

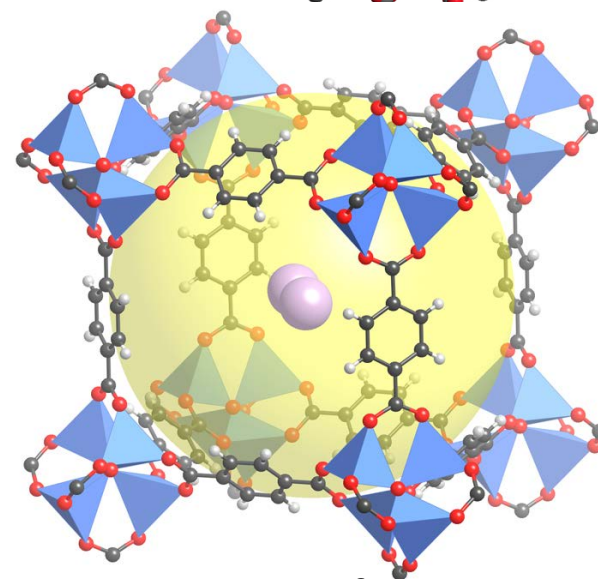
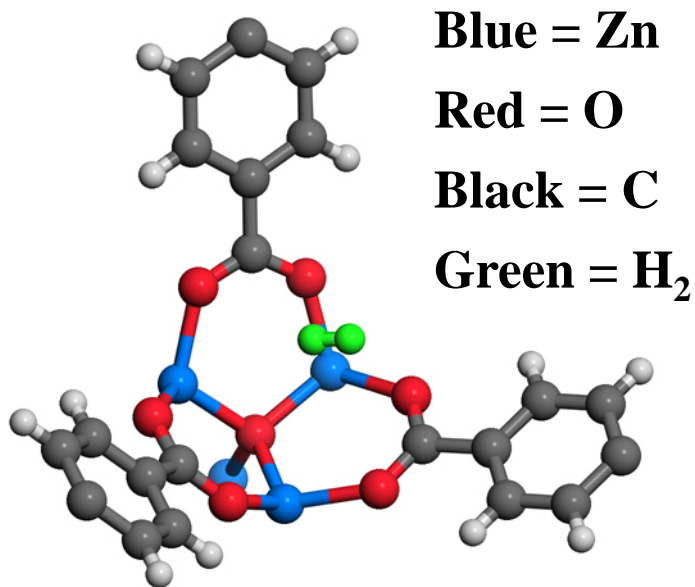
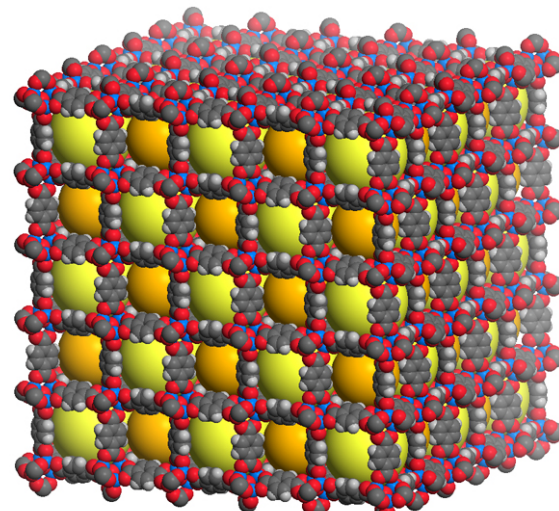
Site Selective Spectroscopy

Interactions of Adsorbed H₂ in MOFs

1. Metal-organic frameworks
2. Infrared spectroscopy and H₂!?
3. Unusual experimental approach
4. Site specific information of H₂···MOF interactions
5. Determining the binding mechanism

Metal-Organic Frameworks

- Act like a 3-D “Tinker Toy”
- Metal ions linked by organic chains
- MOF-5: Cubic lattice with ~ 15 Å voids in the center



Images courtesy of Jesse Rowsell

MOFs: Tunable Highly Porous Structures

1. Gas Storage

Need “post-it note” stickiness

2. Gas Separation

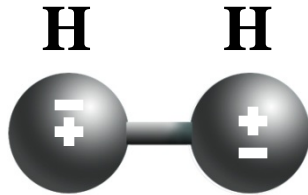
Maximize the difference in interaction energy

3. Catalysis

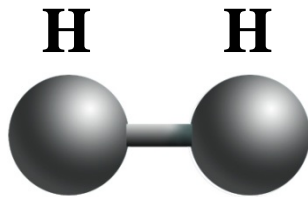
Understand reaction mechanisms and effects of confinement

Need technique to probe adsorbate interactions

Infrared Spectroscopy! Are you crazy?



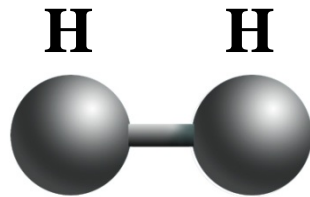
Infrared Spectroscopy! Are you crazy?



The atoms are neutral

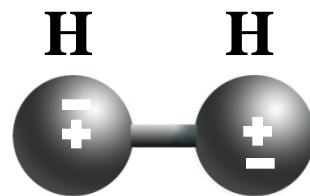
No Dipole moment

Infrared Spectroscopy! Are you crazy?



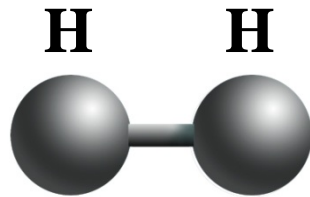
The atoms are neutral

No Dipole moment



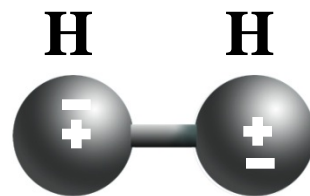
**Interactions with MOF can
polarize H₂**

Infrared Spectroscopy! Are you crazy?



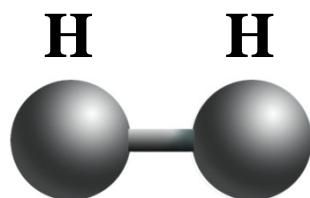
The atoms are neutral

No Dipole moment



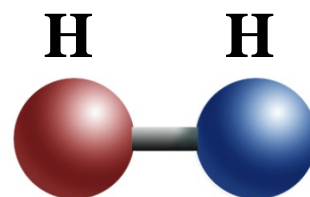
**Interactions with MOF can
polarize H₂**

Infrared Spectroscopy! Are you crazy?



The atoms are neutral

No Dipole moment

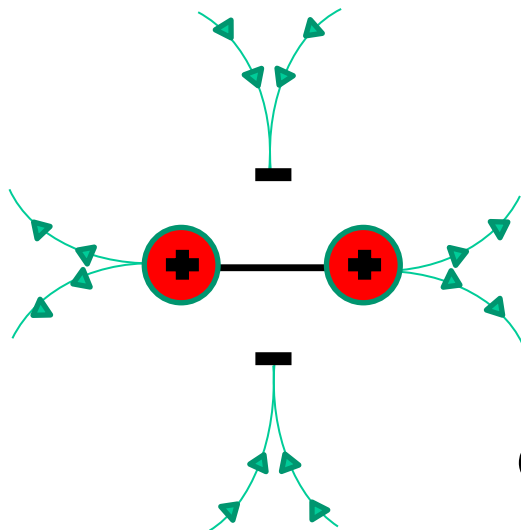


Interactions with MOF can
polarize H₂

H₂ polarizability is almost isotropic

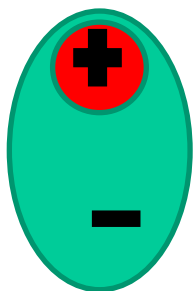
Mostly activates pure vibrational transitions

H₂ Quadrupole Mechanism



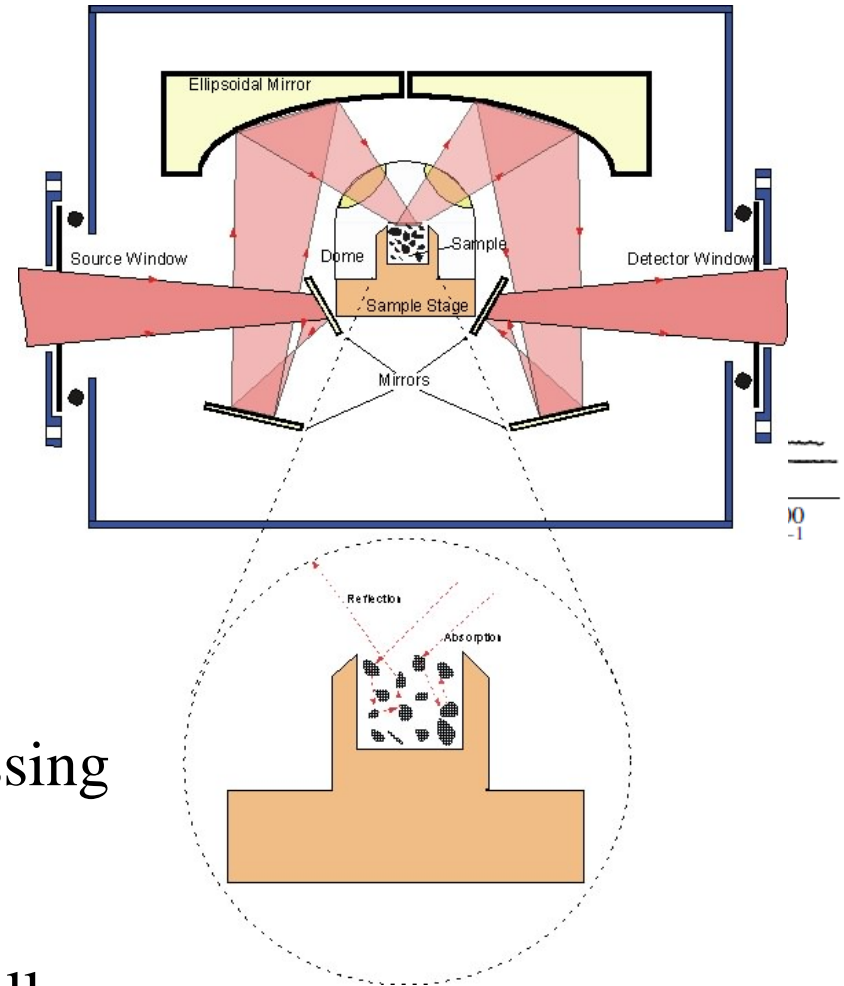
H₂ quadrupole moment can polarize MOF atoms

