# MOF-5: There and Back Again

## Outline

1) MOF-5: The start of a collaboration

2) $H_2$ and infrared: You're crazy

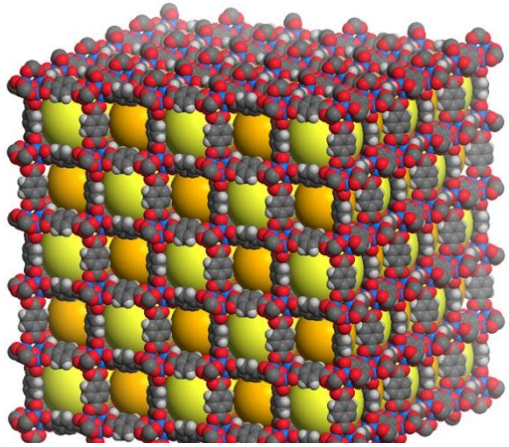
3) MOF-74: The beauty of a systematic series

4) $CO_2$: Something a bit different

5) MOF-5 again: The story continues

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

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

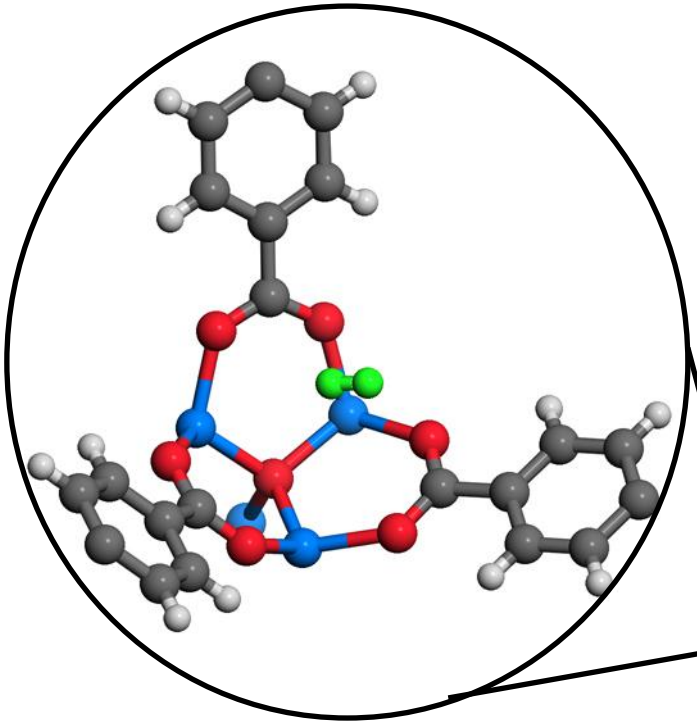


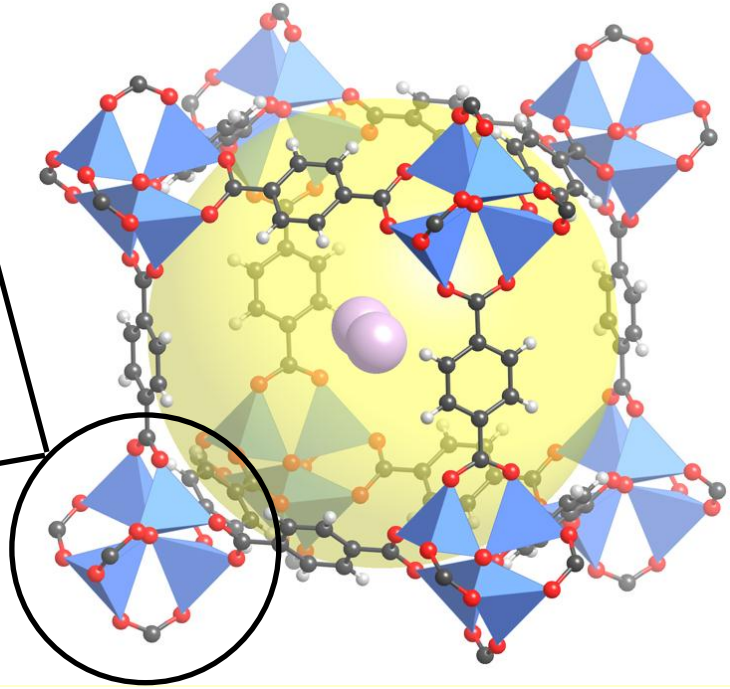
**Blue = Zn**

**Red = O**

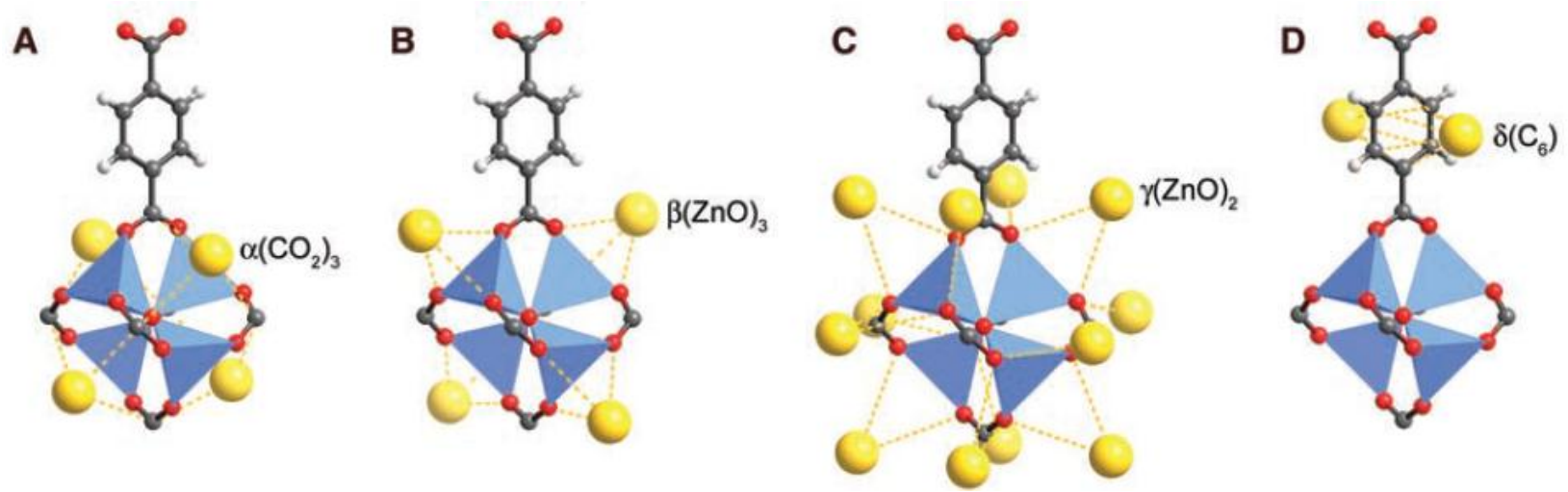
**Black = C**

**Green = $H_2$**



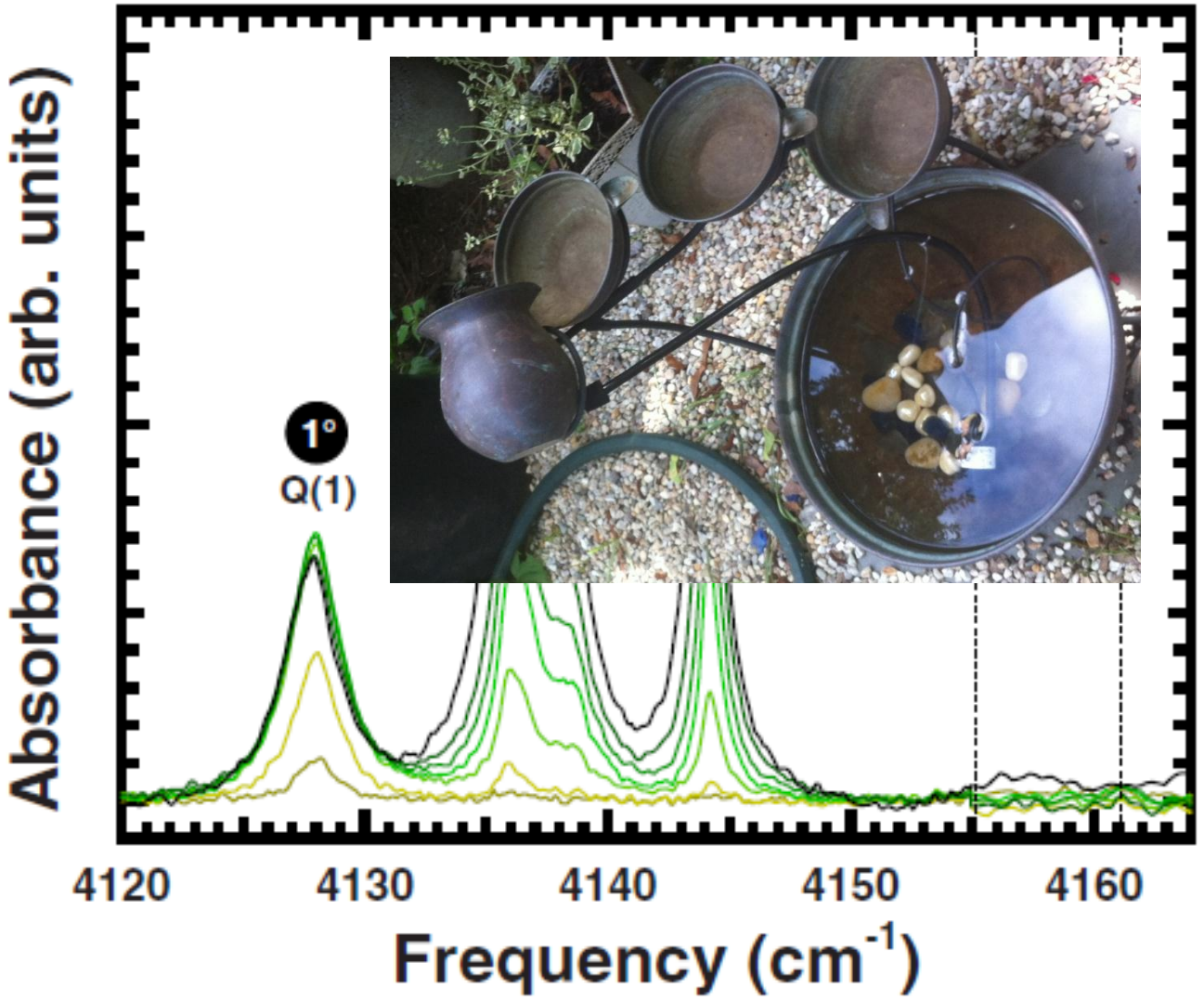


# Secondary Sites




J.L.C. Rowsell, E.C. Spencer, J. Eckert, J. Howard, and O.M. Yaghi, Science, **309**, 1350 (2005)

