Infrared Vibrational Overtone Spectroscopy of H_2 in MOFs

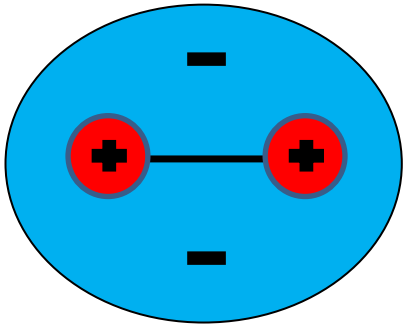
Outline

1) Making H_2 Infrared Active
   Polarizability, Quadrupole Moment

2) Practical Motivation
   Storage, Quantum Sieving, Catalysis

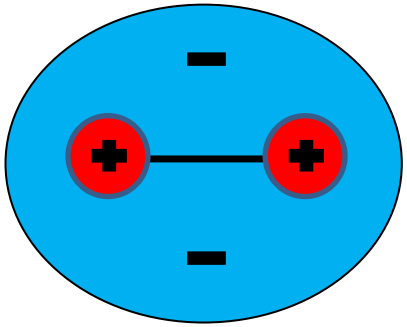
3) Overtone Activation-Anharmonicity
   Frequency and Intensity (Help!)

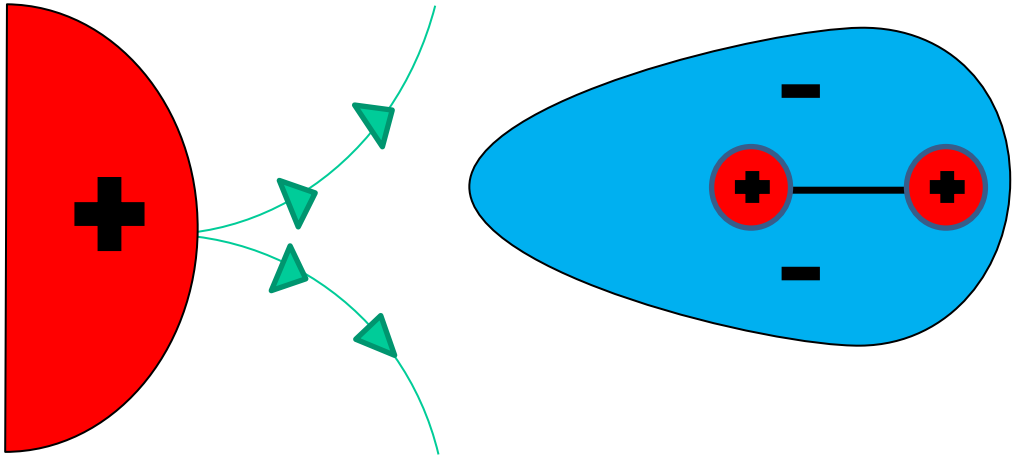
Infrared Spectroscopy! Are you crazy?



No Dipole Moment

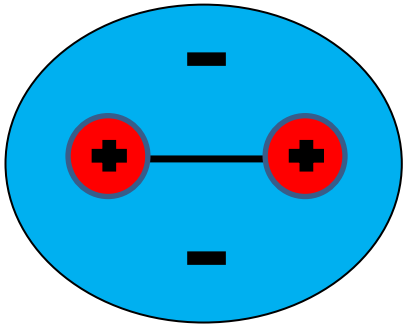
Polarizability Mechanism

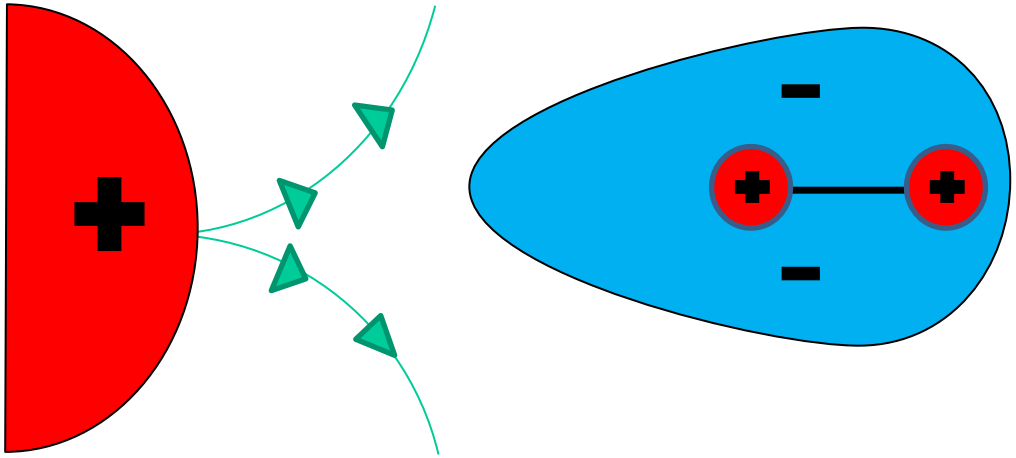




Interactions with “host” can induce a dipole moment

Polarizability Mechanism

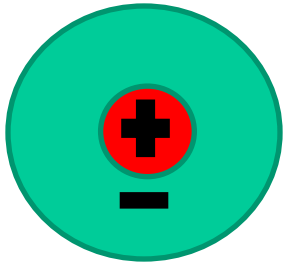




Vibrational Transitions Active
Ro-Vibrational Transitions not very active

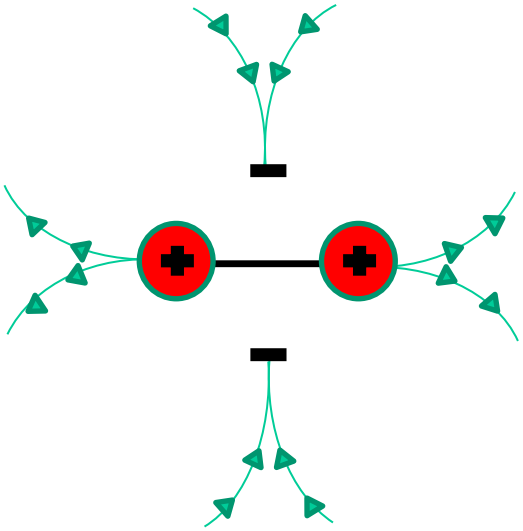
H_2 polarizability is effectively isotropic

Quadrupole Mechanism



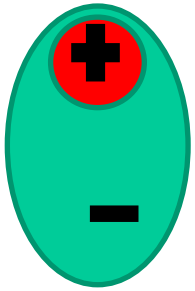
Unpolarized Atom

Quadrupole Mechanism



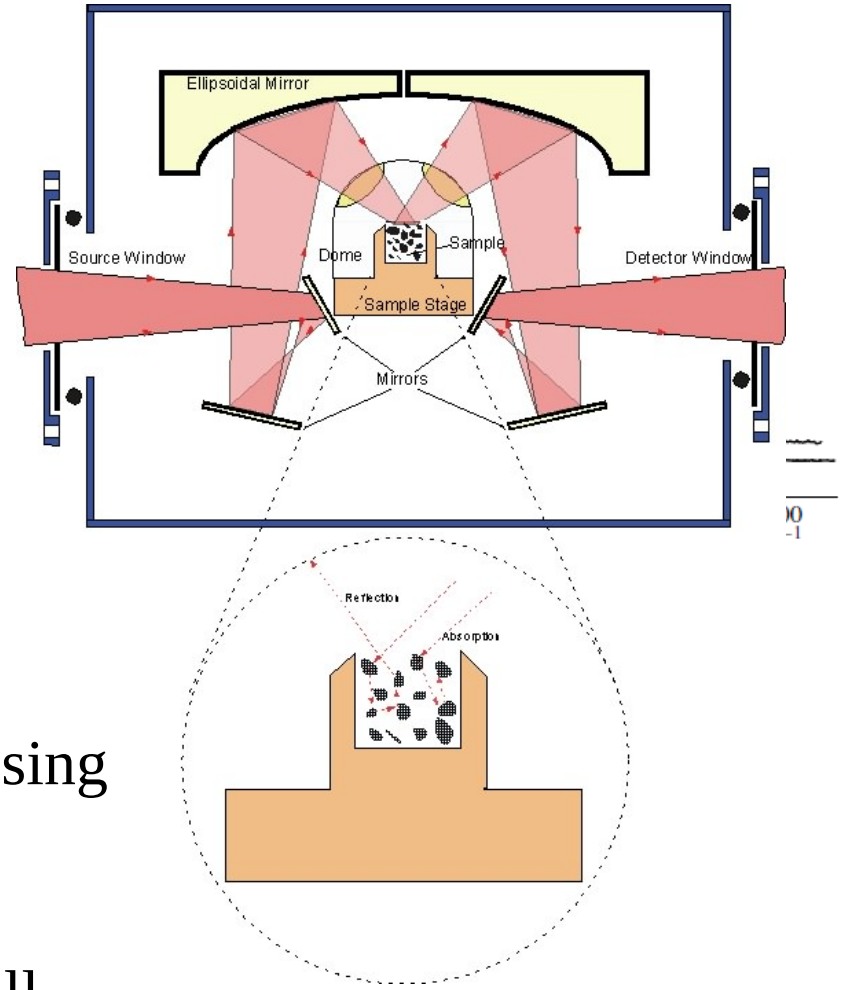
Hydrogen Molecule

Both Vibrations and Ro-vibrations lead to a changing dipole moment



Hydrogen Polarizes Atom

Diffuse Reflectance Infrared Spectroscopy



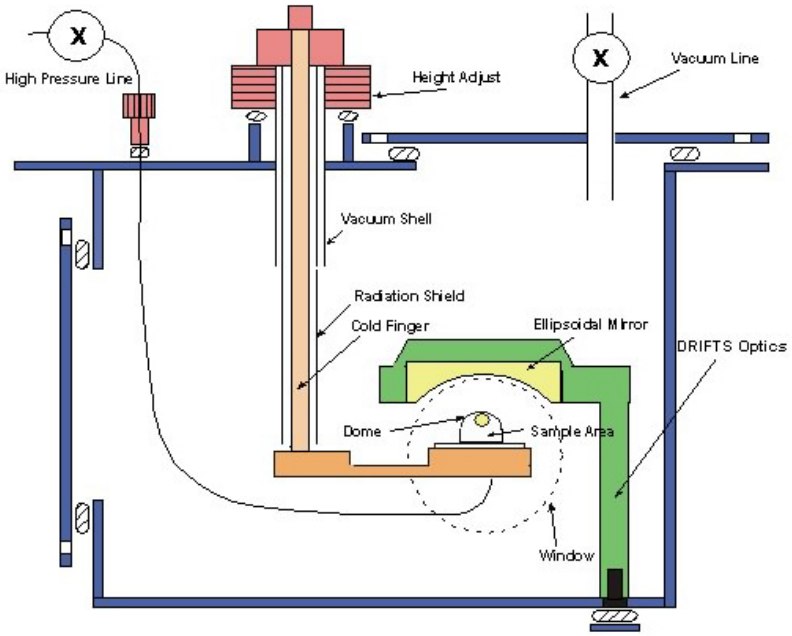
1) Long effective optical path length

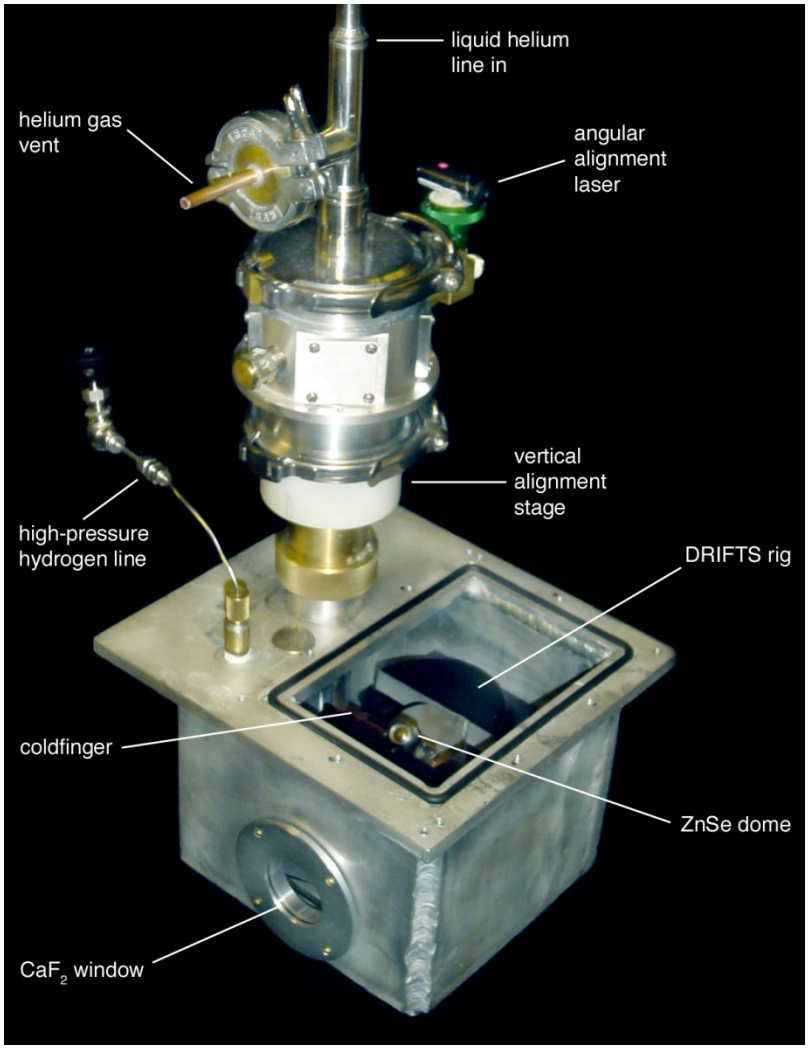
2) Powder sample require no processing

3) Typically use 10 mg of powder

4) Sample chamber can be quite small

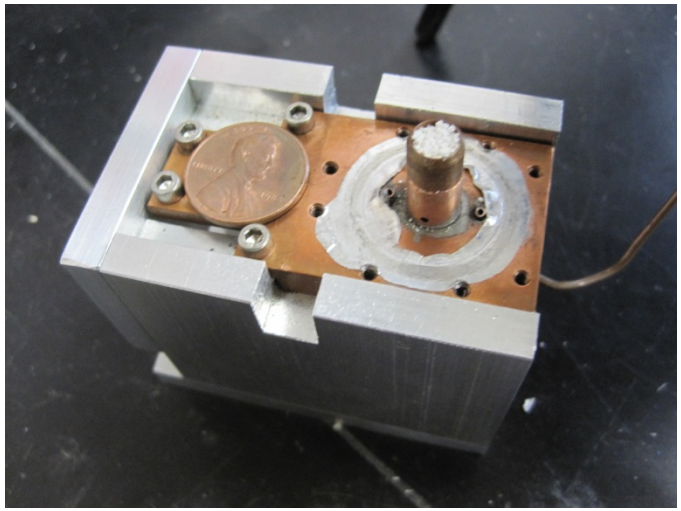
Diffuse Reflectance Spectroscopy: Cryostat Assembly