**Quadrupole moment highly anisotropic
Vibrations and Ro-vibrations are activated**



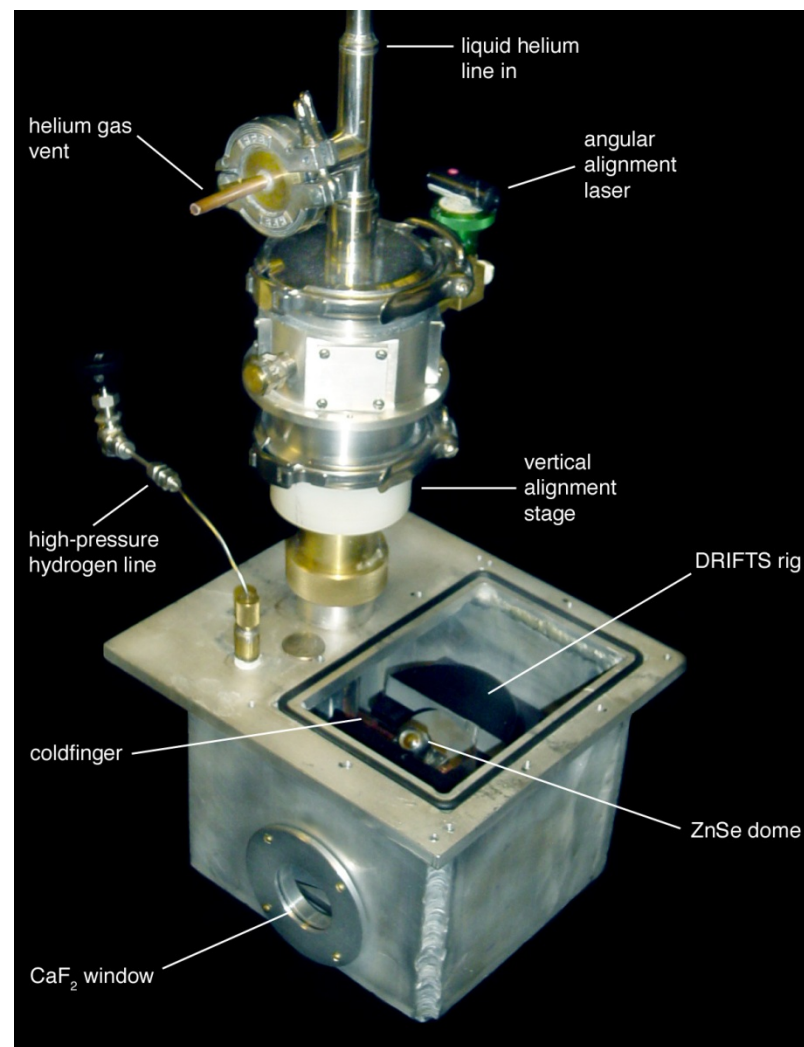
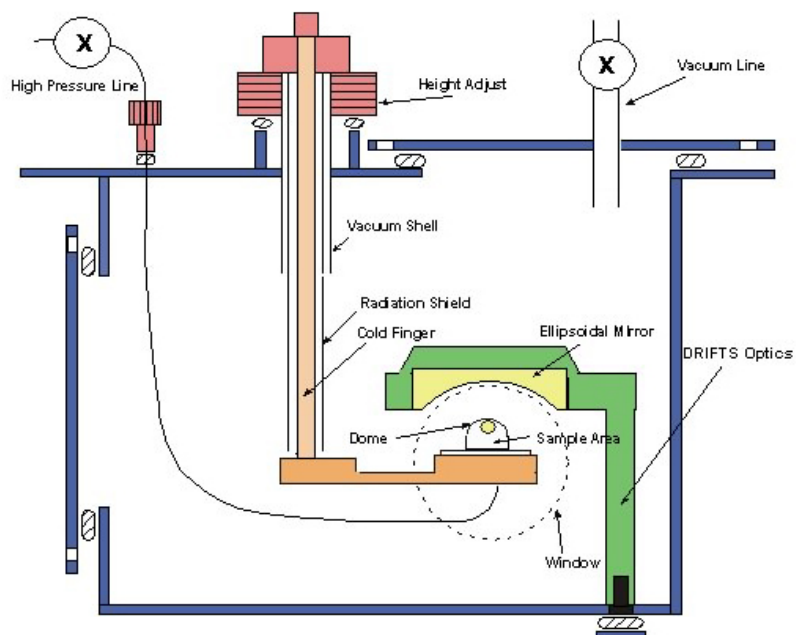
Hydrogen polarizes MOF atoms

Diffuse Reflectance Infrared Spectroscopy



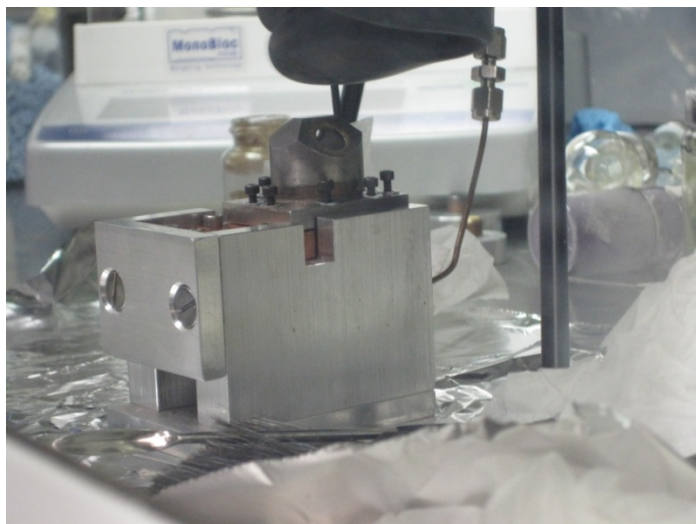
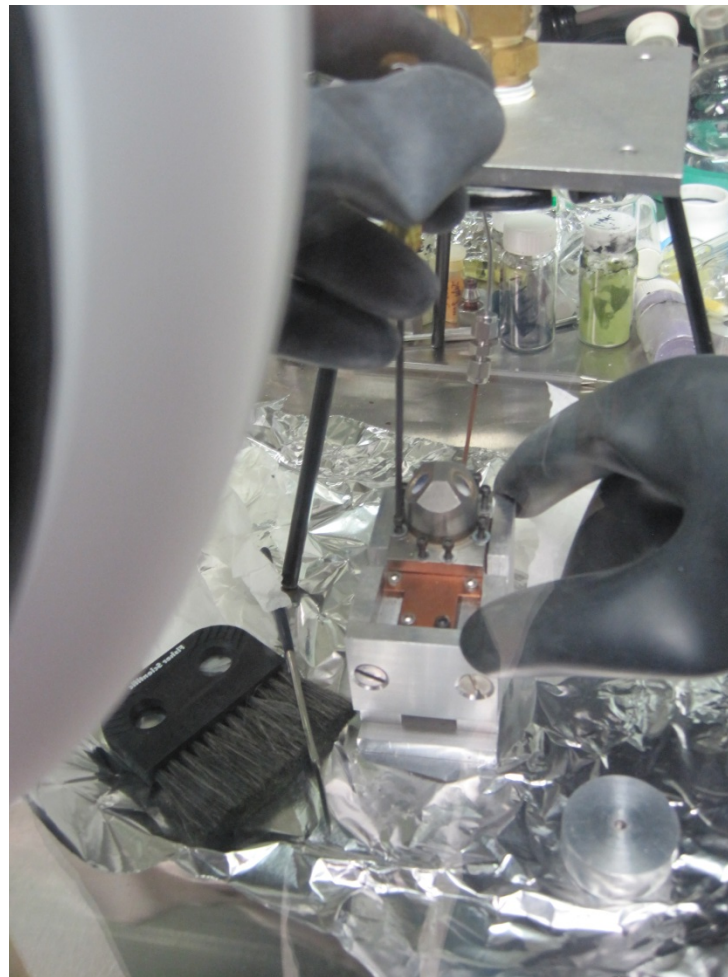
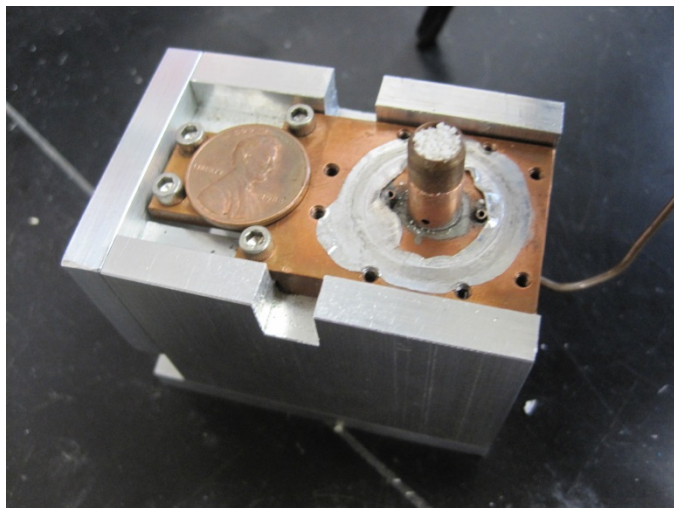
- 1) Long effective optical path length
- 2) Powder sample require no processing
- 3) Typically use 10 mg of powder
- 4) Sample chamber can be quite small