Phys. Rev. B **77**, 224301 (2008)



# Hydrogen Cycle

## Fuel Cell Batteries

$$2H_2 + O_2 \rightleftharpoons 2H_2O + \text{Energy}$$

- **Electrolyze water using renewable energy or otherwise wasted energy**

- **Ideally it would all be done locally**

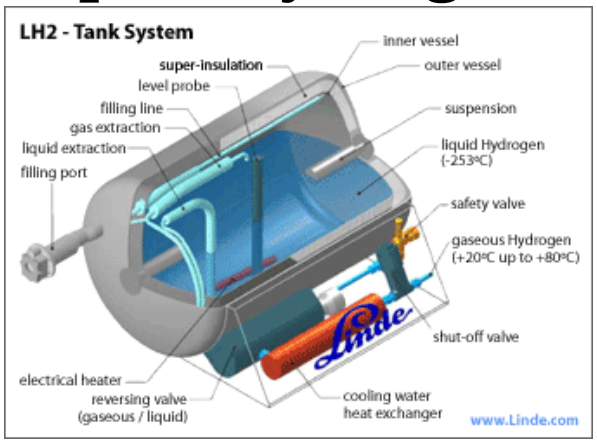
# Hydrogen Storage for Fuel Cells



**High Pressure**

**350-700 bar**

## Liquid Hydrogen



# Need a light weight "hydrogen sponge"

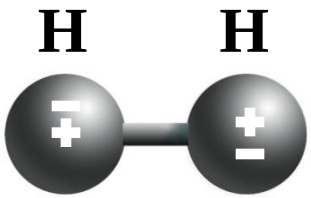
**Highly porous materials exist**

**Problem is hydrogen sticks either too weakly or too strongly**

**Need "post-it note" stickiness**

**Need technique to probe $H_2$ interactions**

# Infrared Spectroscopy! Are you crazy?



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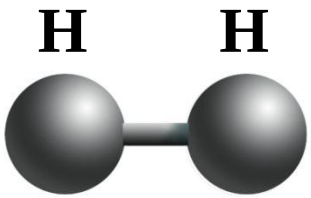
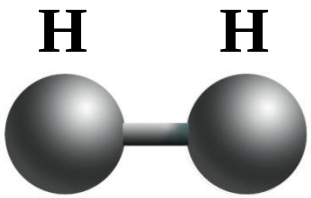
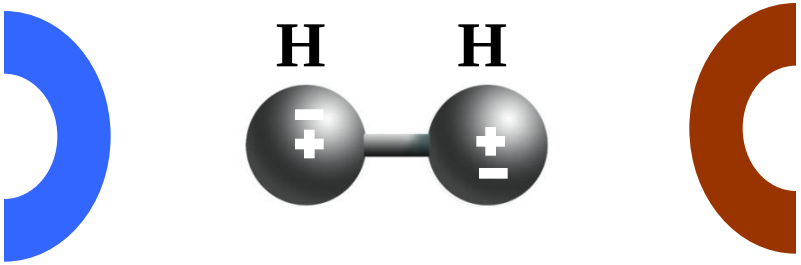



**The atoms are neutral**

# Infrared Spectroscopy! Are you crazy?




**The atoms are neutral**




**Interactions with “sponge” can induce charge separation**

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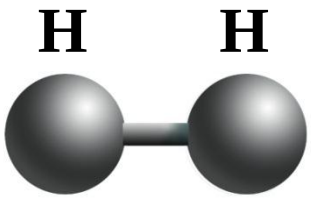


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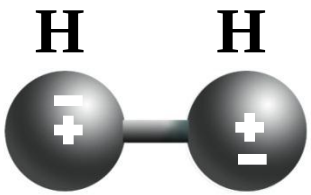


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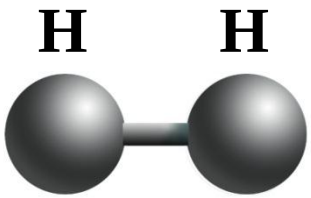


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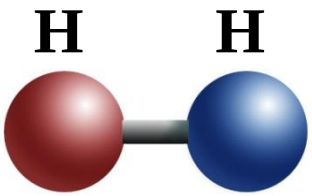
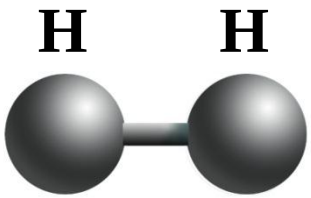
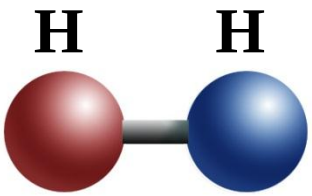