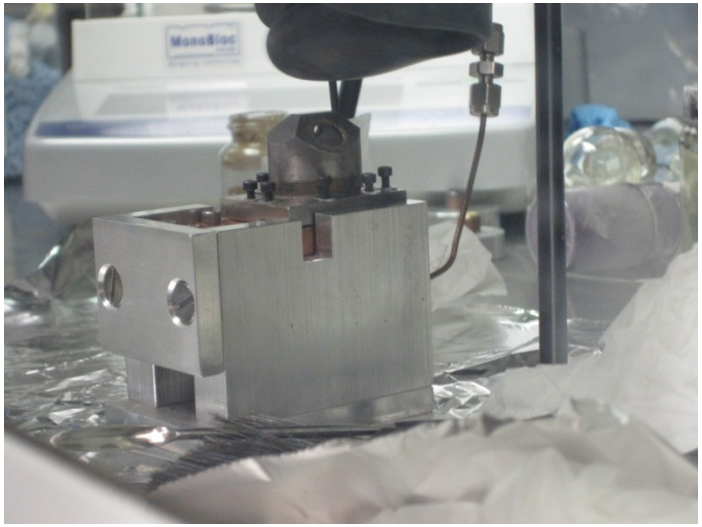


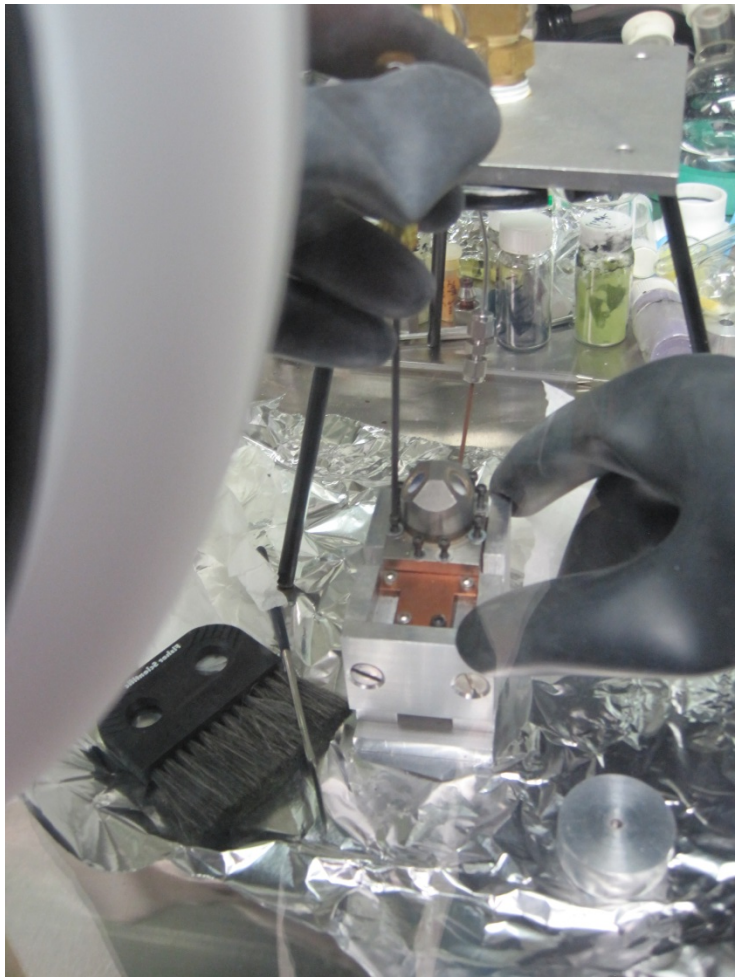


Rev. Sci. Instr. **77**, 093110 (2006)

Samples are mounted in a glove-box







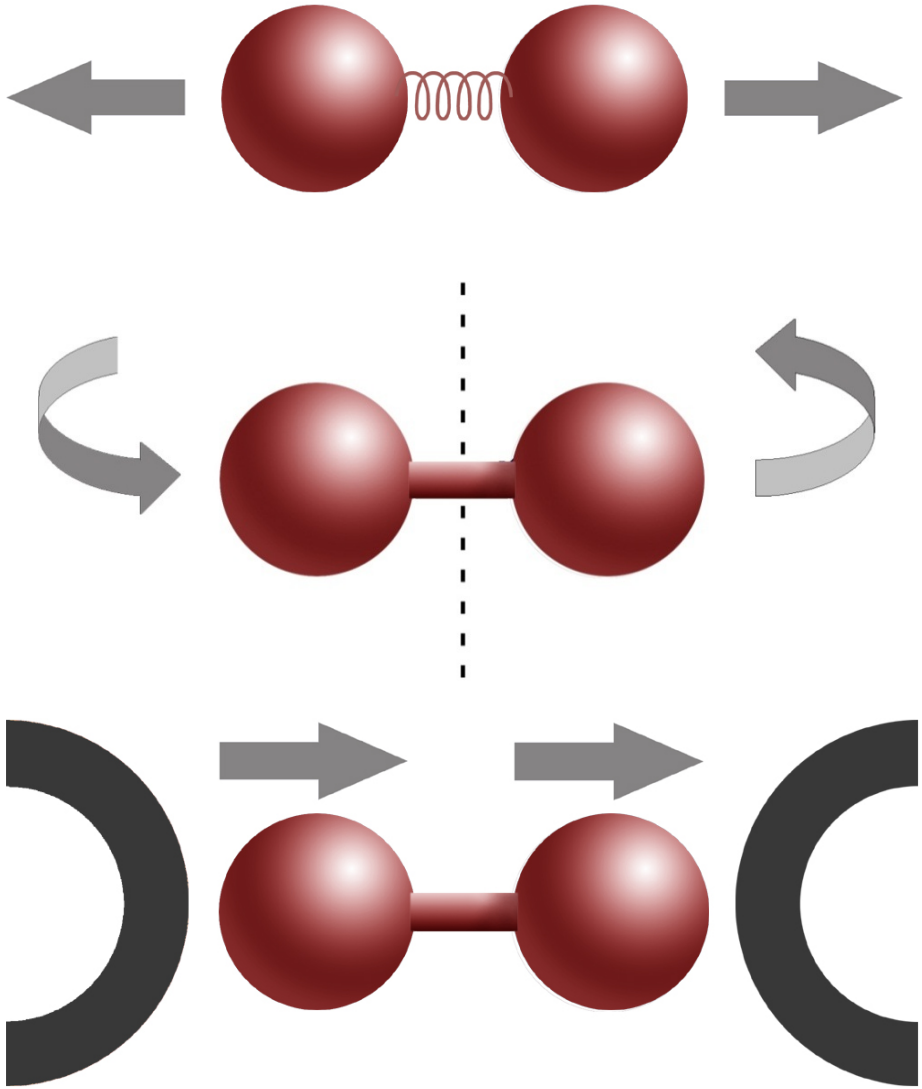
BOMEM
da3
VARIAN

Quantum Dynamics of Adsorbed H_2

- Vibration
  $E_v = (v + 1/2)\, \nu_0$
  ν_0 = 4161 cm^{-1} for free H_2

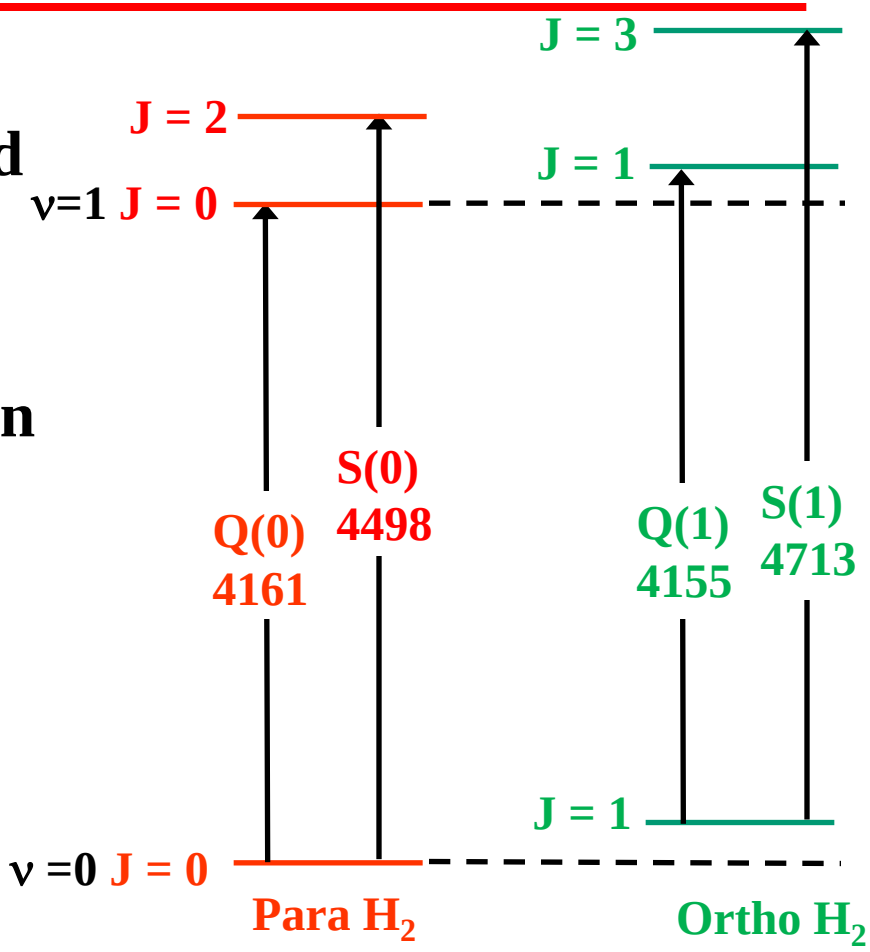
- Rotation
  $E_J = J(J+1)B_0$
  B_0 = 59 cm^{-1} for free H_2

- Translation
  Center-of-mass
  On the order of 100 cm^{-1}



Spectroscopic notation of possible transitions

- **Pure Vibrational modes called Q transitions $\Delta J = 0$**
- **Q(0) and Q(1) are very close in energy ~ 6 cm^{-1} apart**
- **Rotational Sidebands called S Transitions $\Delta J = 2$**

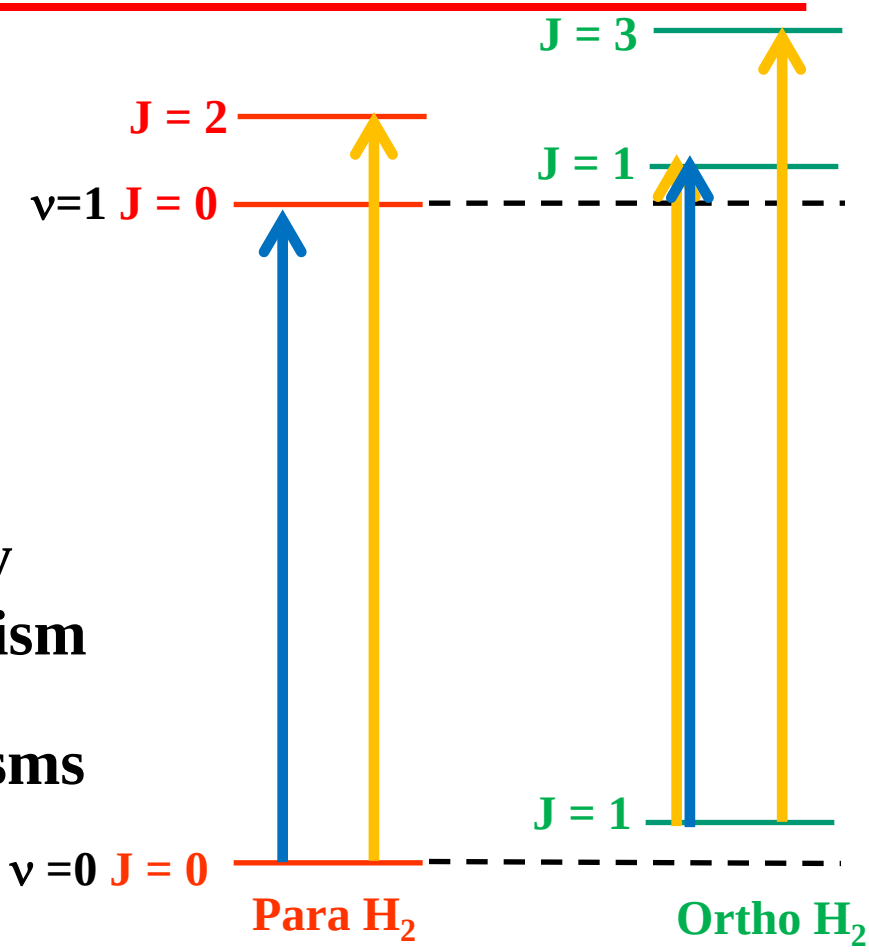


Mechanisms

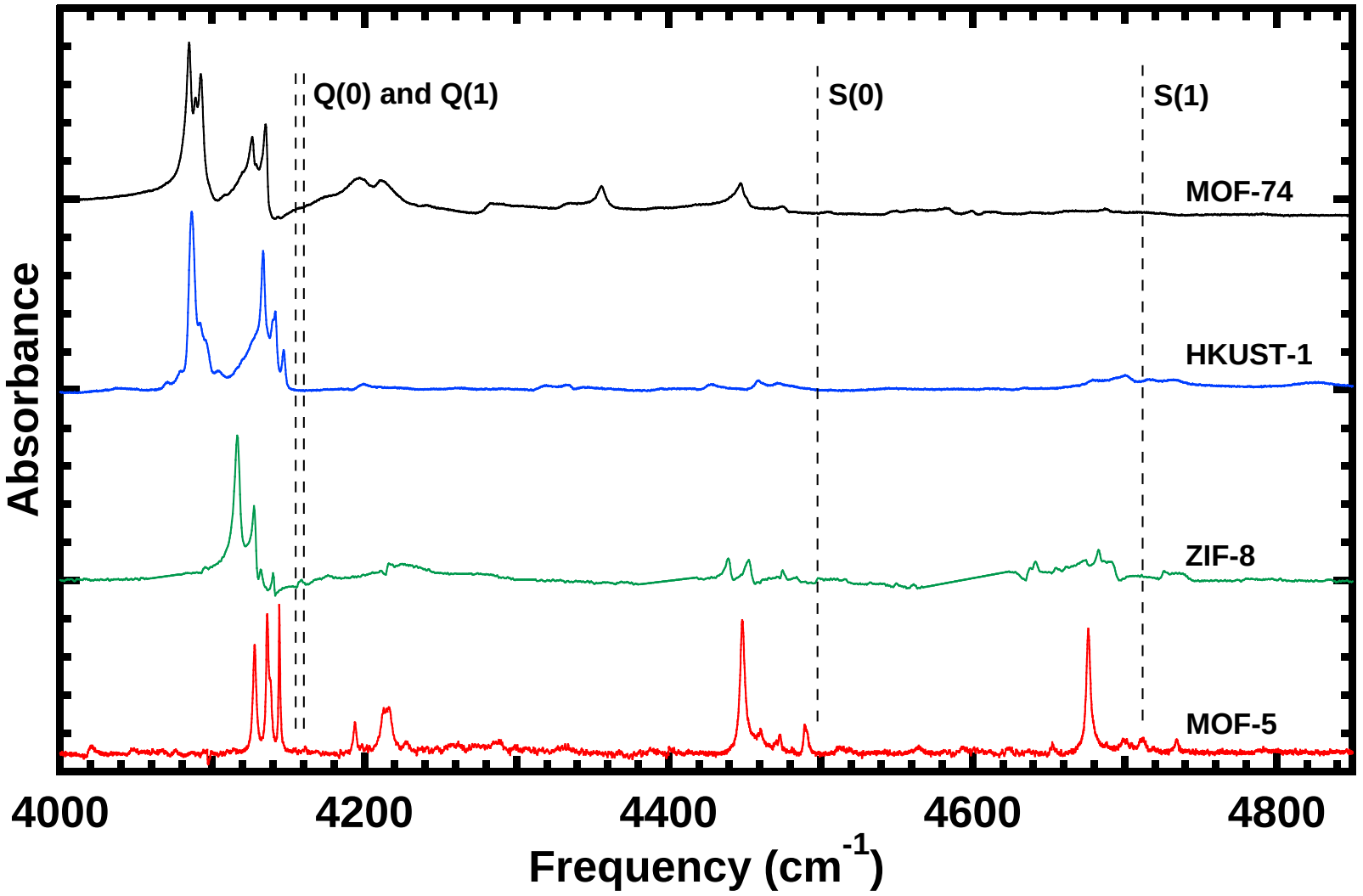
Because J = 0 is spherical
No Quadrupole moment
Q(0) arises solely from polarization mechanism

Because polarization is mostly isotropic S bands dominated by quadrupole induction mechanism