Diffuse Reflectance Spectroscopy: Cryostat Assembly

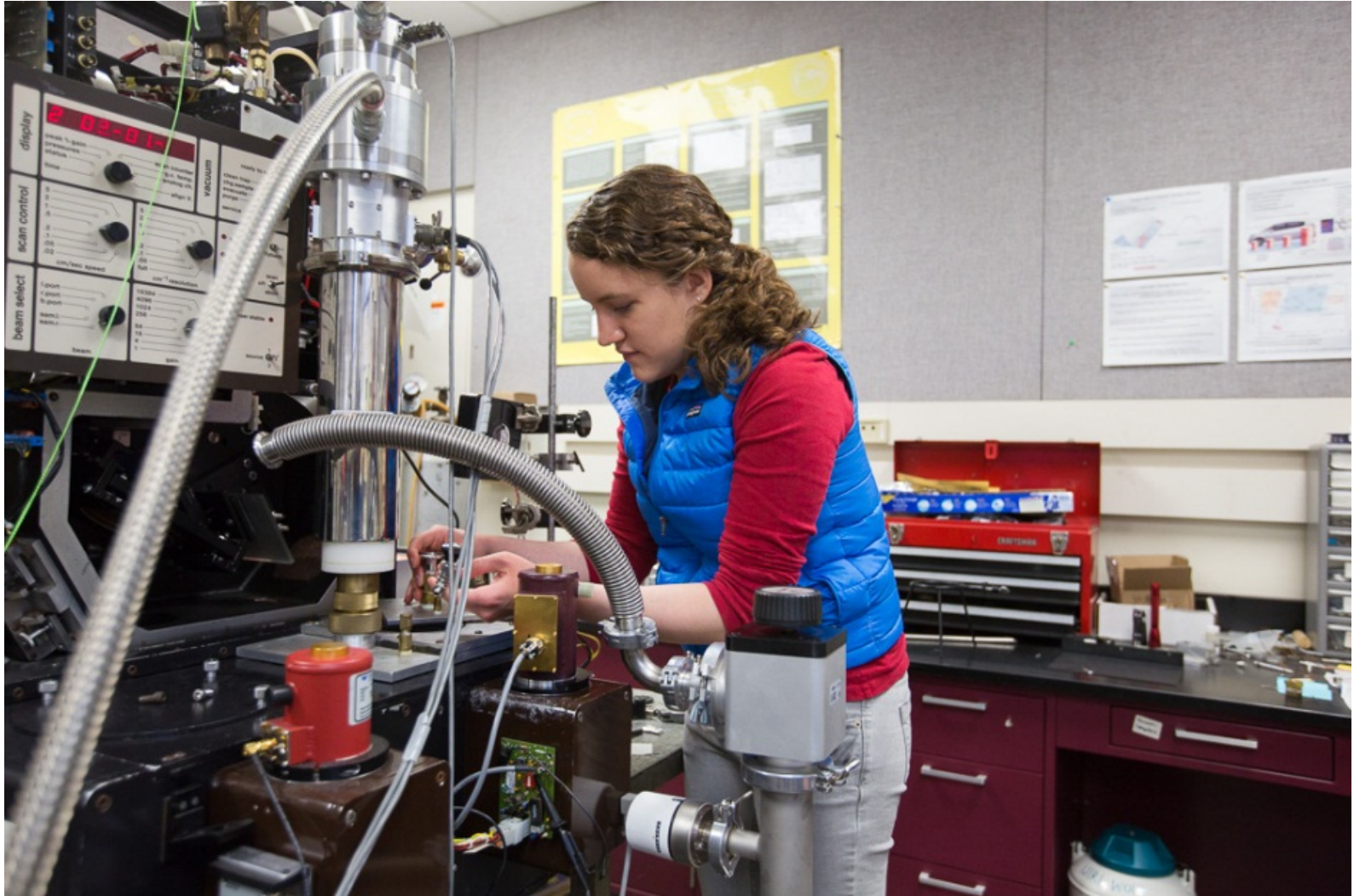


Rev. Sci. Instr. **77**, 093110 (2006)

Samples Loaded and Sealed in a Glove-Box



Spectrometer and Cryostat

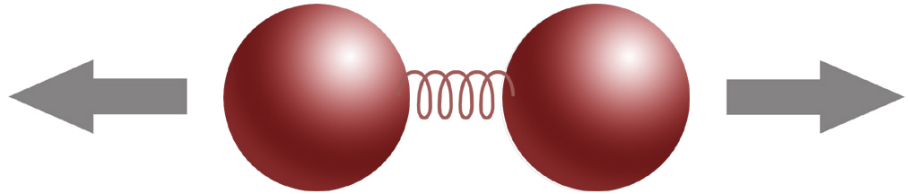


Quantum Dynamics of Adsorbed H₂

- Vibration

$$E_v = (v + 1/2) \nu_0$$

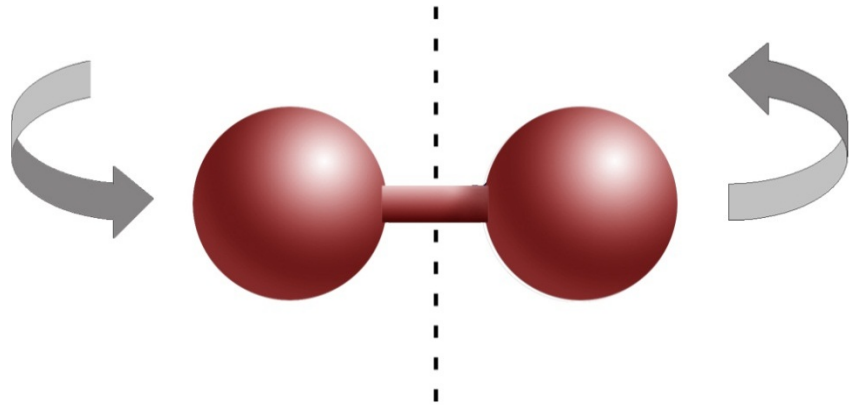
$$\nu_0 = 4161 \text{ cm}^{-1} \text{ for free H}_2$$



- Rotation

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

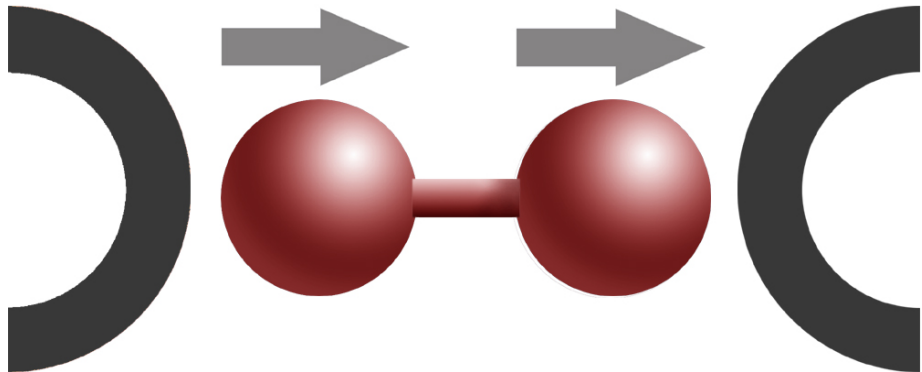
$$B_0 = 59 \text{ cm}^{-1} \text{ for free H}_2$$