**Interactions with “sponge” can induce charge separation**

# Infrared Spectroscopy! Are you crazy?



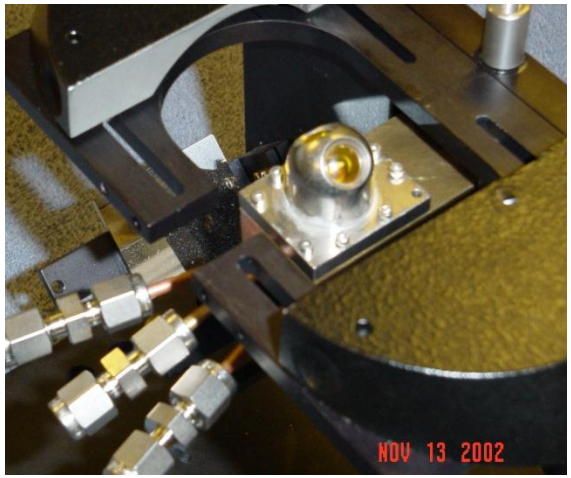



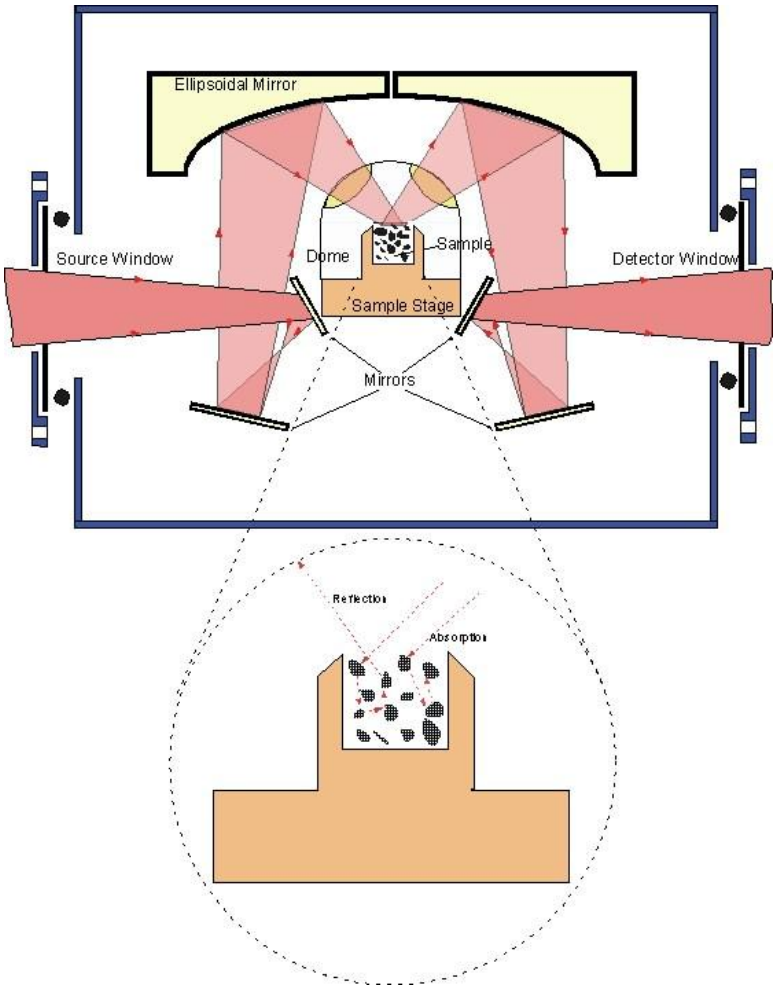

**Interactions with “host” can induce a dipole moment**

**Induced dipole moment is typically weak so special technique is required to enhance signal**

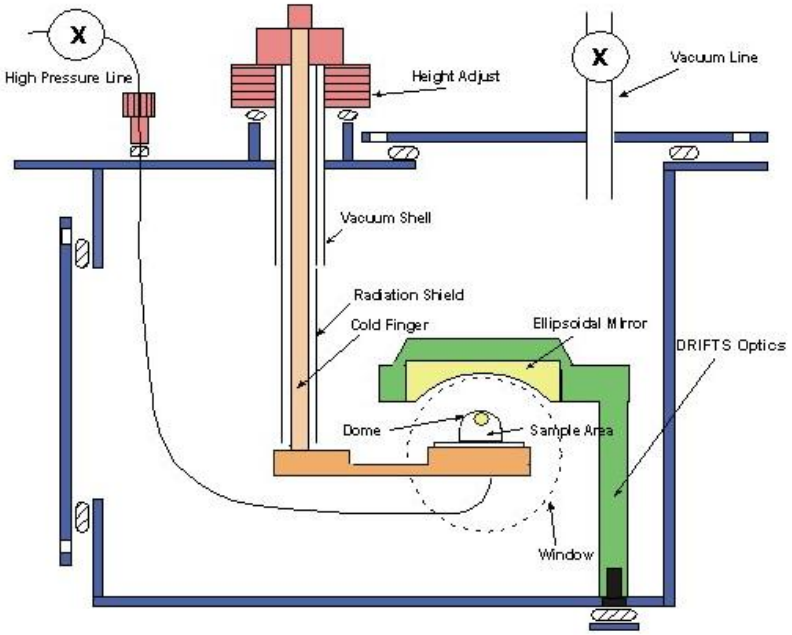
# Diffuse Reflectance Spectroscopy

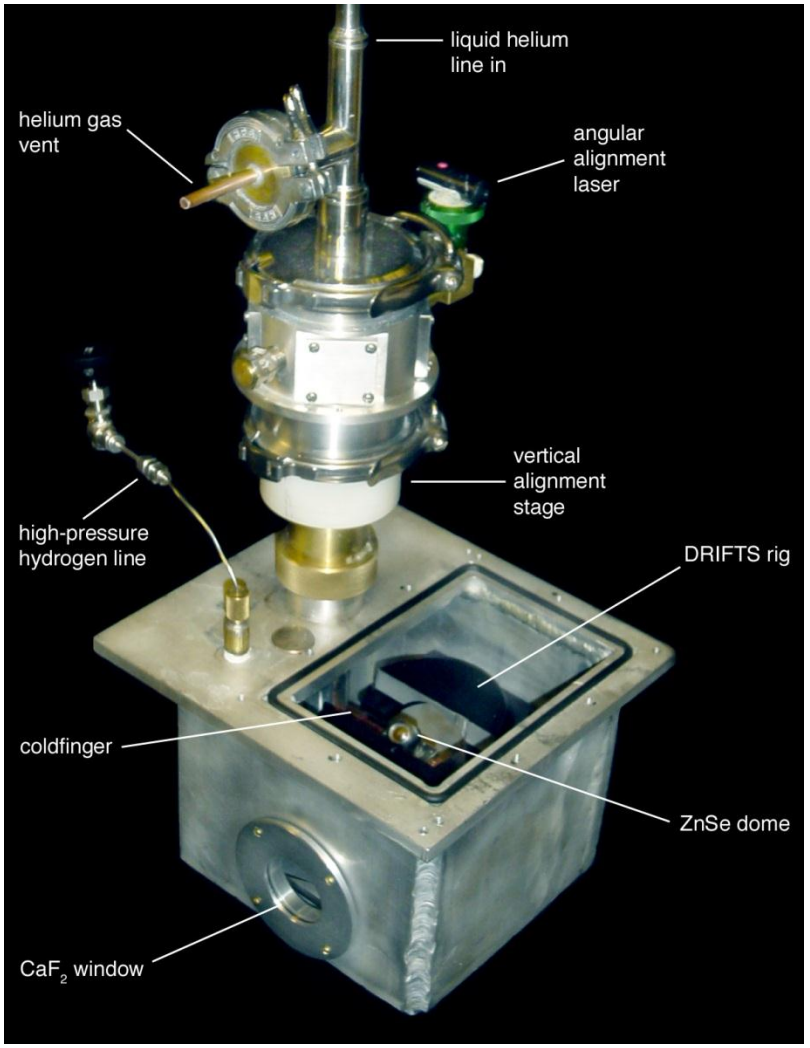
- Light bounces around within powder sample
- Very long path length enhances absorption signal



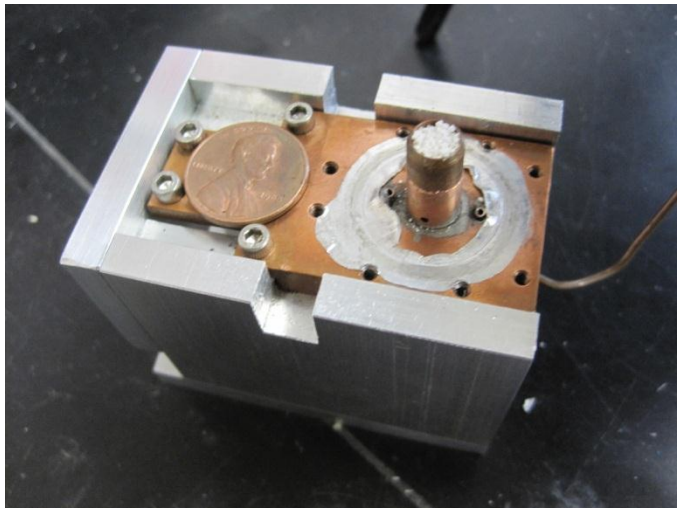
# Diffuse Reflectance Spectroscopy: Cryostat Assembly

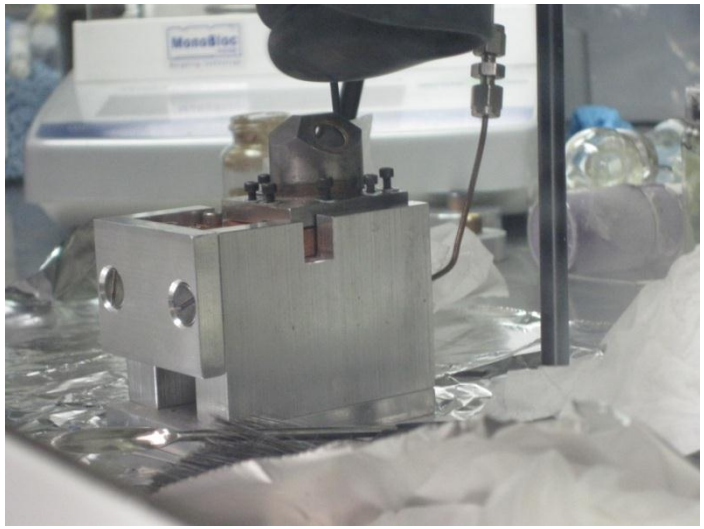


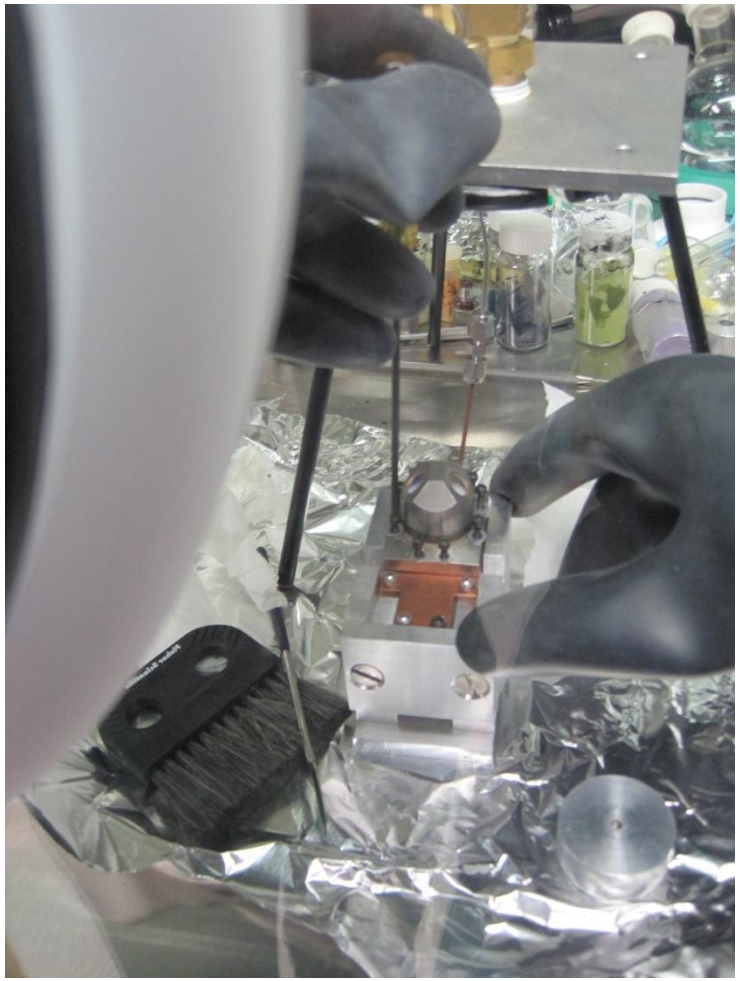




Rev. Sci. Instr. **77**, 093110 (2006)