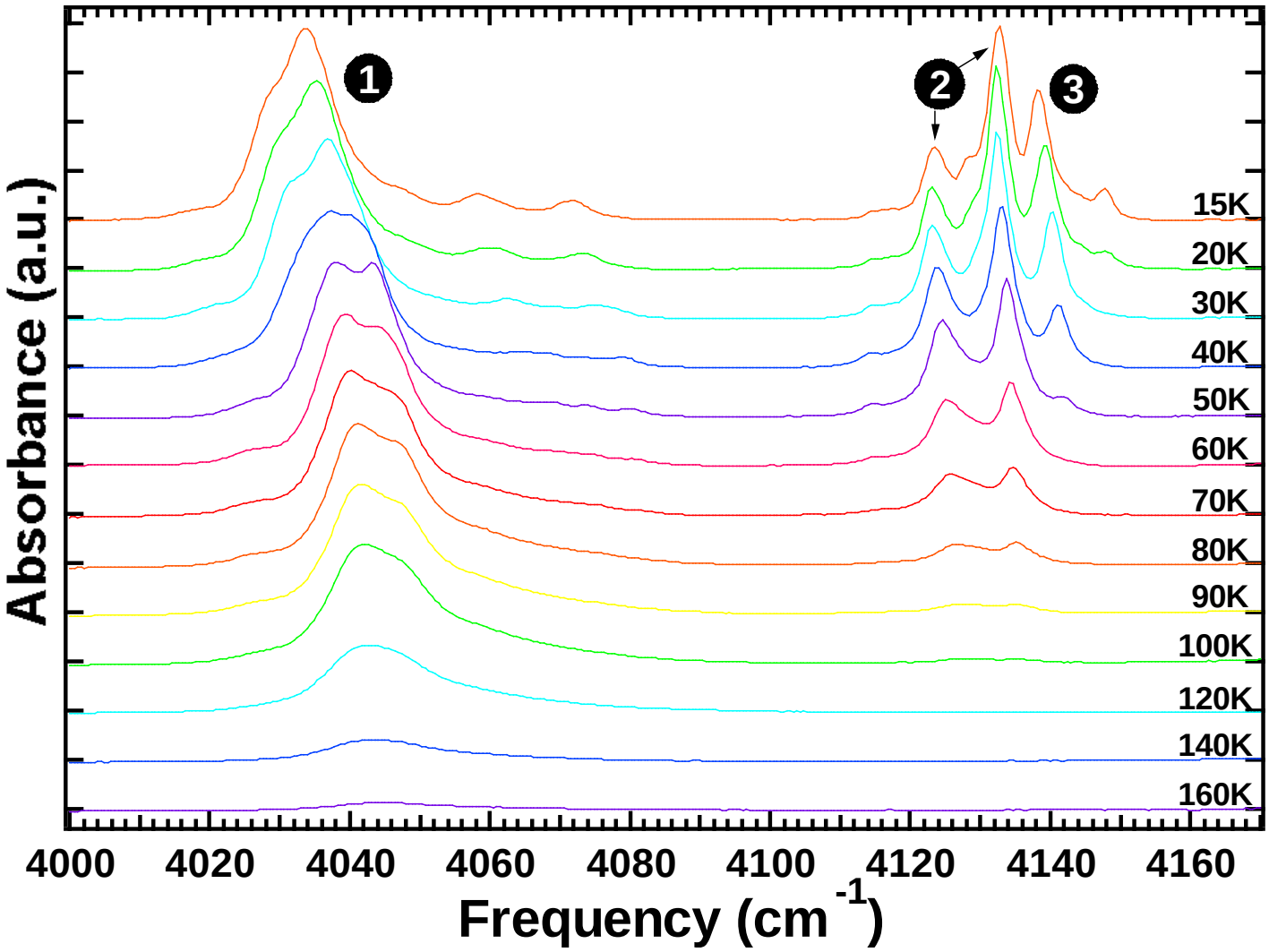
Q(1) arises from both mechanisms



Typical Spectra for H_2 in MOFs at 30 K

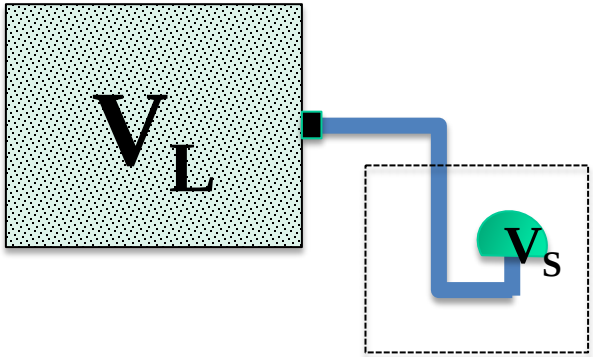


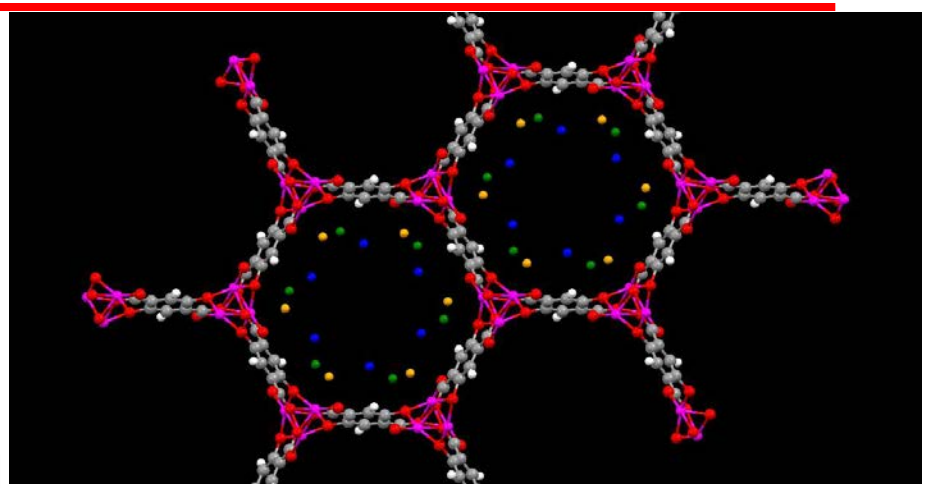
Temperature Dependent Spectra Co-MOF-74

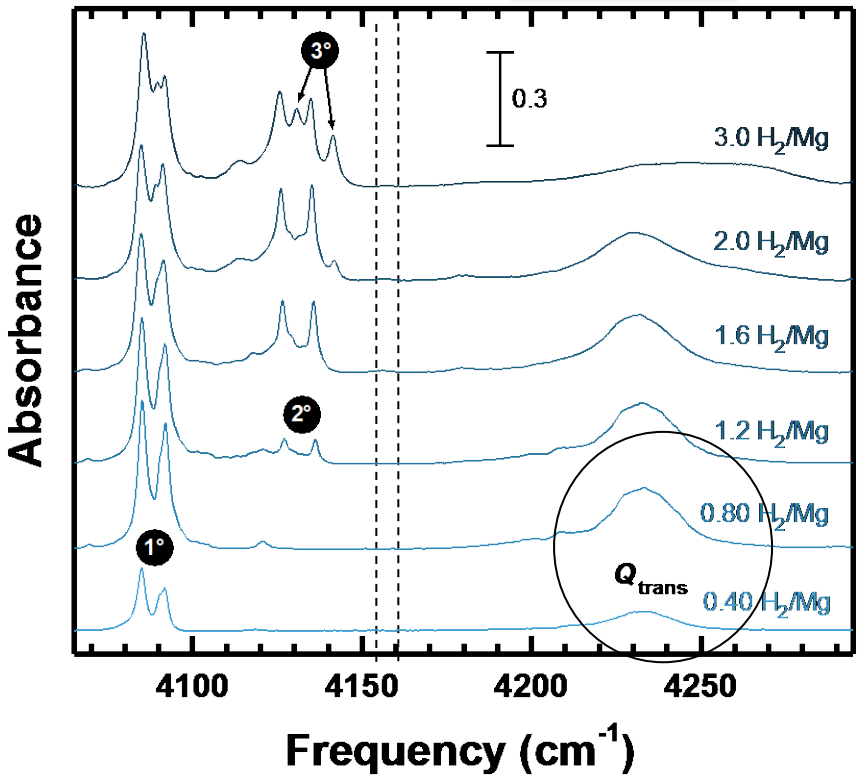


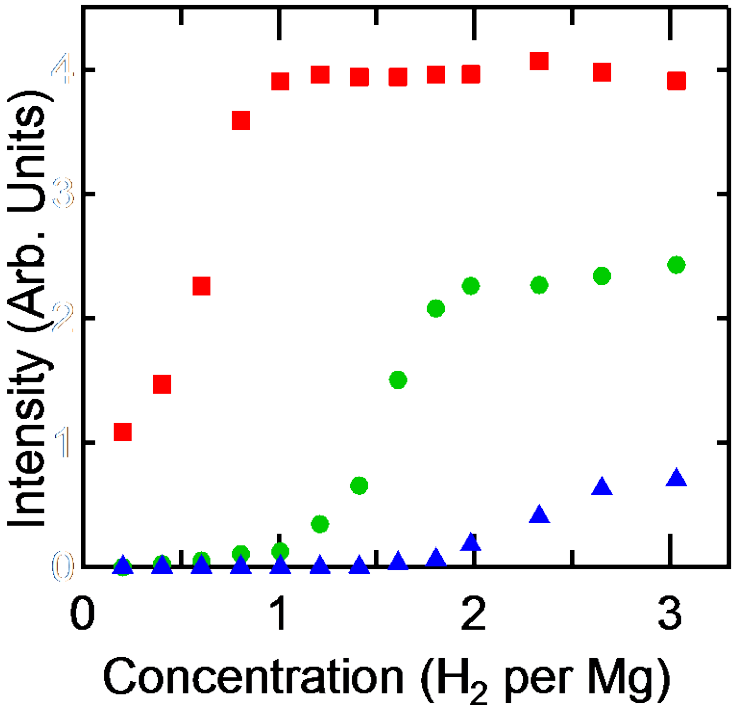
Spectra as a function of concentration (Mg-MOF-74 at 35 K)

J. Am. Chem. Soc. 2011,133, 20310









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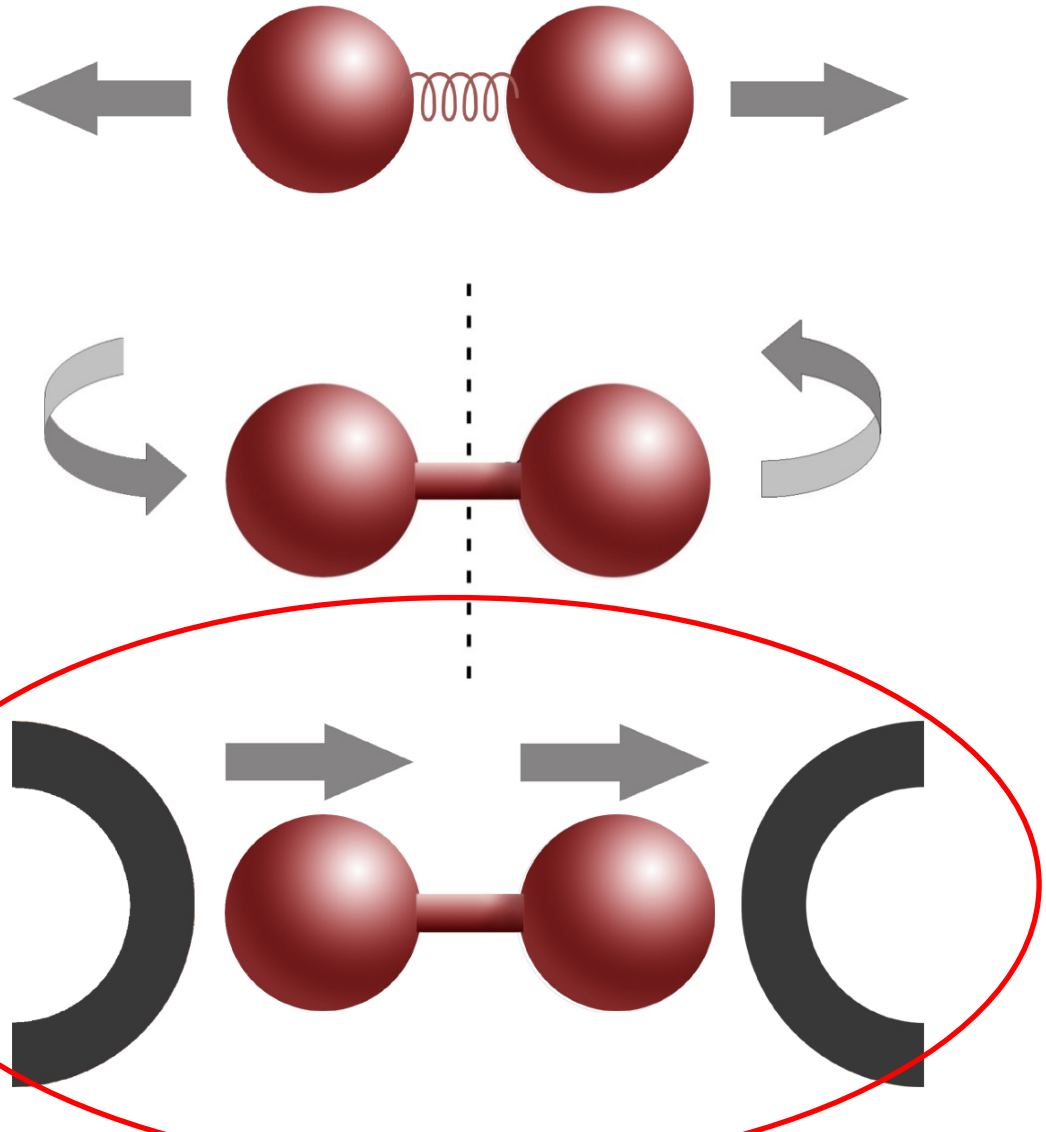
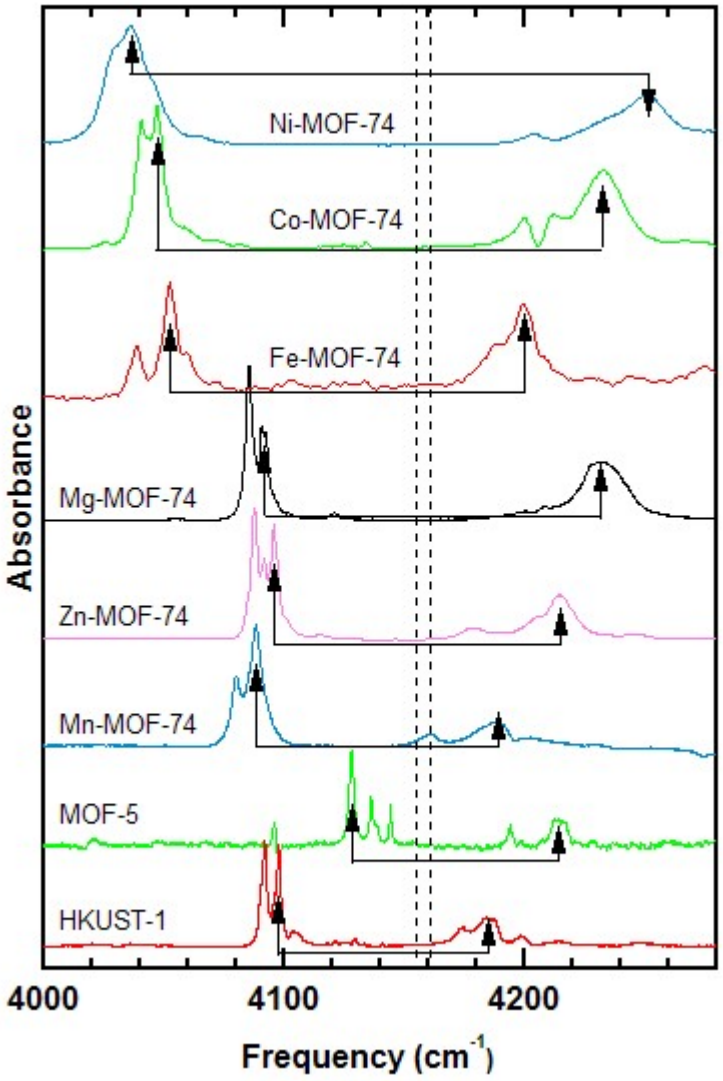
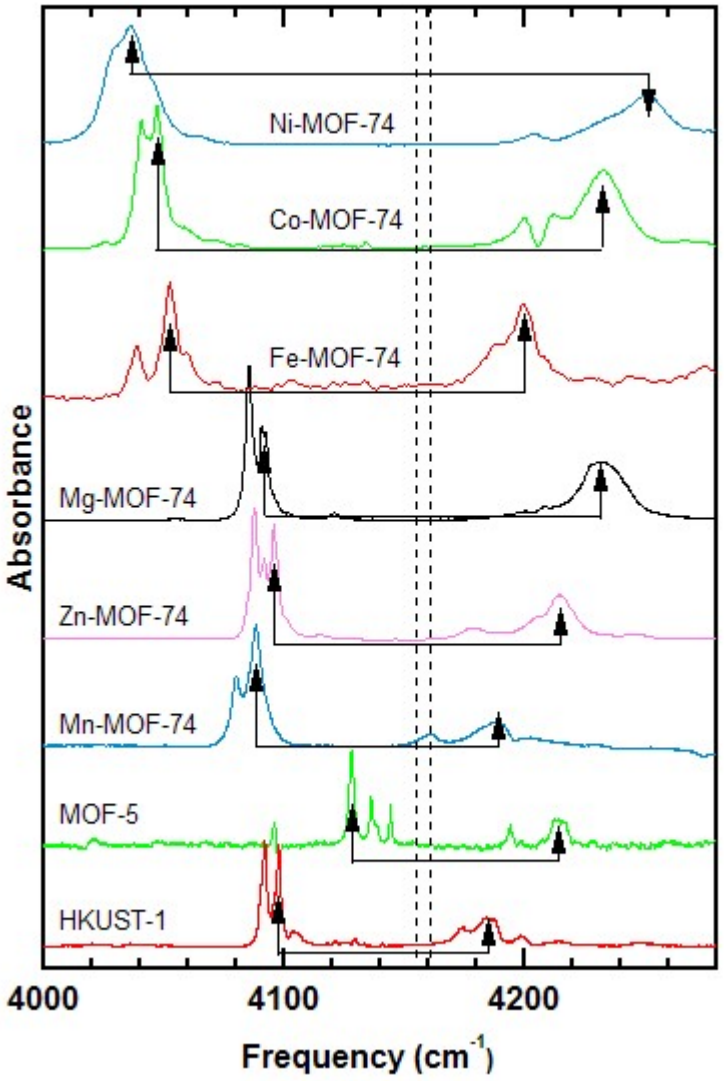
  On the order of 150 cm^{-1}



Translational mode energy (quantum sieving?)