- Translation

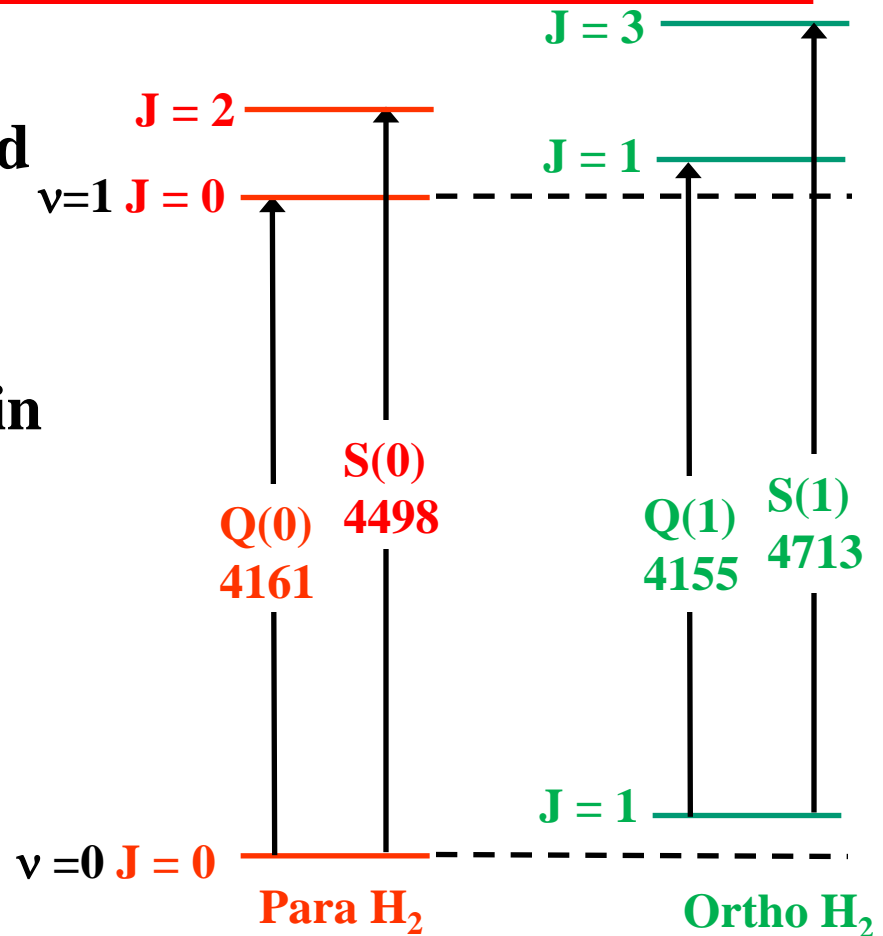
Center-of-mass

On the order of 100 cm^{-1}

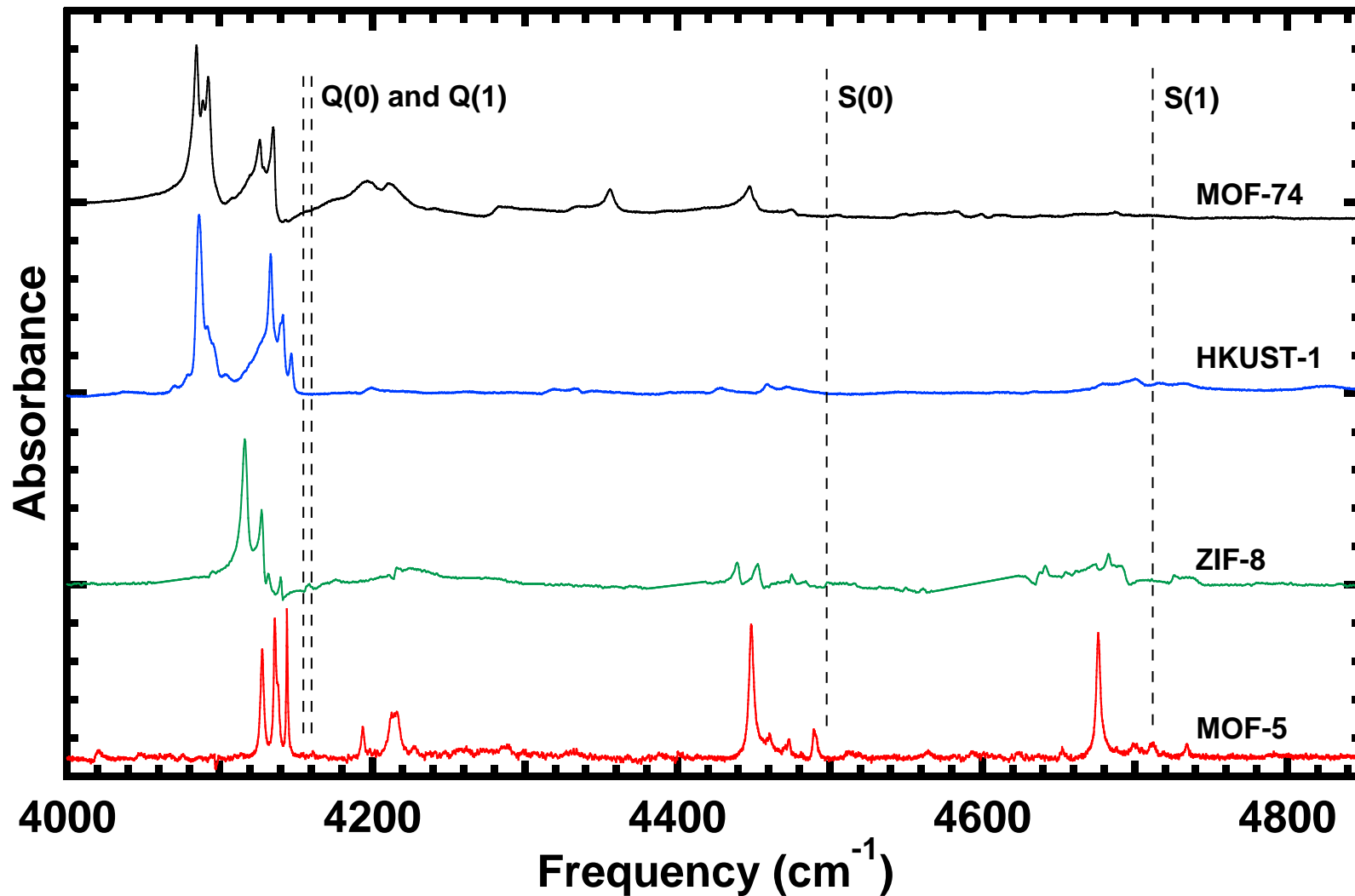


Spectroscopic Notation of Possible Transitions

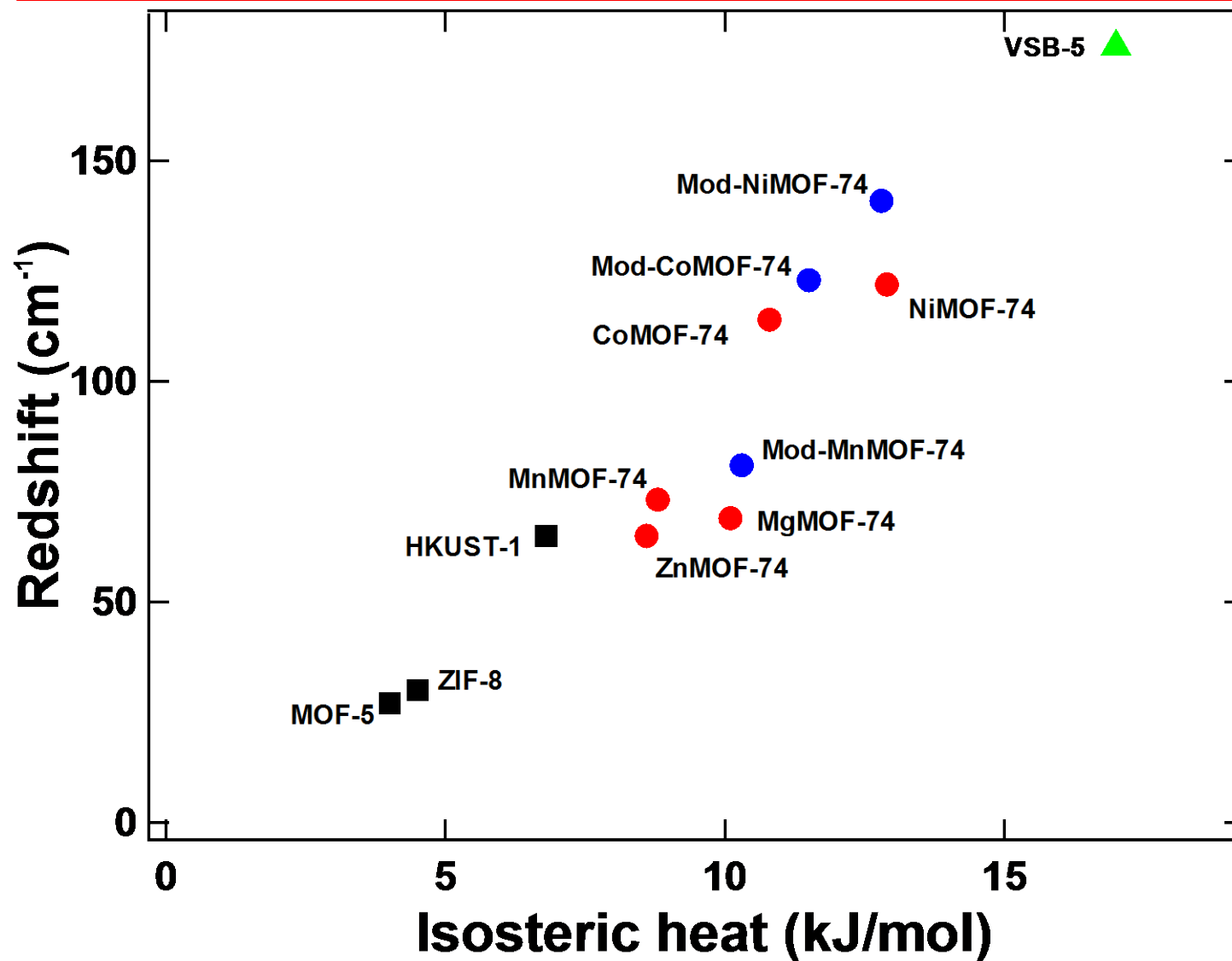
- Pure Vibrational modes called Q transitions $\Delta J = 0$
- Q(0) and Q(1) are very close in energy $\sim 6 \text{ cm}^{-1}$ apart
- Rotational Sidebands called S Transitions $\Delta J = 2$