# Samples are mounted in a glove-box





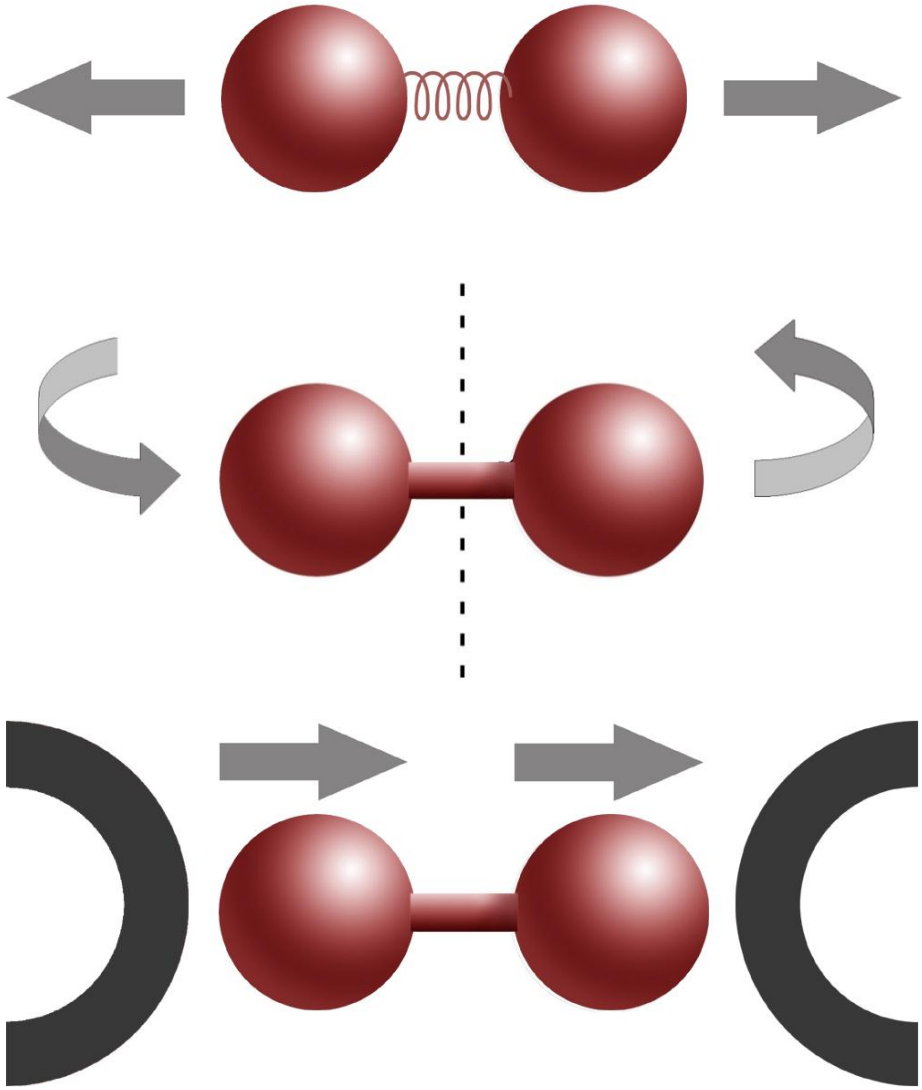


# Quantum Dynamics of Adsorbed $H_2$

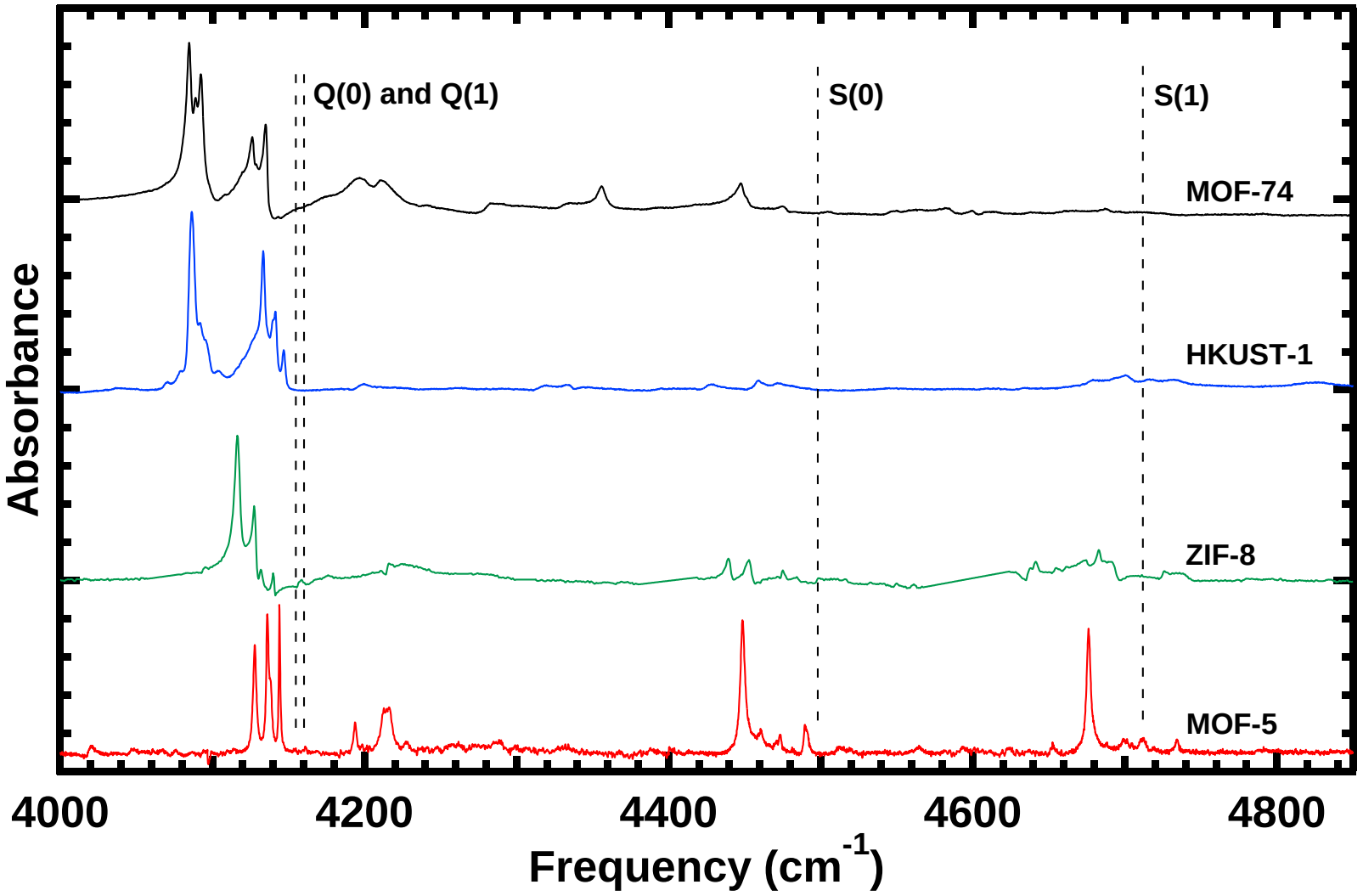
- Vibration
  $E_v = (v + 1/2)\, \nu_0$
  $\nu_0$ = 4161 $cm^{-1}$ for free $H_2$

- 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 150 $cm^{-1}$

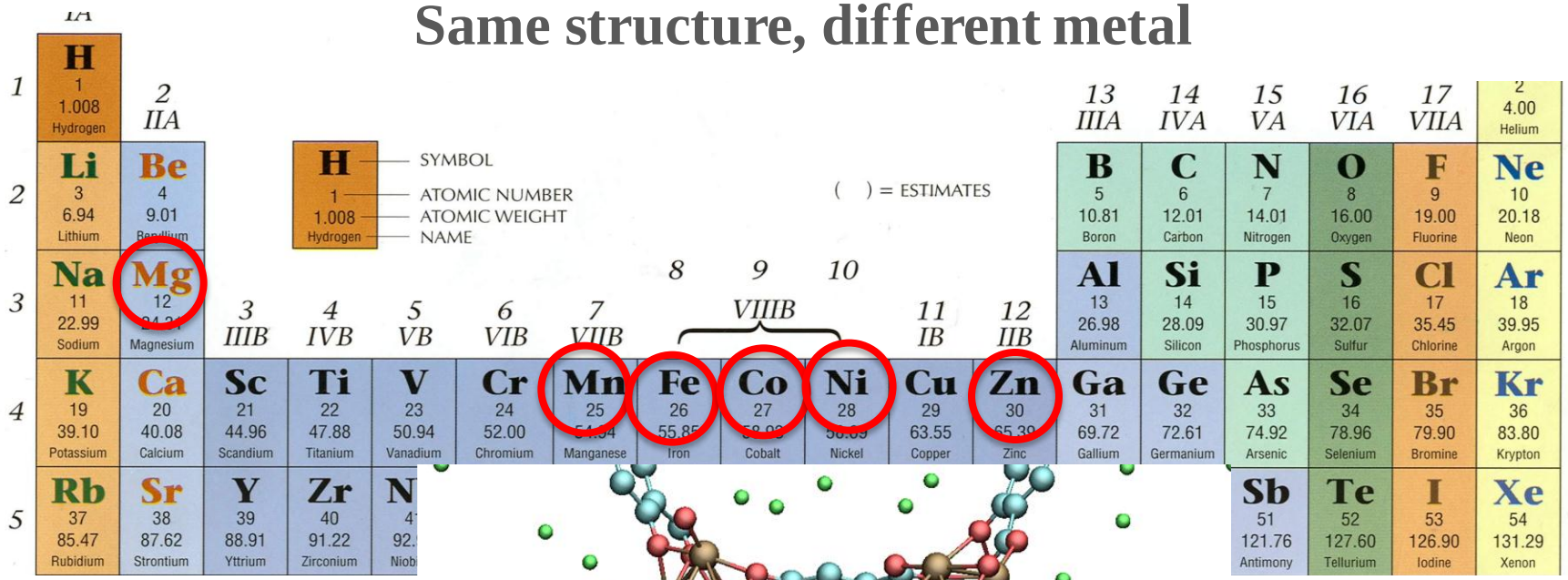


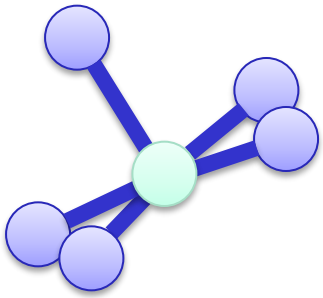
# Typical Spectra for $H_2$ in MOFs at 30 K

