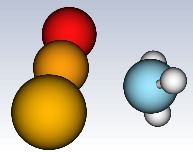
$OCS\text{-}NH_3$

Polarized Molecule with Strong Dipole Moment
Prototype to Study C-S$\cdots$N bond



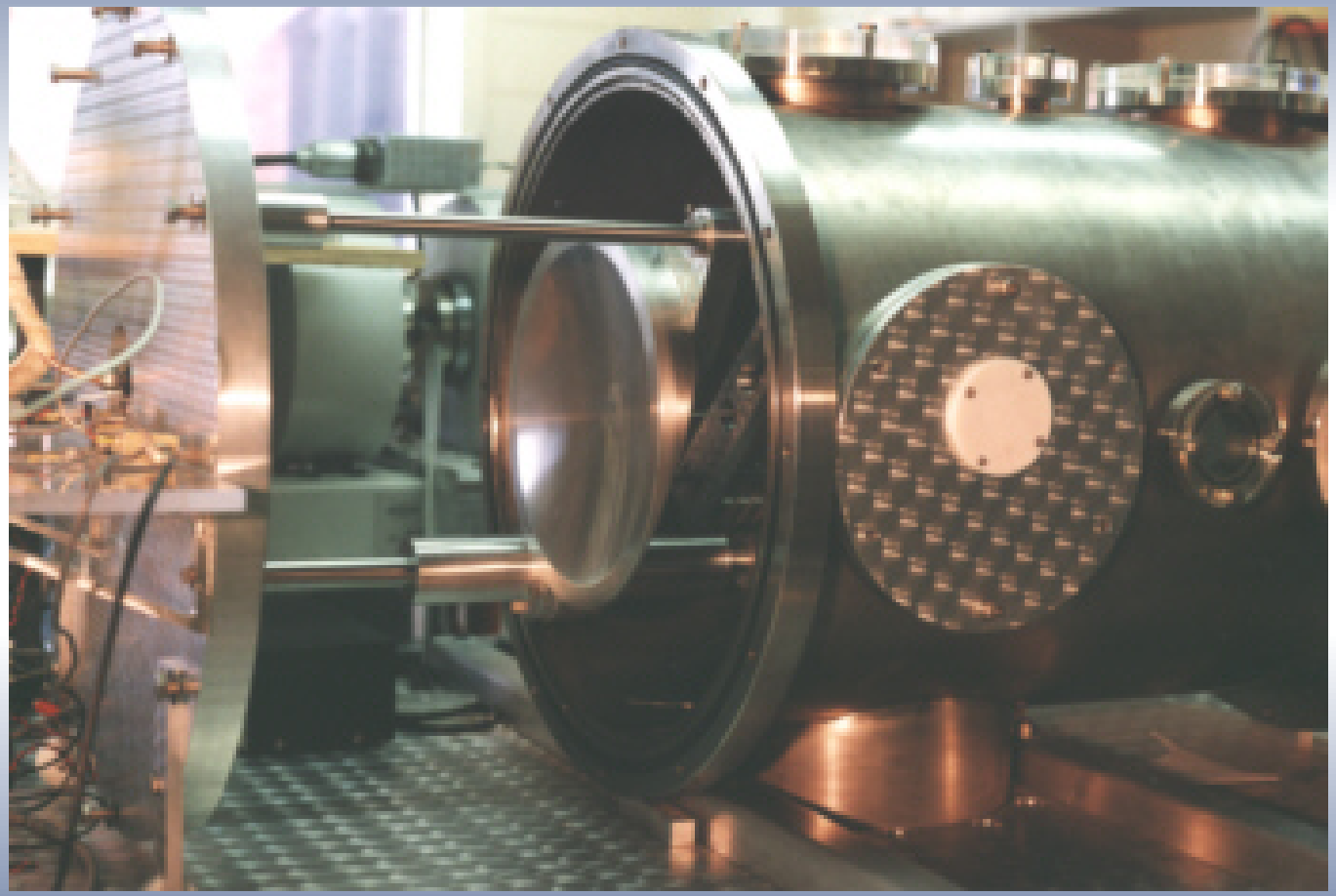
Symmetric Top "T-Shaped"?

Ab initio Calculation

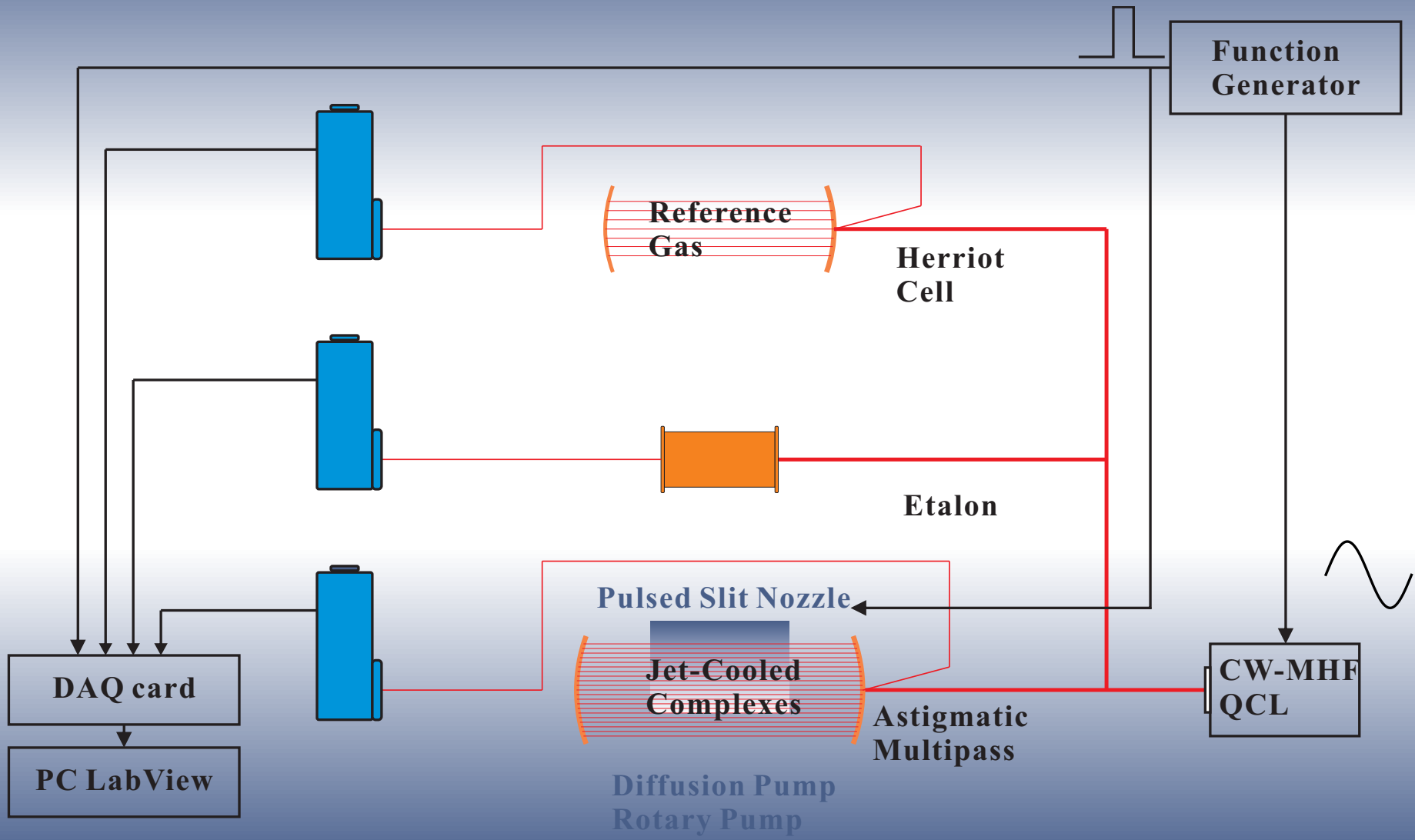
			
ΔE_0 BSSE+**har**-ZPE (kJ/mol) MP2/aug-cc-pVTZ	9.2	6.4	4.8
ΔE_0 BSSE+**anh**-ZPE (kJ/mol) MP2/aug-cc-pVTZ	10.2	7.0	4.8
ΔE_0 BSSE+**scaled-har**-ZPE (kJ/mol) CCSD(T)/6-311+G(3df,2p)[a]	9.3		

[a] M. Hartmann and L. Radom, *J. Phys. Chem. A*, 2000, **104**, 968

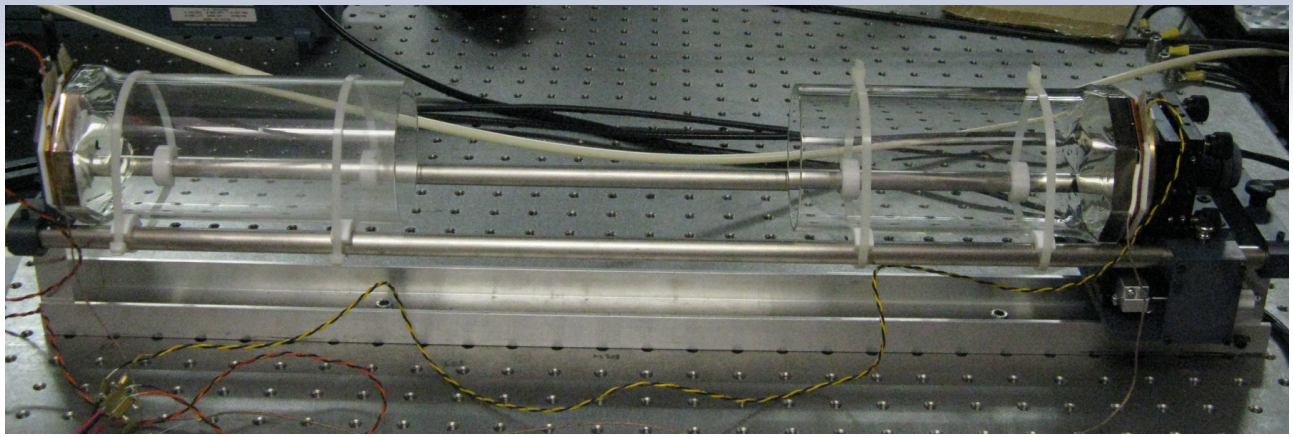
Pulsed Molecular Beam Fourier Transform Microwave Spectrometer