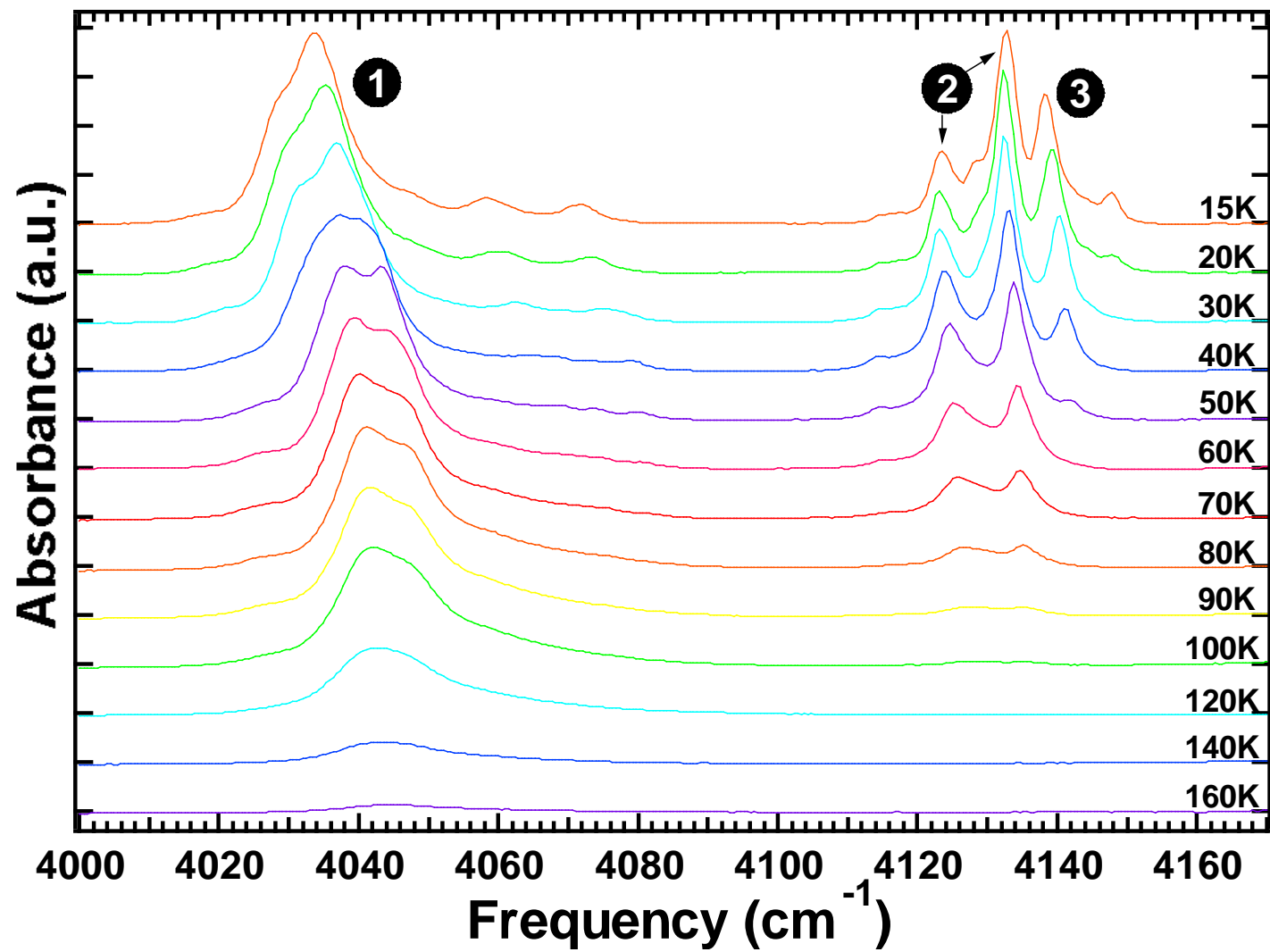
Typical Spectra for H₂ in MOFs at 30 K



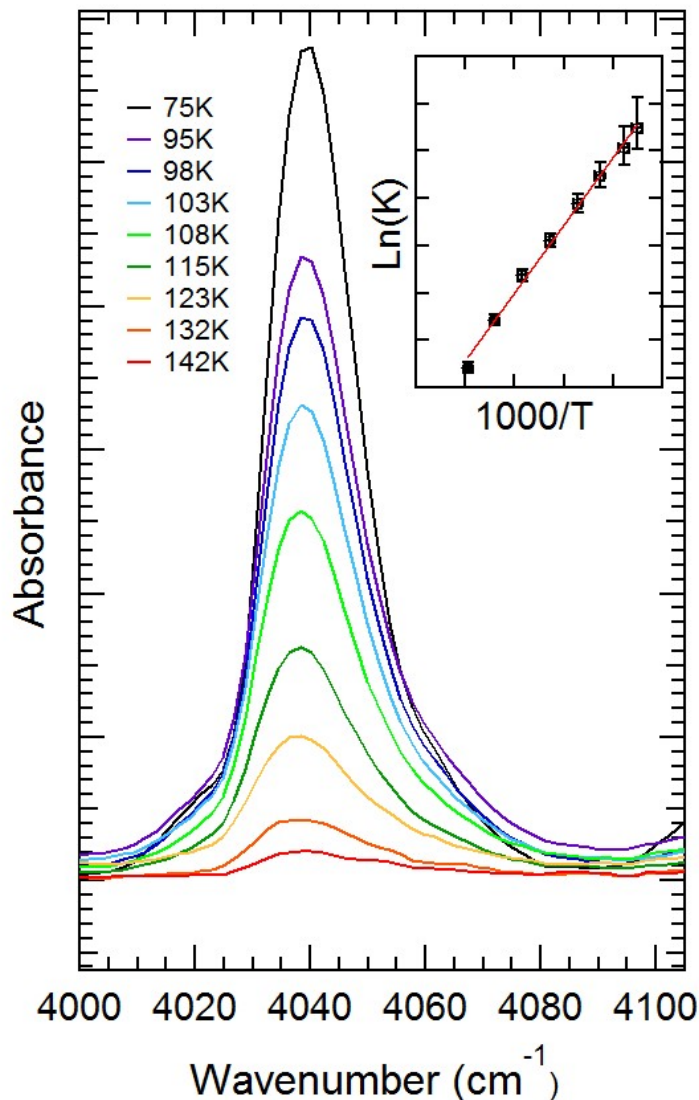
Vibrational Redshift as a Function of Binding Energy