Back of the Envelope Calculation



$ZPE = 3/2\ \hbar\omega$

$\omega \approx 200\ cm^{-1}$

$\Rightarrow ZPE = 300\ cm^{-1} = 420K$

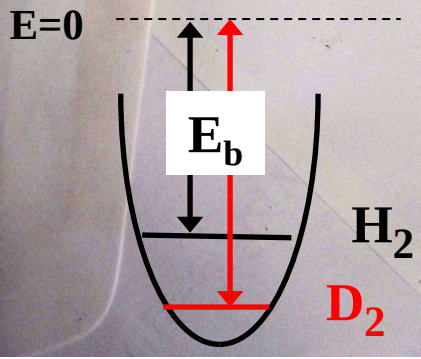
$\omega_{D_2} = 1/\sqrt{2}\ \omega_{H_2}$

$\Rightarrow ZPE_{D_2} \approx 300K$

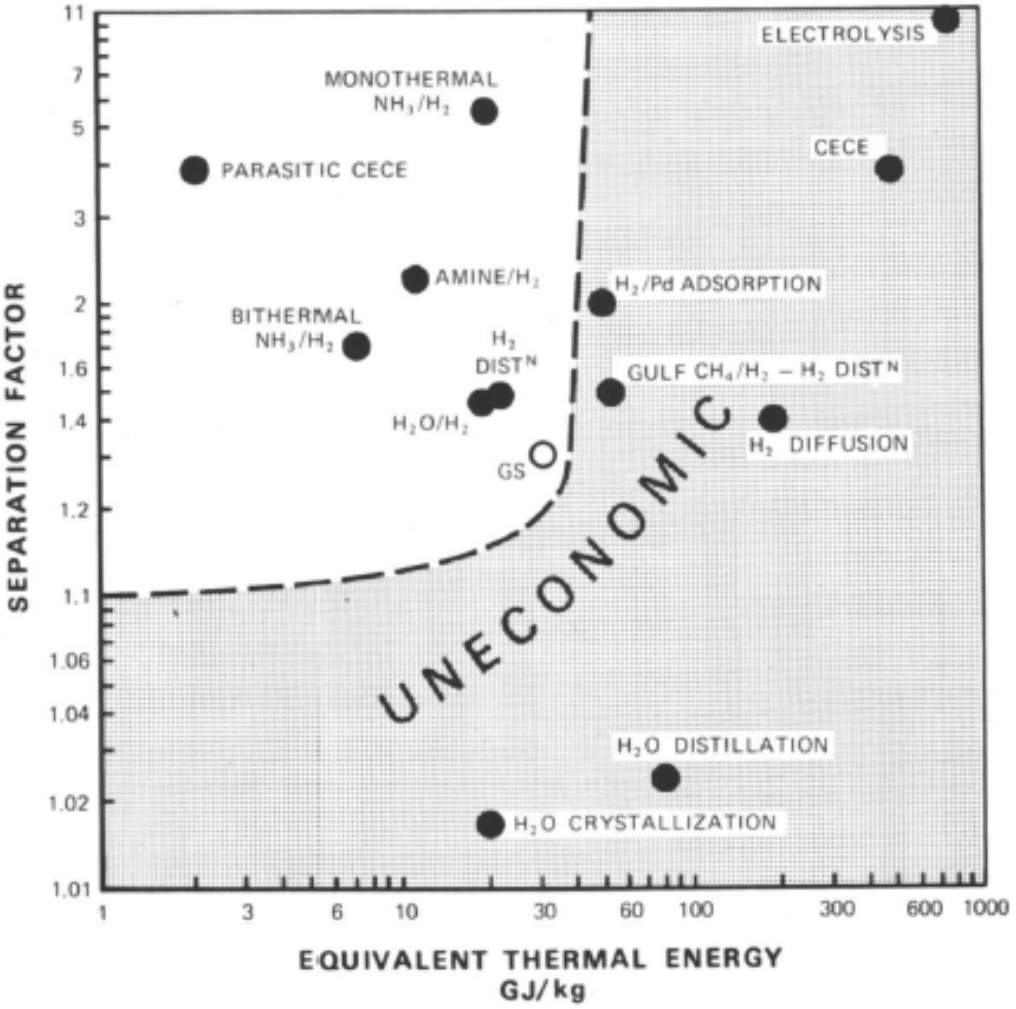
$\Delta ZPE = 120K$

$e^{\Delta E/KT}$ at 77 K

$e^{120/77} = 4.75$

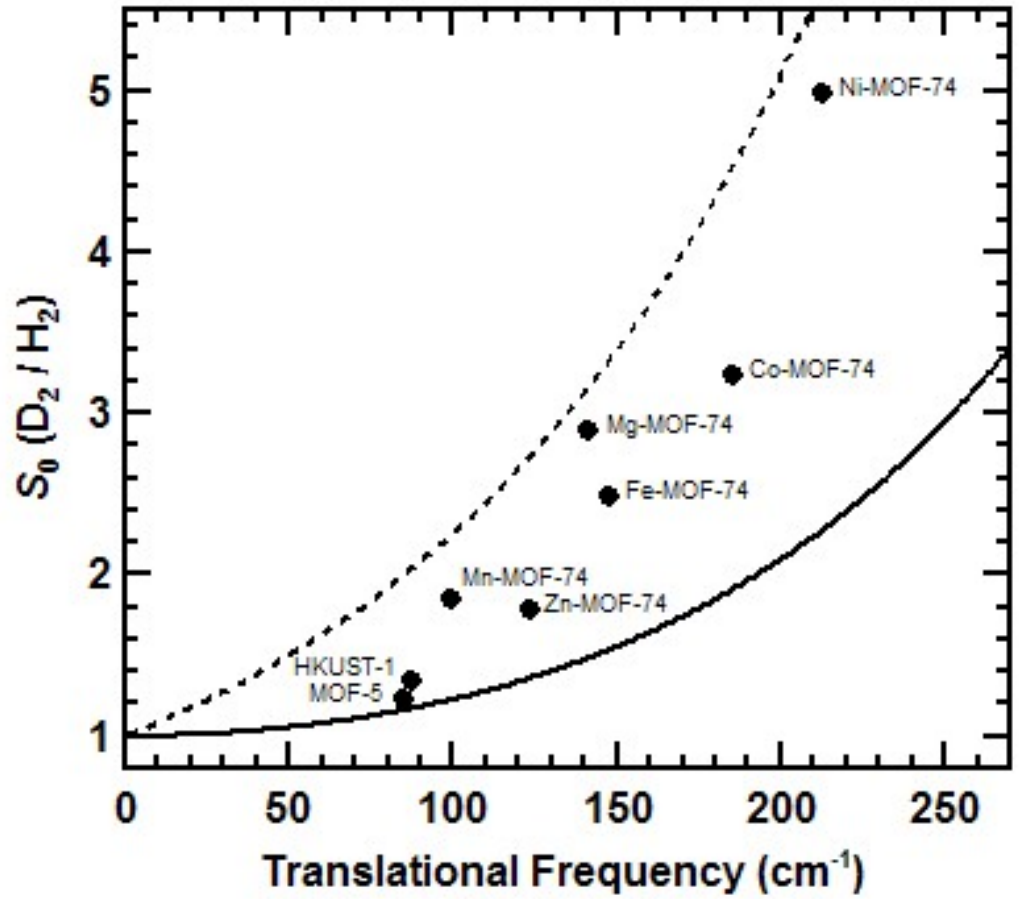


Standard Separation Techniques



Rae, H. K. *Selecting Heavy Water Processes*; ACS Symposium Series 68, American Chemical Society: Washington, DC1978.

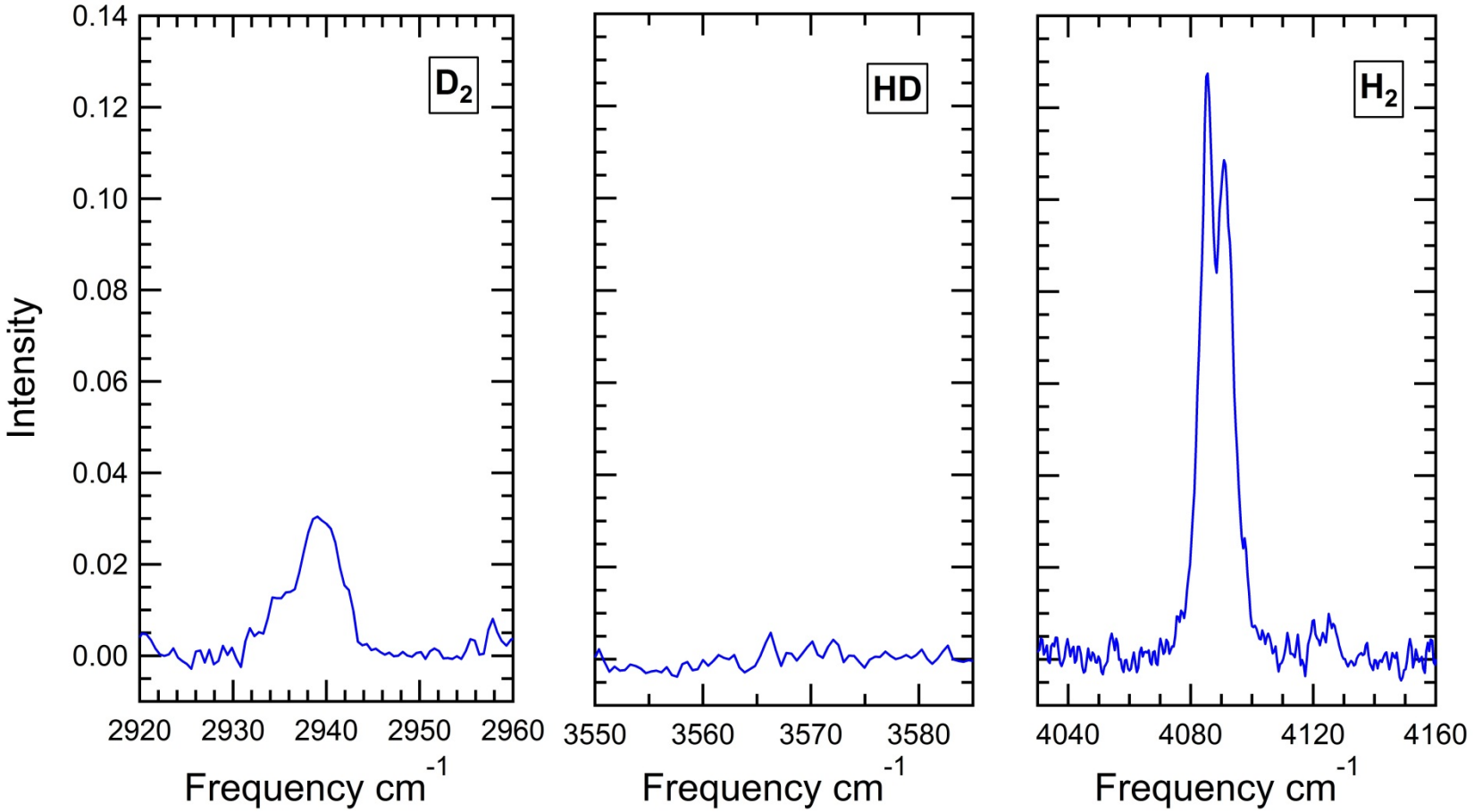
Selectivity vs Translational Frequency



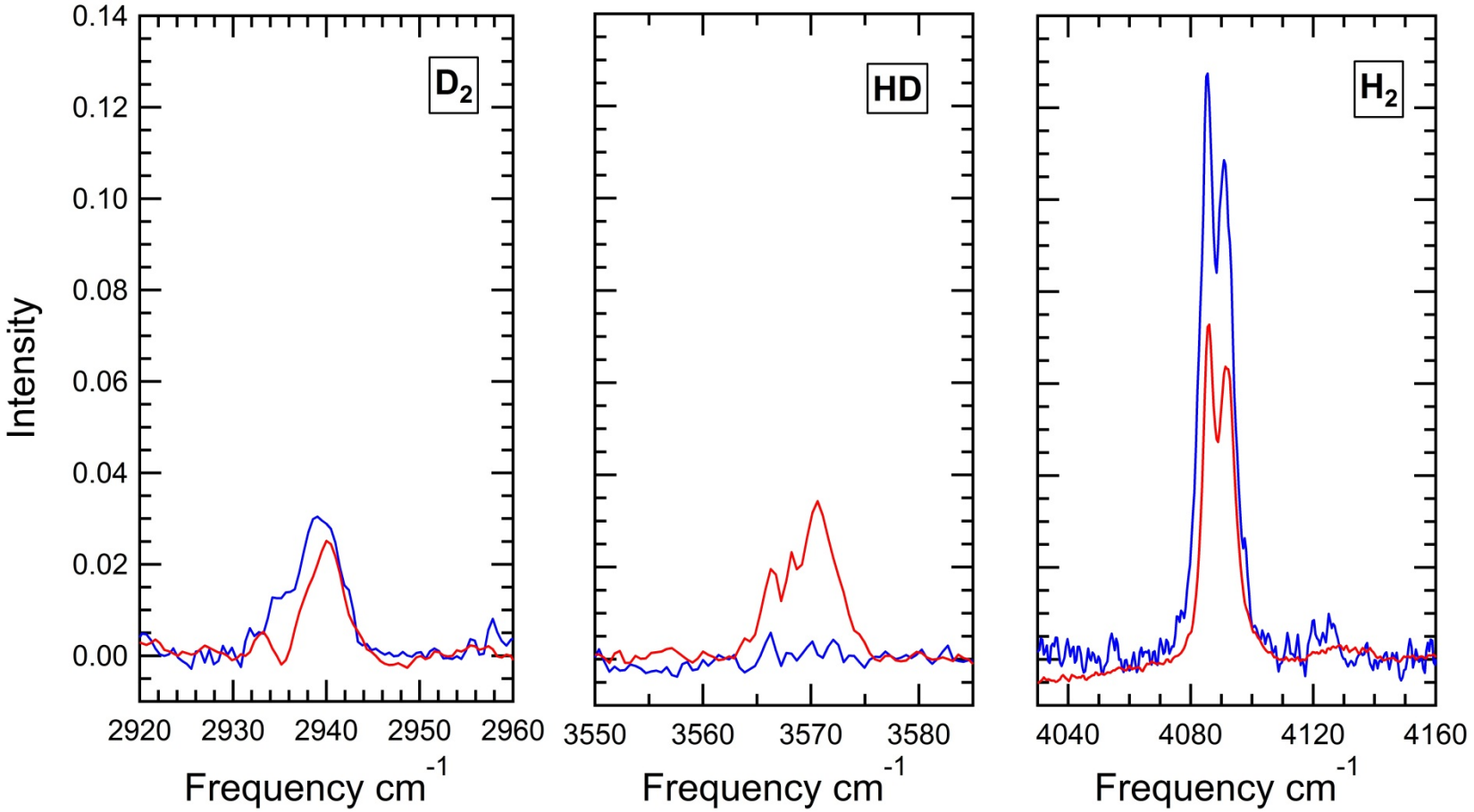
J. Am. Chem. Soc.
2013, 135, 9458−9464

Dashed line shows simple back of the envelope
Solid line shows full (harmonic) thermodynamic calculation

