

MOF-5: There and Back Again

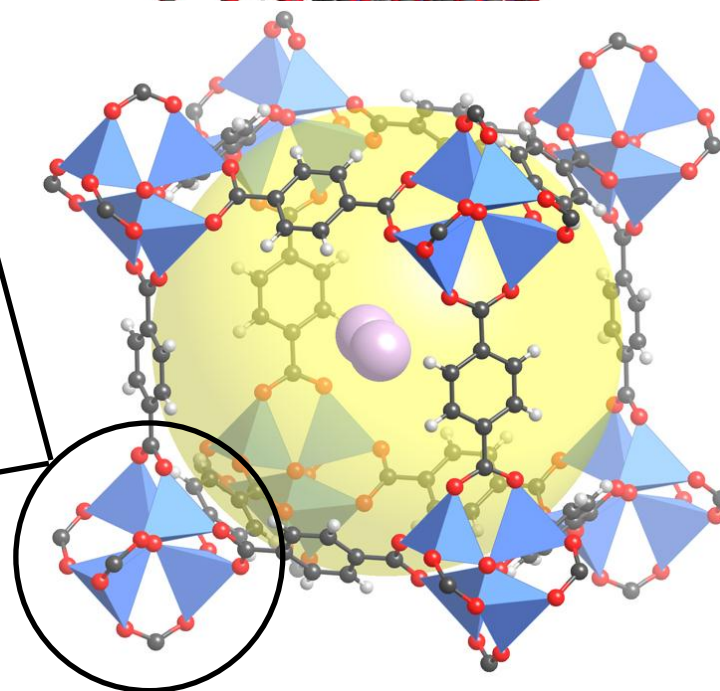
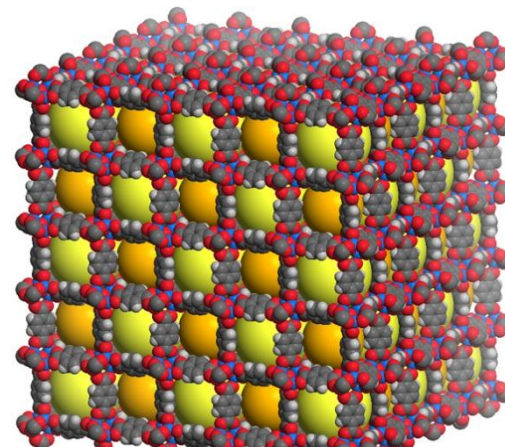
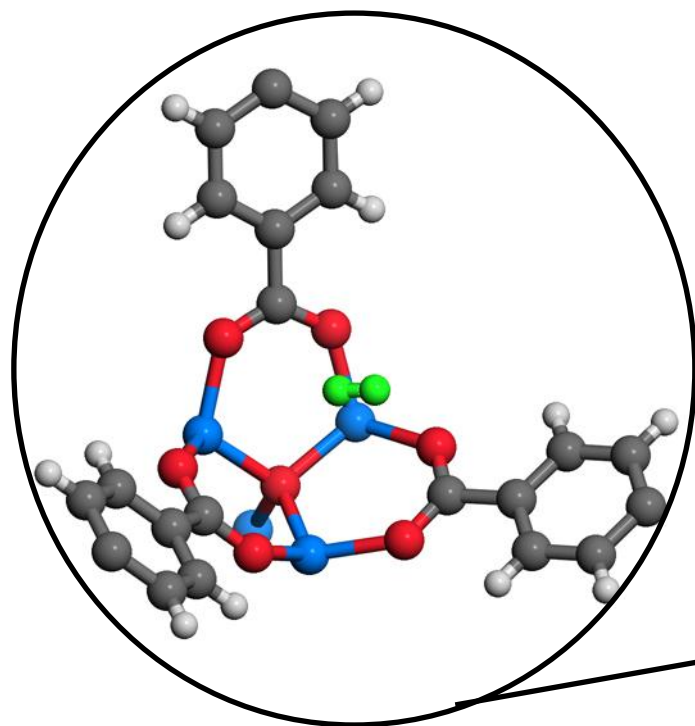
Outline

- 1) MOF-5: The start of a collaboration
- 2) H₂ and infrared: You're crazy
- 3) MOF-74: The beauty of a systematic series
- 4) CO₂: Something a bit different
- 5) MOF-5 again: The story continues

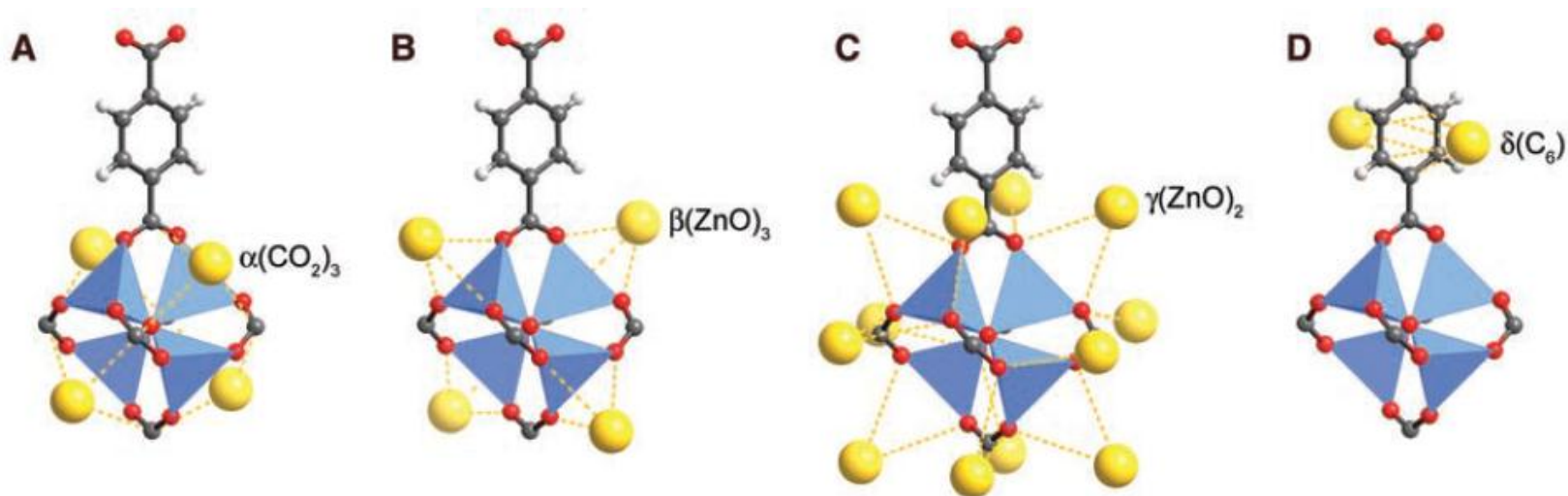
MOF-5: $Zn_4O(BDC)_3$

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

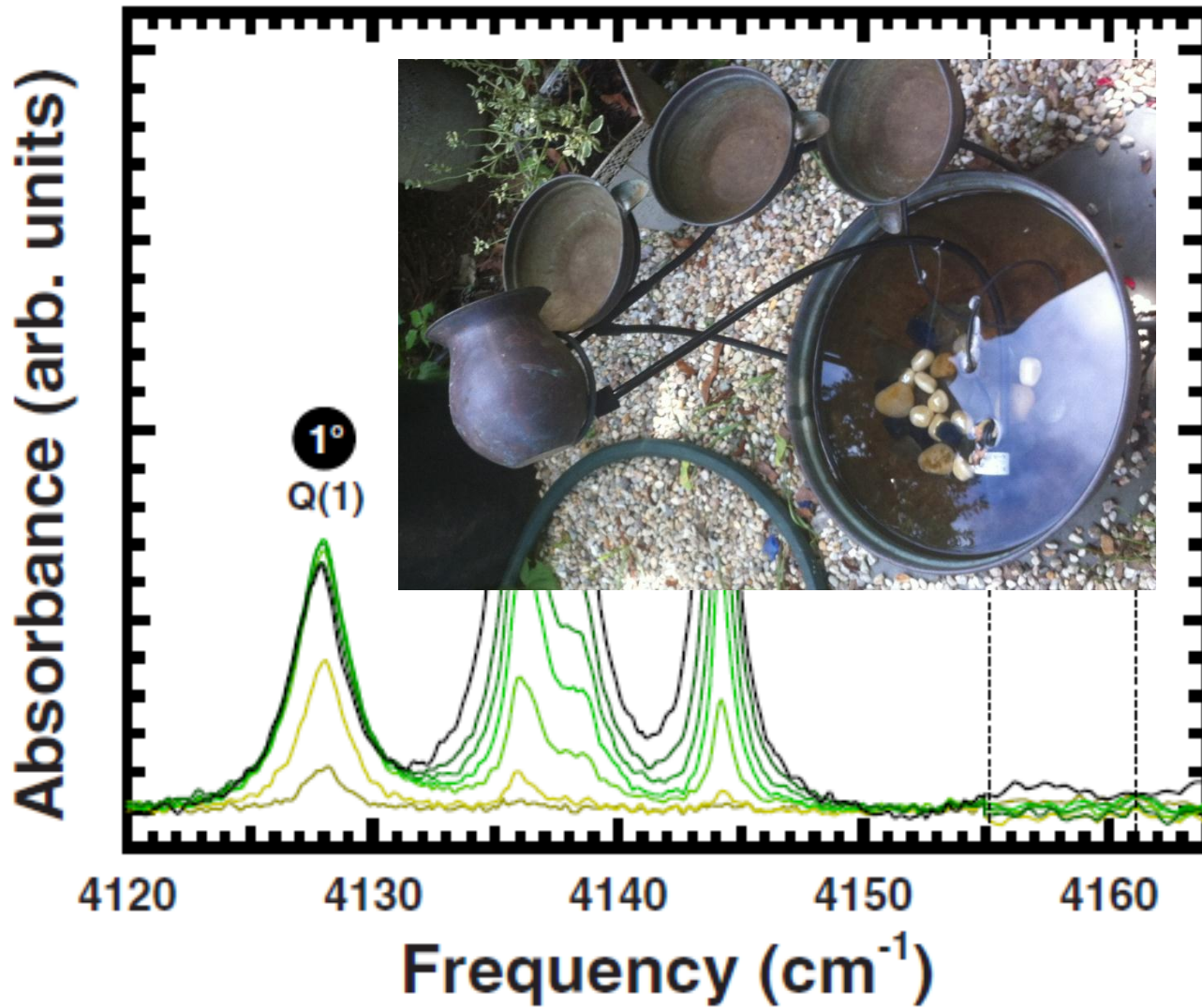
Blue = Zn
Red = O
Black = C
Green = H₂



Secondary Sites

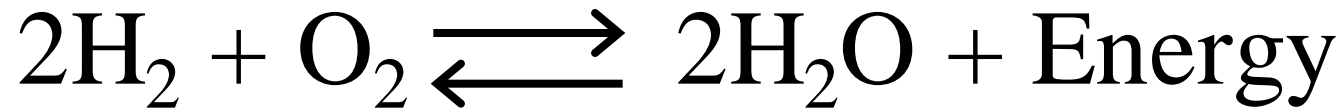


J.L.C. Rowsell, E.C. Spencer, J. Eckert, J. Howard, and O.M. Yaghi, *Science*, **309**, 1350 (2005)