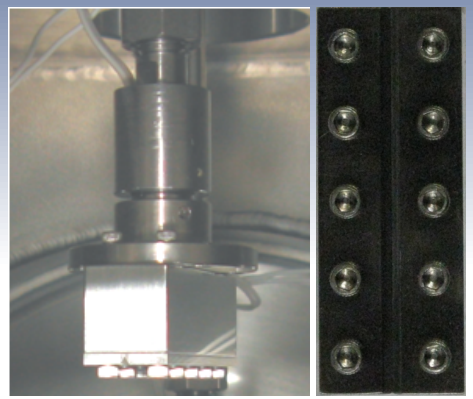


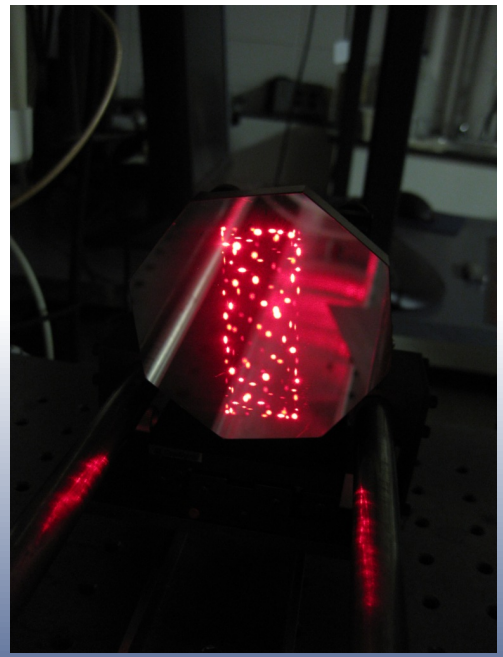
Quantum Cascade Laser Multipass Absorption Spectrometer



Astigmatic Multipass Cell
Supersonic Jet Expansion from Slit Nozzle



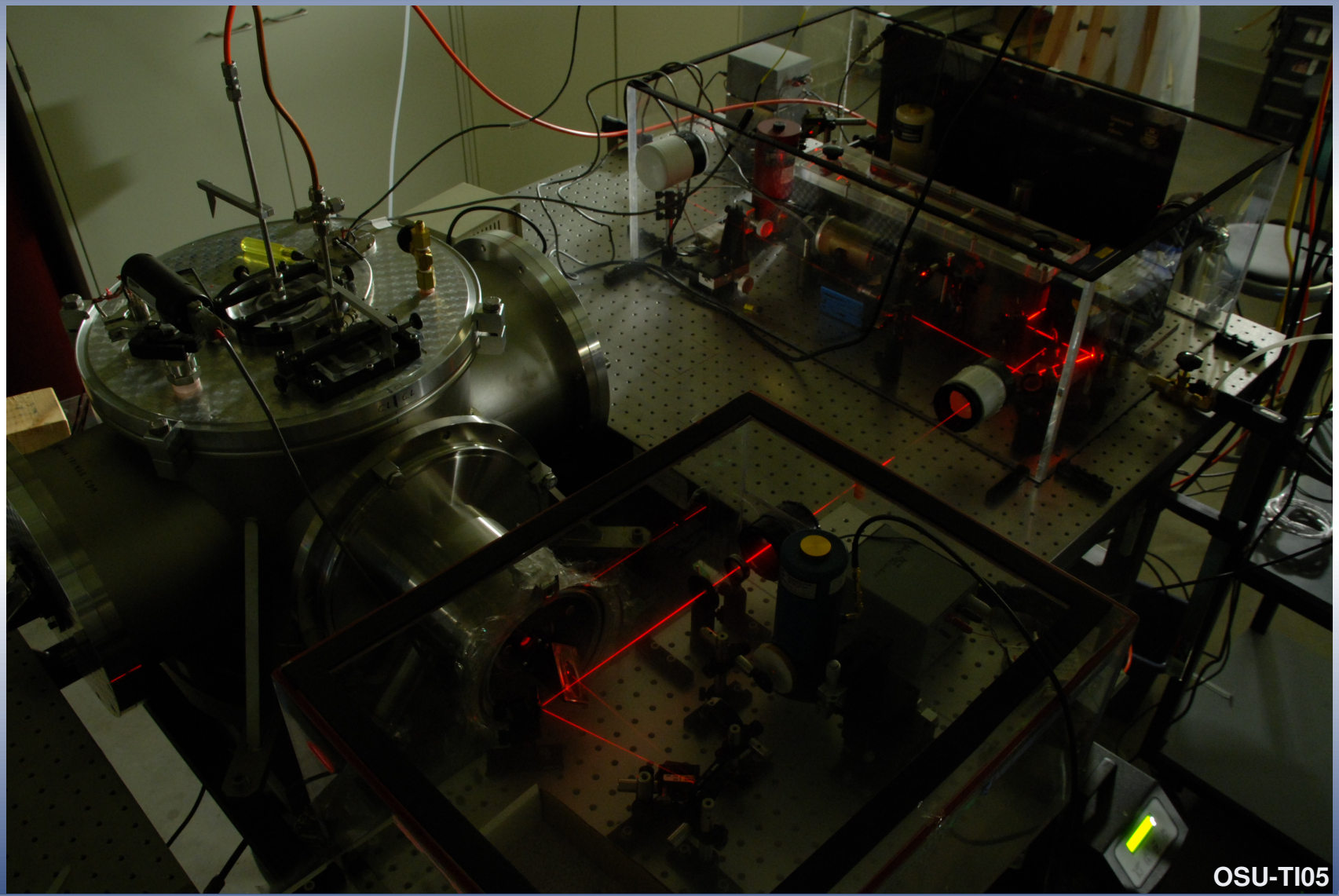




- Astigmatic multipass cell
  mirror distance 55 cm, aligned for 366 passes
- supersonic jet expansion
  home-made slit-nozzle