Temperature Dependent Spectra Co-MOF-74



Extracting Enthalpy Change



Chem. Soc. Rev., **34**, 846 (2005)
Edoardo Garrone and Carlos Arean

Assume Langmuir-Isotherm

$$\theta = A/A_M = k(T) p / [1 + k(T)p]$$

$$k(T) = \exp(-\Delta H/RT) \exp(\Delta S/R)$$

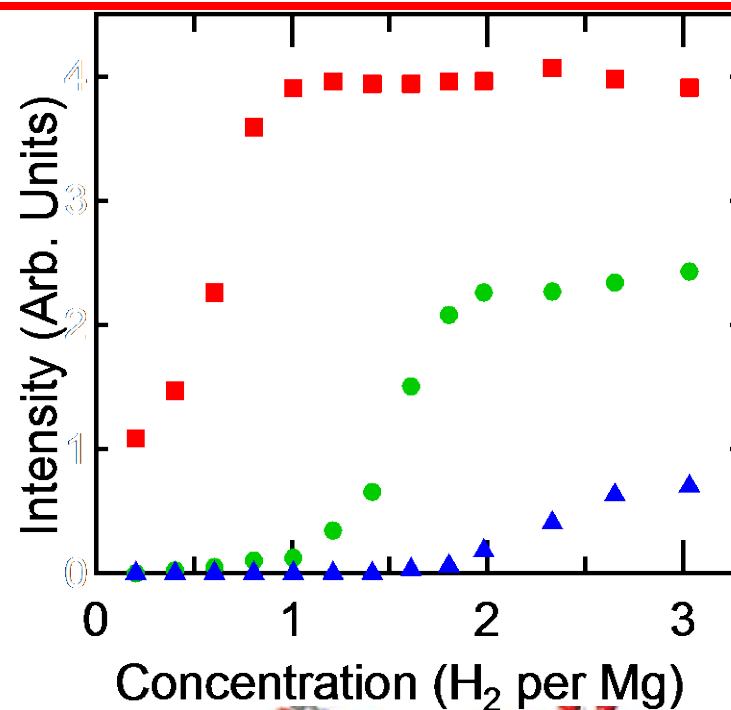
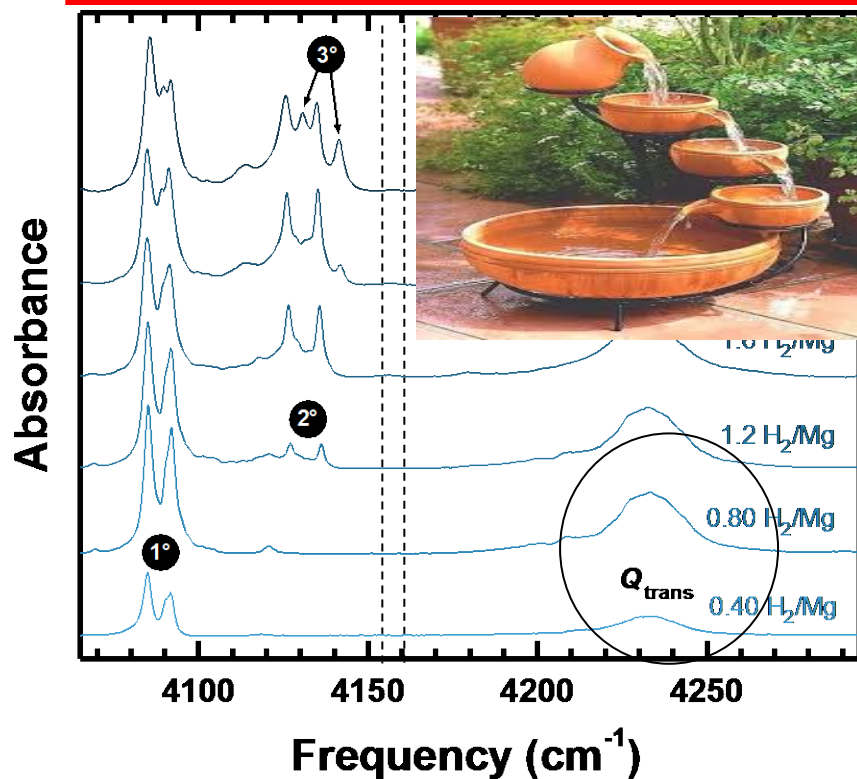
$$\ln[A/(A_M - A)p] = -\Delta H/RT + \Delta S/R$$

Data indicate Co-MOF-74
with a modified linker

$$\Delta H = -12 \text{ kJ/mol}$$

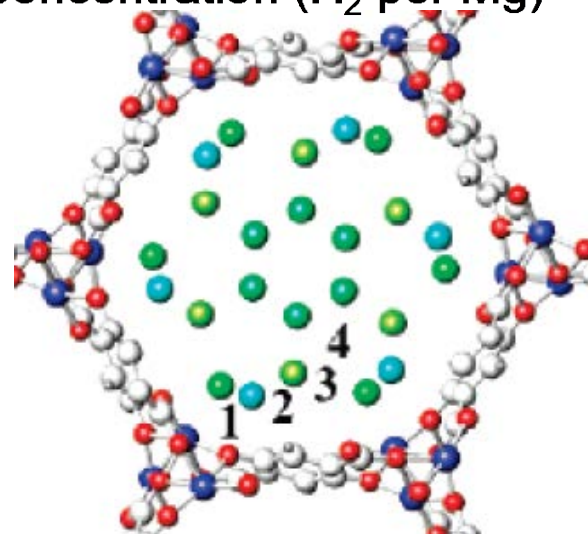
$$\Delta S = -140 \text{ J mol}^{-1} \text{ K}^{-1}$$

Spectra as a Function of Concentration



J. Am. Chem. Soc. **133**, 20310 (2011)

Neutron Diffraction Data
Langmuir **24**, 4772 (2008)

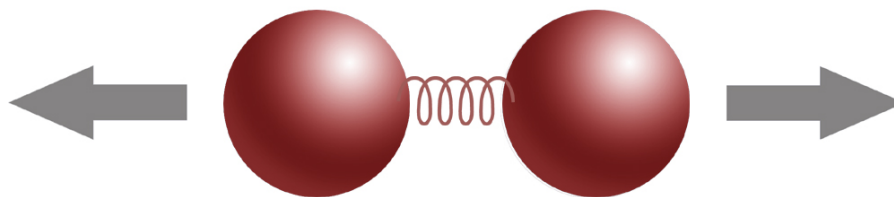


Quantum Dynamics of Adsorbed H₂

- Vibration

$$E_v = (v + 1/2) \nu_0$$

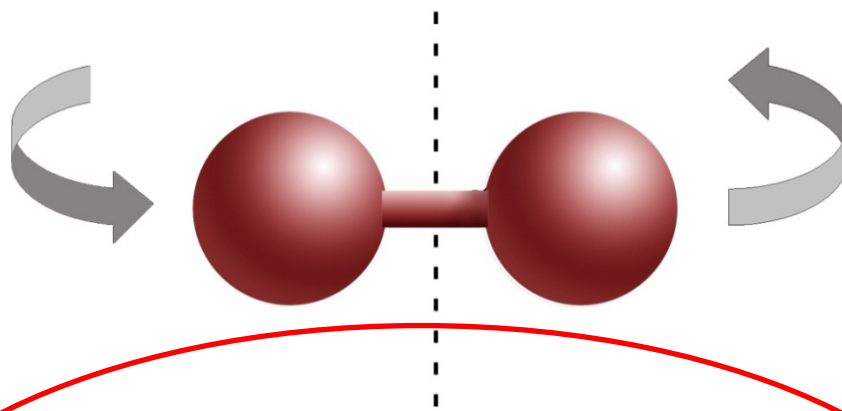
$\nu_0 = 4161 \text{ cm}^{-1}$ for free H₂