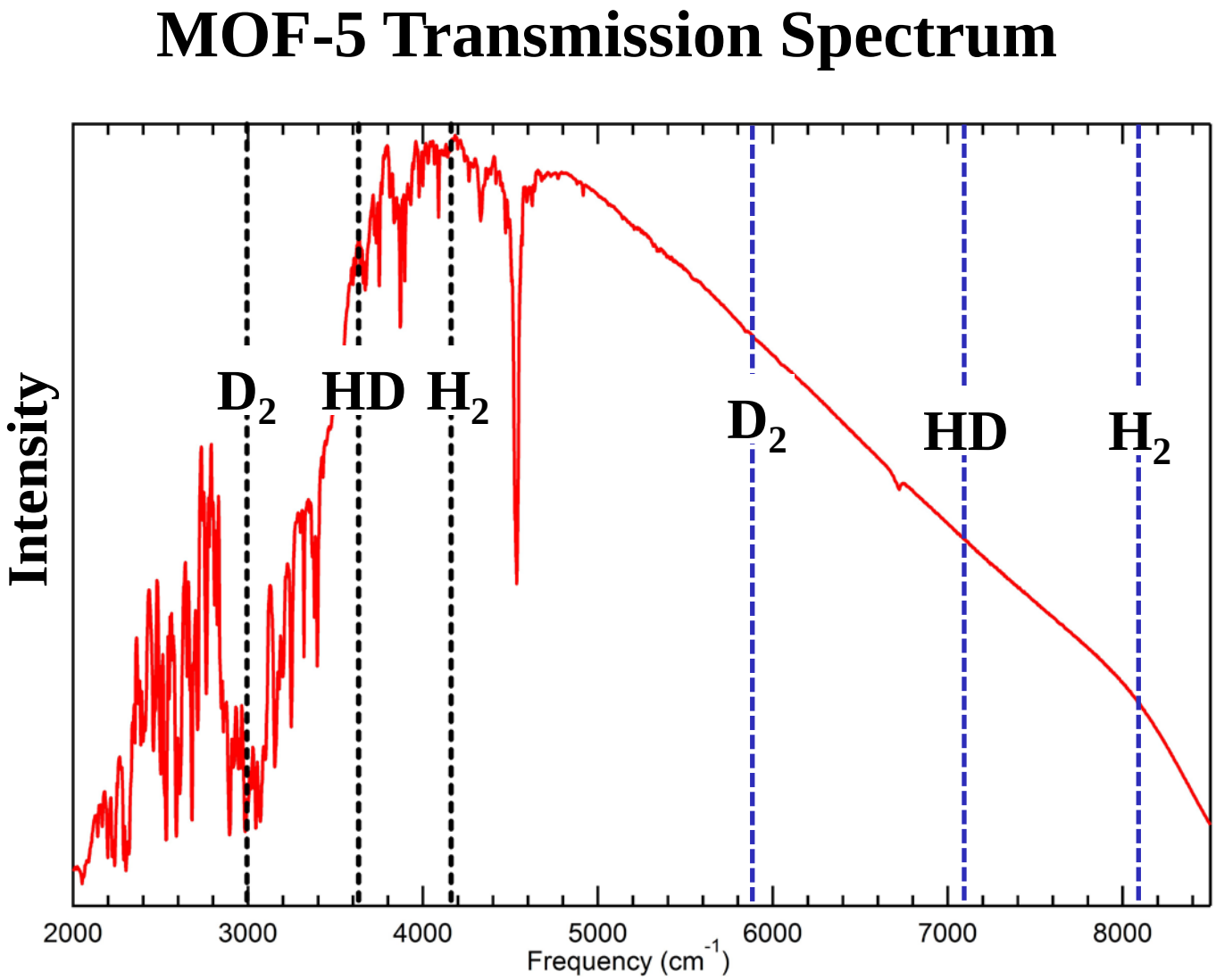
H_2 and D_2 Mixtures in Mg-MOF-74



H_2 and D_2 Mixtures (After sitting at room temperature)

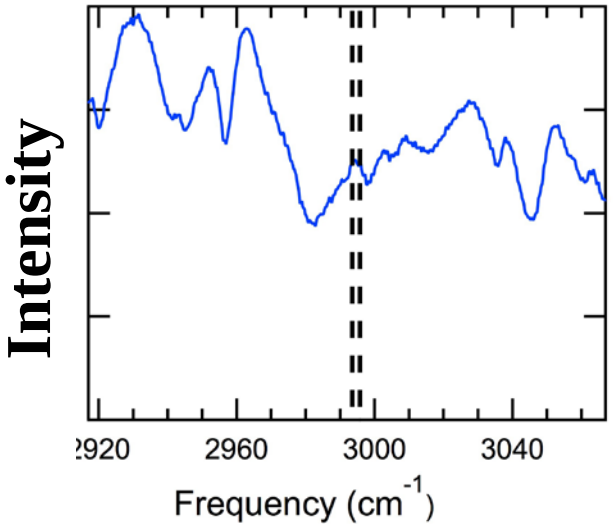


Will Overtone show D_2 more Clearly?

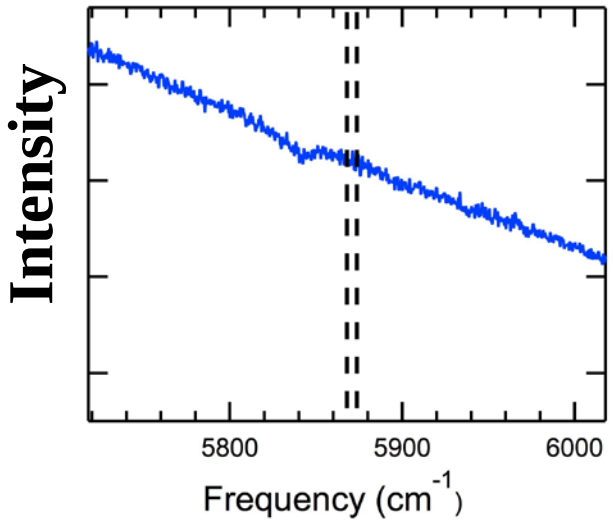


Deuterium in MOF-5

Pure MOF-5 —



Fundamental

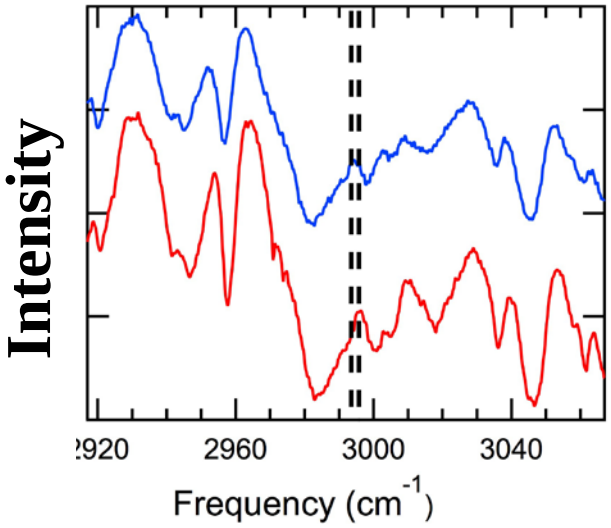


Overtone

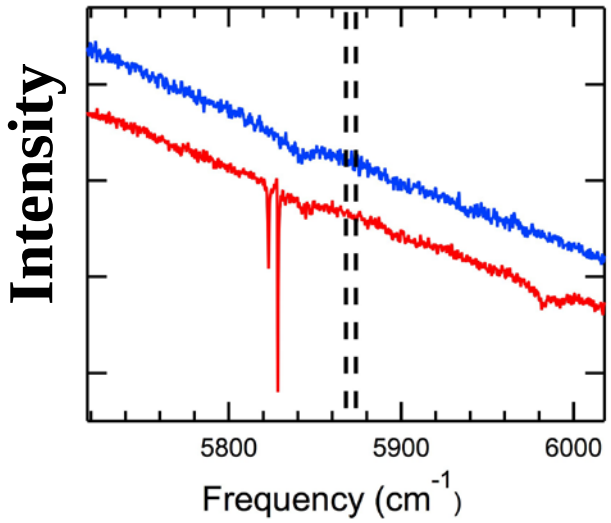
Deuterium in MOF-5

Pure MOF-5

MOF-5 with D_2



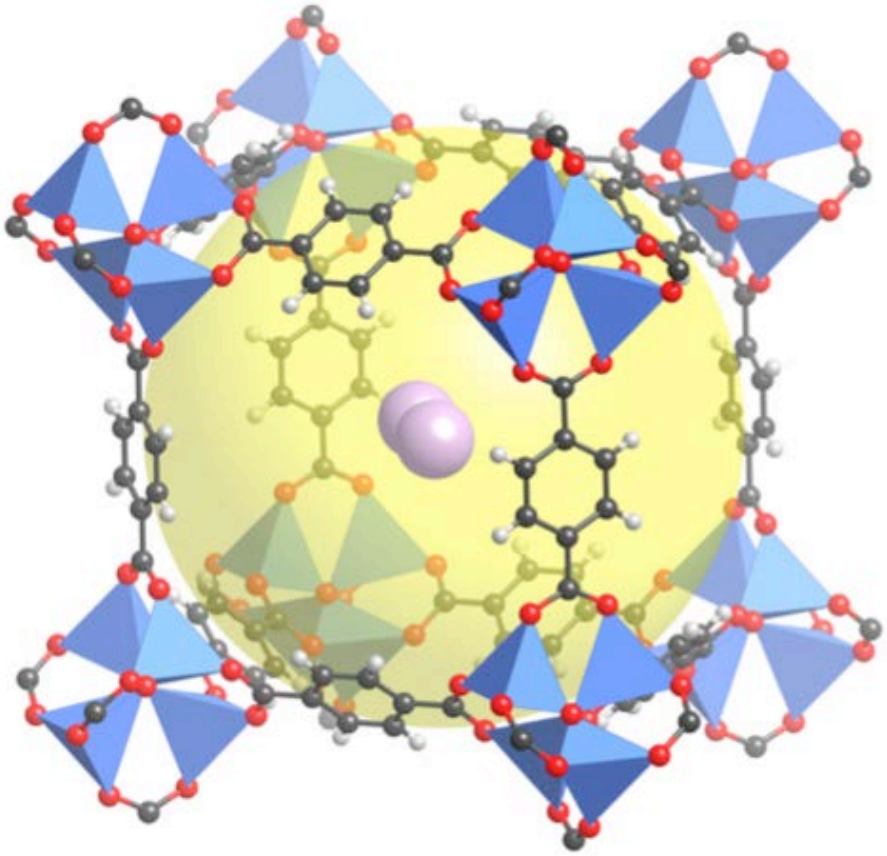
Fundamental



Overtone

MOF-5 ($Zn_4O(BDC)_3$

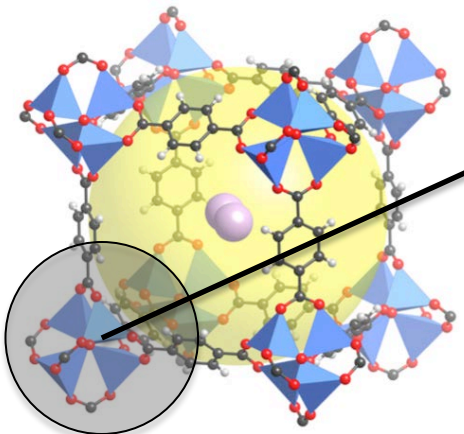
- Each collection of Zn_4O tetrahedra (blue) forms a metal binding site

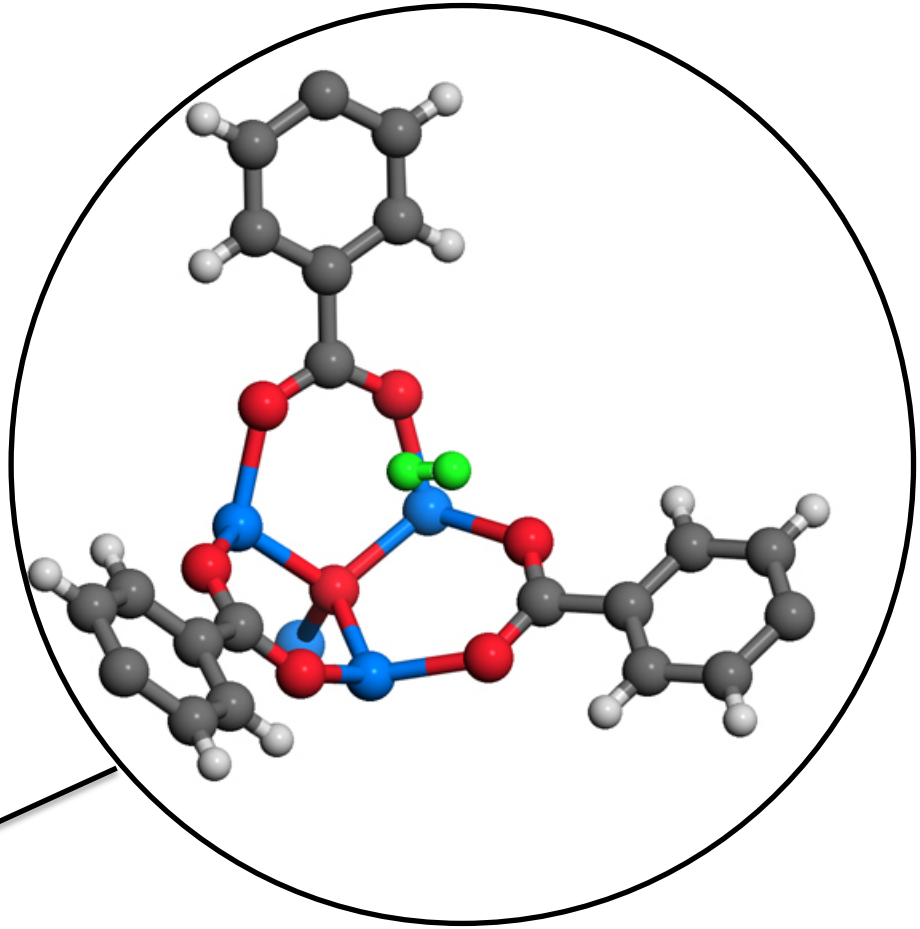


E. Spencer, J. Howard, G. McIntyre, J. L. C. Rowsell, and O. M. Yaghi, Chem. Commun. 3, 278 (2006).

MOF-5 ($Zn_4O(BDC)_3$)

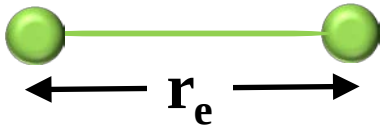
- Each collection of Zn_4O tetrahedra (blue) forms primary binding site
- Hydrogen binds preferentially to this "cup site"





Potential Energy and Frequency Shift

Isolated H_2



$$\rho = \frac{r - r_e}{r_e}$$

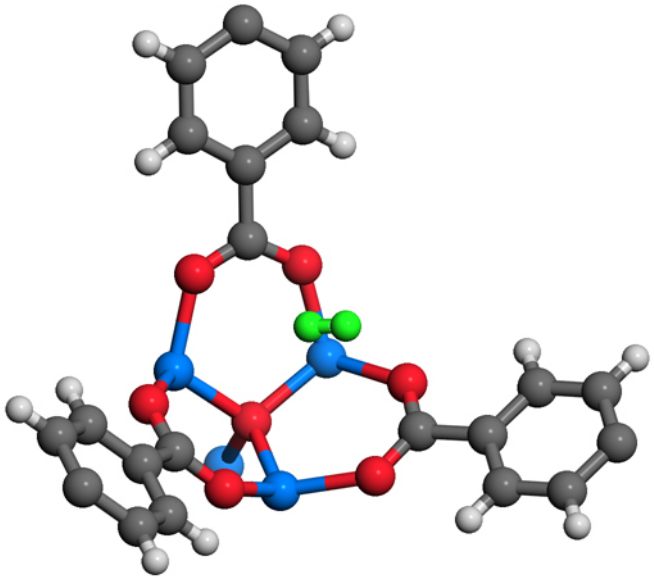
$$U_0(\rho) = \frac{hc\omega_e{}^2}{4B_e}\left(\rho^2 + a\,\rho^3 + b\,\rho^4 + \cdots\right)$$