Hydrogen Cycle

Fuel Cell **Batteries**



- **Electrolyze water using renewable energy or otherwise wasted energy**
- **Ideally it would all be done locally**

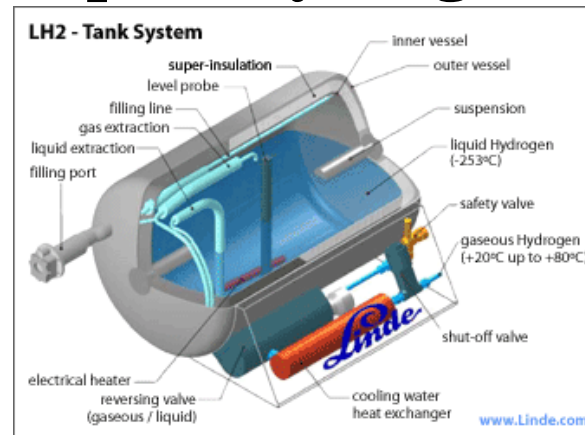


Hydrogen Storage for Fuel Cells



High Pressure
350-700 bar

Liquid Hydrogen



Need a light weight “hydrogen sponge”

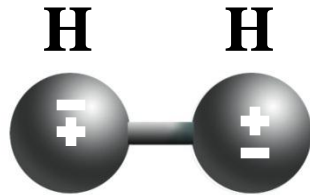
Highly porous materials exist

Problem is hydrogen sticks either too weakly or too strongly

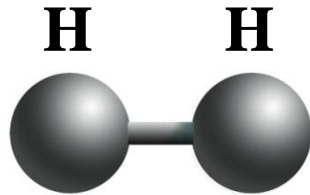
Need “post-it note” stickiness

Need technique to probe H₂ interactions

Infrared Spectroscopy! Are you crazy?

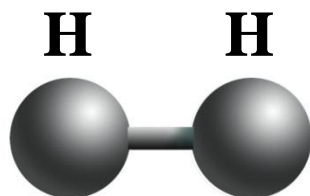


Infrared Spectroscopy! Are you crazy?

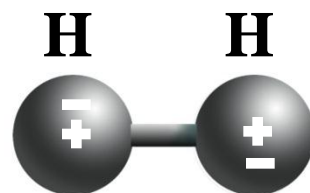


The atoms are neutral

Infrared Spectroscopy! Are you crazy?

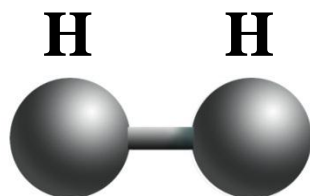


The atoms are neutral

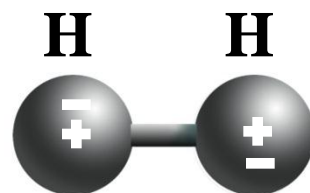


**Interactions with “sponge”
can induce charge
separation**

Infrared Spectroscopy! Are you crazy?

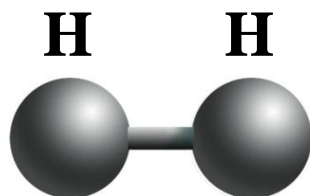


The atoms are neutral

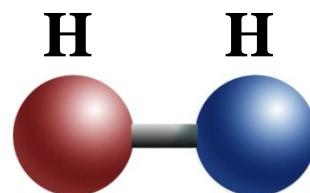


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Infrared Spectroscopy! Are you crazy?

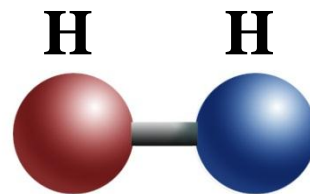
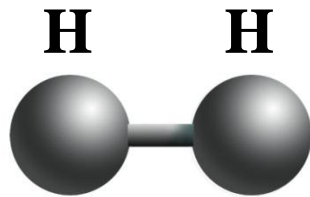


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Infrared Spectroscopy! Are you crazy?

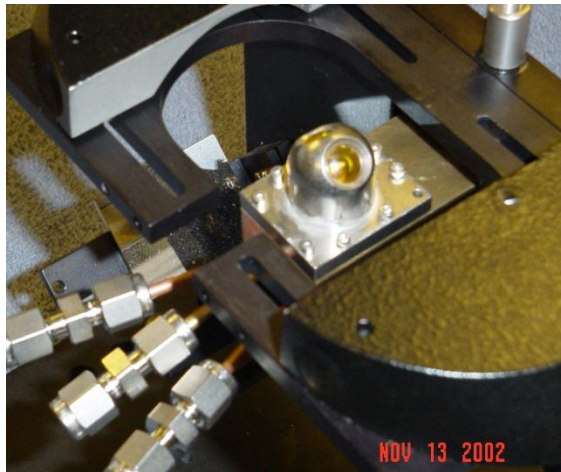
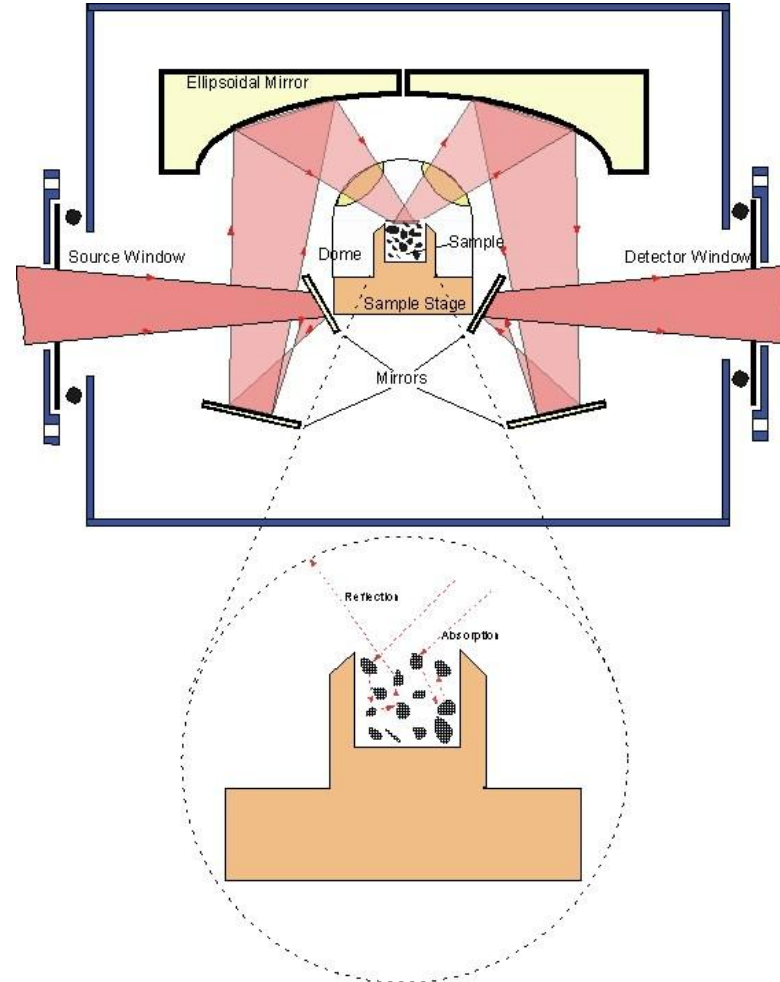