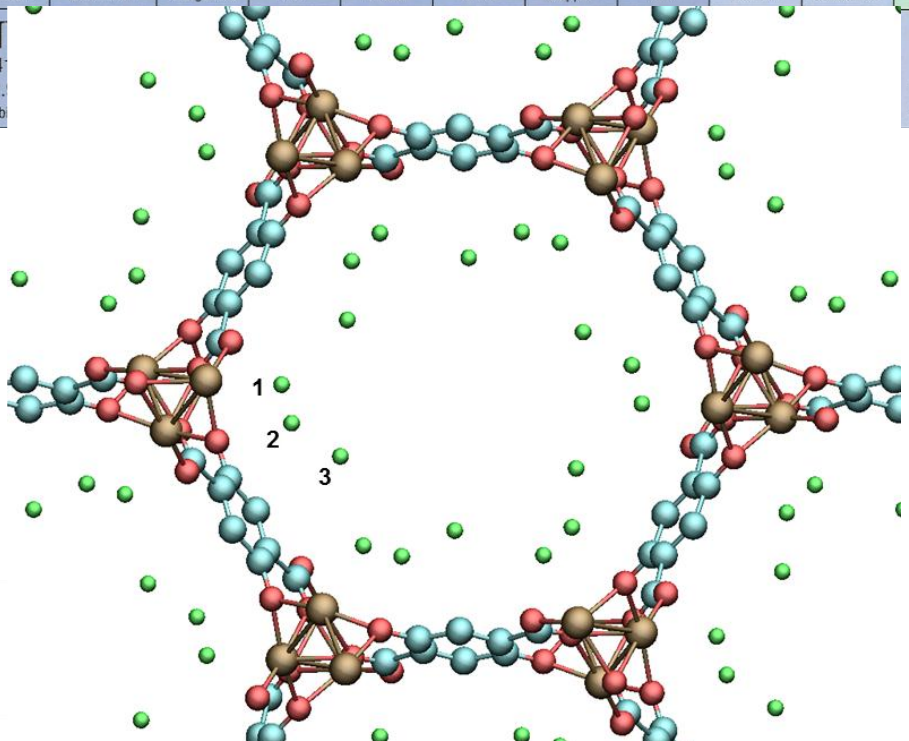


# MOF-74 Isostructural Series

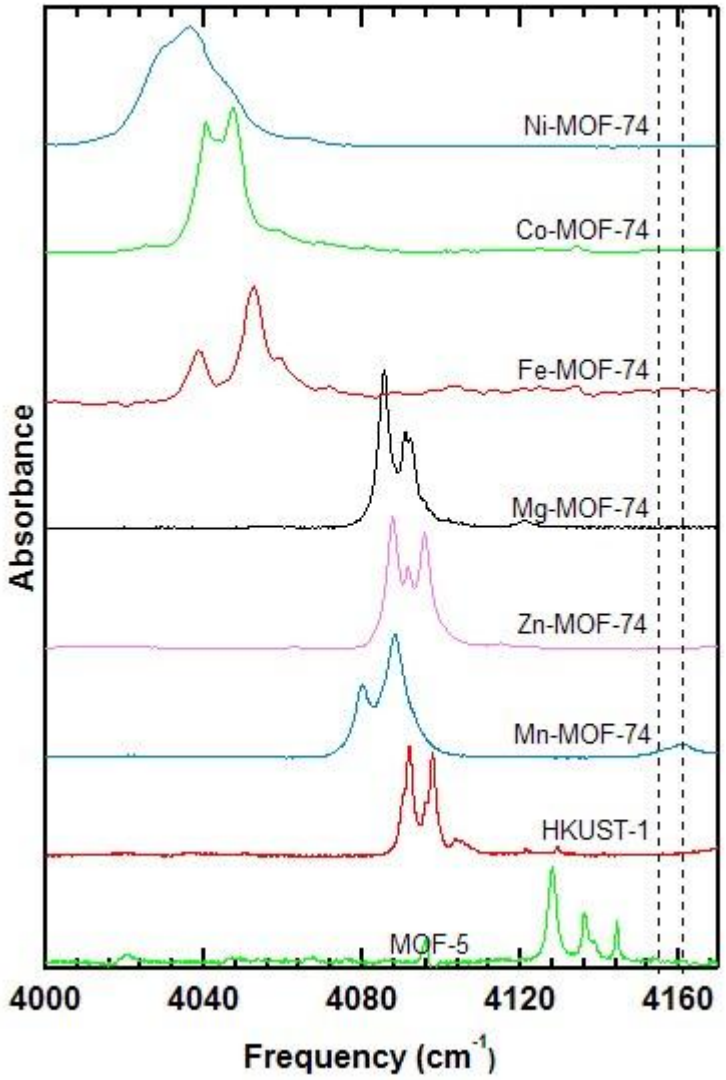
## Same structure, different metal

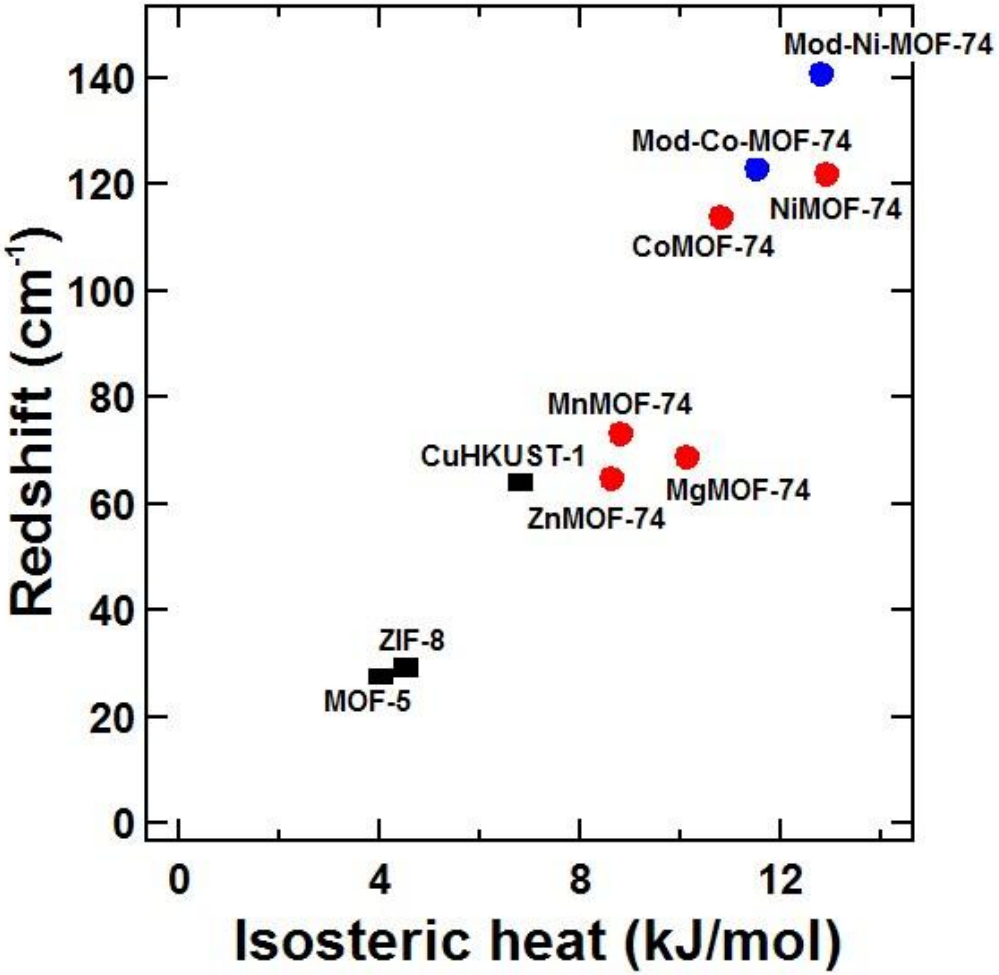




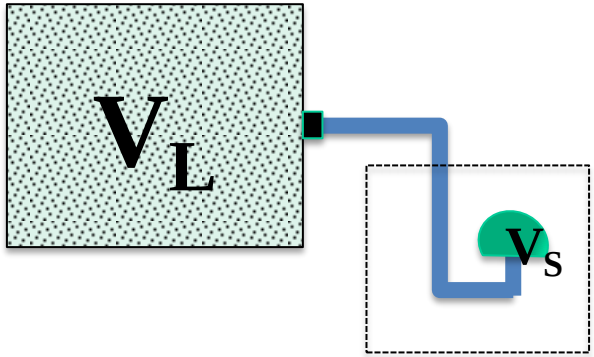
# Vibrational shift and binding energy?

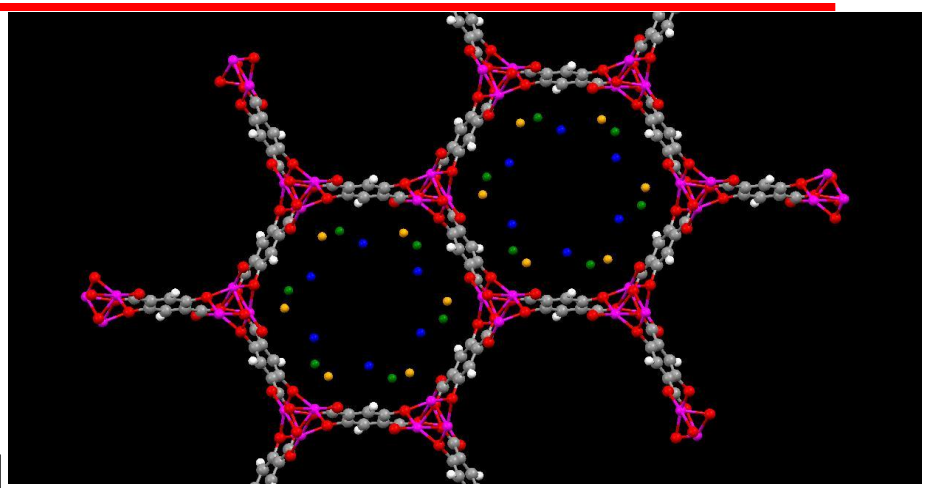


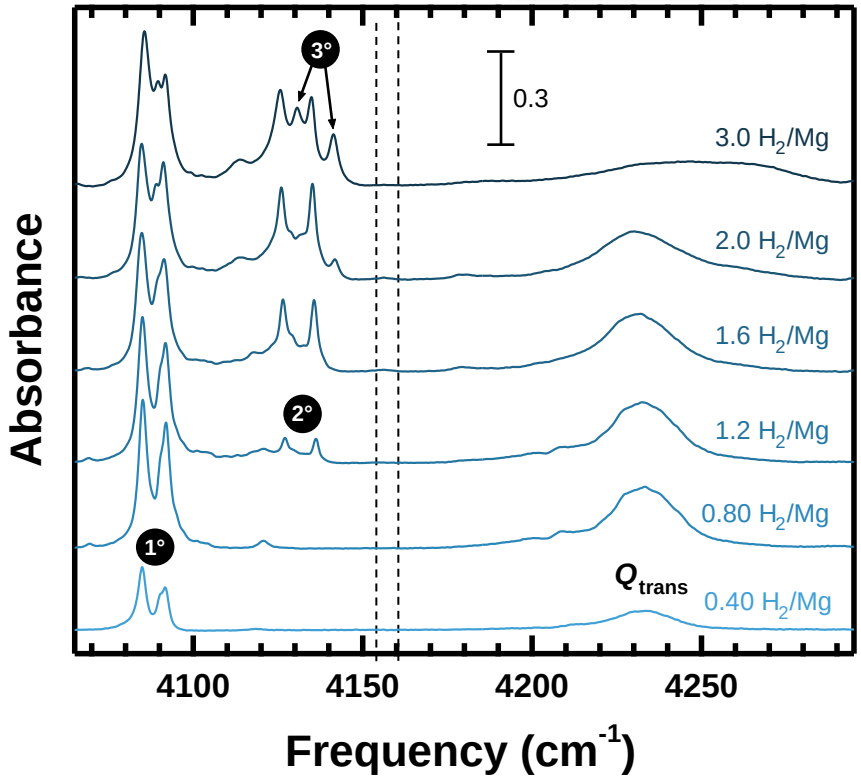



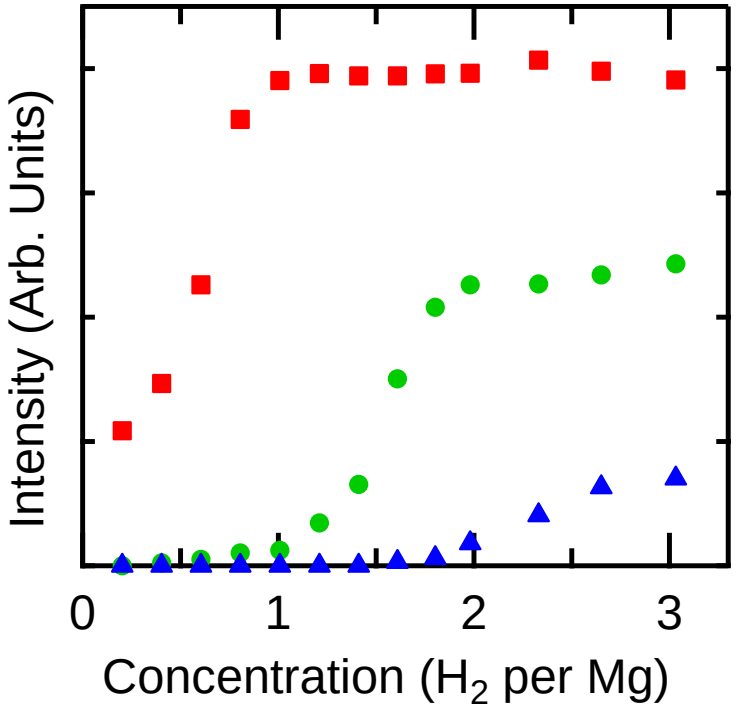
# Spectra as a function of concentration (Mg-MOF-74 at 35 K)