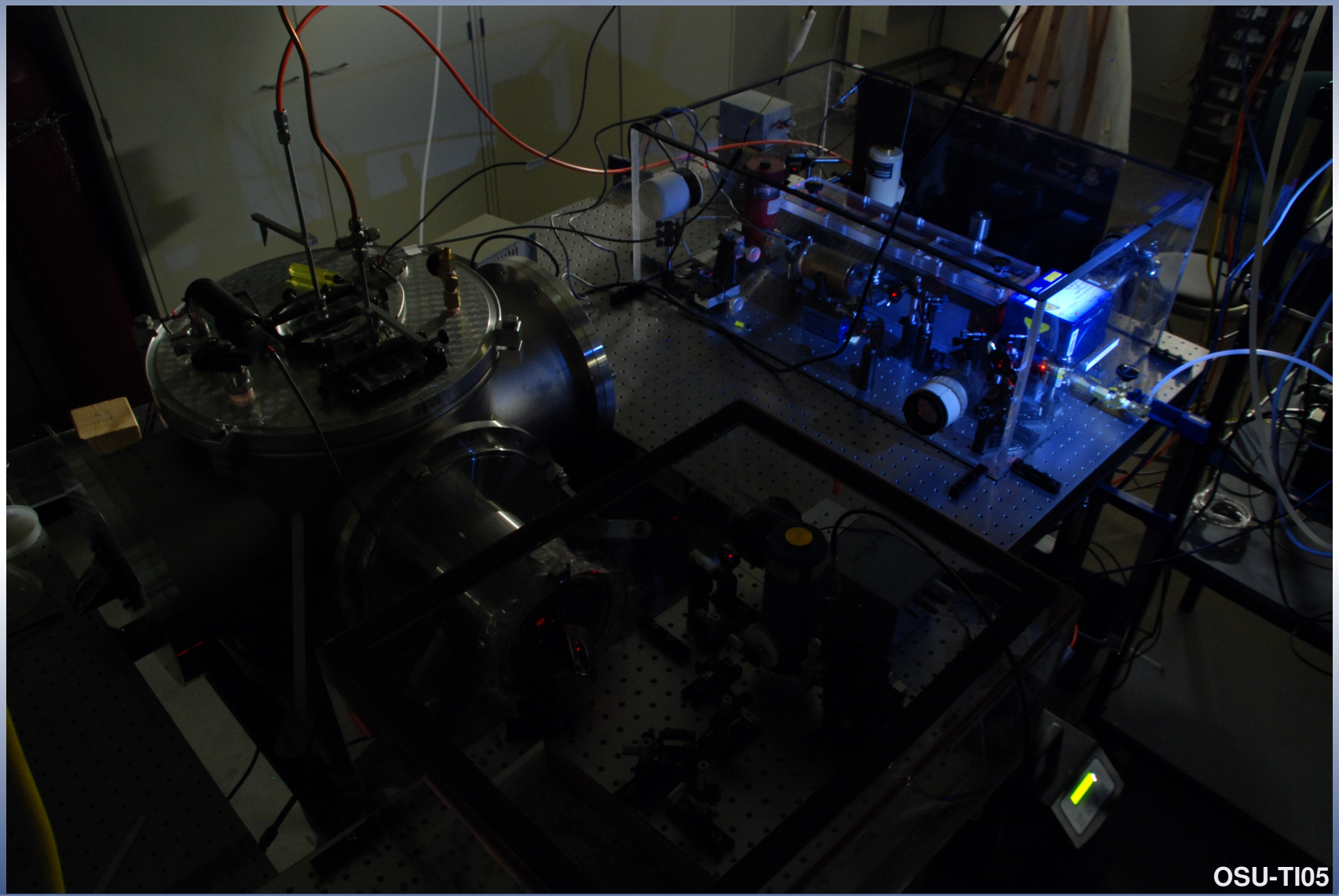
Infrared Spectrum

Multipass Absorption spectrometer



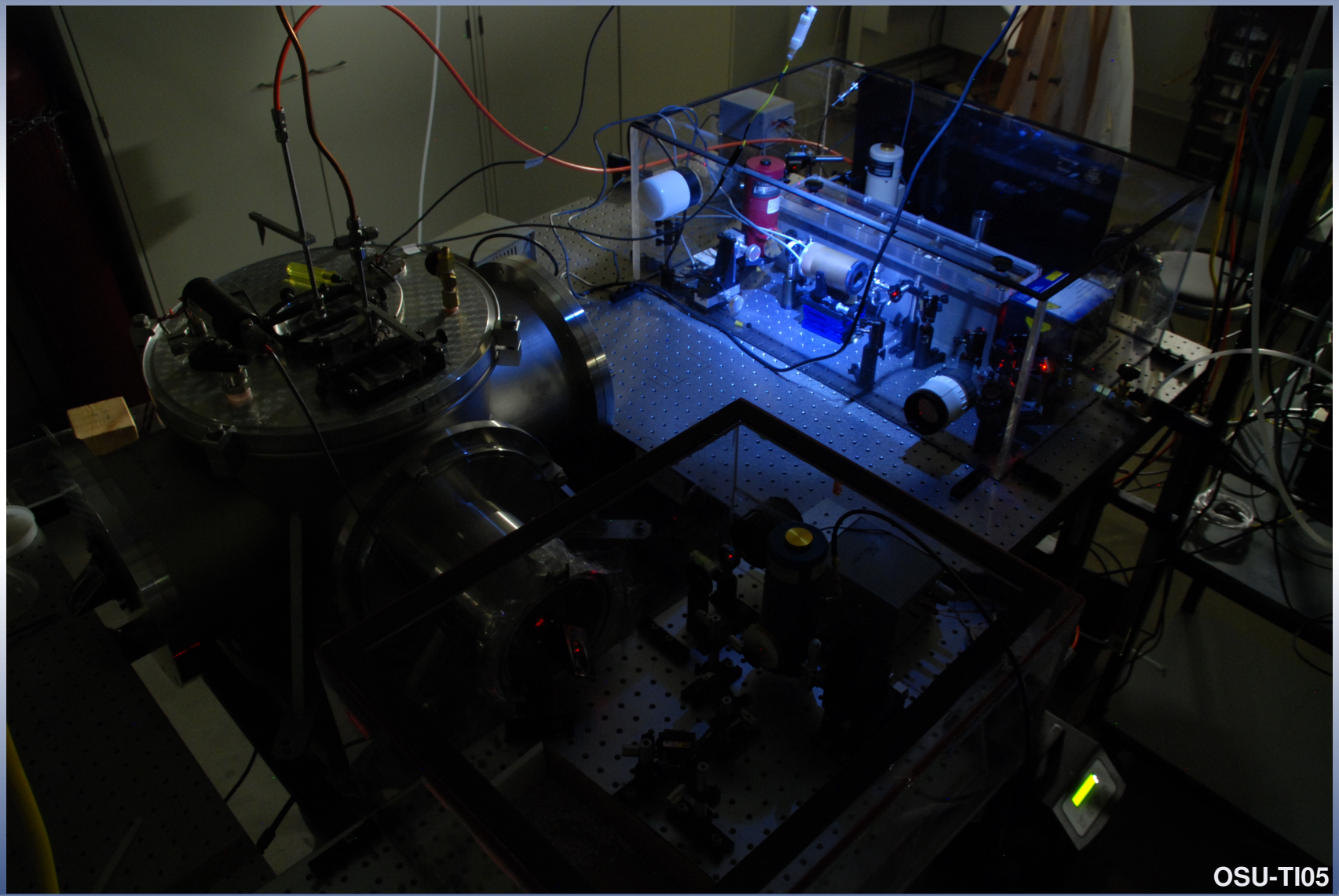
Infrared Spectrum

Multipass Absorption spectrometer



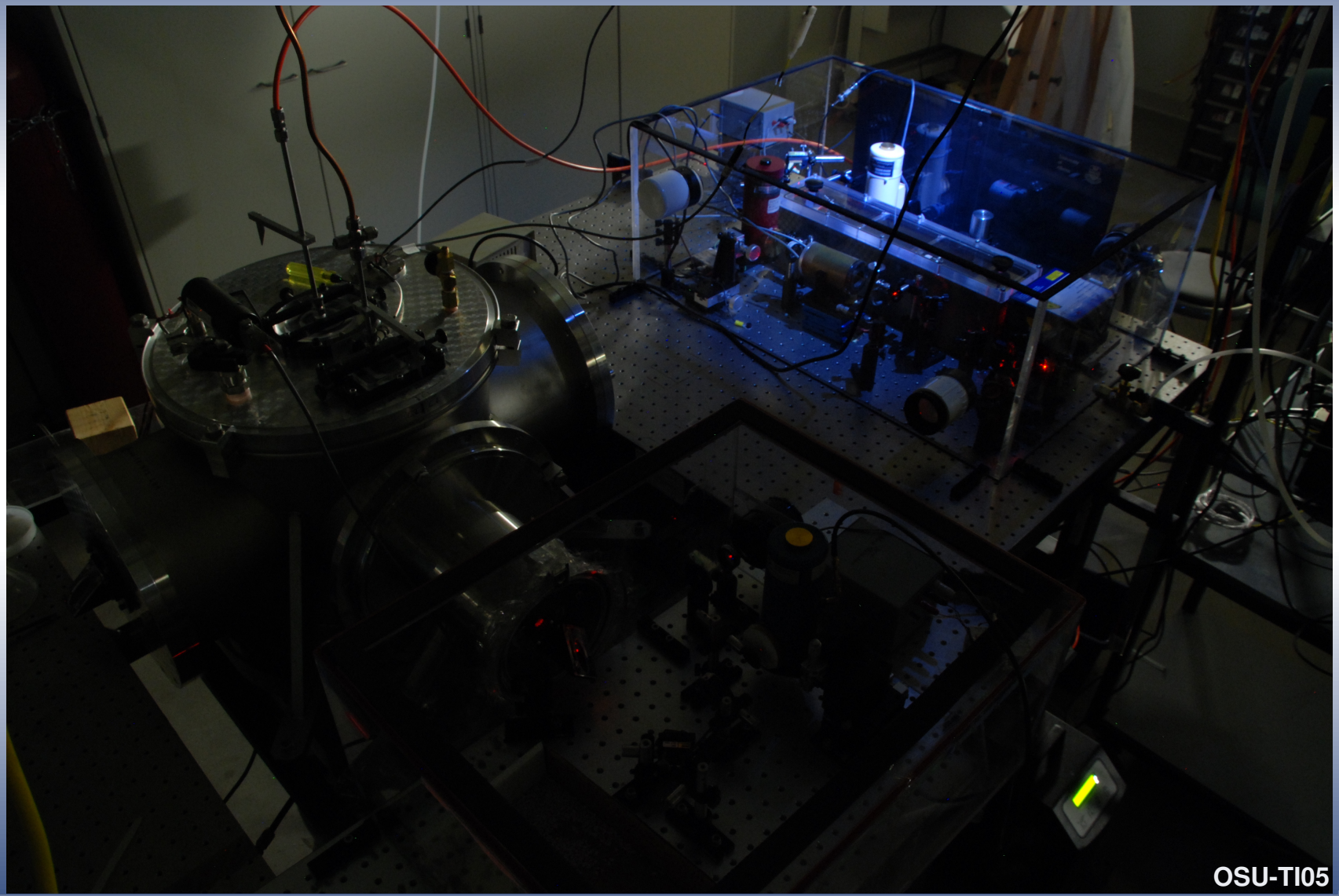
Infrared Spectrum

Multipass Absorption spectrometer