Interactions with “host”
can induce a dipole moment

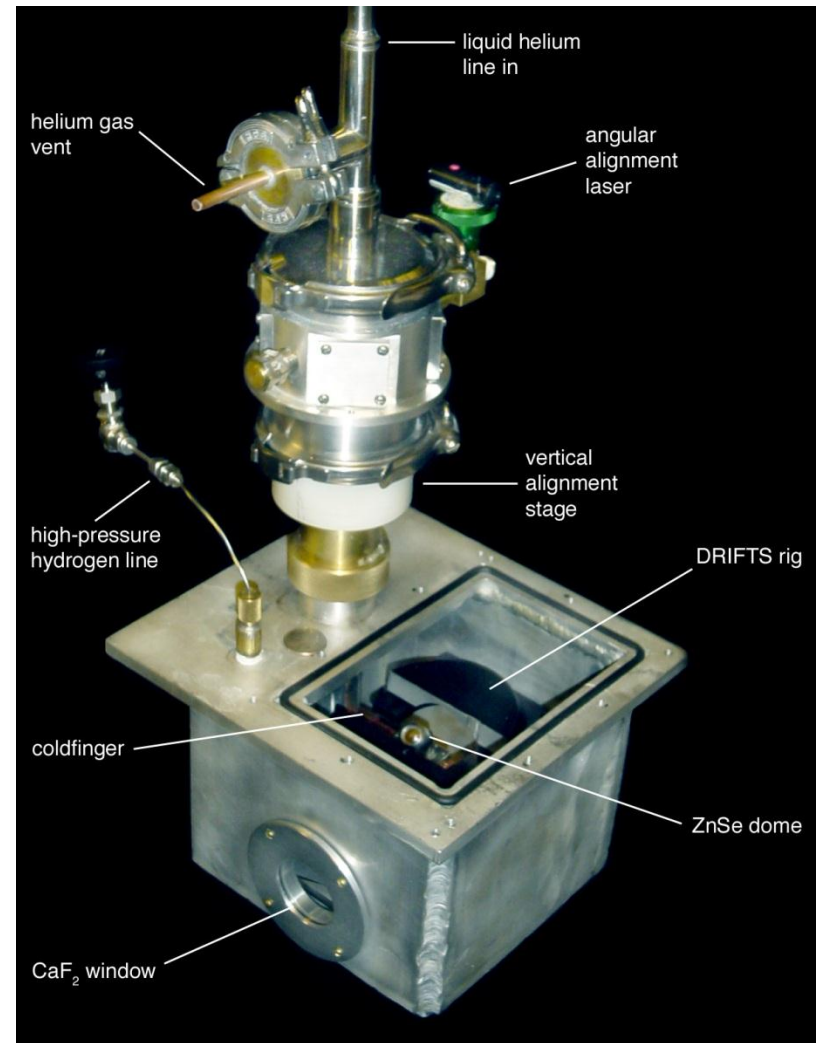
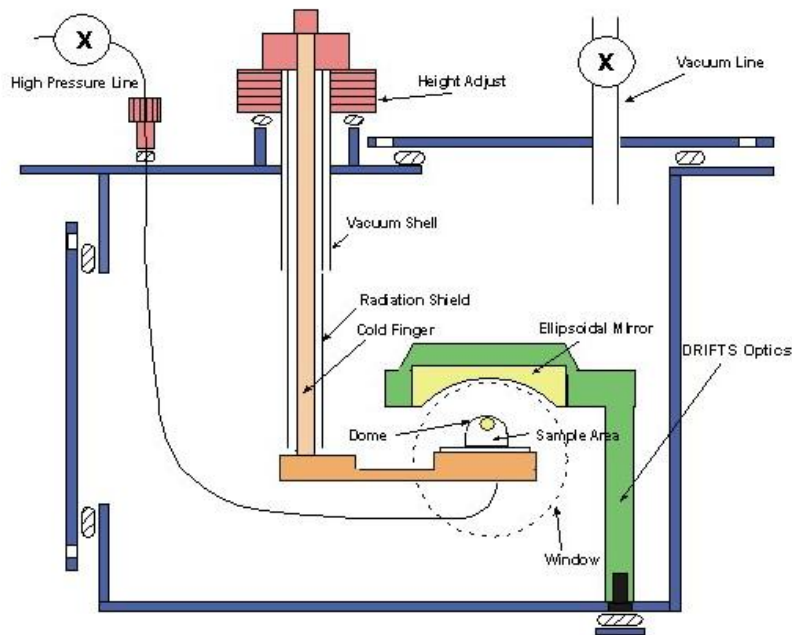
**Induced dipole moment is typically weak so
special technique is required to enhance signal**

Diffuse Reflectance Spectroscopy

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

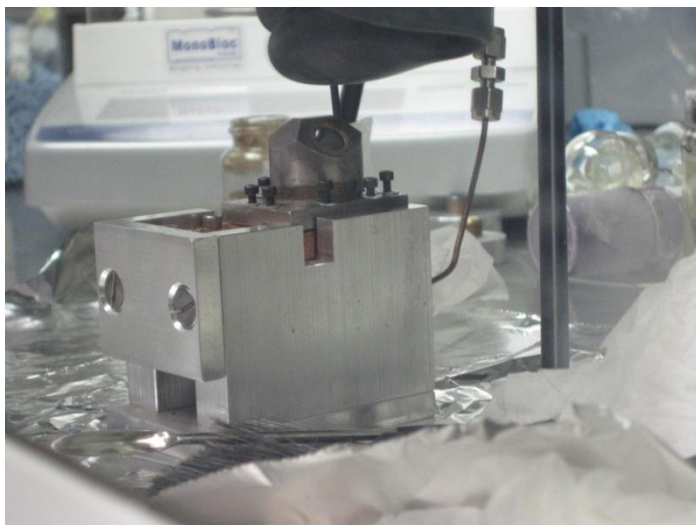
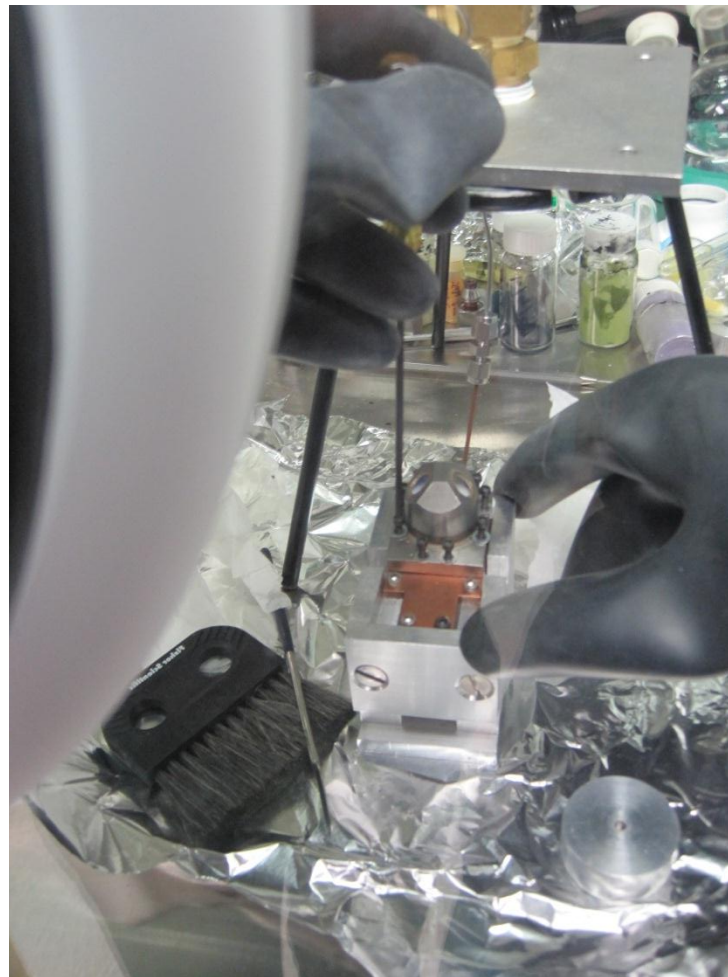
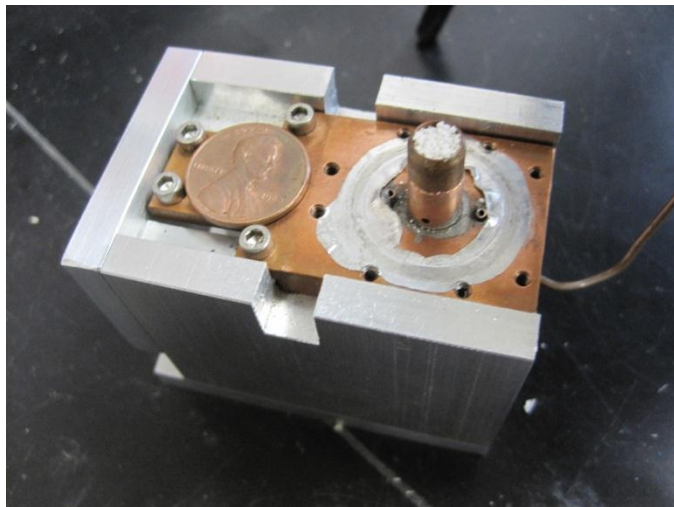


Diffuse Reflectance Spectroscopy: Cryostat Assembly



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

Samples are mounted in a glove-box

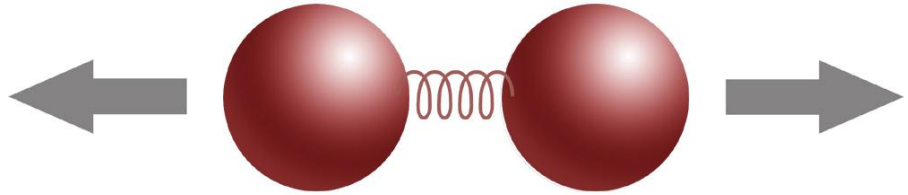


Quantum Dynamics of Adsorbed H₂

- Vibration

$$E_\nu = (\nu + 1/2) \nu_0$$

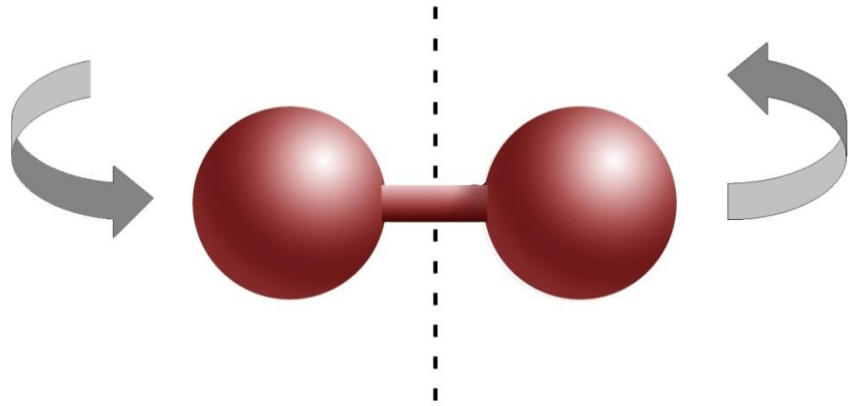
$$\nu_0 = 4161 \text{ cm}^{-1} \text{ for free H}_2$$



- Rotation

$$E_J = J(J + 1)B_0$$

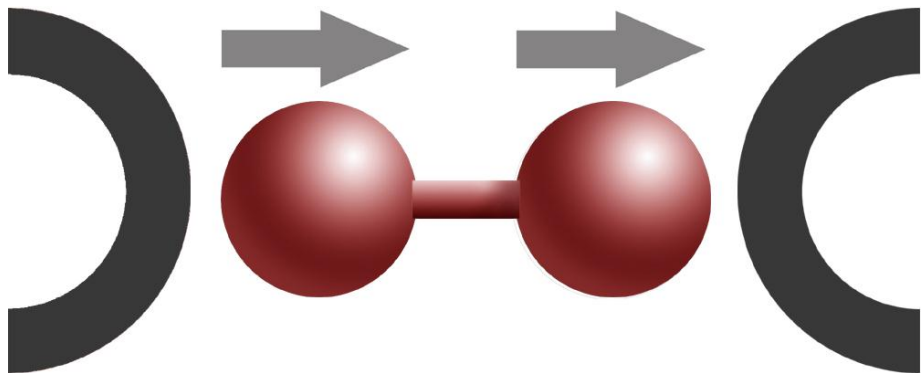
$$B_0 = 59 \text{ cm}^{-1} \text{ for free H}_2$$