Adsorbed H_2

$$U_{Adsorbate} = U_0 + U_{MOF}$$

$$U_{MOF} = U_{\rho=0} + U'\rho + U"\rho^2 + \cdots$$

$$\Delta\omega_{0\to n} \propto n\frac{B_e}{\omega_e}\left(U" - 3a\,U'\right) + O\left(\frac{B_e}{\omega_e}\right)^2$$



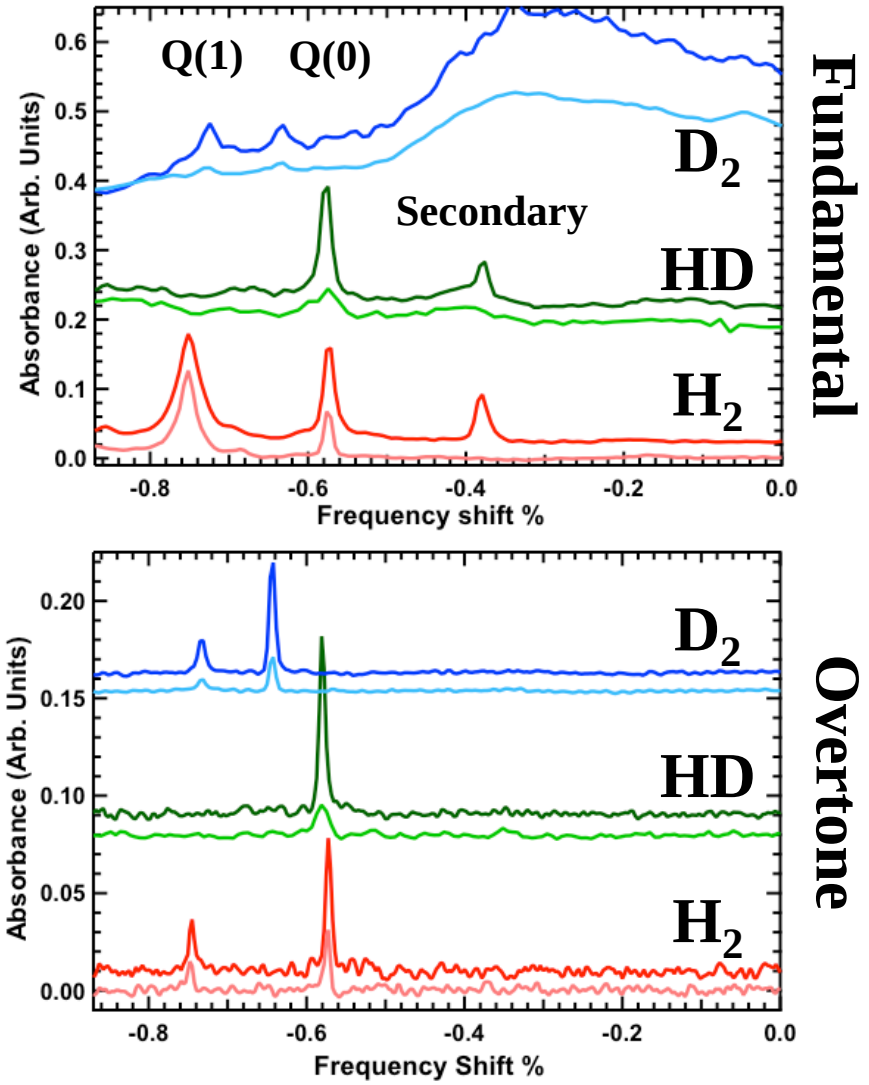
Frequency Shift Fundamental versus Overtone

$$\frac{\Delta\omega_{0\to n}}{\omega_e} \propto n\frac{B_e}{{\omega_e}^2}(U'' - 3a\,U')$$

$$\Delta\omega_{0\to 2} = 2\,\Delta\omega_{0\to 1}$$

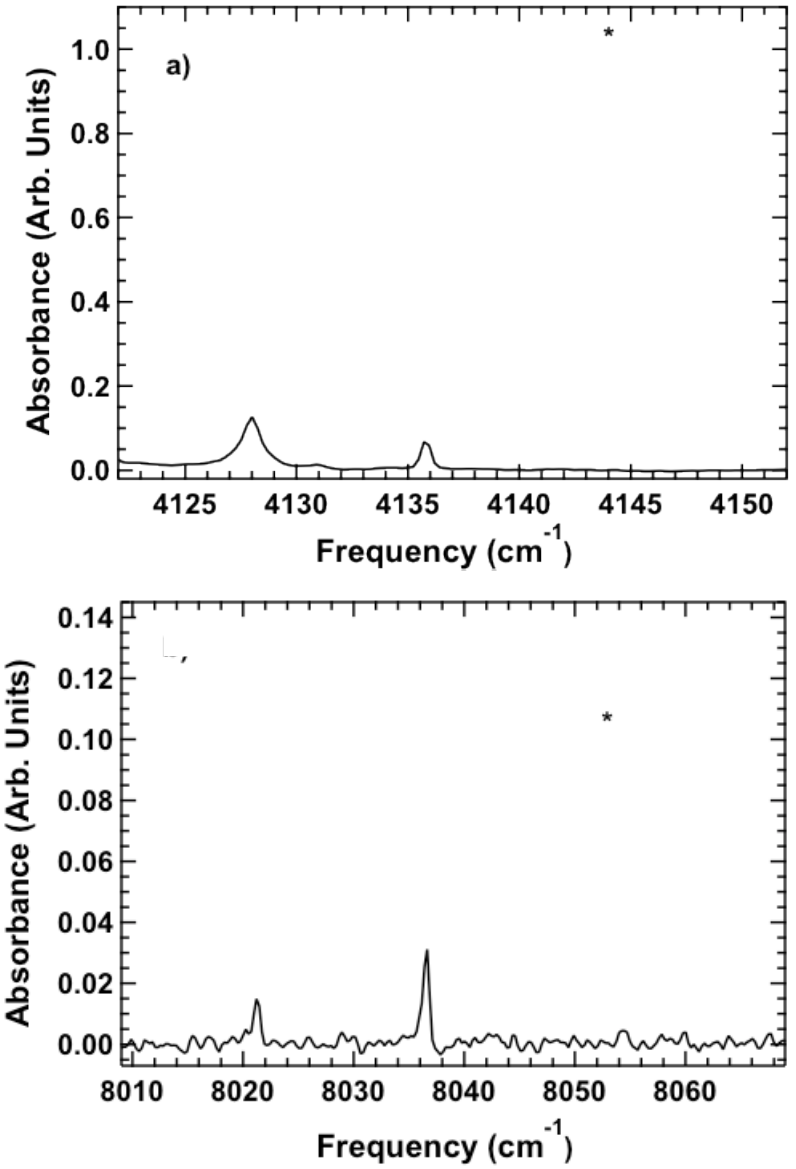
$$\frac{B_e}{{\omega_e}^2} \approx \text{constant for diatomic}$$

Fractional frequency shift for all isotopologues and overtones should be the same.



Hydrogen Concentration

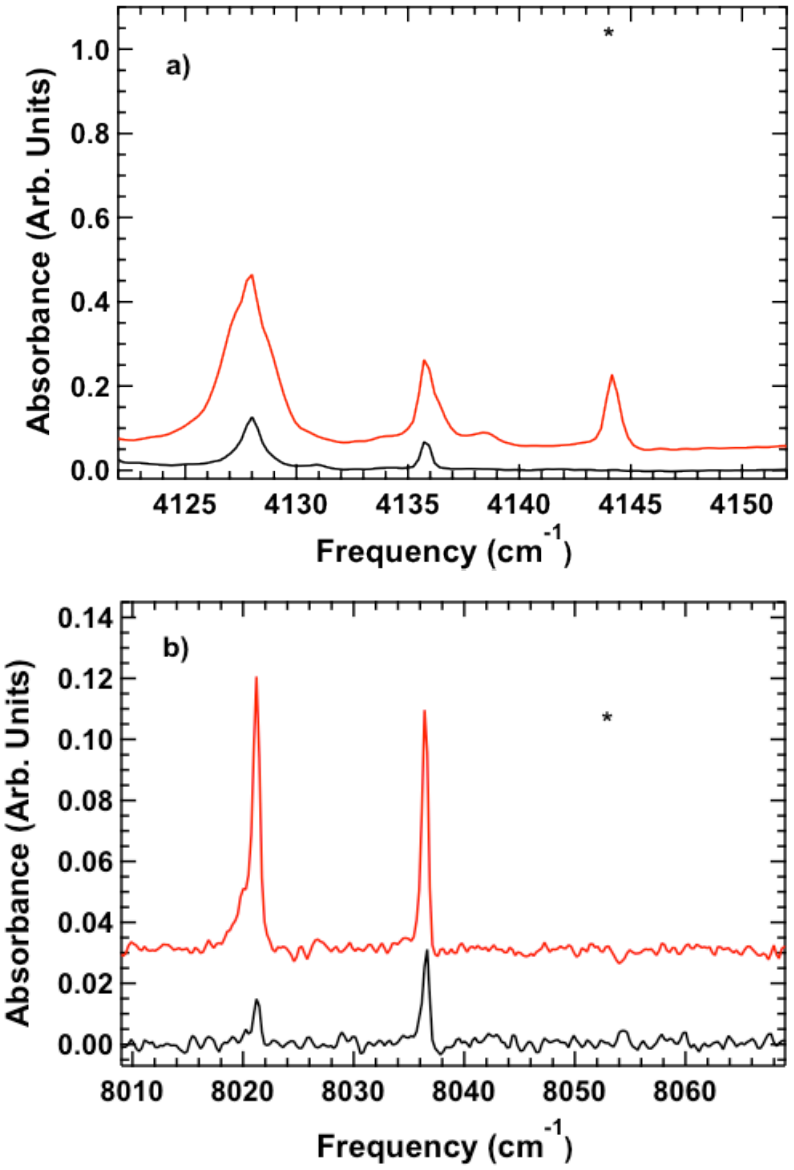
0.2 H_2/metal



Hydrogen Concentration

0.2 H_2/metal

1 H_2/metal



Hydrogen Concentration

0.2 H_2/metal

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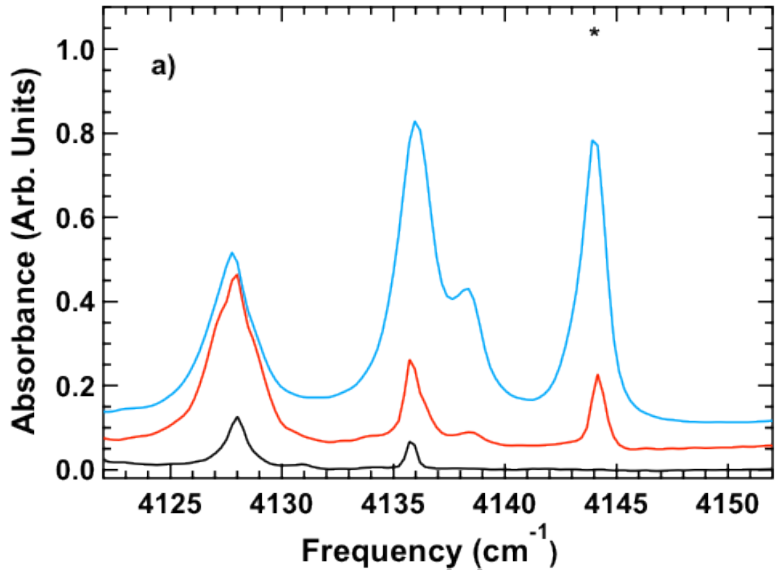
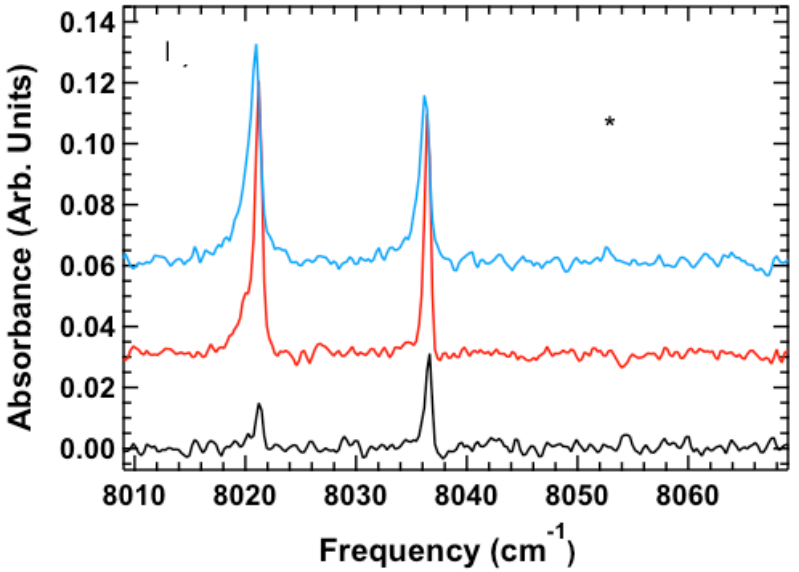
2 H_2/metal





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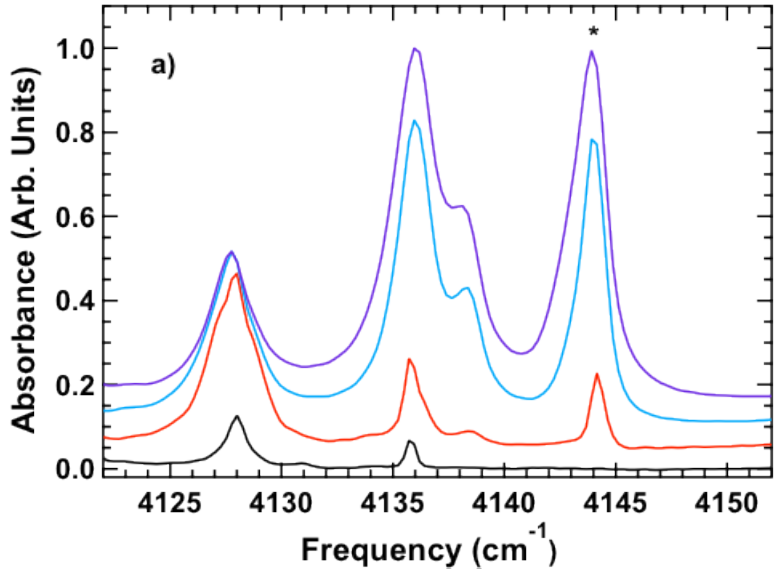
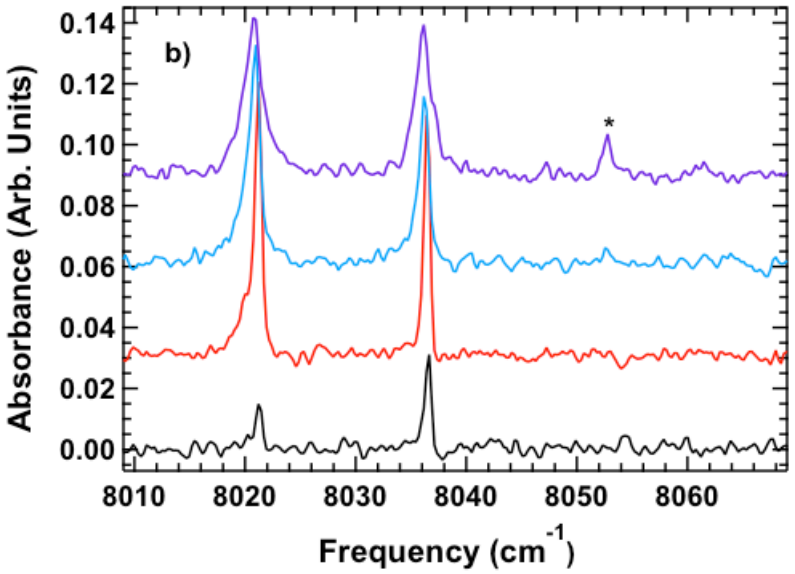
2 H_2/metal
3 H_2/metal