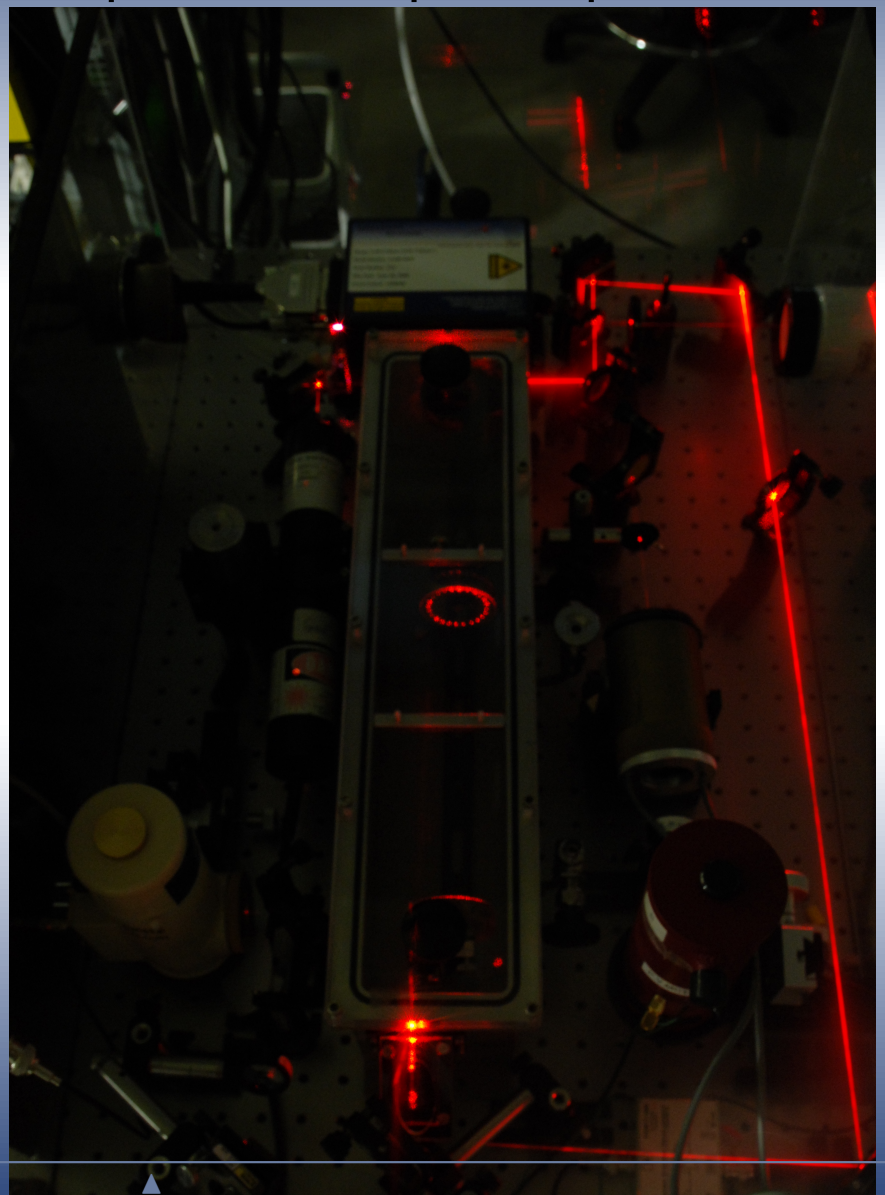
Infrared Spectrum

Multipass Absorption spectrometer



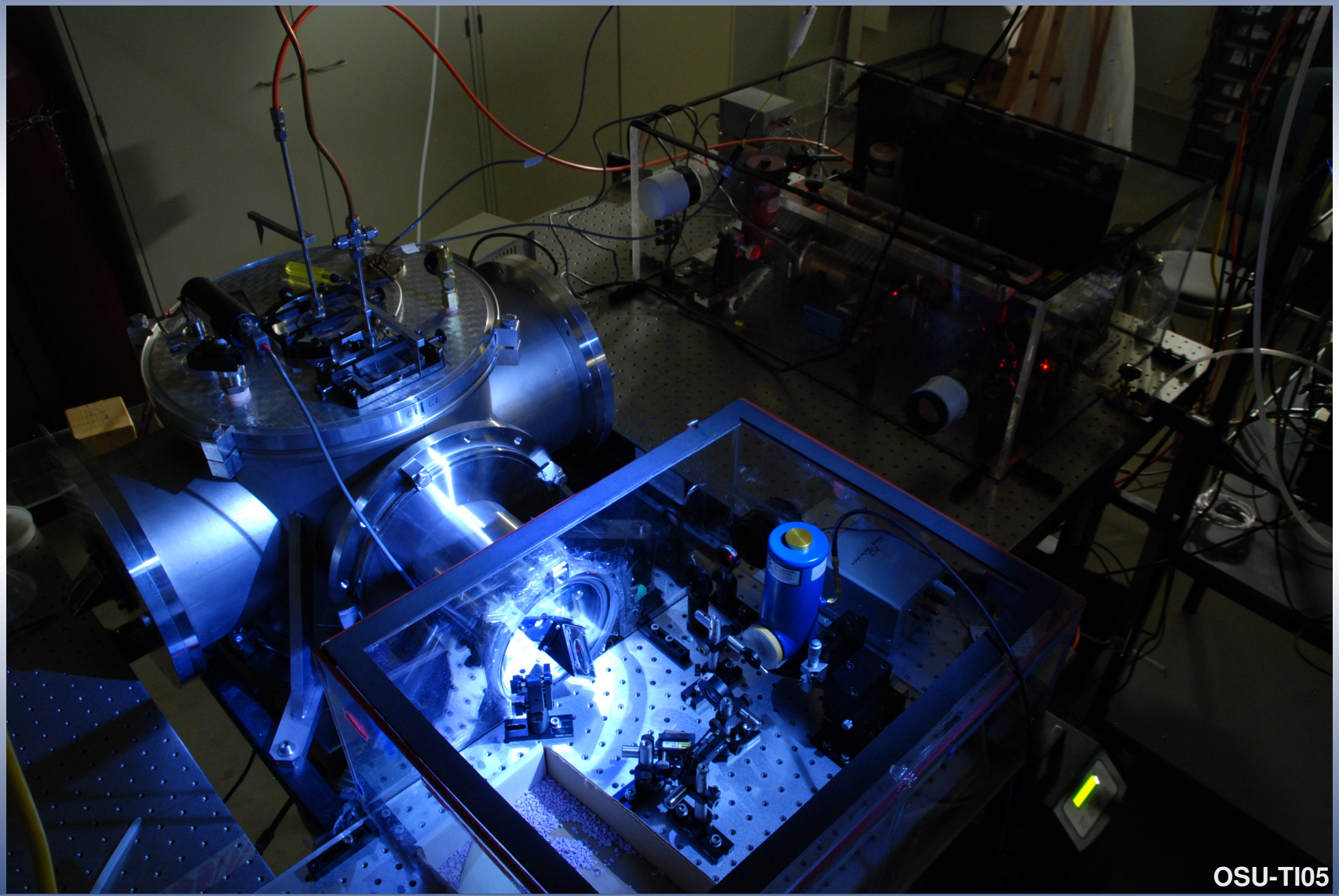
Infrared Spectrum

Multipass Absorption spectrometer



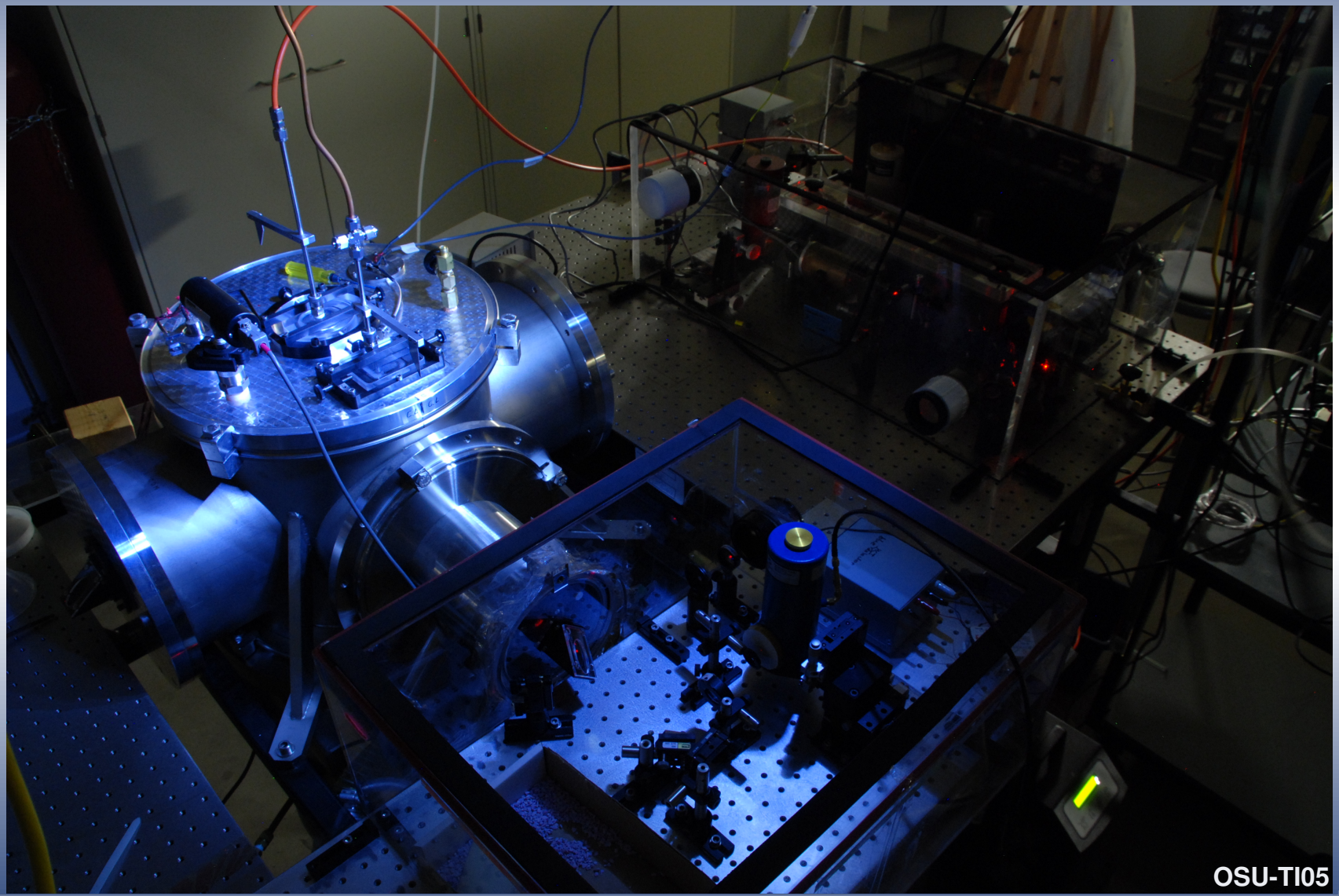
Infrared Spectrum

Multipass Absorption spectrometer