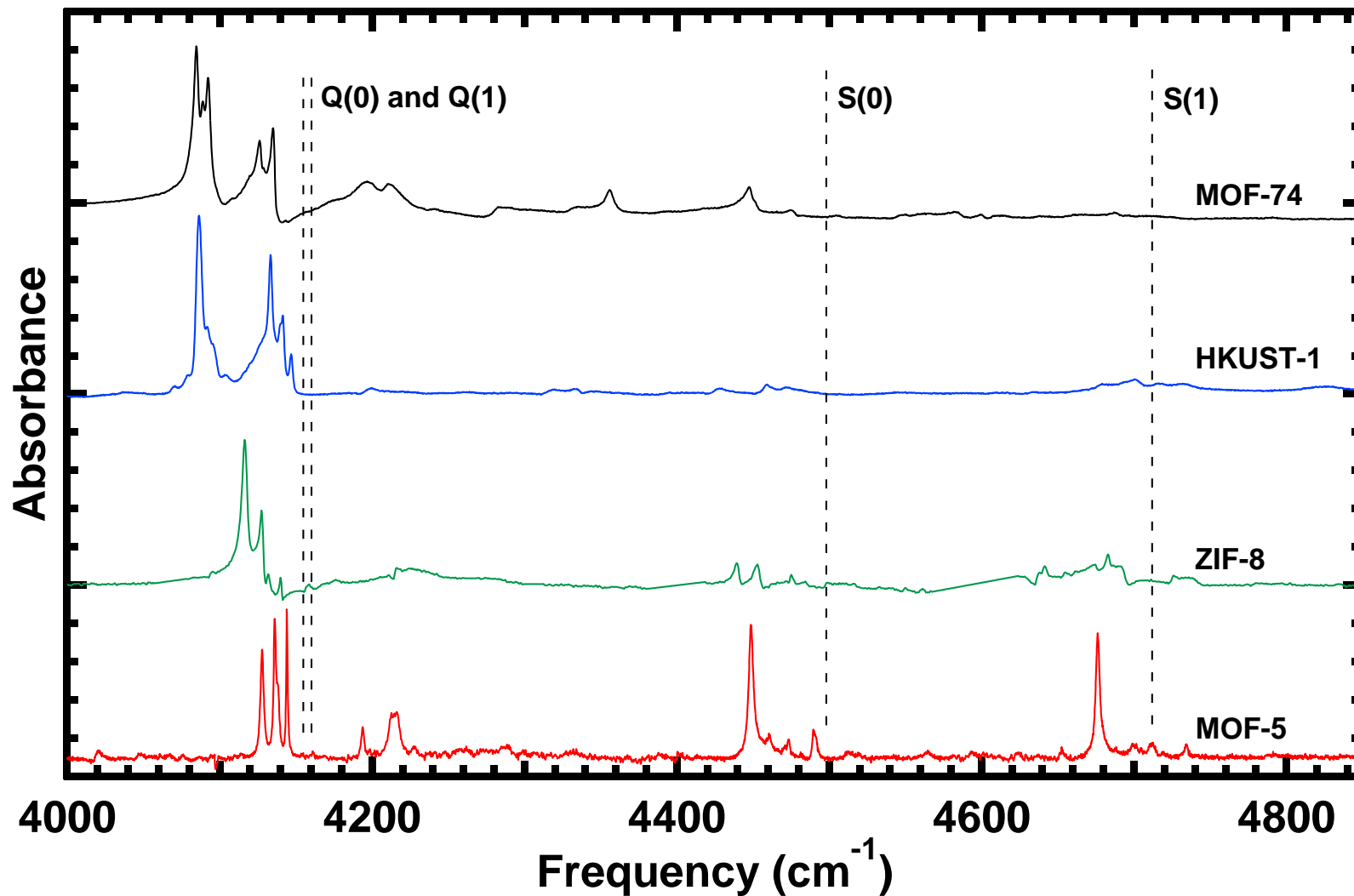
- Translation

Center-of-mass

On the order of 150 cm⁻¹



Typical Spectra for H₂ in MOFs at 30 K



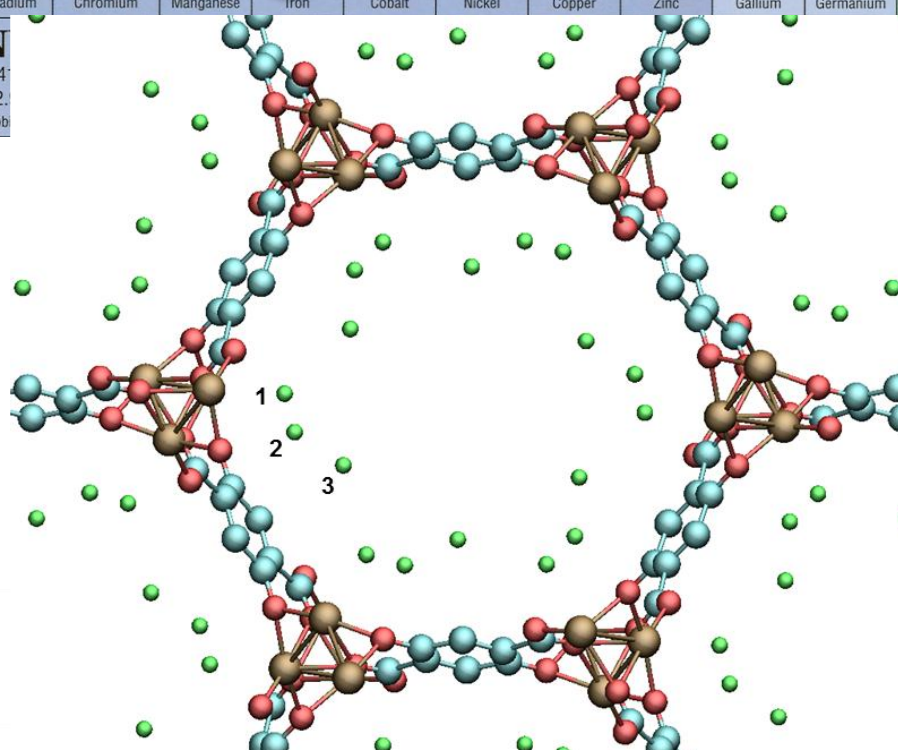
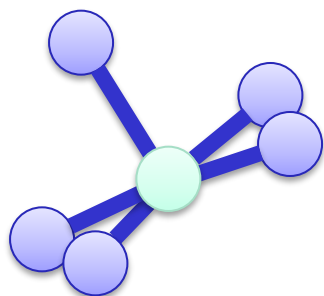
MOF-74 Isostructural Series