- Rotation

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

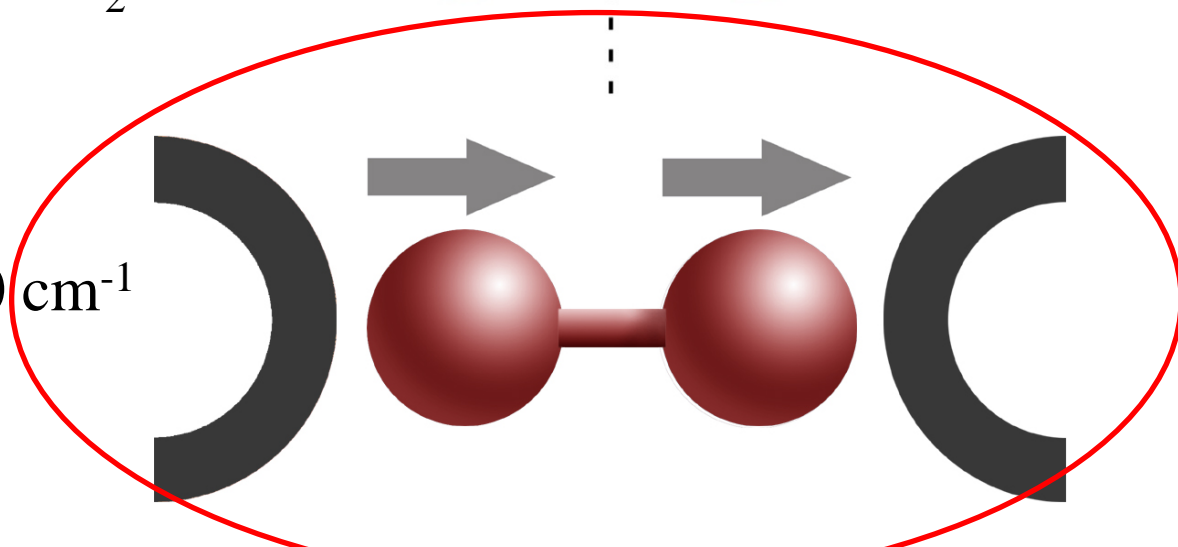
$B_0 = 59 \text{ cm}^{-1}$ for free H₂



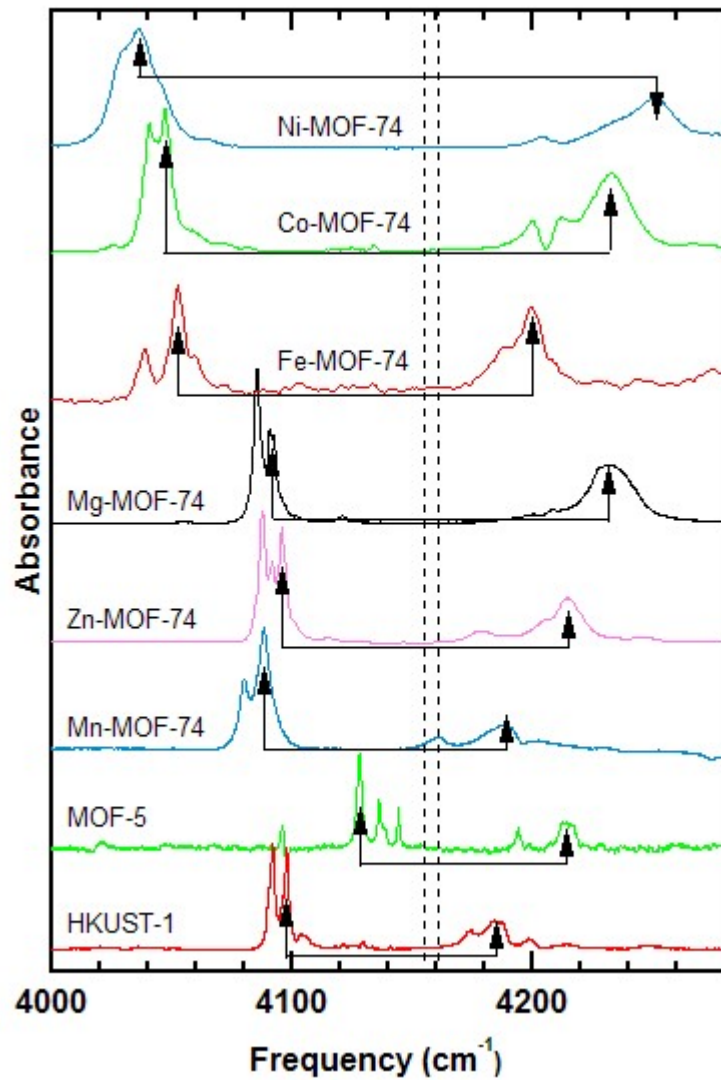
- Translation

Center-of-mass

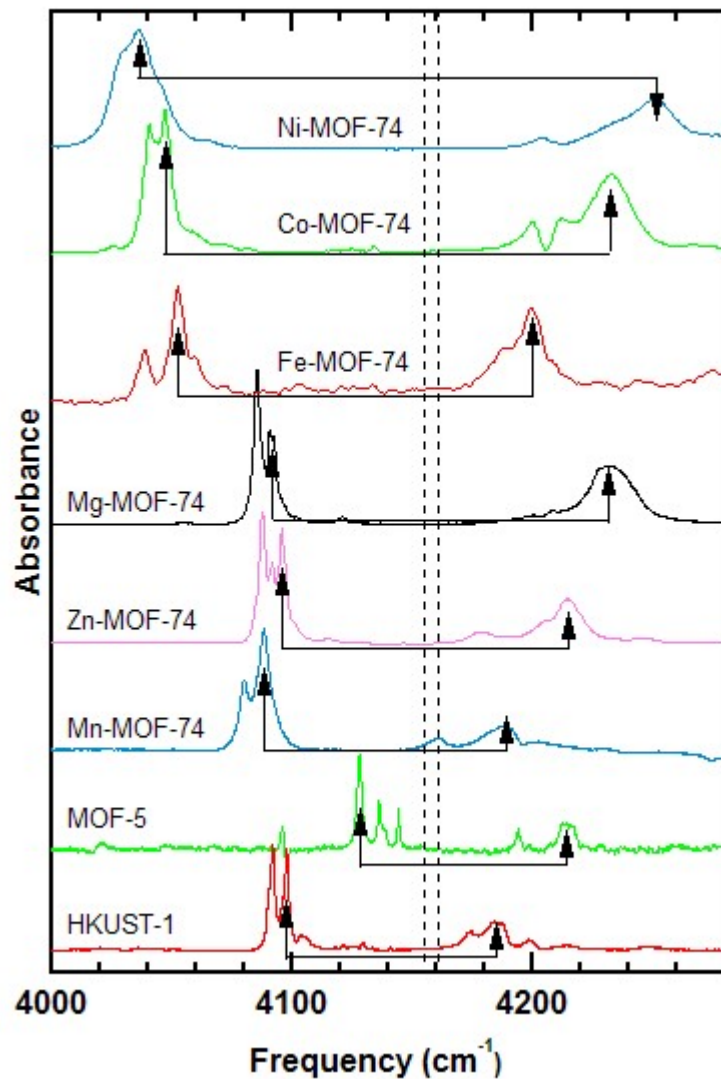
On the order of 150 cm^{-1}



Translational mode energy (quantum sieving?)



Back of the Envelope Calculation



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

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

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

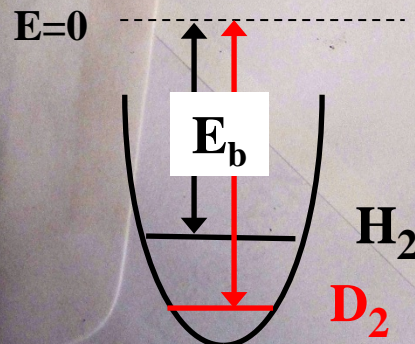
$$\omega_{D_2} = \frac{1}{\sqrt{2}} \omega_{H_2}$$