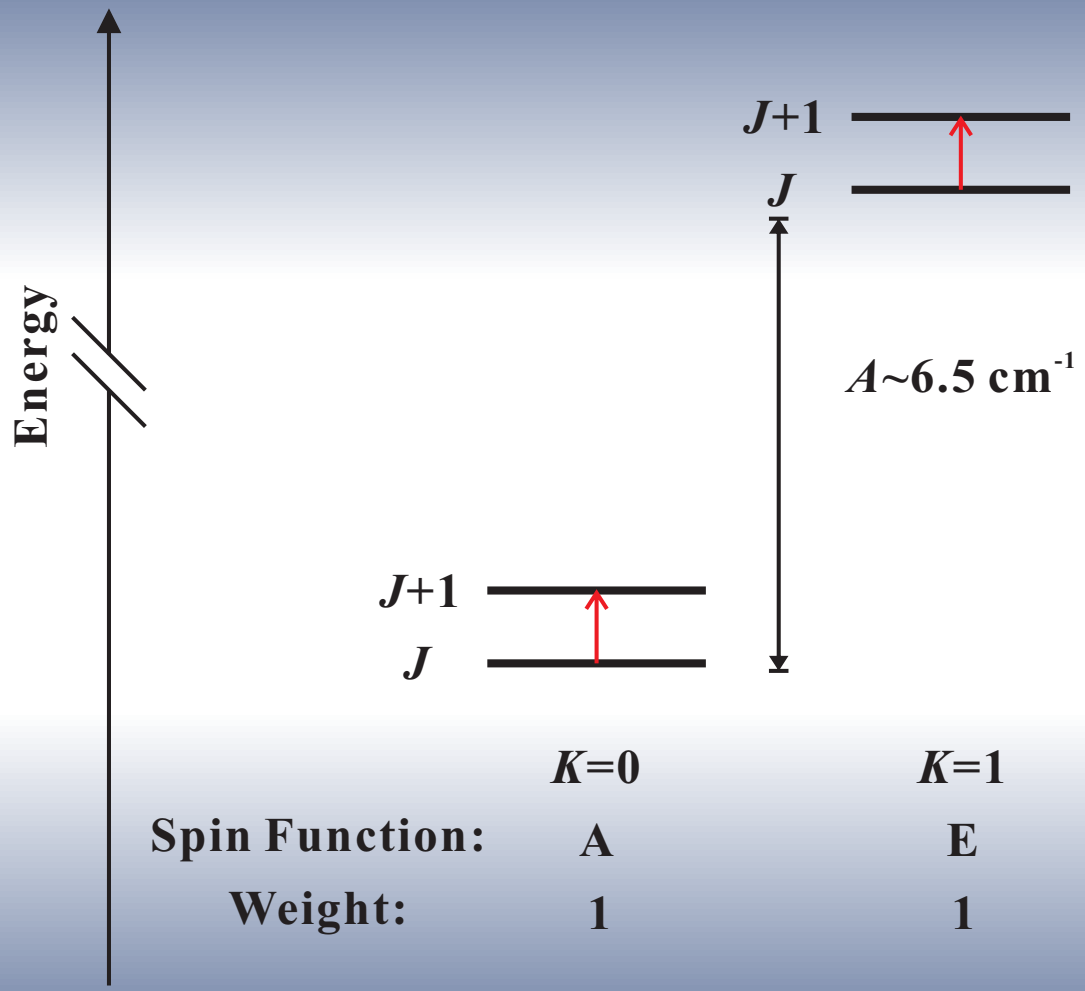


Infrared Spectrum

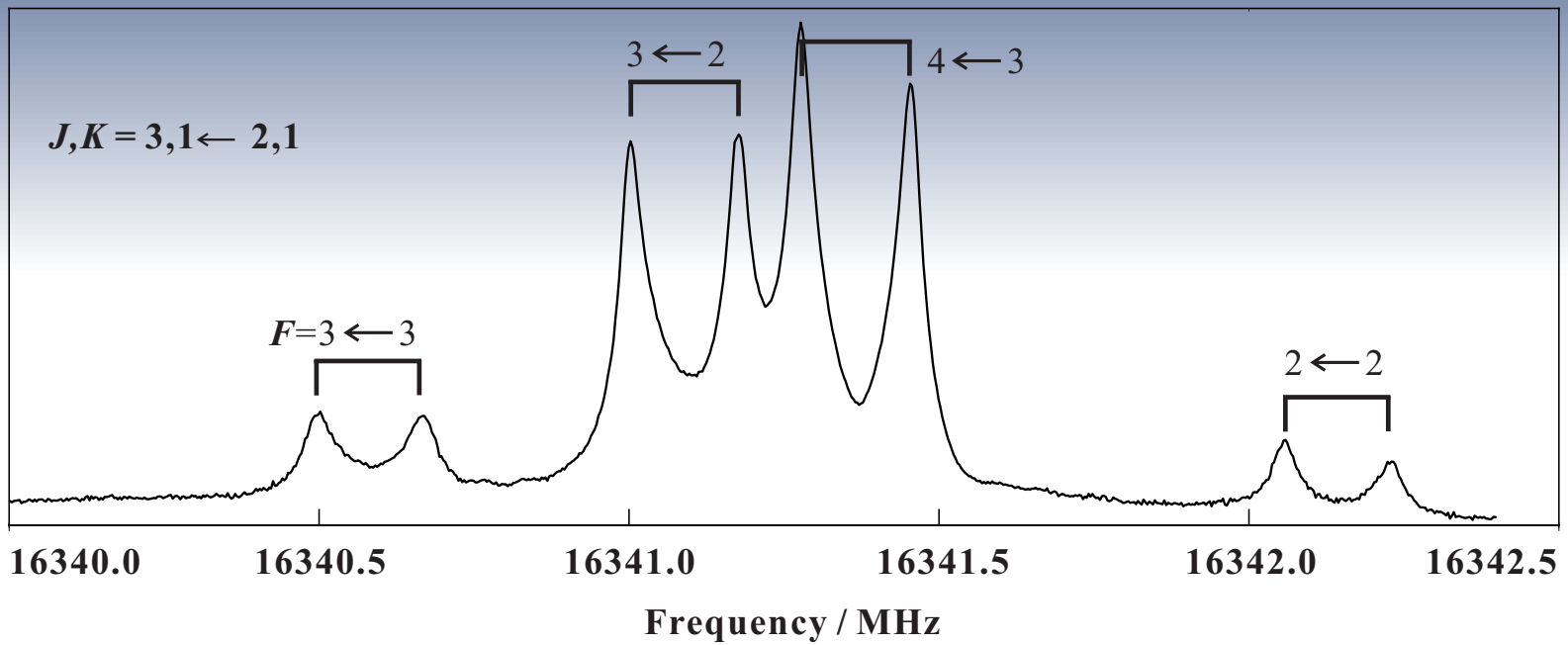
Multipass Absorption spectrometer



Microwave spectra of HCCH-NH_3

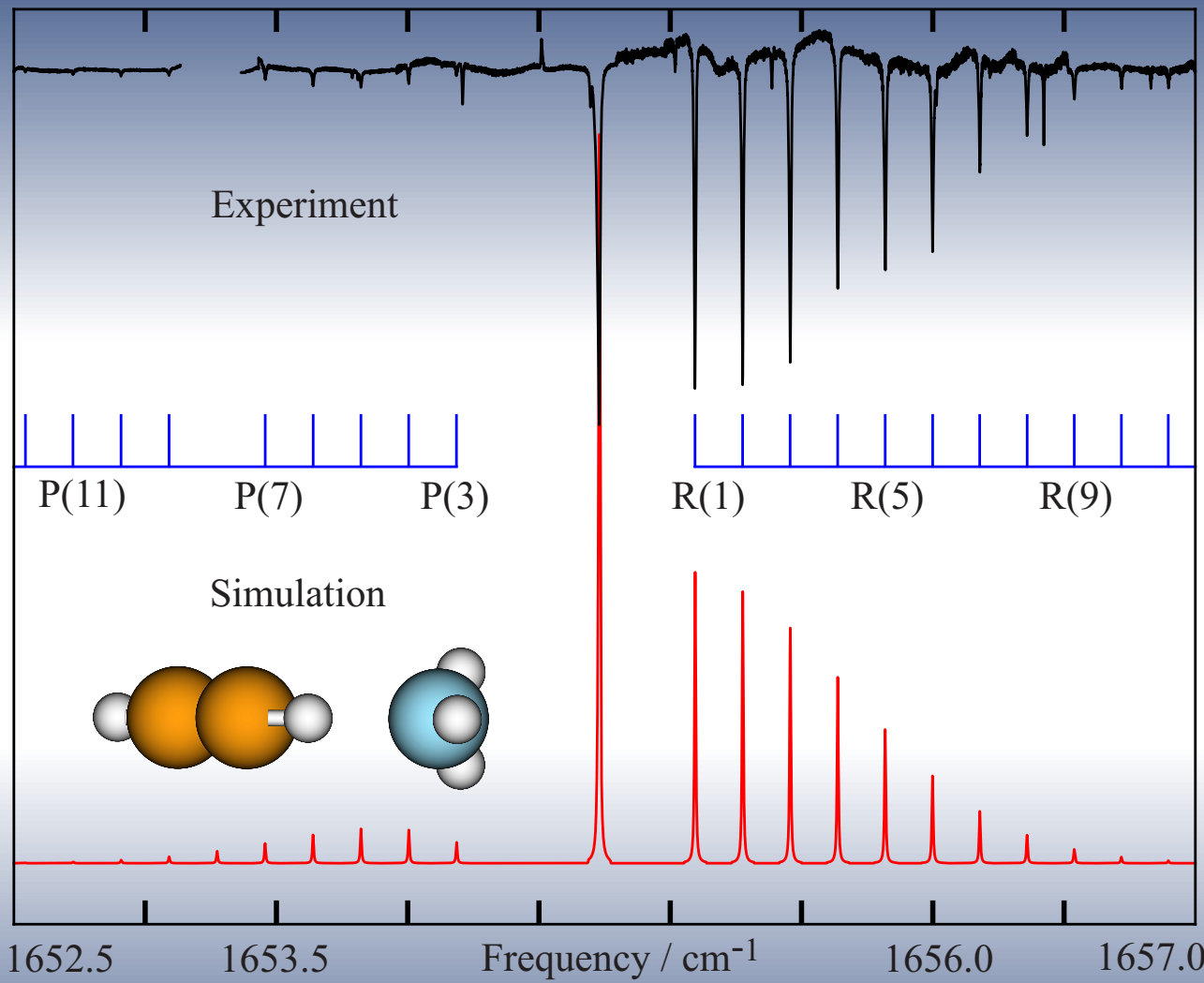


Microwave transitions of HCCH-NH_3