Same structure, different metal

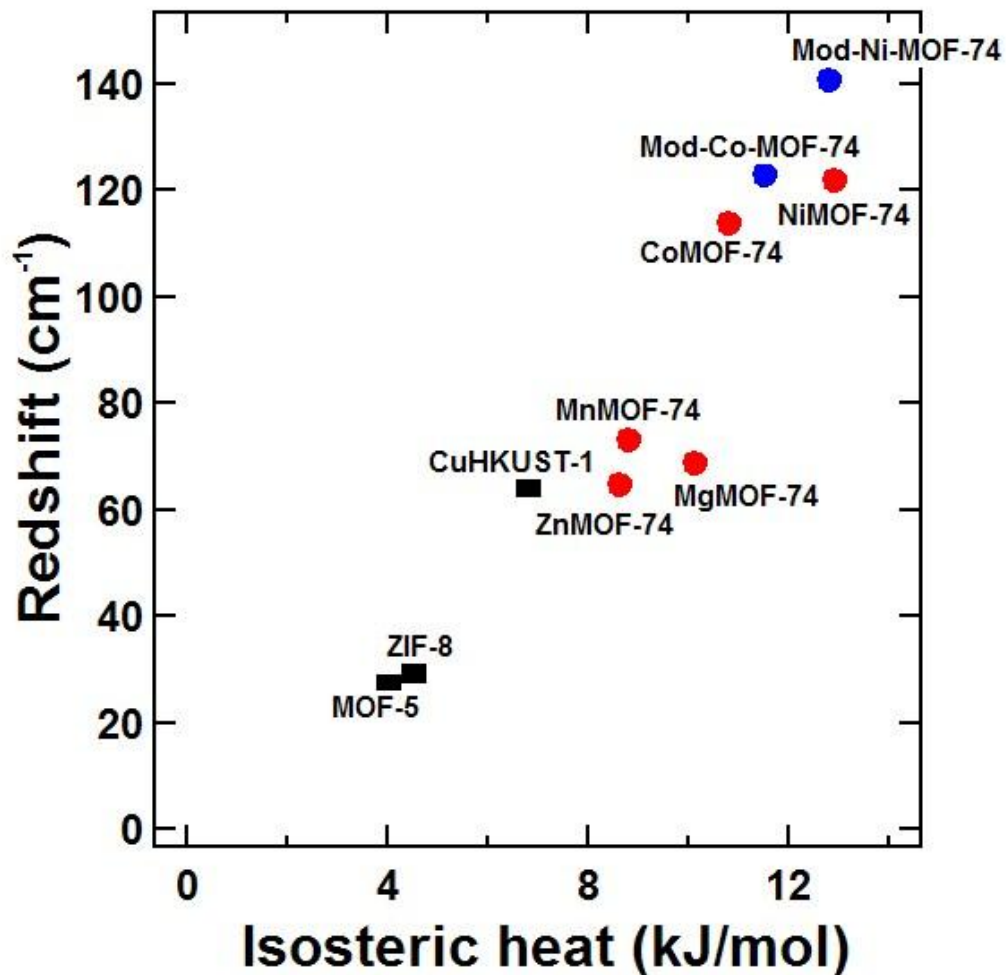
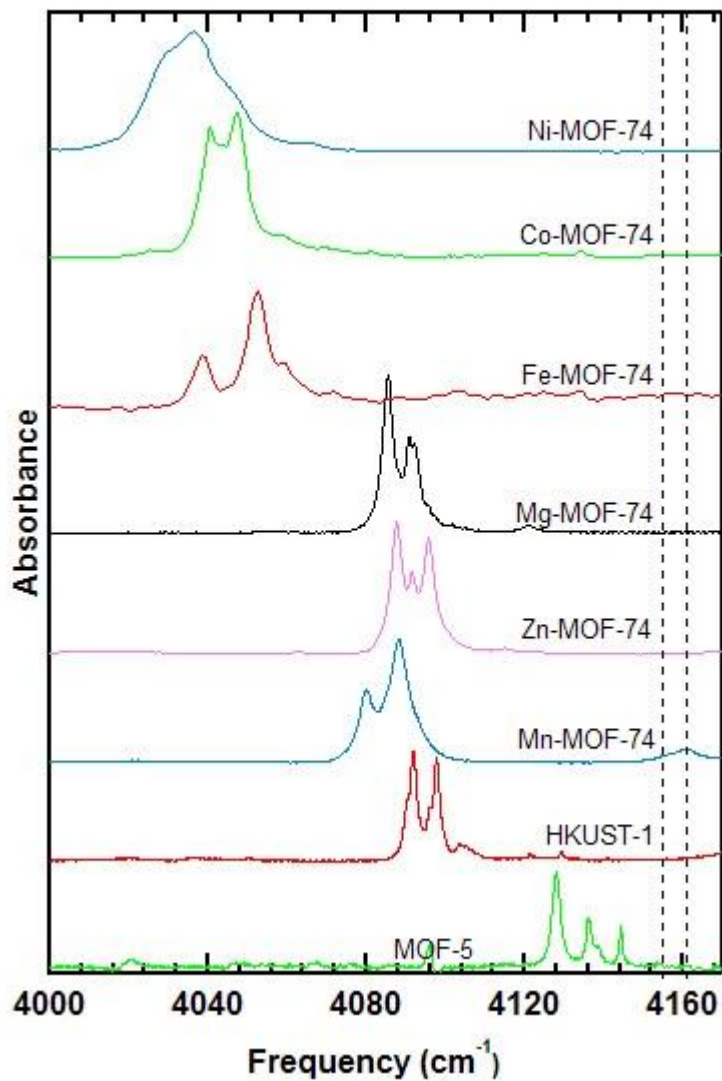
1	H 1 1.008 Hydrogen											13	14	15	16	17	2	
2	Li 3 6.94 Lithium	Be 4 9.01 Beryllium											B 5 10.81 Boron	C 6 12.01 Carbon	N 7 14.01 Nitrogen	O 8 16.00 Oxygen	F 9 19.00 Fluorine	Ne 10 20.18 Neon
3	Na 11 22.99 Sodium	Mg 12 24.31 Magnesium	3 <i>IIIB</i>	4 <i>IVB</i>	5 <i>VB</i>	6 <i>VIB</i>	7 <i>VII B</i>	8	9	10	11 <i>IB</i>	12 <i>IIB</i>	Al 13 26.98 Aluminum	Si 14 28.09 Silicon	P 15 30.97 Phosphorus	S 16 32.07 Sulfur	Cl 17 35.45 Chlorine	Ar 18 39.95 Argon
4	K 19 39.10 Potassium	Ca 20 40.08 Calcium	Sc 21 44.96 Scandium	Ti 22 47.88 Titanium	V 23 50.94 Vanadium	Cr 24 52.00 Chromium	Mn 25 54.94 Manganese	Fe 26 55.85 Iron	Co 27 58.93 Cobalt	Ni 28 58.69 Nickel	Cu 29 63.55 Copper	Zn 30 65.39 Zinc	Ga 31 69.72 Gallium	Ge 32 72.61 Germanium	As 33 74.92 Arsenic	Se 34 78.96 Selenium	Br 35 79.90 Bromine	Kr 36 83.80 Krypton
5	Rb 37 85.47 Rubidium	Sr 38 87.62 Strontium	Y 39 88.91 Yttrium	Zr 40 91.22 Zirconium	Nb 41 92.91 Niobium							Sb 51 121.76 Antimony	Te 52 127.60 Tellurium	I 53 126.90 Iodine	Xe 54 131.29 Xenon			

H — SYMBOL
1 — ATOMIC NUMBER
1.008 — ATOMIC WEIGHT
Hydrogen — NAME

() = ESTIMATES

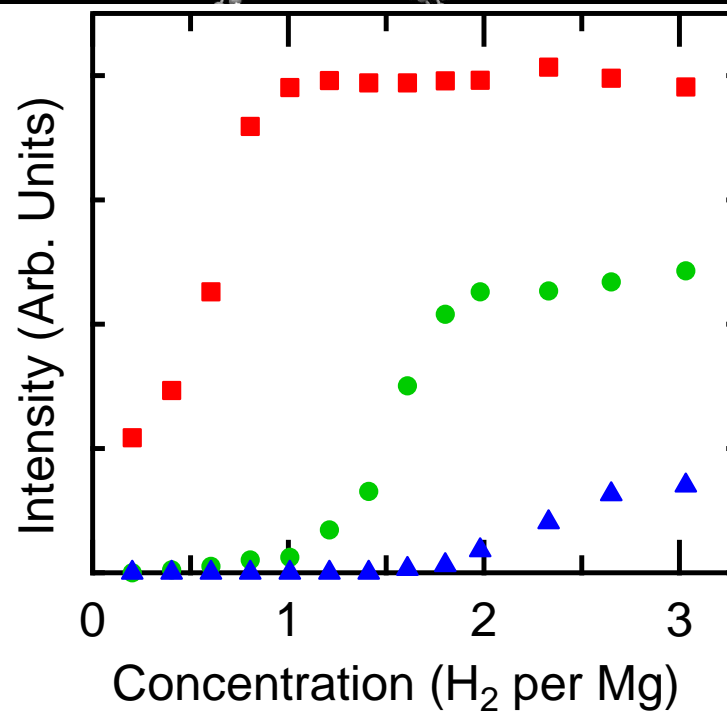
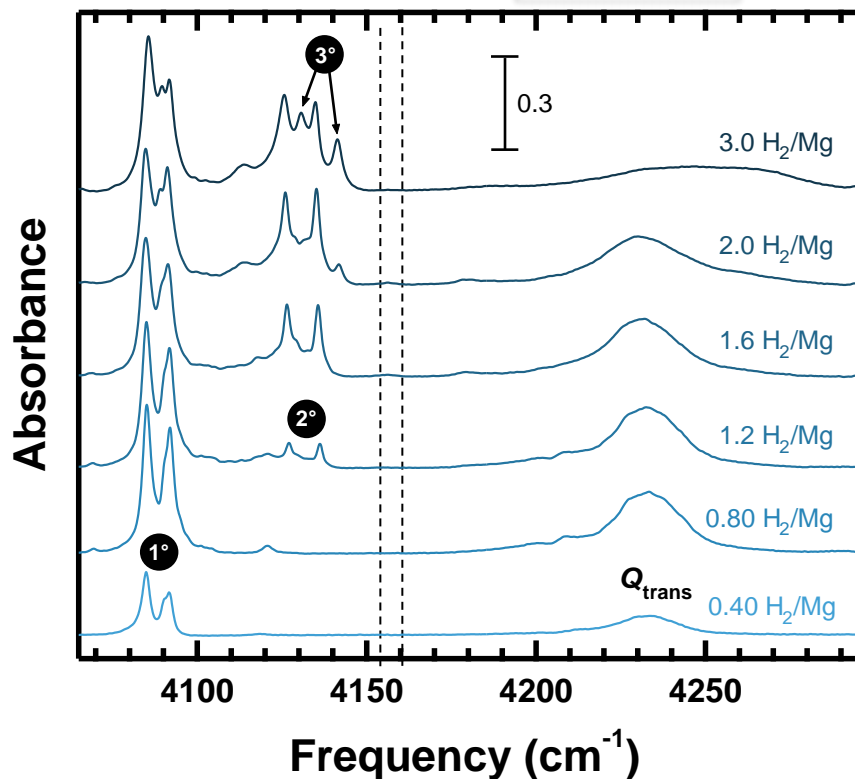
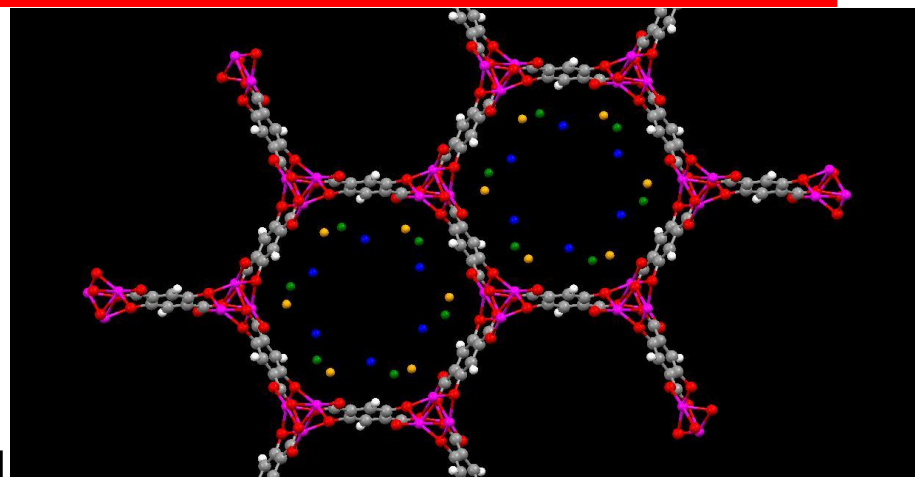
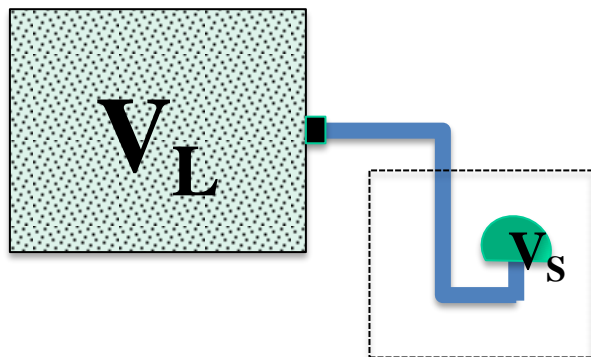


Vibrational shift and binding energy?