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





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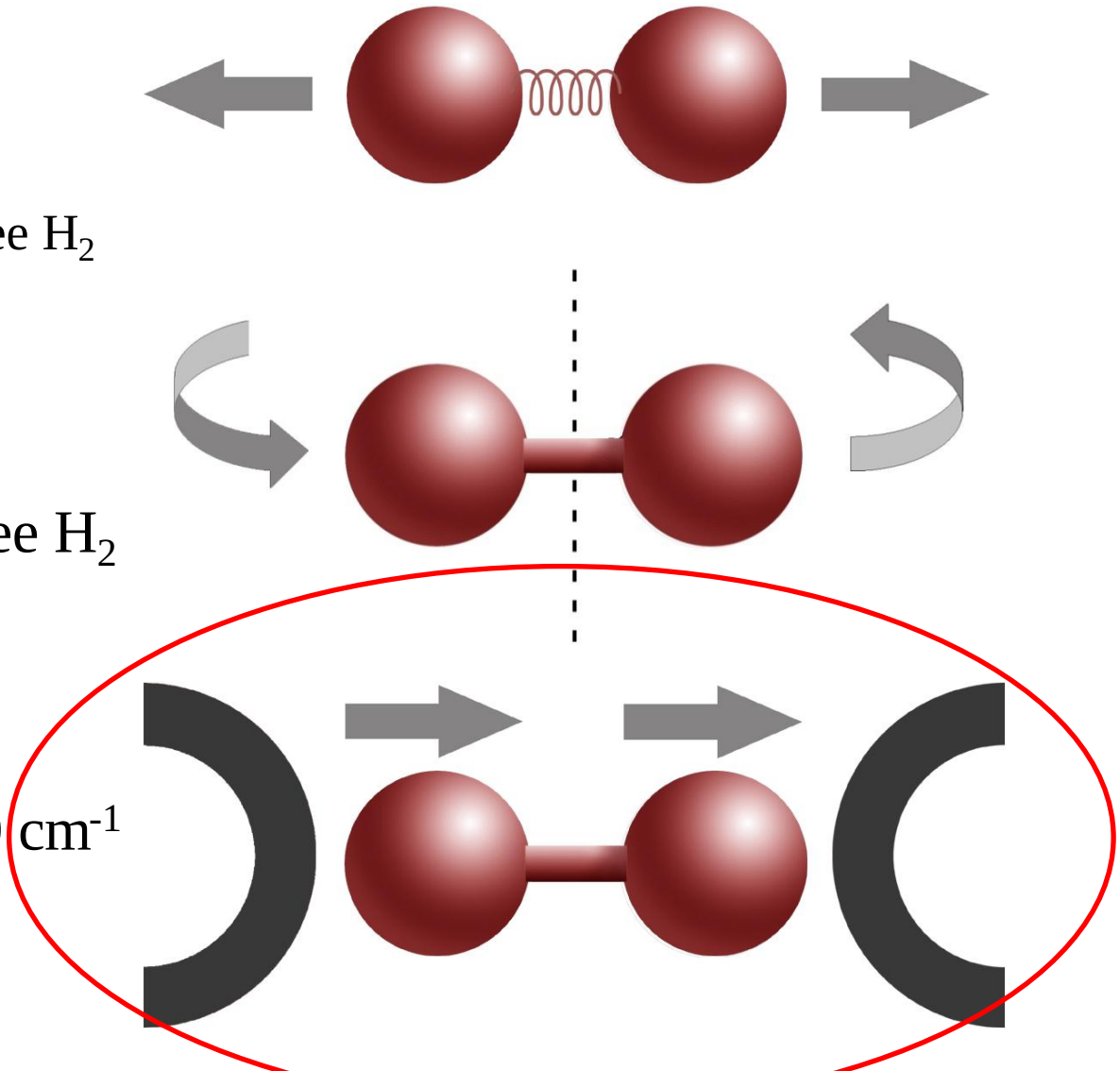
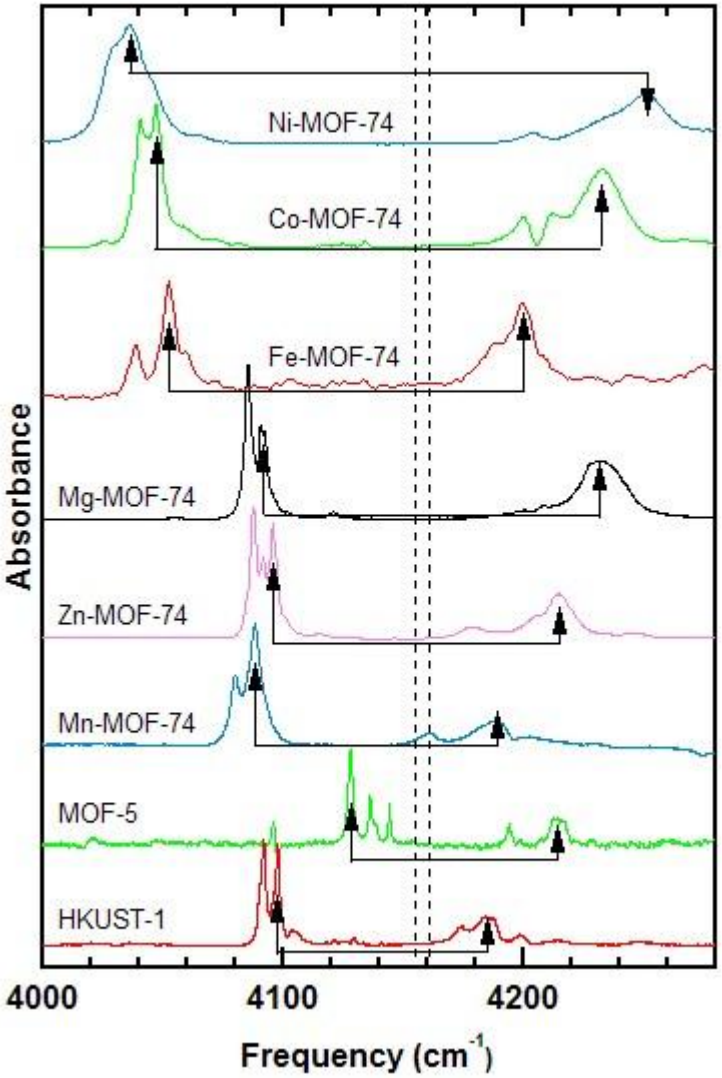
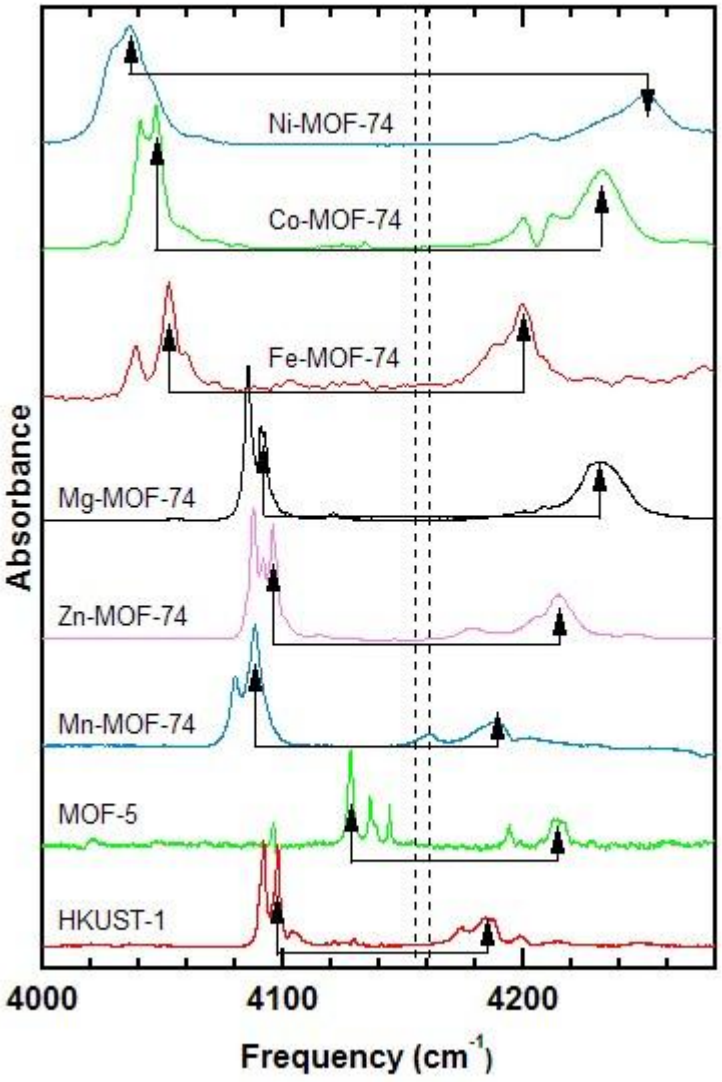


# Translational mode energy (quantum sieving?)



# Back of the Envelope Calculation




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

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

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

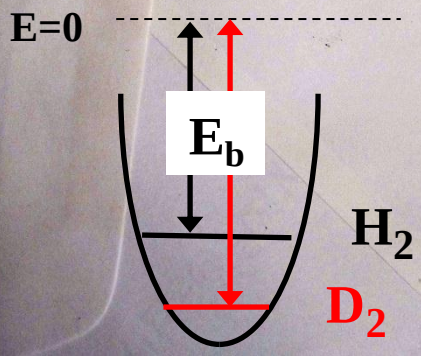
$\omega_{D_2} = 1/\sqrt{2}\ \omega_{H_2}$