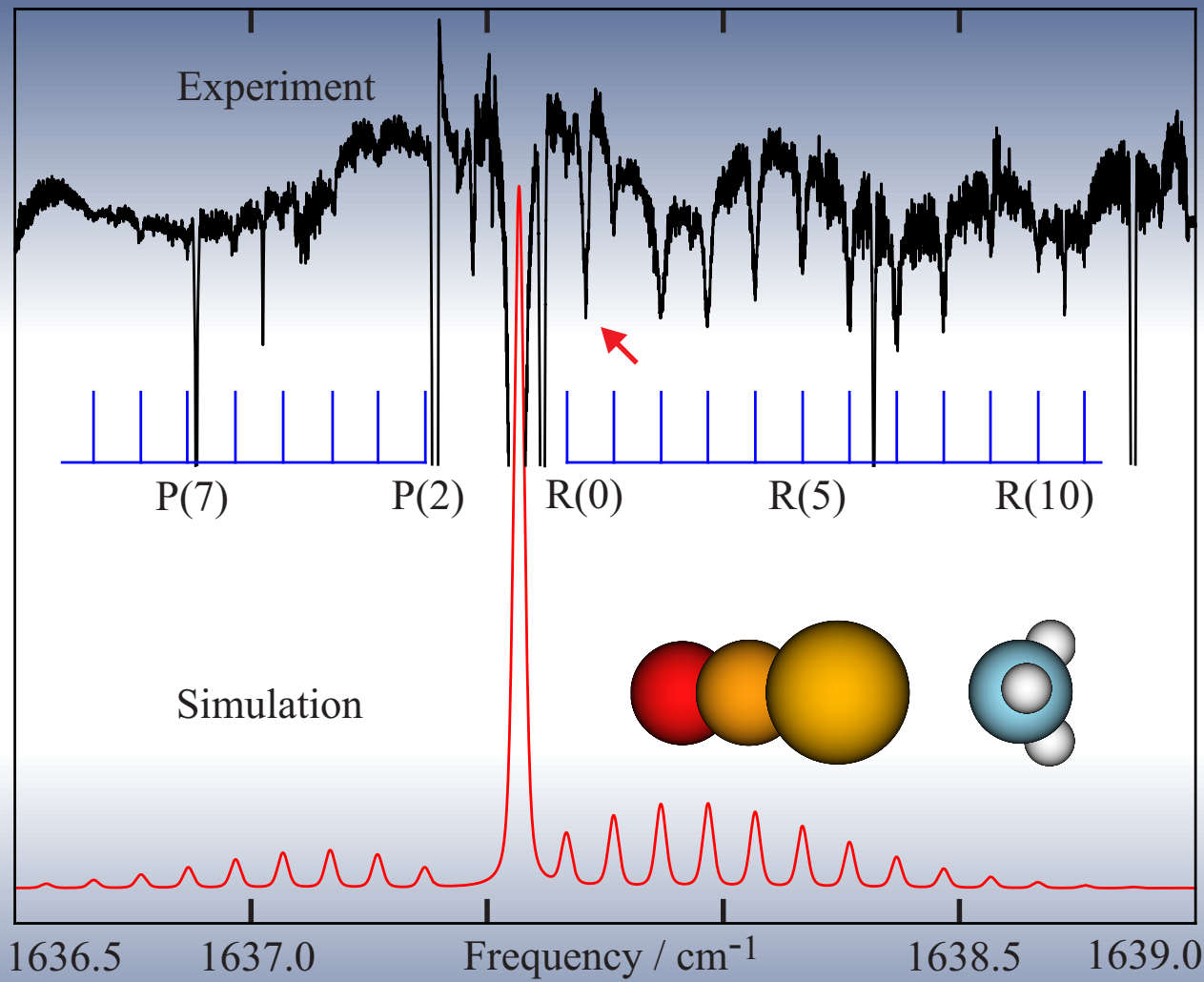
- Extended the measurements to J=3 and K=2
- ^{14}N nuclear quadrupole hyperfine structures fully resolved

Infrared spectra of HCCH-NH_3



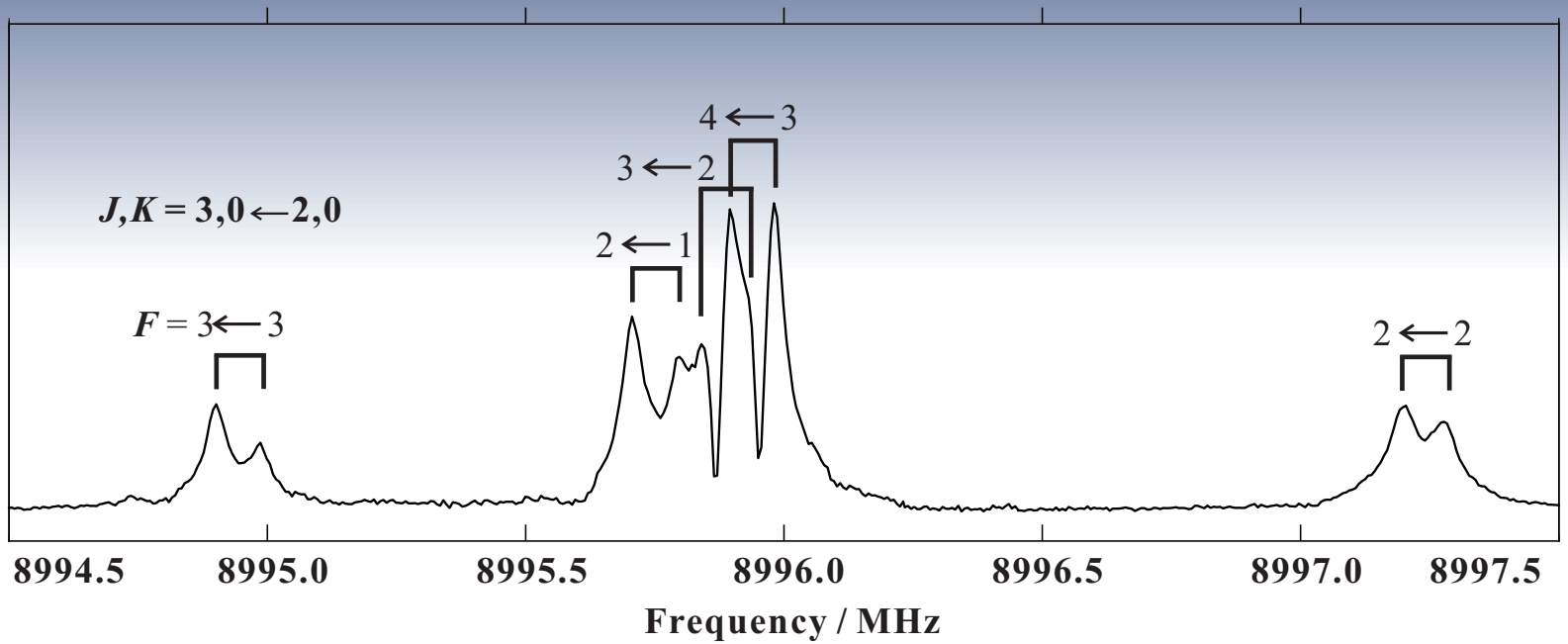
$K = 2 \leftarrow 1$ sub-band with origin at $1654.73202\,\mathrm{cm}^{-1}$