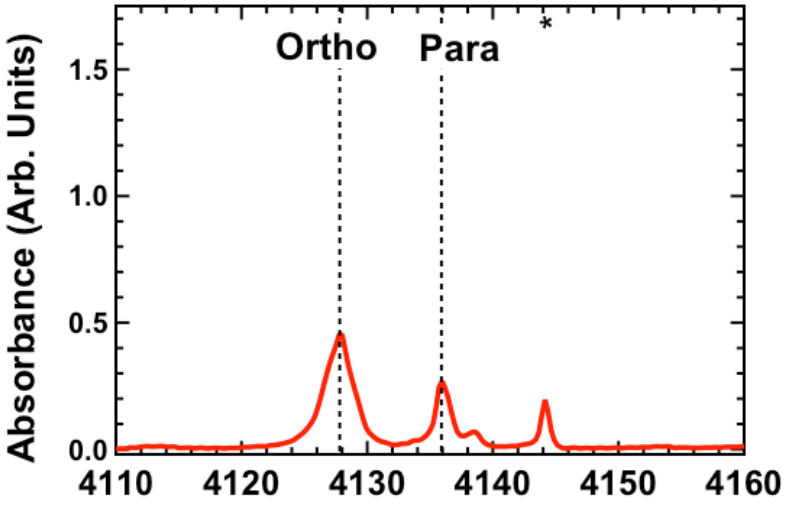




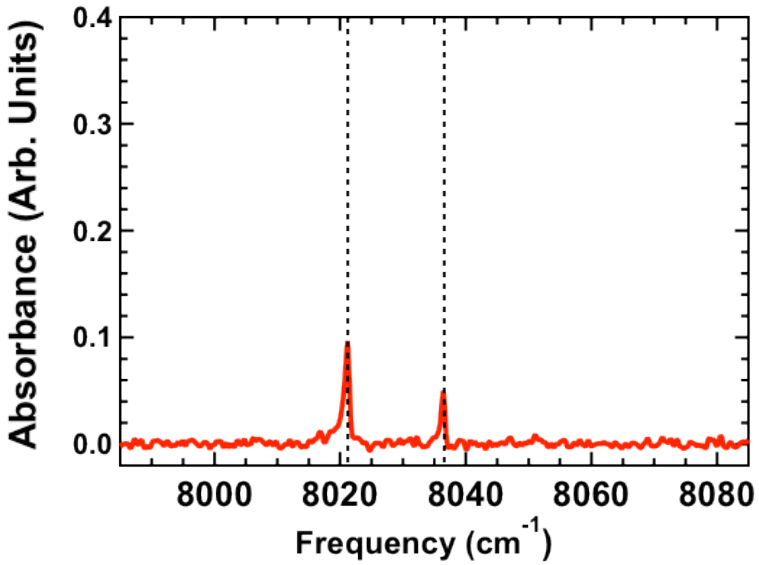
Overtone of hydrogen at Primary site are dramatically enhanced relative to other sites

Ortho to Para Conversion

t = 7 min



Fundamental

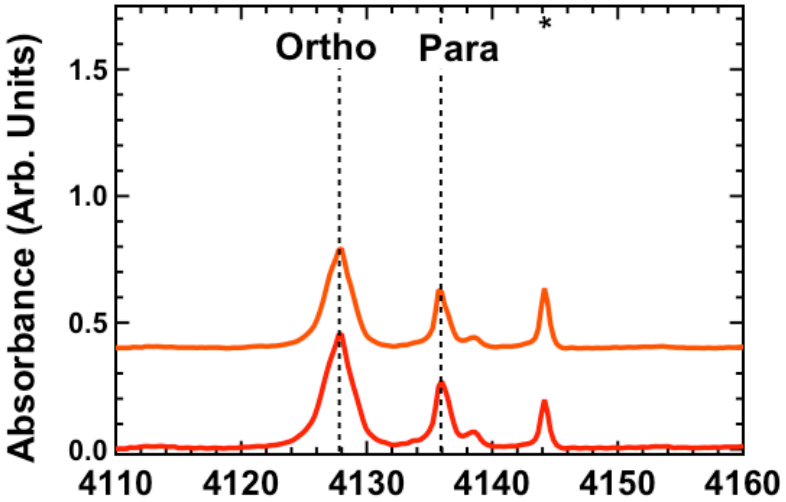


Overtone

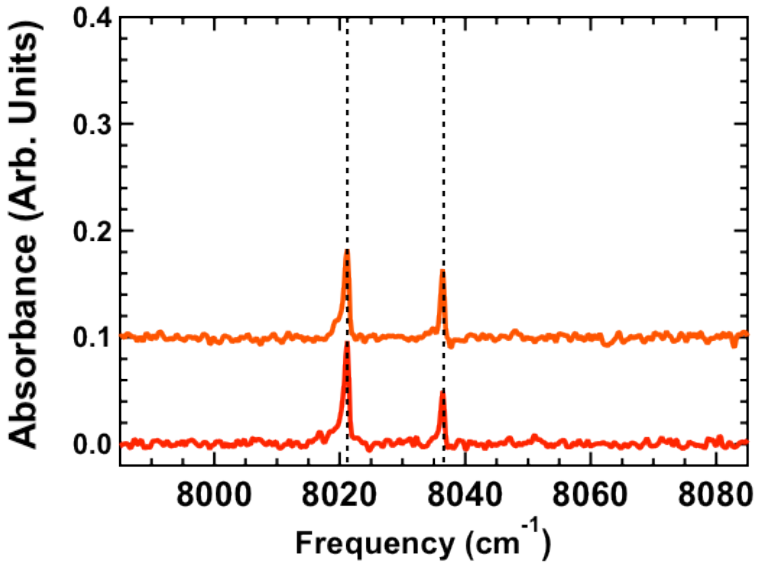
Ortho to Para Conversion

t = 7 min

t = 17 min



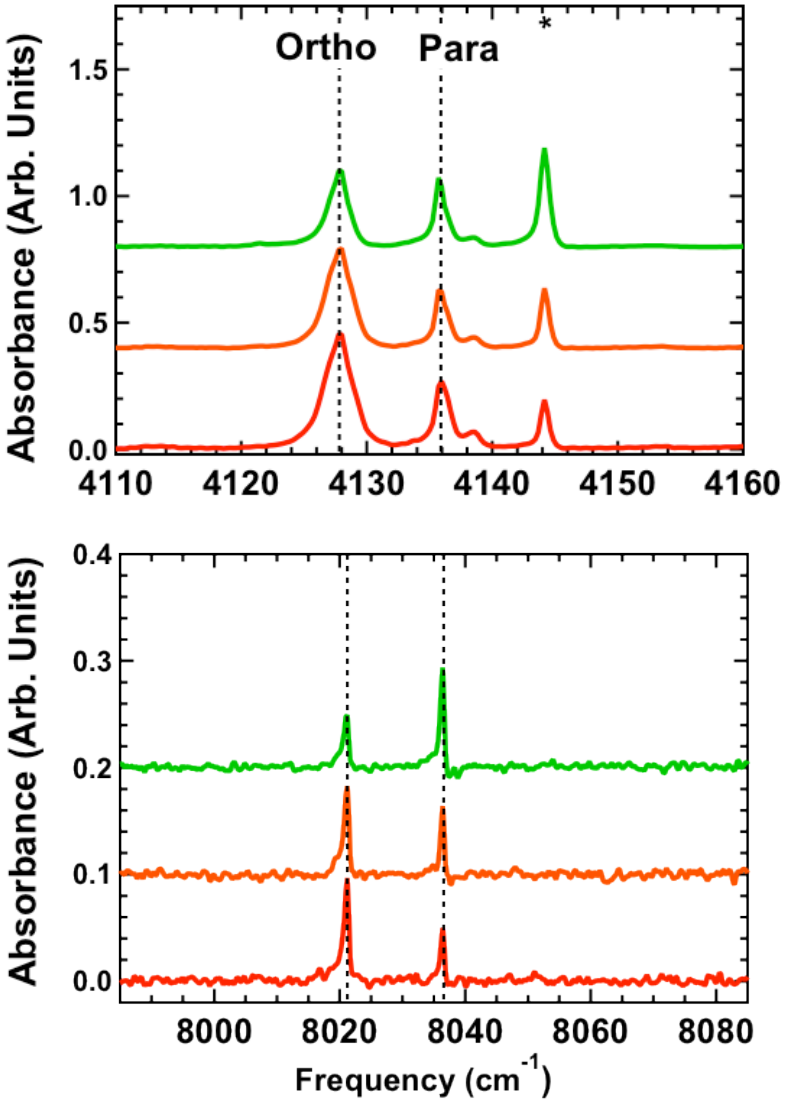
Fundamental



Overtone

Ortho to Para Conversion

t = 7 min
t = 17 min
t = 42 min



Fundamental

Overtone

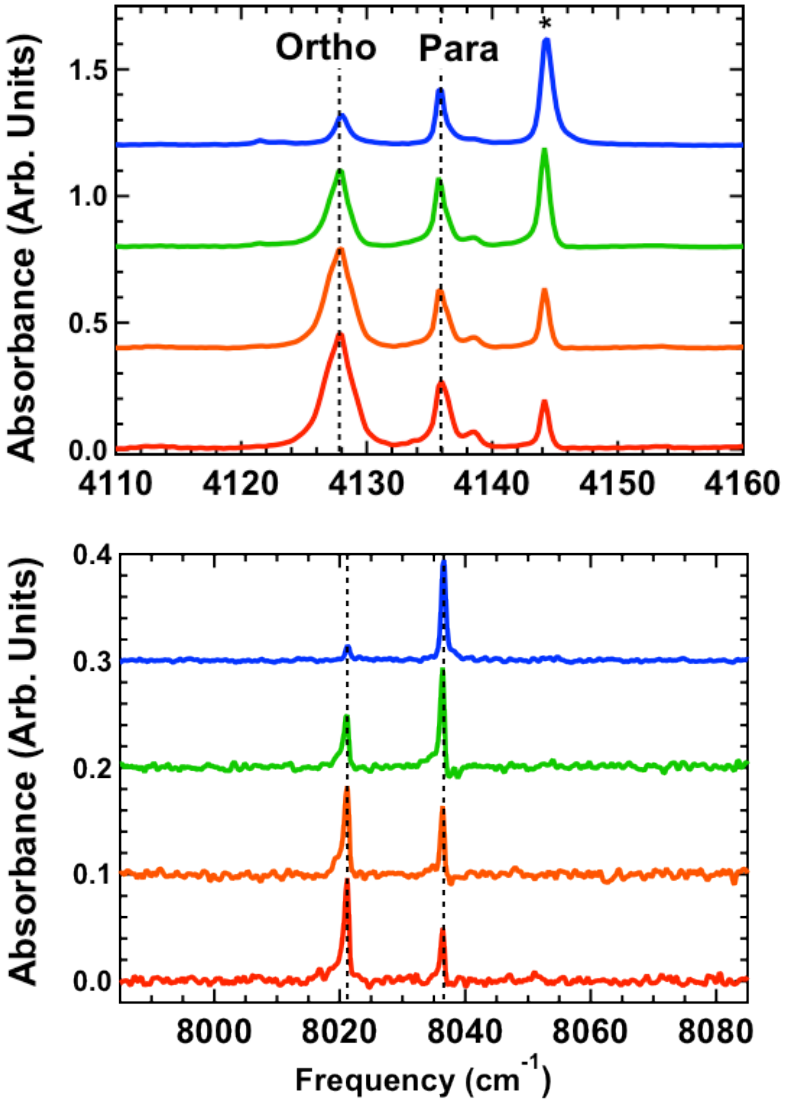
Ortho to Para Conversion

t = 7 min

t = 17 min

t = 42 min

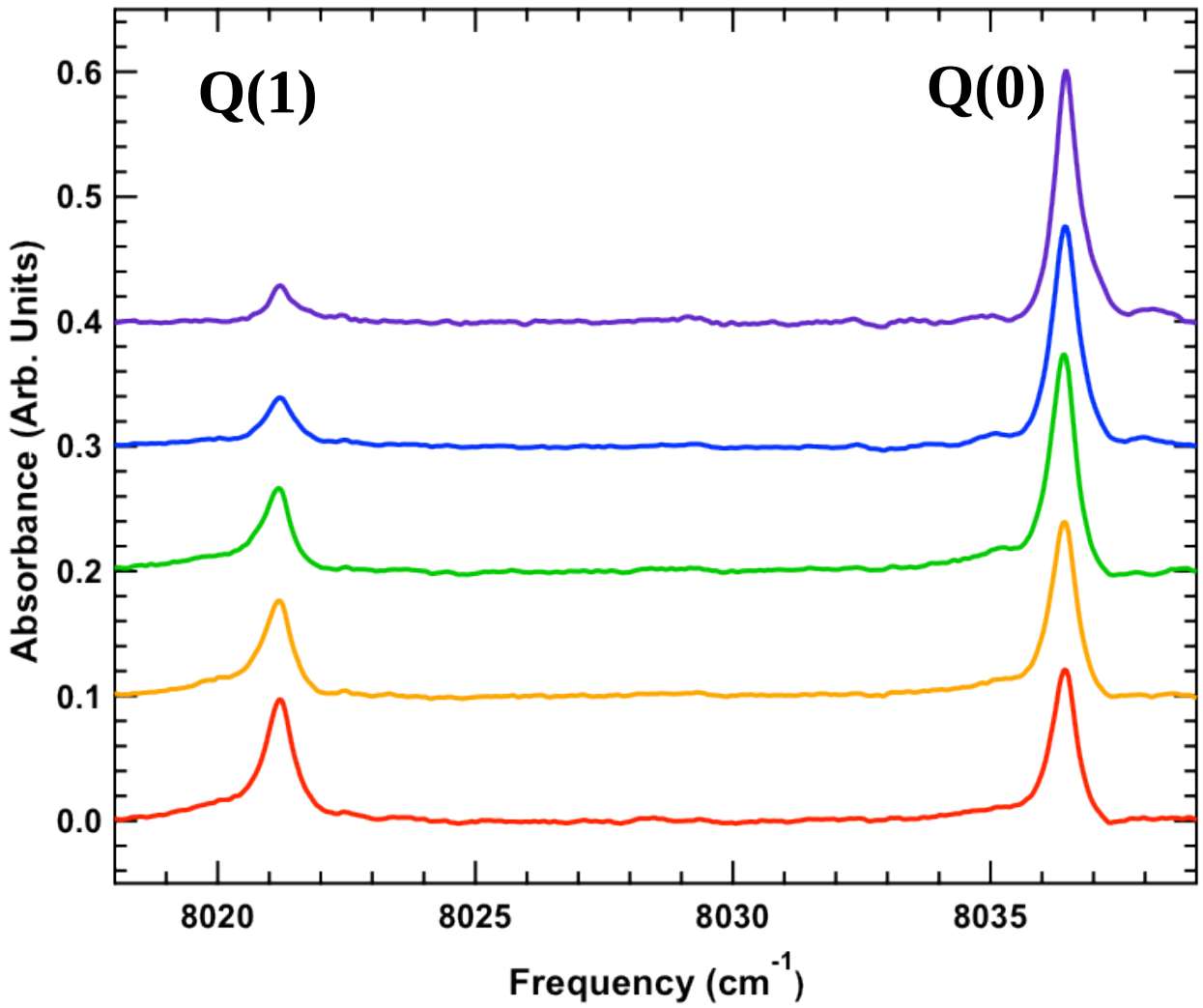
t = 550 min



Fundamental

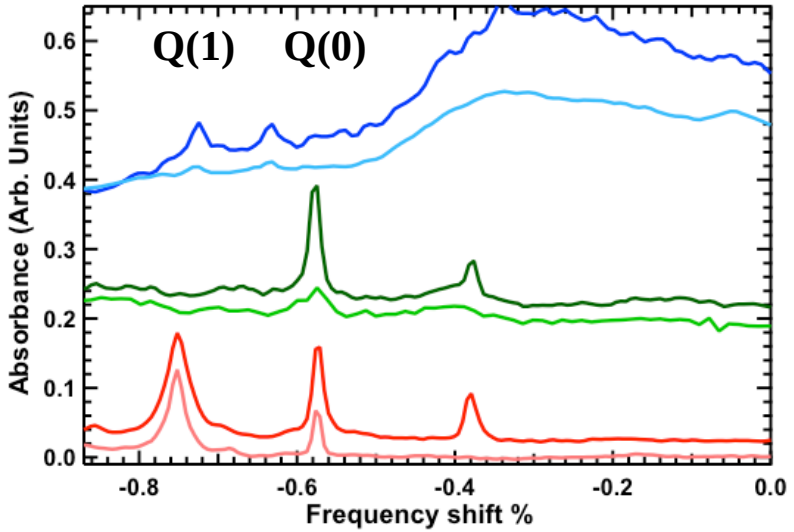
Overtone

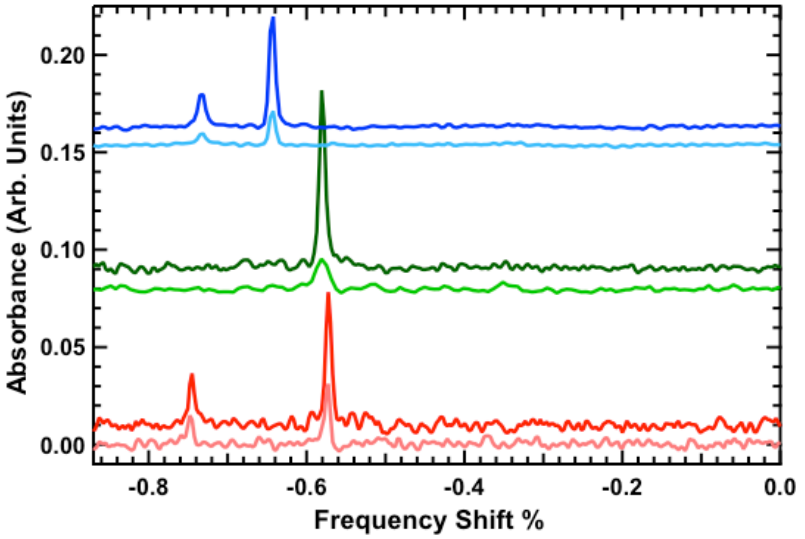
InGaAs Detector plus filter



Relative Intensity of Q(0) and Q(1)

Why is the relative intensity of the Q(0) to Q(1) greater in the overtone than in the fundamental?