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

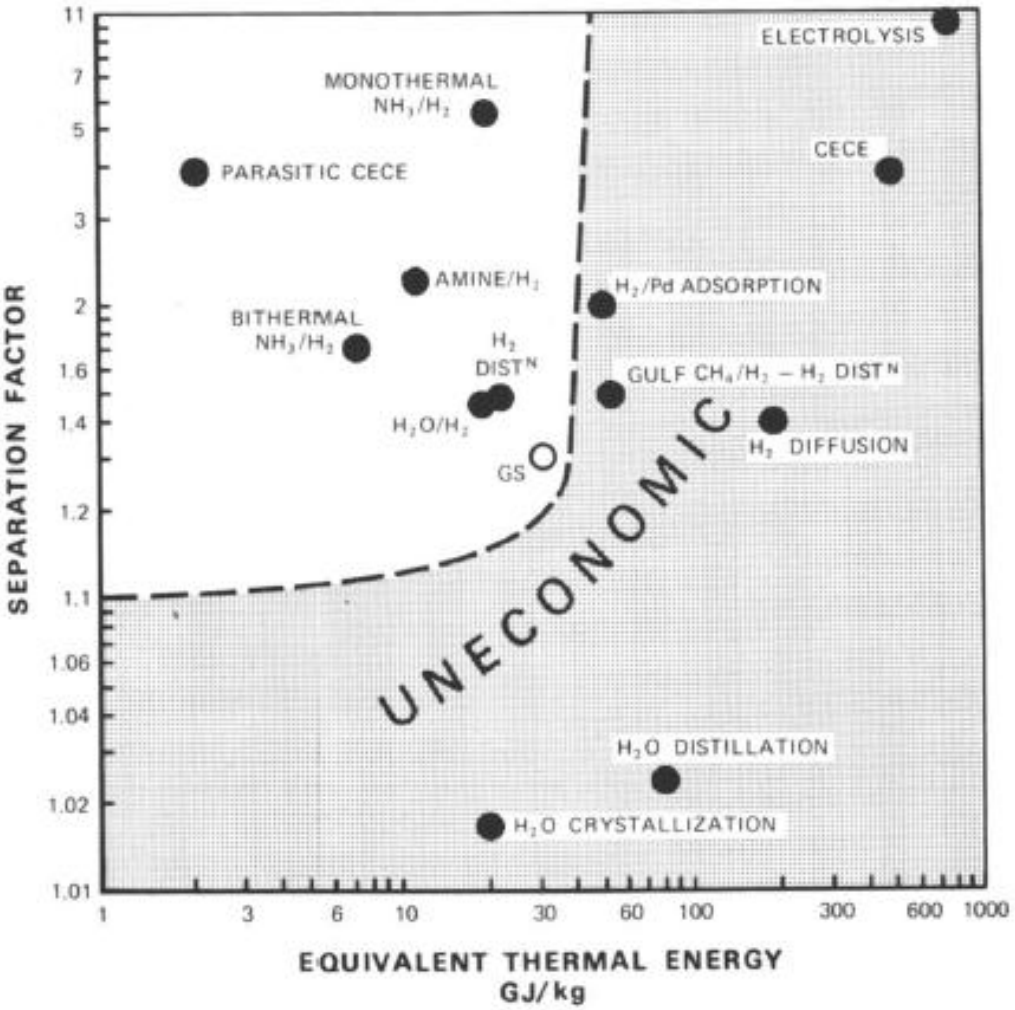
$\Delta ZPE = 120K$

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

$e^{120/77} = 4.75$

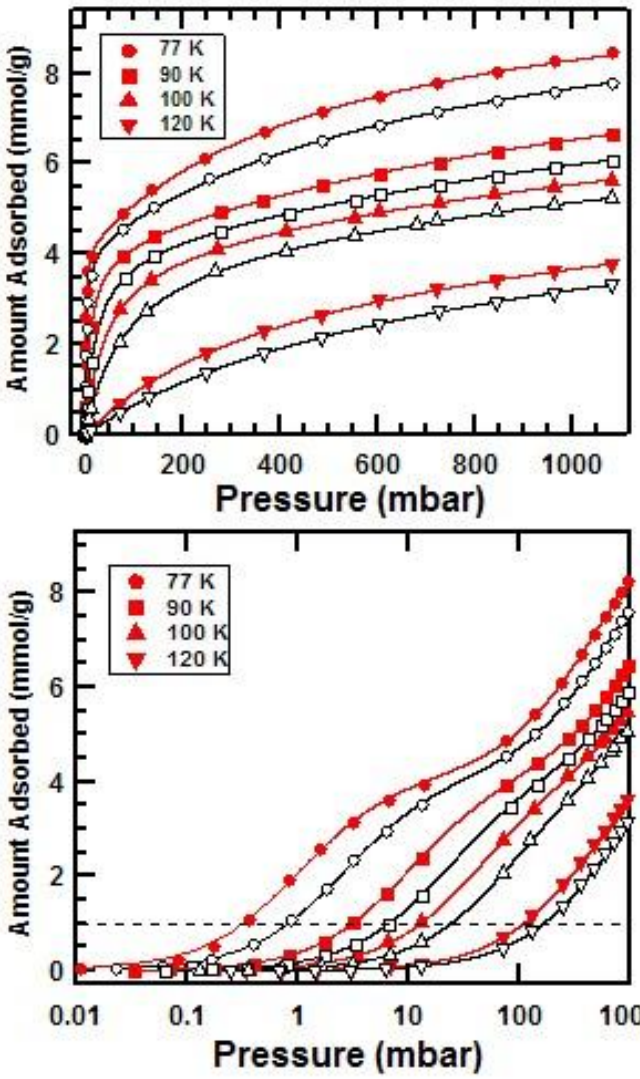


# Standard Separation Techniques




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

# $D_2$ vs $H_2$ Isotherms in Fe-MOF-74



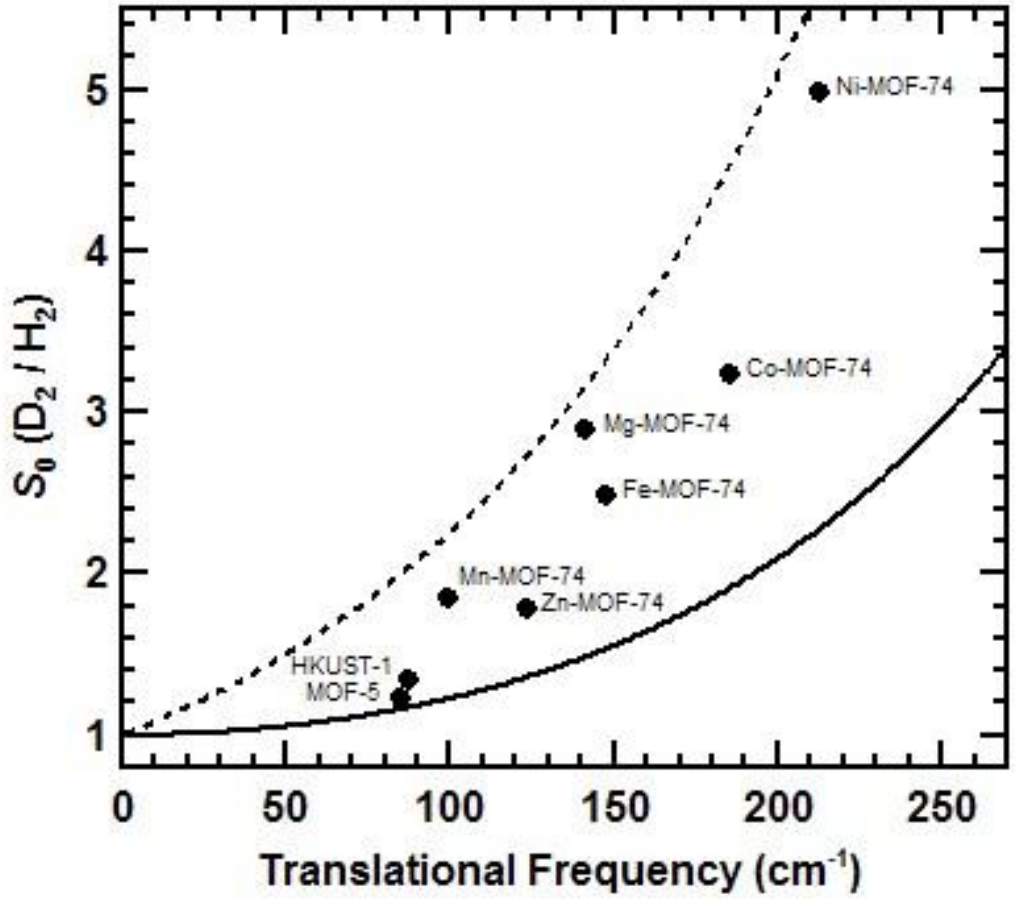

*J. Am. Chem. Soc.*, 2013, **135**, 9458

**Fits are based on constrained two-site Langmuir isotherm**

**$D_2$ (red) consistently higher than $H_2$ (black)**

**$D_2/H_2$ Ratio increases with decreasing temperature**

# Selectivity vs Translational Frequency

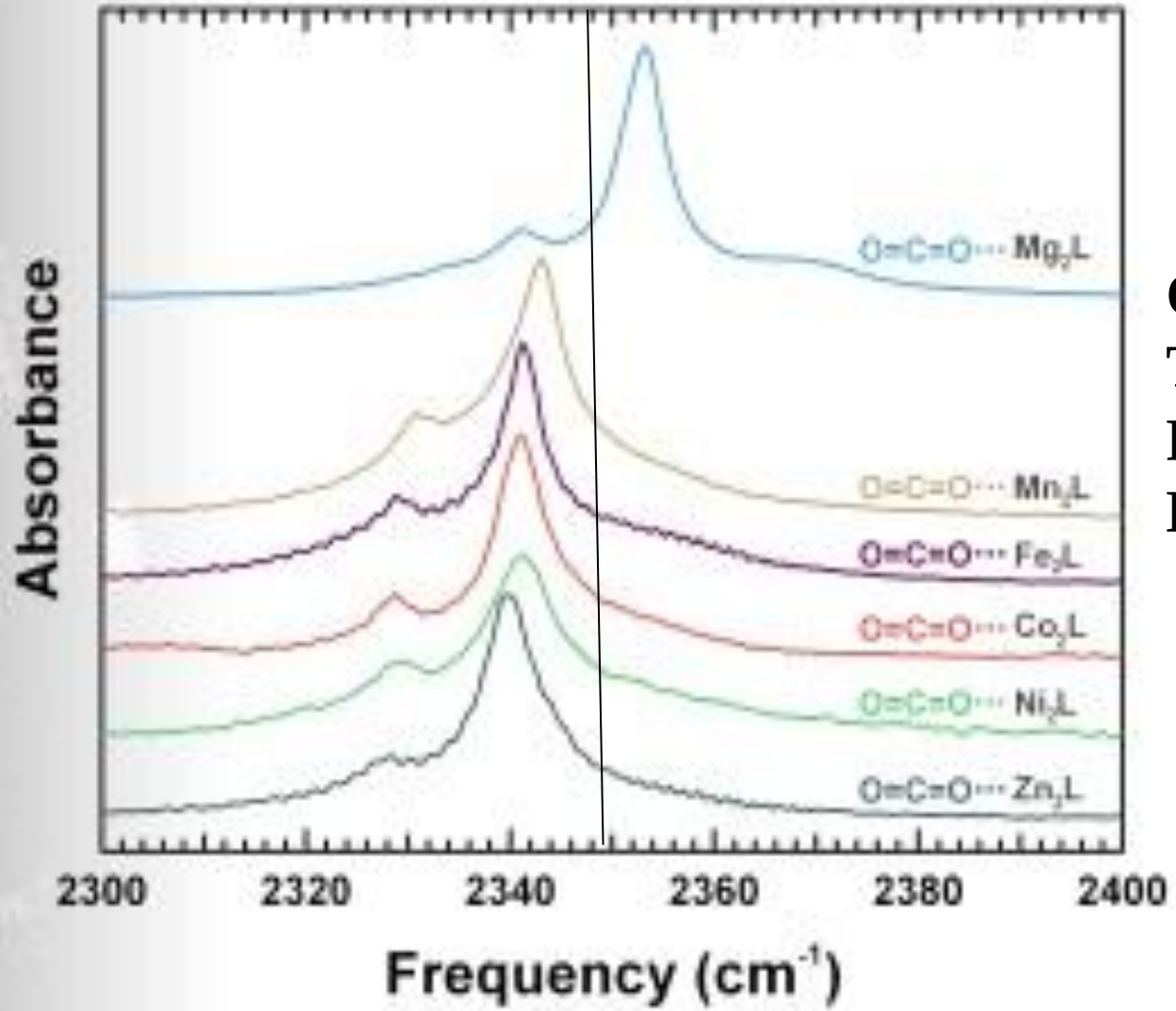