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

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

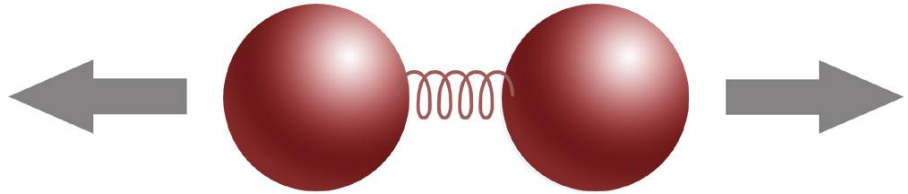


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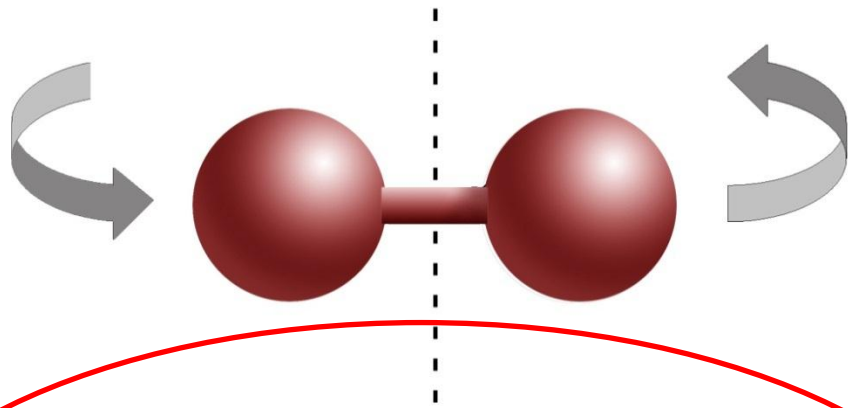
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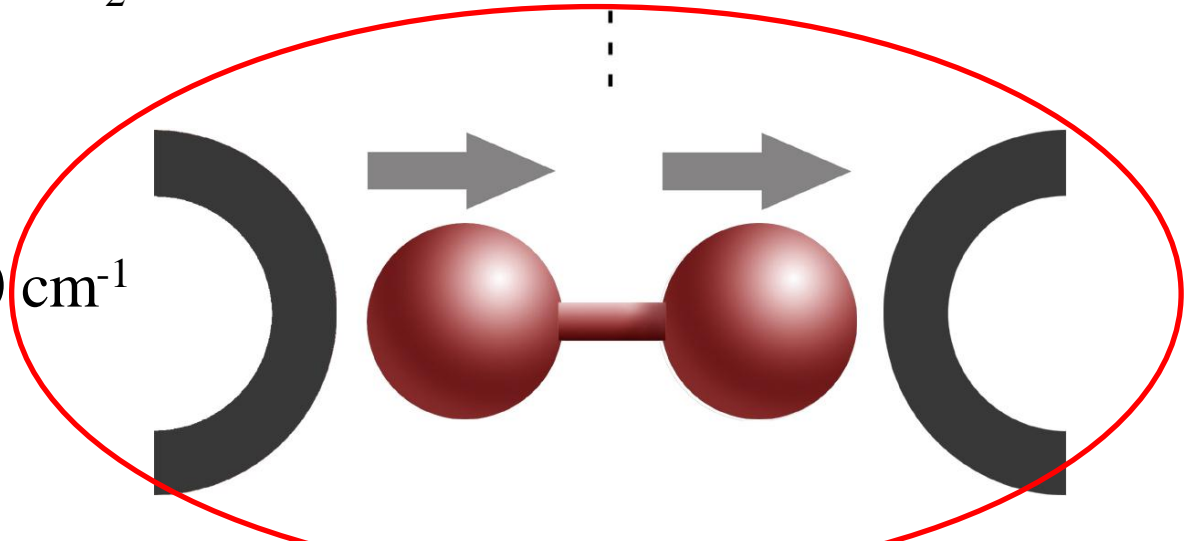
$$B_0 = 59 \text{ cm}^{-1} \text{ for free H}_2$$



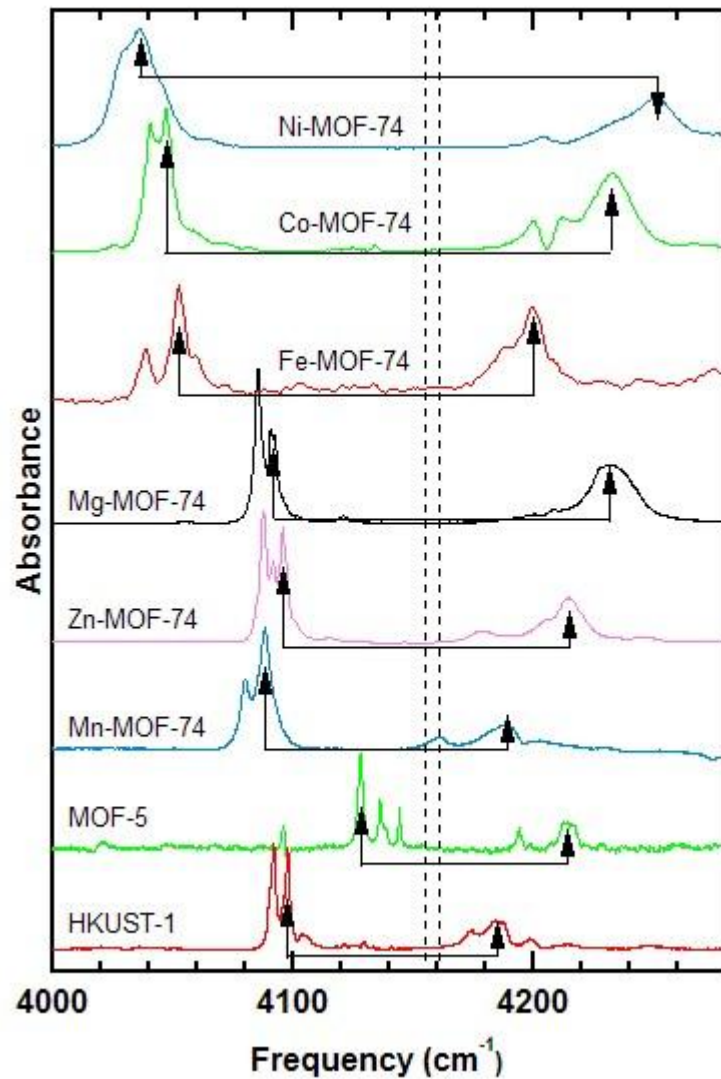
- Translation

Center-of-mass

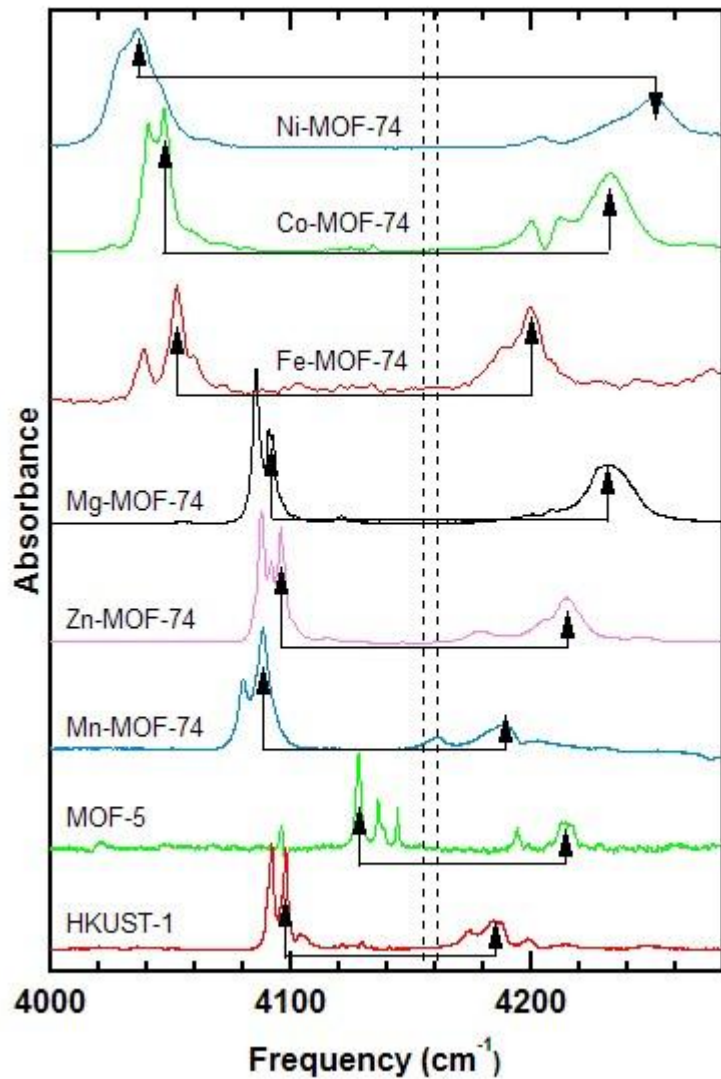
On the order of 150 cm⁻¹



Translational mode energy (quantum sieving?)