Infrared spectra of OCS-NH_3



$K = 1 \leftarrow 0$ subband with origin at 1637.56882 cm^{-1}

Microwave transitions of HCCH-NH_3



- Extended the measurements to J=5 and K=1
- ^{14}N nuclear quadrupole hyperfine structures fully resolved

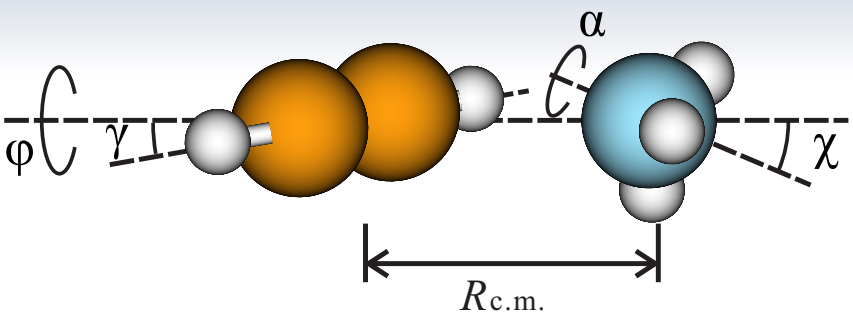
Experimental spectroscopic constants

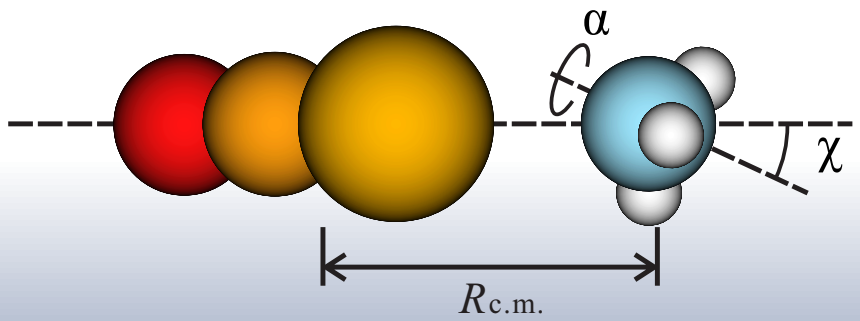
	ν_0	ν_4=1
HCCH-NH_3		$K = 2 \leftarrow 1$
ν (cm^{-1})	0.0	1654.73202(18)
B_0 (MHz)	2724.56497(45)	2724.69(16)
D_J (kHz)	6.789(94)	8.89(90)
D_{JK} (kHz)	896.27(33)	896.27[a]
H_J (Hz)	-11.8(51)	-11.8[a]
H_{JK} (Hz)	753(34)	753[a]
H_{KJ} (Hz)	131.3(214)	131.3[a]
eQq^N_{aa} (MHz)	-3.13073(94)	
OCS-NH_3		$K = 1 \leftarrow 0$
ν (cm^{-1})	0.0	1637.56882(16)
B_0 (MHz)	1499.349248(52)	1499.021(73)
D_J (kHz)	1.87152(101)	1.87152[a]
D_{JK} (kHz)	425.461(81)	425.461[a]
eQq^N_{aa} (MHz)	-2.97507(84)	

[a] Fixed at the corresponding vibrational ground state value.

van der Waals Vibration

$$eQq_{aa}^{N} = eQq_{NH_3}^{N}\langle P_2(\cos\chi)\rangle = eQq_{NH_3}^{N}\left(\frac{3\langle\cos^2\chi\rangle - 1}{2}\right)$$





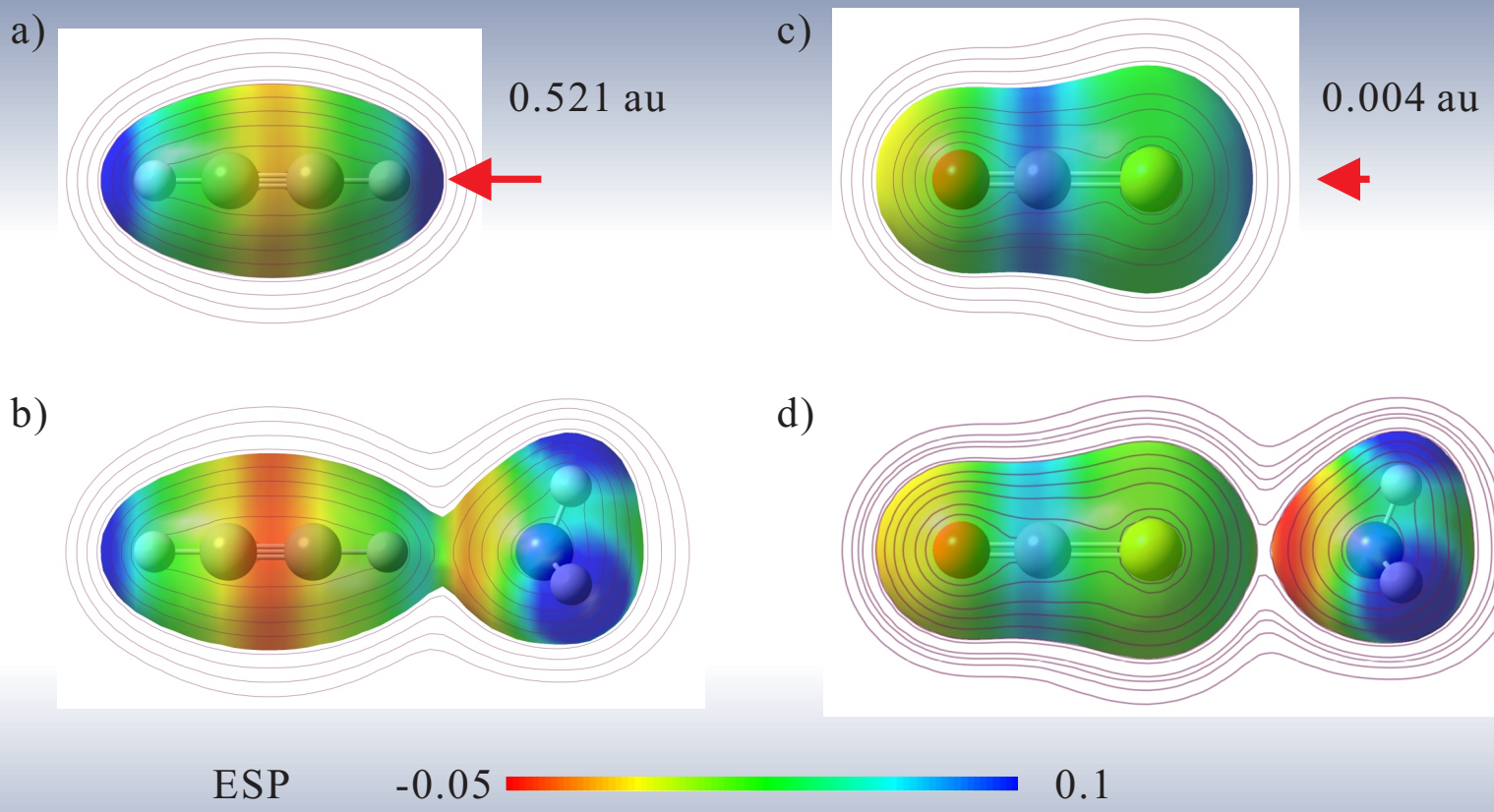
$$I_b = \mu_R\langle R_{c.m.}^2\rangle + I_b^{NH_3}\left(\frac{1+\langle\cos^2\chi\rangle}{2}\right) + I_c^{NH_3}\left(\frac{\langle\sin^2\chi\rangle}{2}\right) + I_b^{C_2H_2}\left(\frac{1+\langle\cos^2\gamma\rangle}{2}\right)$$

$$k_s = \frac{\hbar^4\mu_R}{2D_J h}\frac{I_{AB} - I_A - I_B}{I_{AB}^4} \qquad \Delta E_0 = \frac{1}{72}k_s R_{c.m}^2$$