**Dashed line shows simple back of the envelope**

**Solid line shows full (harmonic) thermodynamic calculation**

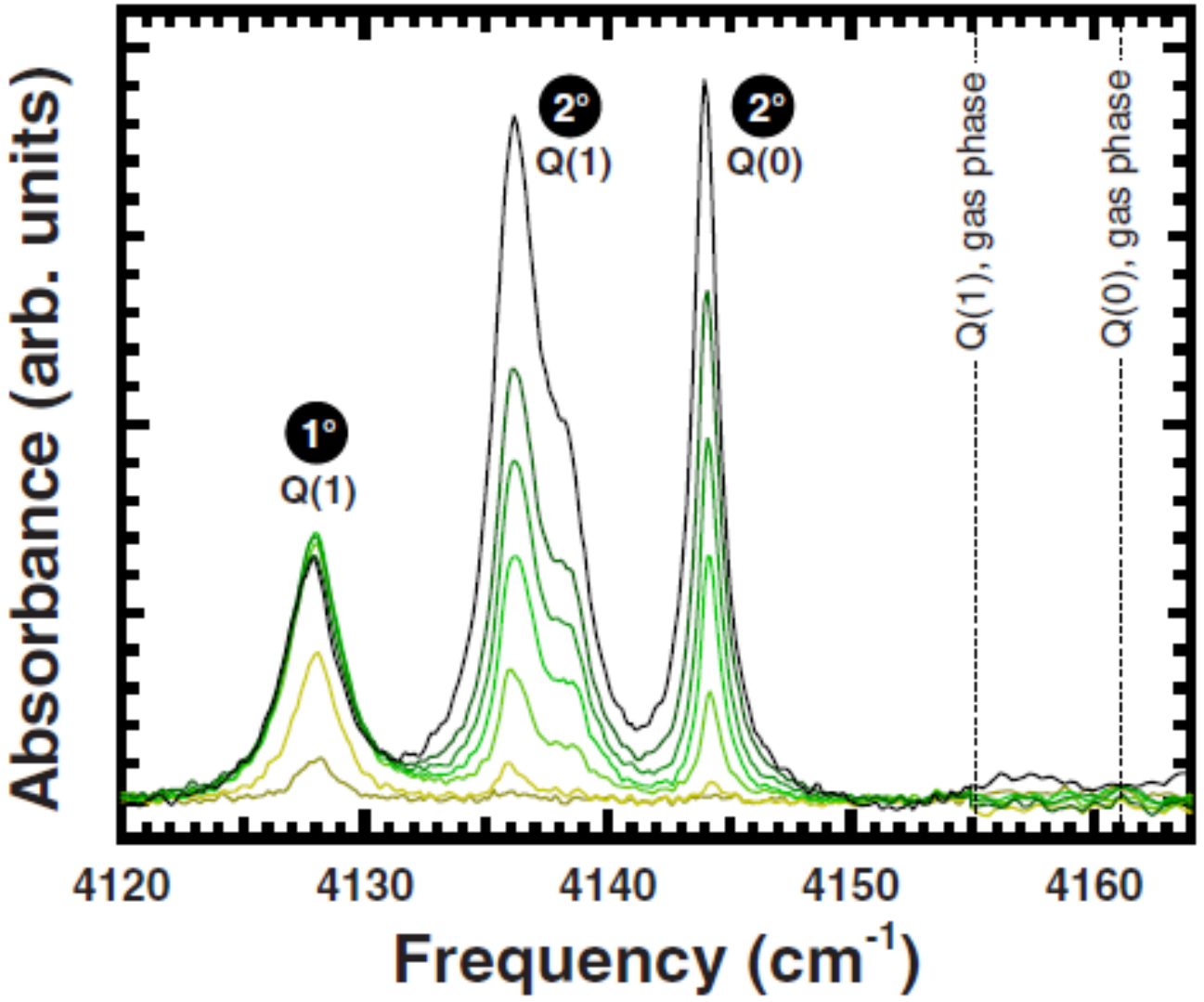
# $CO_2$ in Different Metal MOF-74

J. Phys. Chem. C 2015, 119, 5293-5300

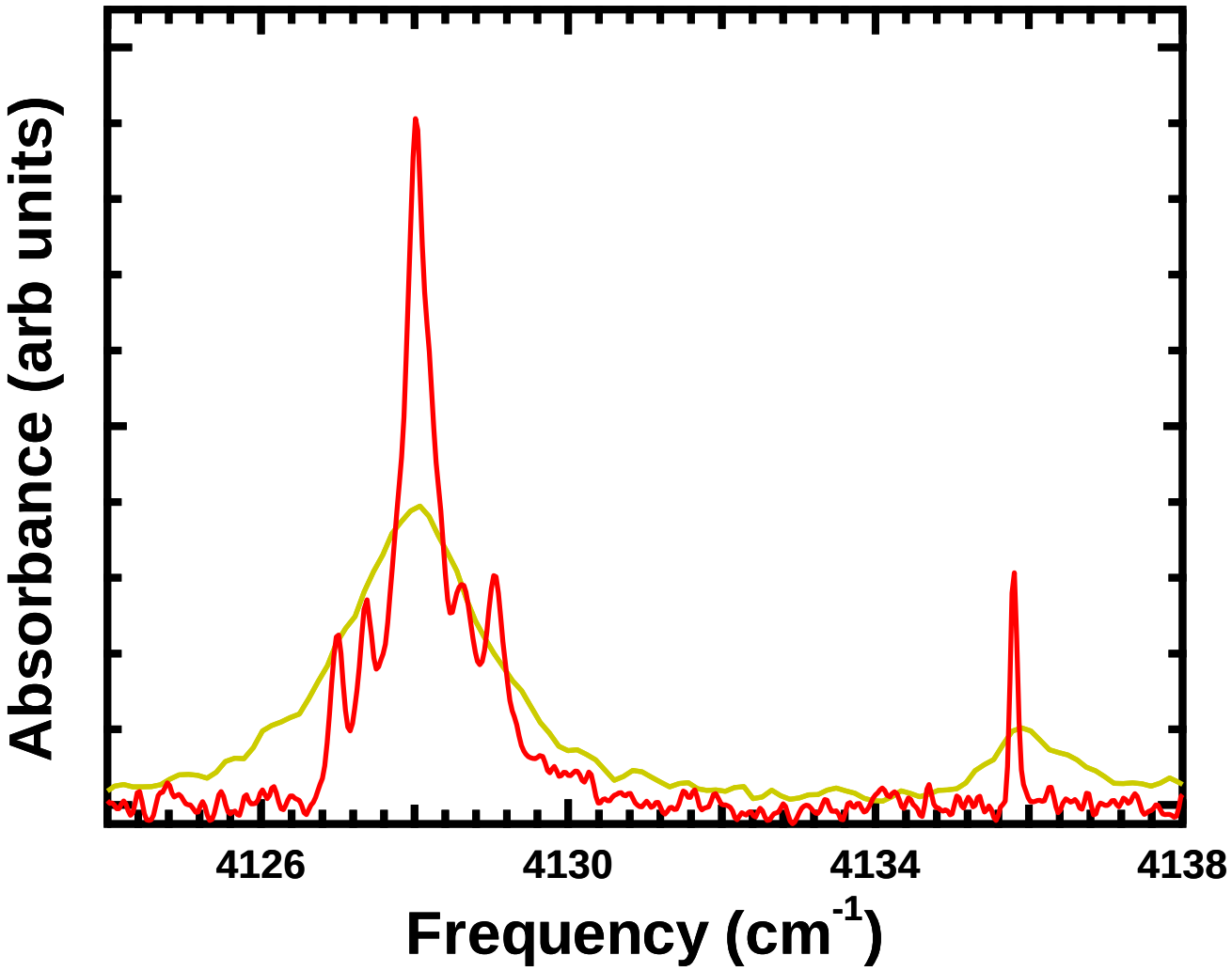



**One Shift**
**Two Shift**
**Red Shift**
**Blue Shift**

Phys. Rev. B **77**, 224301 (2008)



# MOF-5 Again



# Students on Our Papers

Kelty Allen

Ross Myers

Jenny Schloss

Jesse Hopkins

Brian Burkholder

Chris Pierce

Patrick Landreman

Michael Friedman

Elizabeth Gilmour

John Matters

Ben Thompson

Jocienne Nelson