Back of the Envelope Calculation



$$ZPE = \frac{3}{2} h \omega$$

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

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

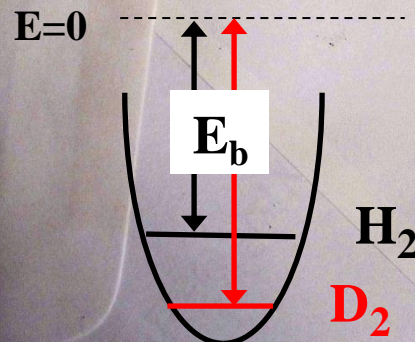
$$\omega_{D_2} = \frac{1}{\sqrt{2}} \omega_{H_2}$$

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

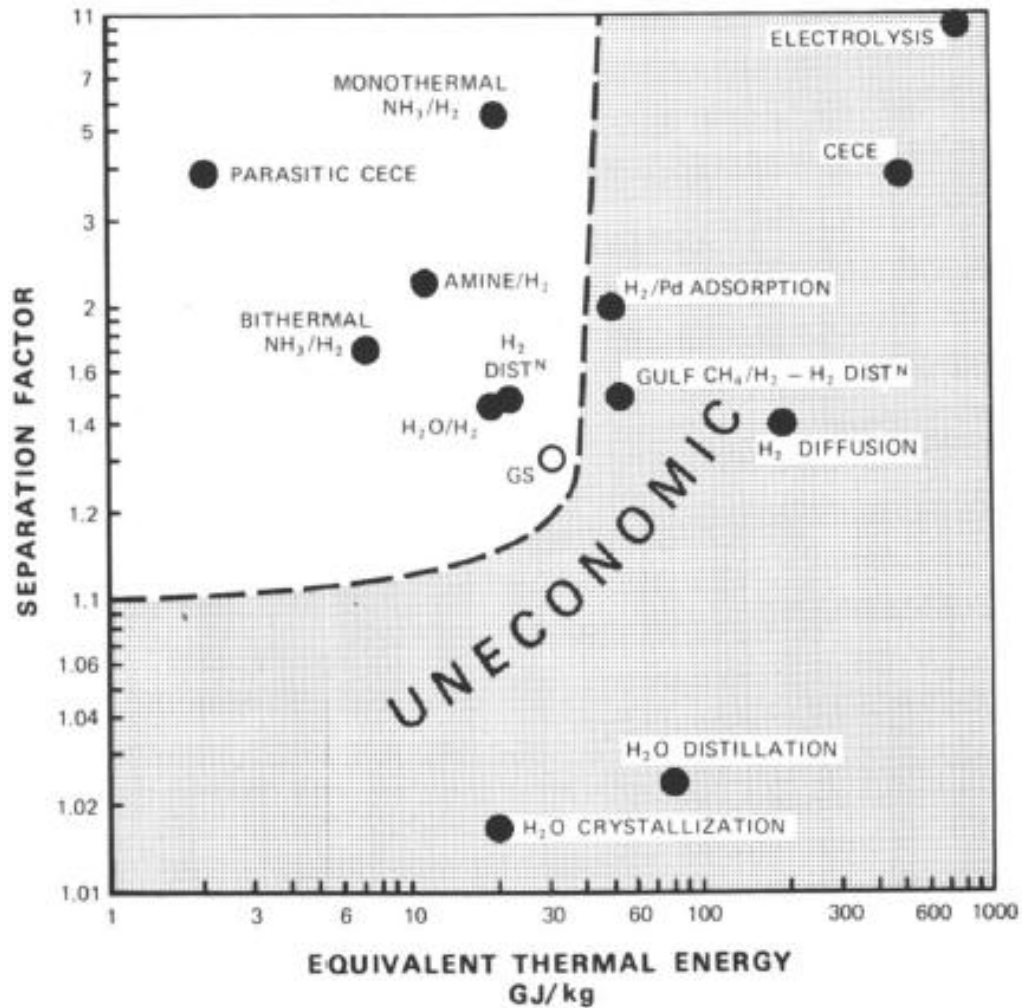
$$\Delta ZPE = 120 \text{ K}$$

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

$$e^{120/77} = 4.75$$

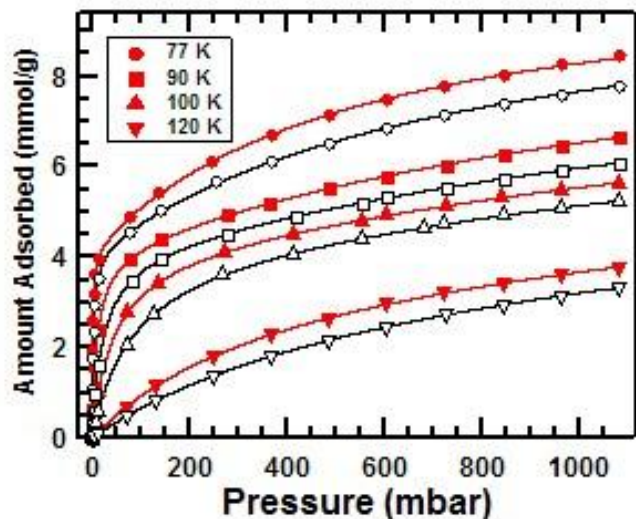


Standard Separation Techniques



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

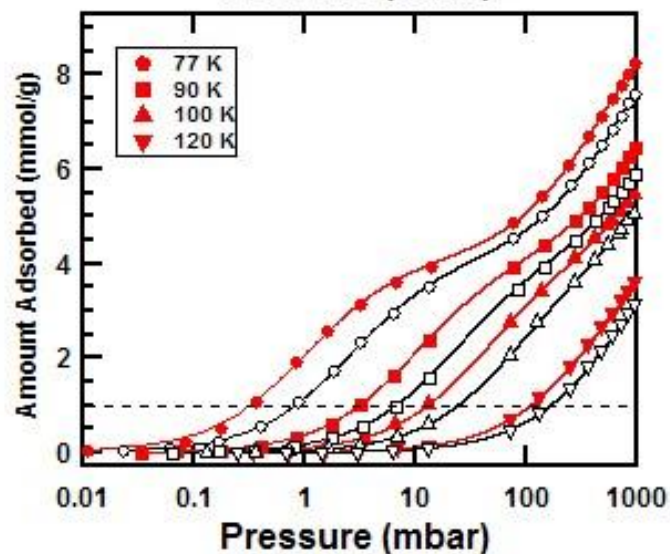
D₂ vs H₂ Isotherms in Fe-MOF-74



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

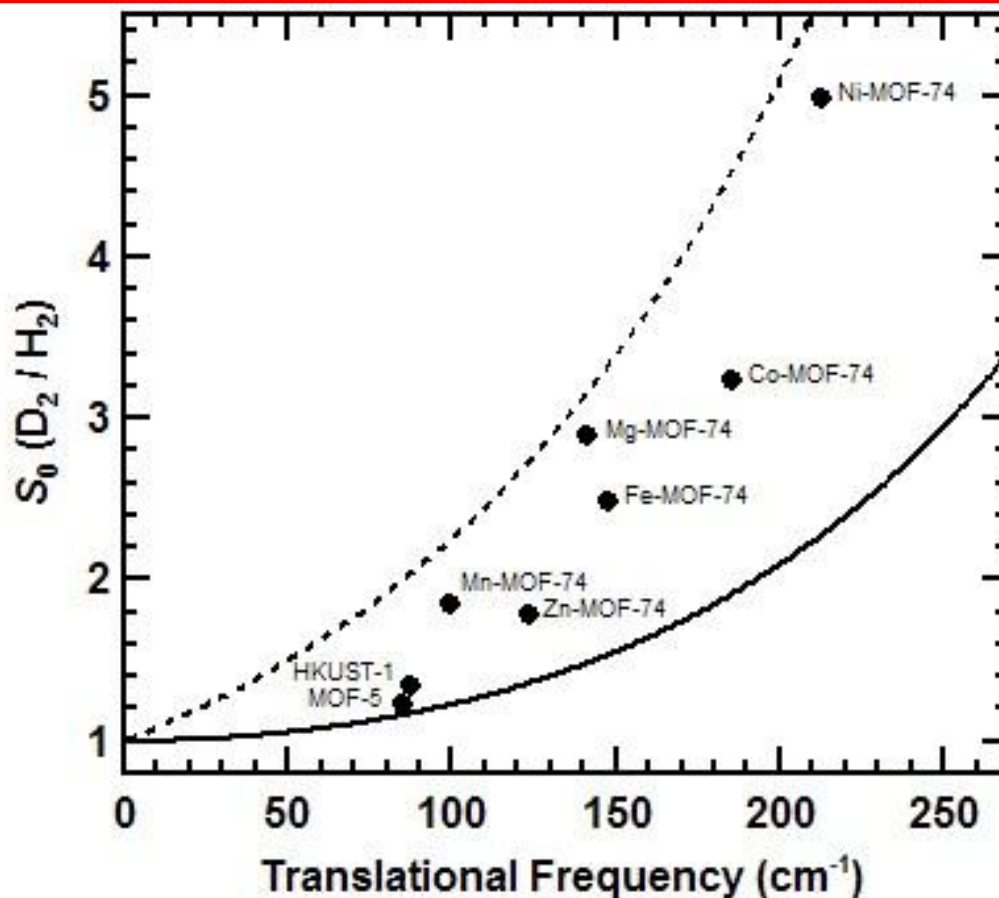
Fits are based on constrained two-site Langmuir isotherm

D₂ (red) consistently higher than H₂ (black)