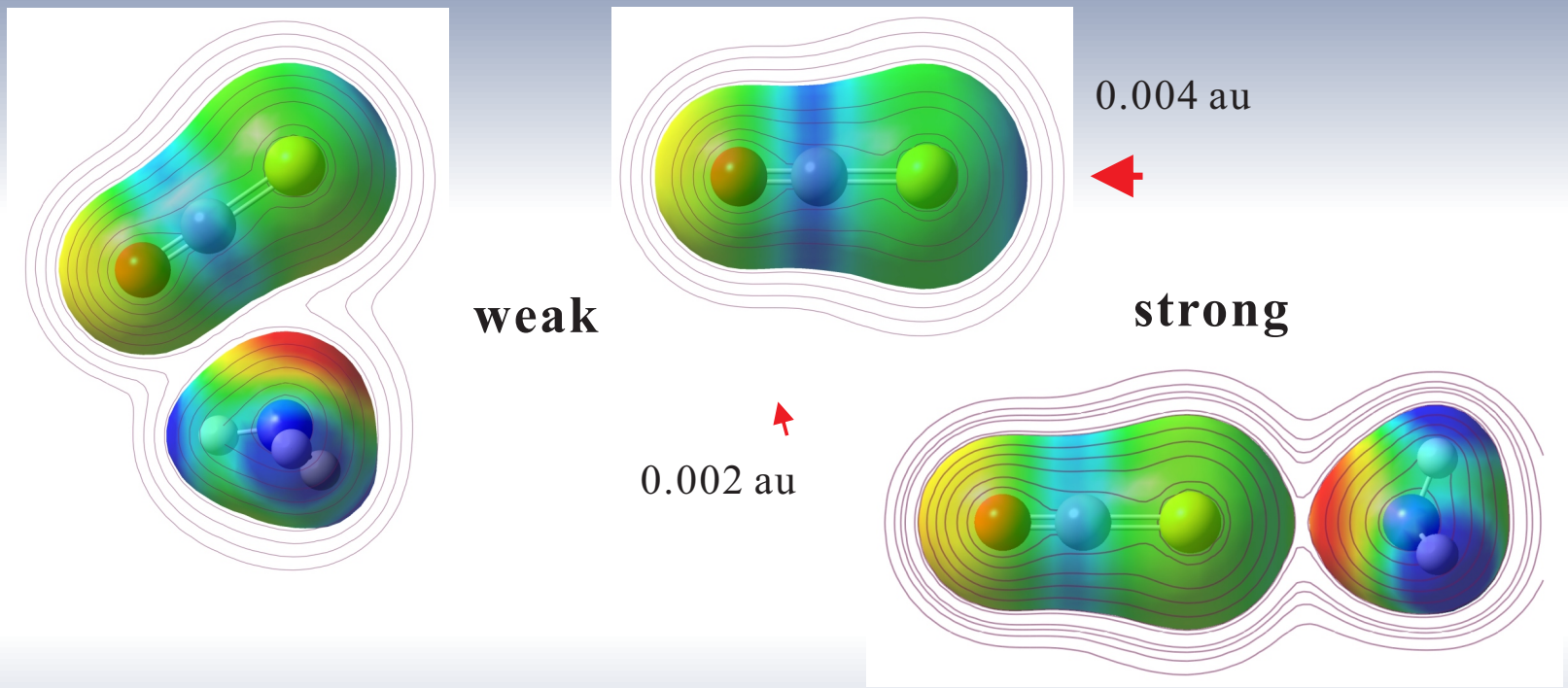
Structure Parameters

	HCCH-NH_3	OCS-NH_3
χ	23.29(2)°	25.23(2)°
$R_{c.m.}$ (Å)	4.05941(79)	4.360748(27)
$R_{H/S\cdots N}$ (Å)	2.3981(27)	3.3232(1)
k_s (N/m)	7.34(10)	4.6872(25)
ν_s (cm^{-1})	110.0(8)	77.45(2)
ΔE_0 (kJ/mol)	10.1(1)	7.455(4)

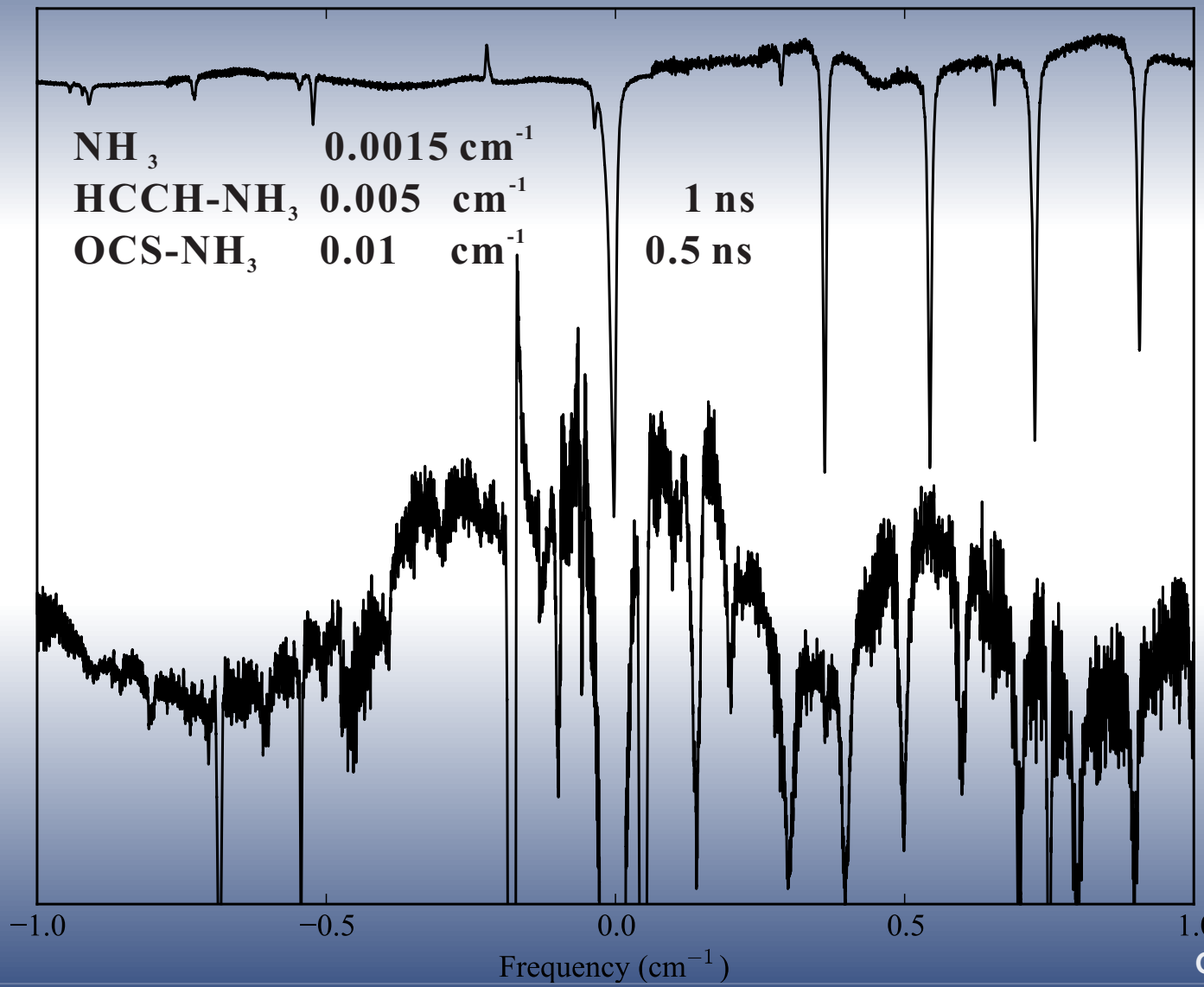
Electrostatic Interaction



Electrostatic Interaction



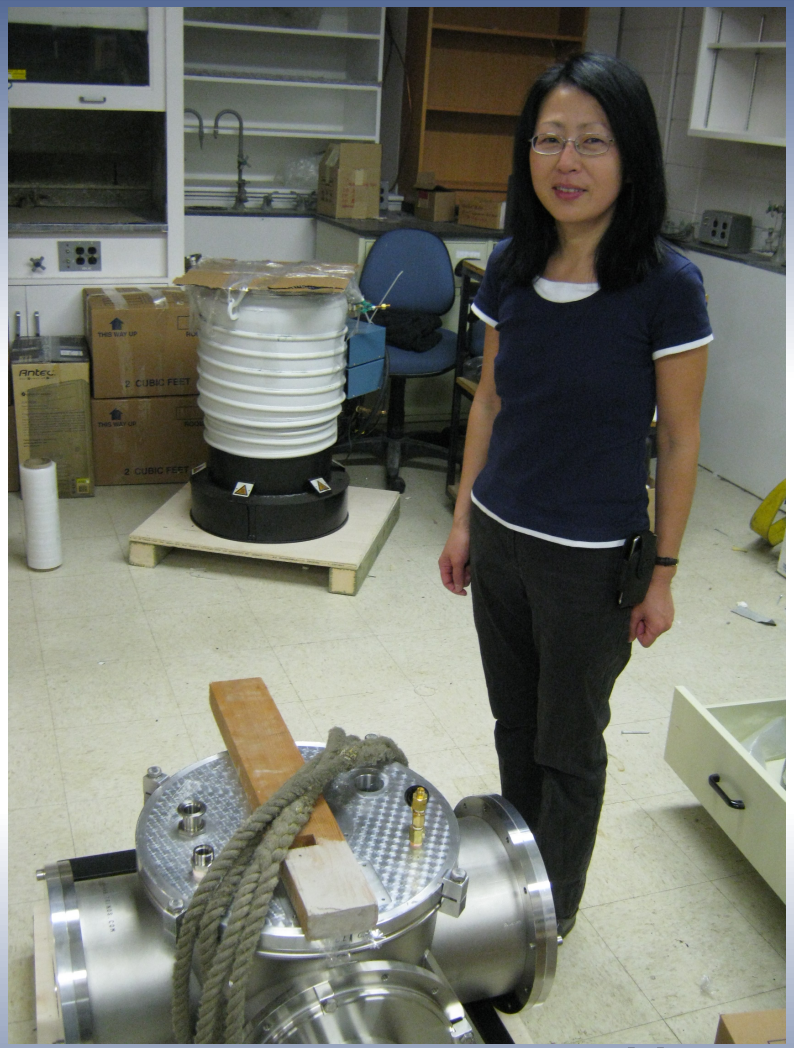
Excited state lifetime from linewidth



Summary and Future Work

- Microwave and high resolution infrared spectra are measured for HCCH-NH_3 and OCS-NH_3 complexes
- Both structure are axially symmetric (T-shaped OCS-NH_3 is less stable)
- Weak C-H$\cdots$N hydrogen bond in HCCH-NH_3 is stronger than C-S$\cdots$N interaction in OCS-NH_3
- NH_3-Ne/Ar, NH_3-Ne/Ar_2 spectra have been measured and assigned

Acknowledgement



Xu and Jäger groups
Dr. Wolfgang Jäger

Thank you for suggestion and comments