Two Induction Mechanisms

$$\vec{\mu}_{sys} = \vec{\mu}_{polar} + \vec{\mu}_{quad}$$

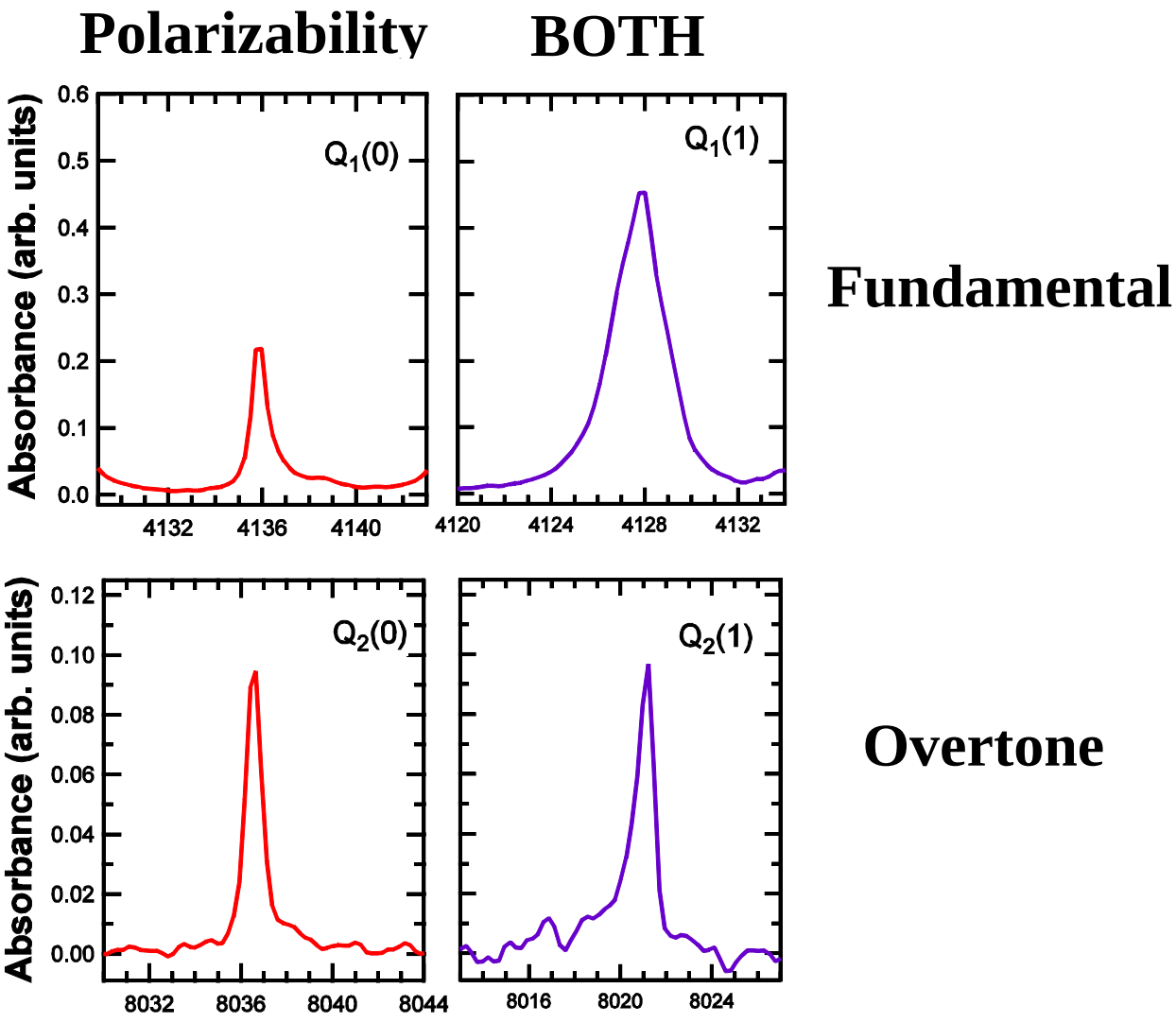
$$\vec{\mu}_{polar} = \vec{E}_{MOF} \cdot \alpha_{H_2}$$

$$\vec{\mu}_{quad} = \sum_i \vec{E}_{Q_H} \cdot \alpha_{i,MOF}$$

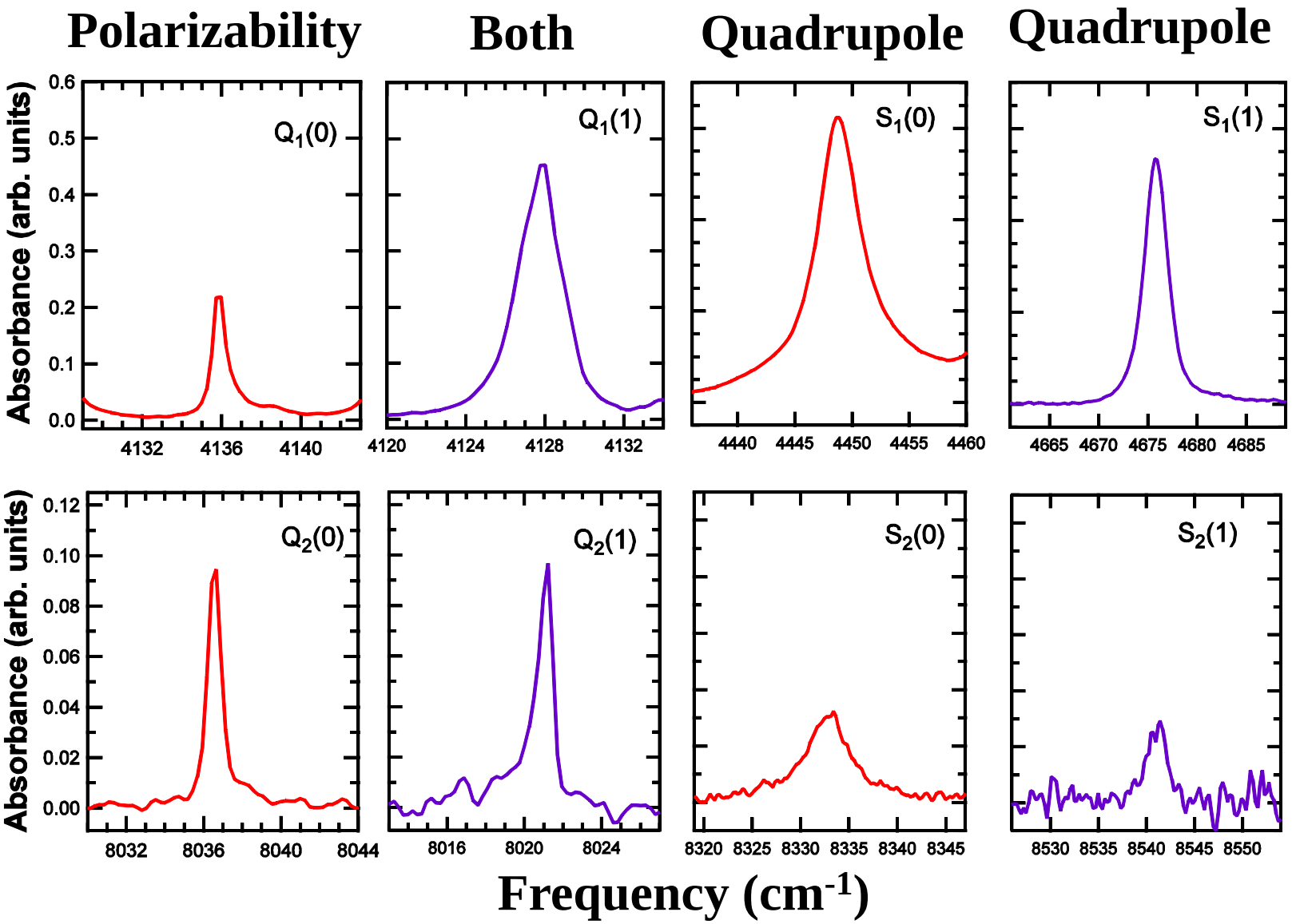
$$I_{0JM \rightarrow \nu' J' M'} \propto |\langle 0JM|\vec{\mu}_{sys}|\nu' J' M'\rangle|^2 =$$

$$|C\langle 0JM|\alpha_{H_2}|\nu' J' M'\rangle + D\langle 0JM|Q|\nu' J' M'\rangle|^2$$

Relative Intensity



Relative Intensity



Experimental Intensities

	Vibrational		**Rovibrational ΔJ =2**	
	$Q(0)$	$Q(1)$	$S(0)$	$S(1)$
Mechanism	Polar	Both	Quad	Quad
$I_{2\leftarrow0}/I_{1\leftarrow0}$ (Theory)	$1/60$	$\left(\boldsymbol{C(1/8)+D(1/5)}\right)^2$	$1/20$	$1/20$
$I_{2\leftarrow0}/I_{1\leftarrow0}$ (MOF-5 Exp)	$1/(2.5\pm0.5)$	$1/(14\pm3)$	$1/(17\pm1)$	$1/(22\pm4)$

It appears that the polarizability mechanism is enhanced by more than an order of magnitude relative to gas phase, but quadrupole induction mechanism is largely unchanged.

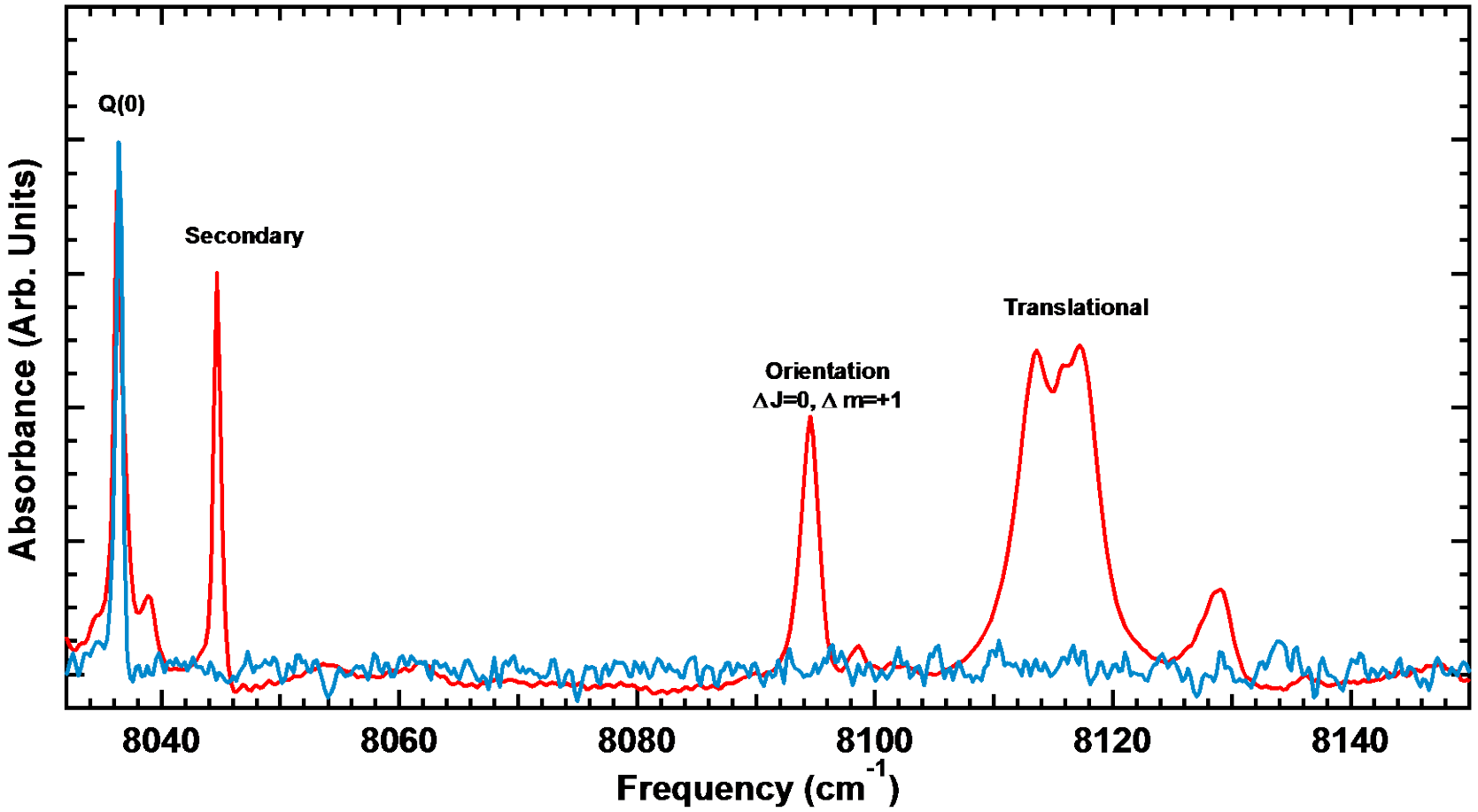
Q(0) Relative Intensity Overtone vs Fundamental

$$\frac{I_{0\rightarrow 2}}{I_{0\rightarrow 1}} = \frac{B_e}{\omega_e}\left(a + \frac{\bar{\alpha}''}{\bar{\alpha}'}\right)^2$$

in gas phase $a = -1.607$ and $\frac{\bar{\alpha}''}{\bar{\alpha}'} = 0.537$

For MOF-5 would need $\left(a + \frac{\alpha''}{\alpha'}\right)^2 \approx 30$

Translational Peaks ?



Fundamental shifted by ~ 3900 cm^{-1} and x 0.35

Conclusion

- **Overtone IR spectroscopy is a useful tool in studying adsorbed gas behavior**
- **Leads to peaks away from background**
  Adds another site specific tool
  Greatly facilitates in ortho/para studies
- **Relative intensity of overtone peaks provides detailed information about adsorbate**
- **Theoretical models are needed**

Acknowledgements

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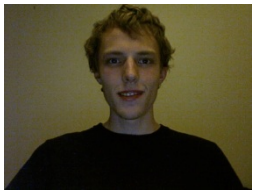
MOF samples: Jesse Rowsell (Oberlin) Jeff Long (Berkeley)

Undergraduate Students

Chris 

Jocienne

Elizabeth

Jesse

Brian

Jenny

Michael

Ben

Sujoy