D₂/H₂ Ratio increases with decreasing temperature

Selectivity vs Translational Frequency

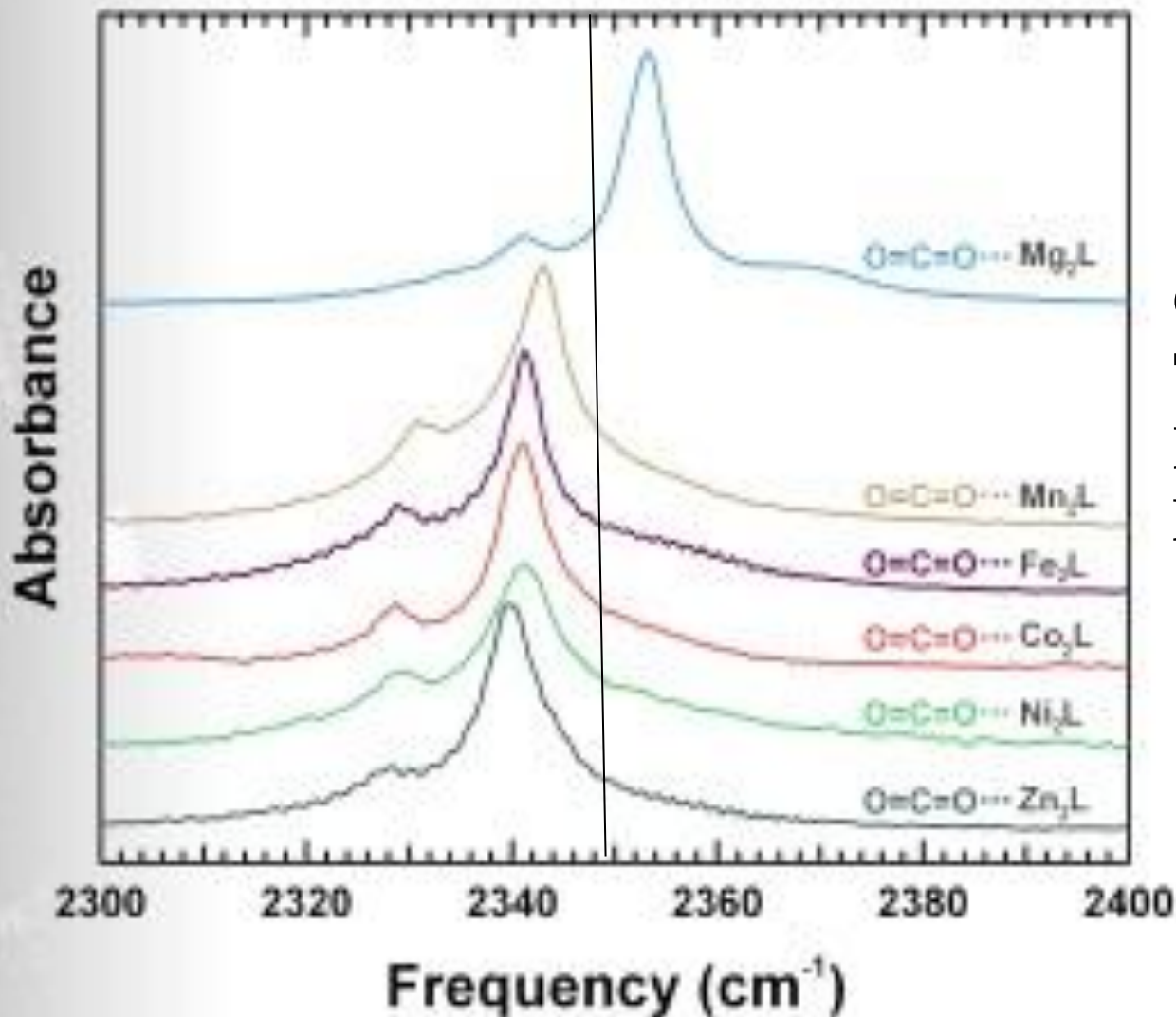


Dashed line shows simple back of the envelope

Solid line shows full (harmonic) thermodynamic calculation

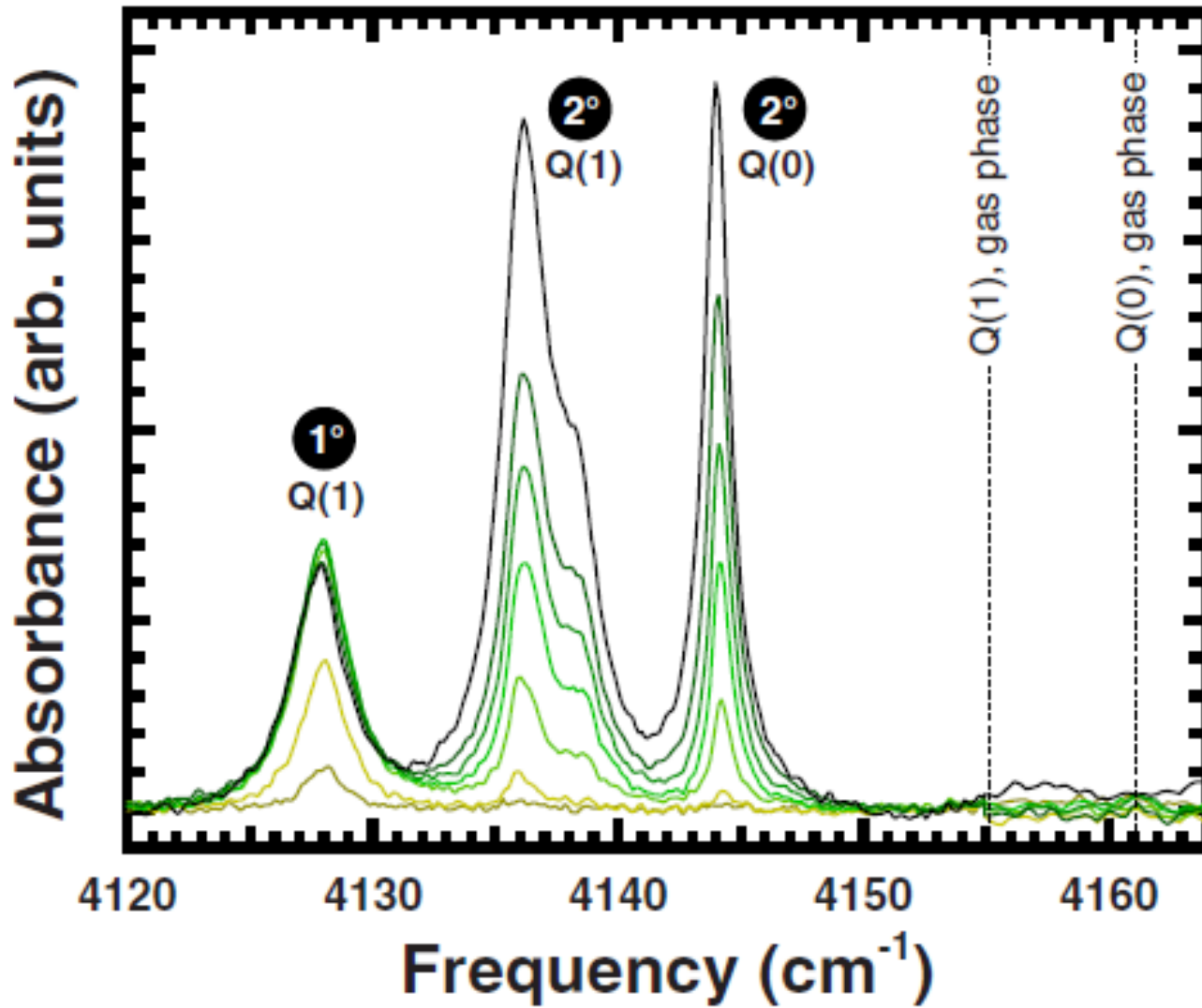
CO₂ in Different Metal MOF-74

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

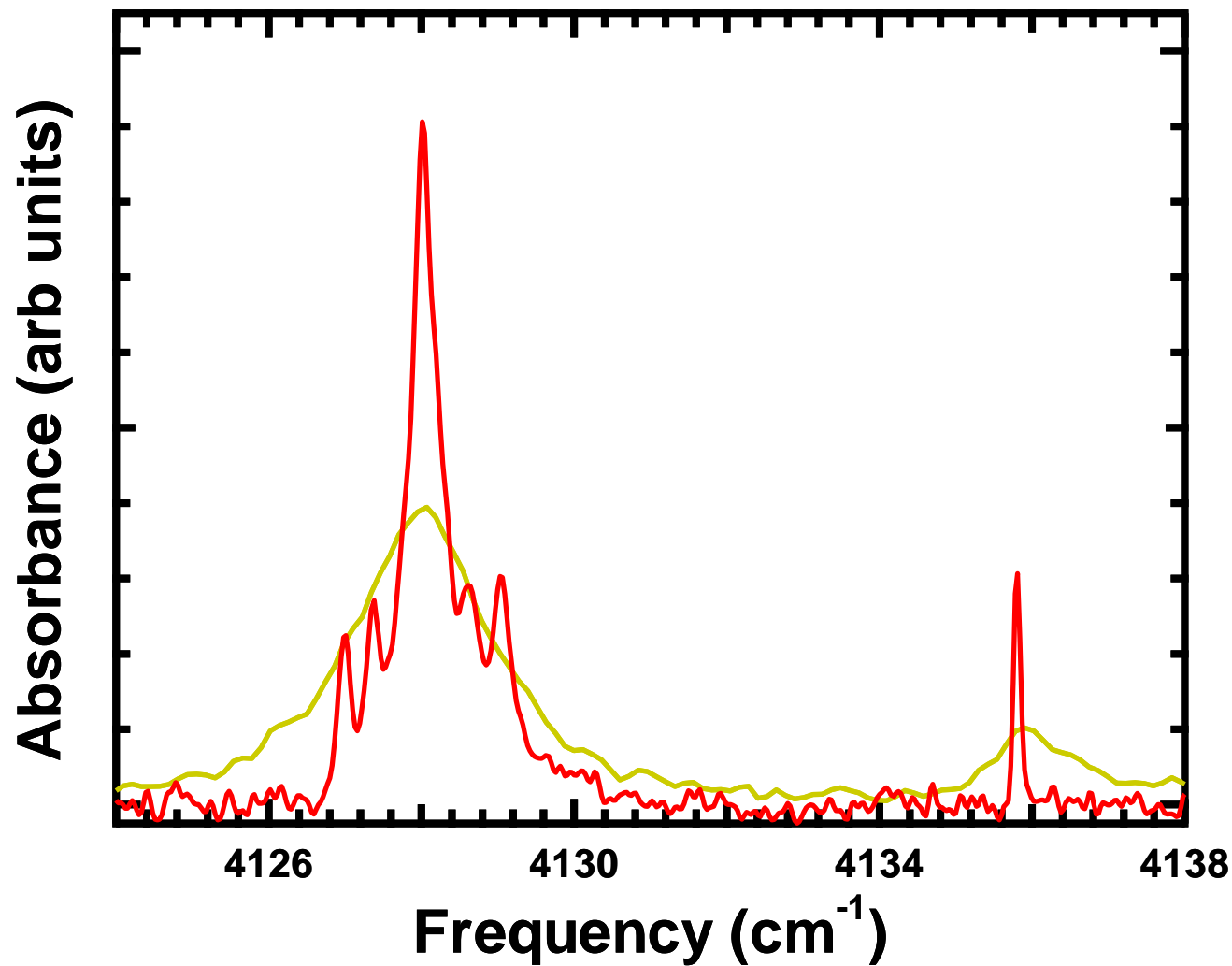


One Shift
Two Shift
Red Shift
Blue Shift

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**