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

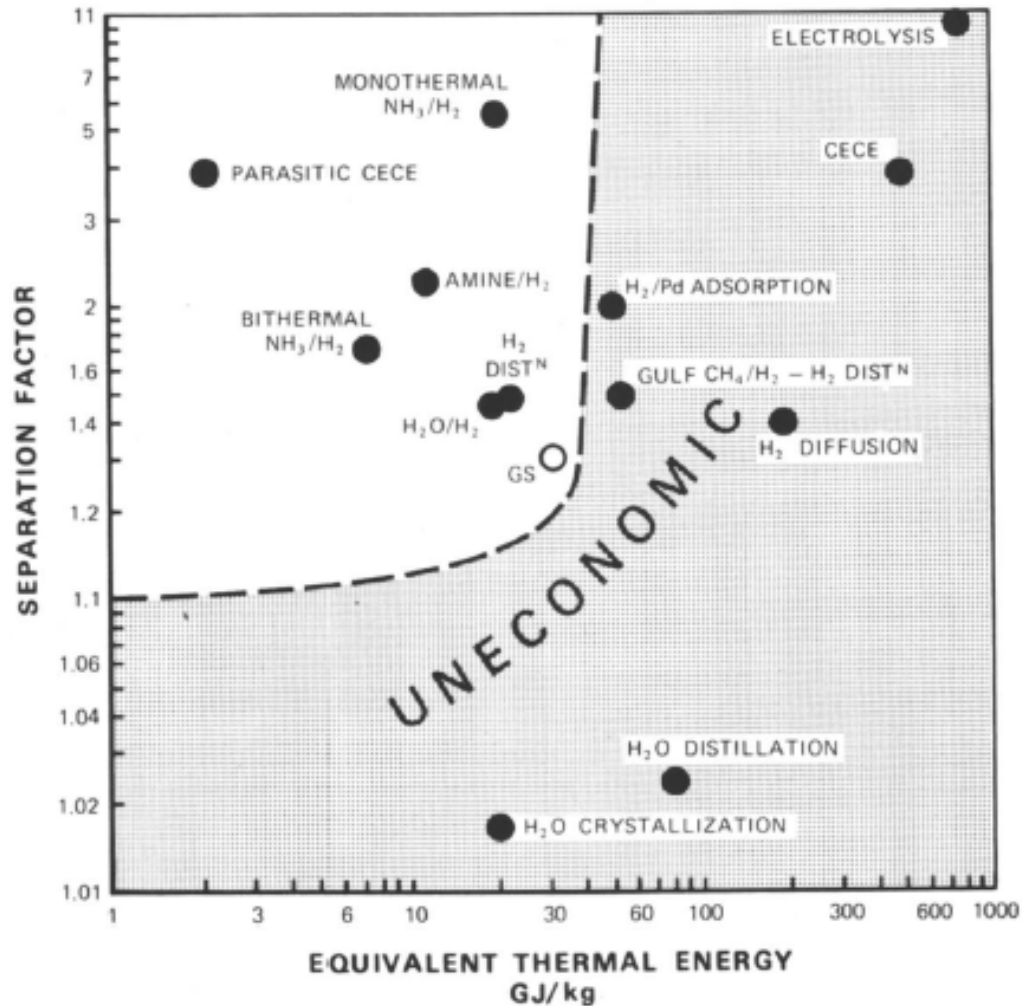
$$\Delta ZPE = 120 \text{ K}$$

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

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

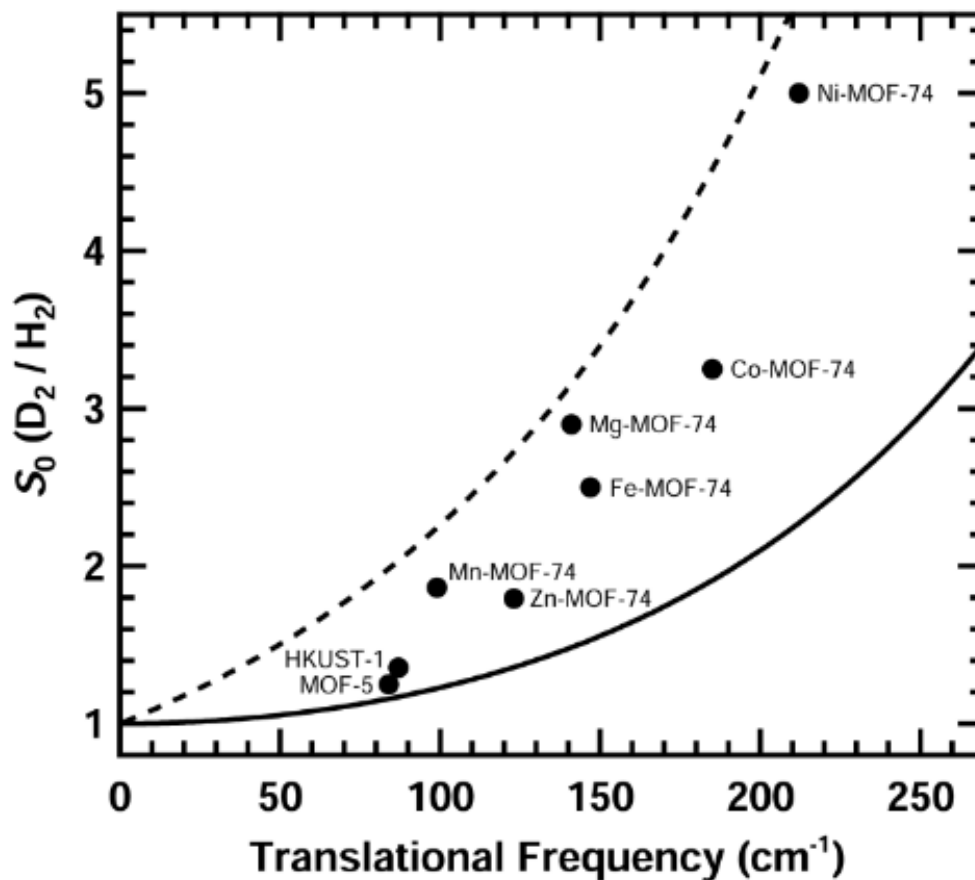


Standard Separation Techniques



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

Selectivity vs Translational Frequency



Dashed line: back of the envelope

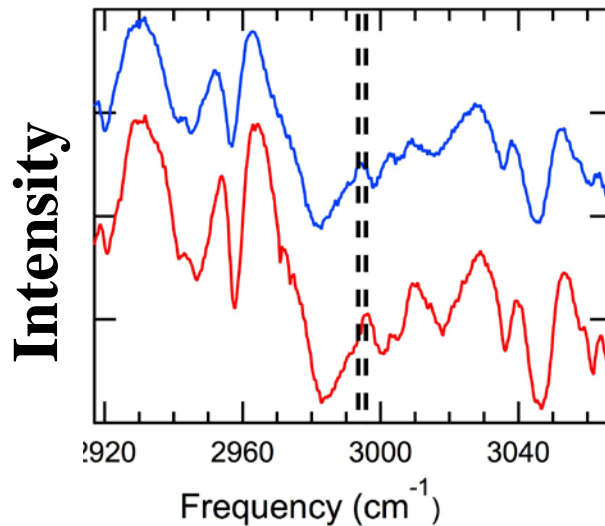
Solid line: thermodynamic calculation (harmonic)

Deuterium in MOF-5

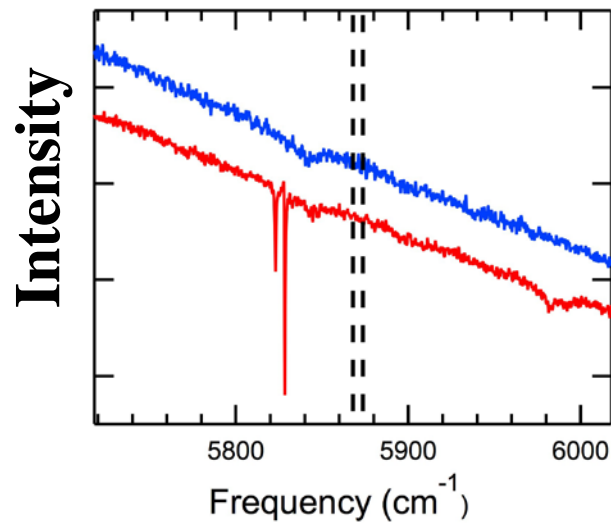
Pure MOF-5



MOF-5 with D₂



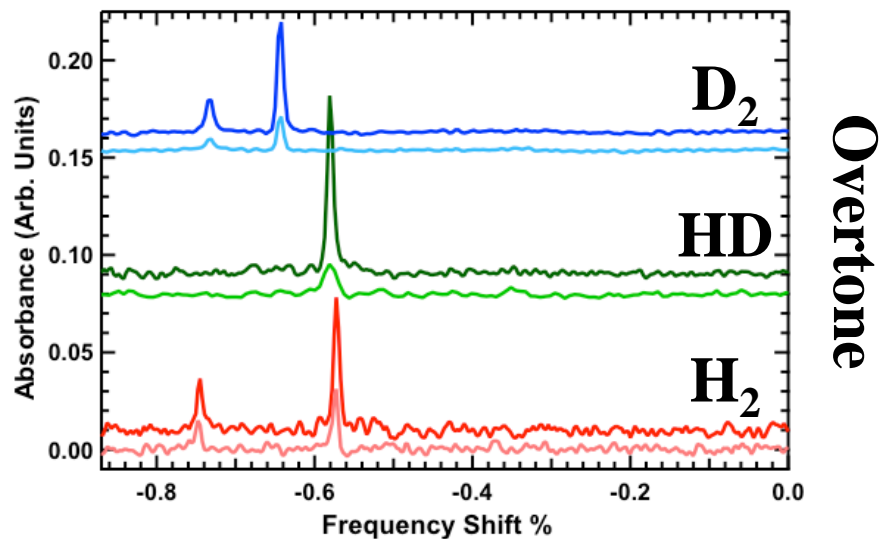
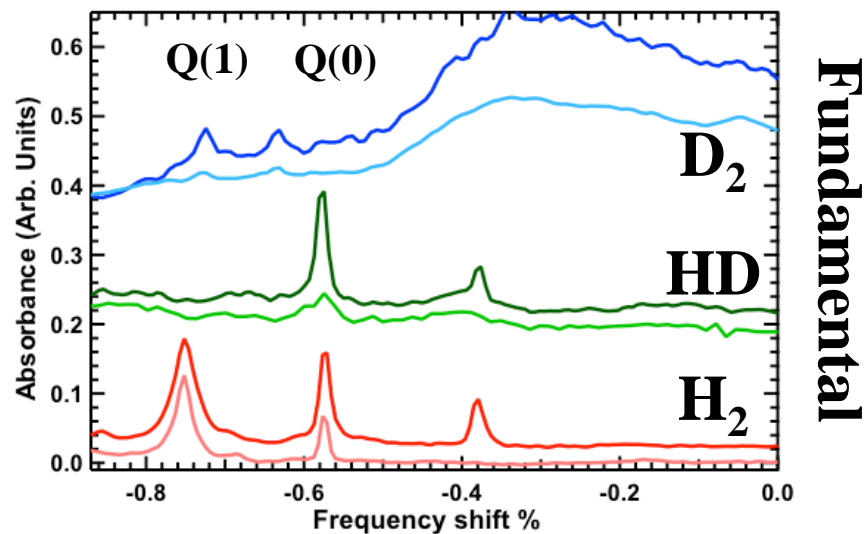
Fundamental



Overtone

Frequency Shift Fundamental versus Overtone

J. Mol. Spectroscopy. **307**, 20 (2015)



Extra adsorption and adsorbate superlattice formation in metal–organic frameworks

Hae Sung Cho^{1*}, Hexiang Deng^{2,3*}, Keiichi Miyasaka^{4*}, Zhiyue Dong², Minhyung Cho¹, Alexander V. Neimark⁵, Jeung Ku Kang¹, Omar M. Yaghi^{3,5,6} & Osamu Terasaki^{1,7}

Metal–organic frameworks (MOFs) have a high internal surface area and widely tunable composition^{1,2}, which make them useful for applications involving adsorption, such as hydrogen, methane or carbon dioxide storage^{3–6}. The selectivity and uptake capacity of the adsorption process are determined by interactions involving the adsorbates and their porous host materials. But, although the interactions of adsorbate molecules with the internal MOF surface^{10–17} and also amongst themselves within individual pores^{18–22} have been extensively studied, adsorbate–adsorbate interactions across pore walls have not been explored. Here we show that local strain in the MOF, induced by pore filling, can give rise to collective and long-range adsorbate–adsorbate interactions and the formation of adsorbate superlattices that extend beyond an original MOF unit cell. Specifically, we use *in situ* small-angle X-ray scattering to track and map the distribution and ordering of adsorbate molecules in five members of the mesoporous MOF-74 series along entire adsorption–desorption isotherms. We find in all cases that the capillary condensation that fills the pores gives rise to the formation of ‘extra adsorption domains’—that is, domains spanning several neighbouring pores, which have a higher adsorbate density than non-domain pores. In the case of one MOF, IRMOF-74-V-hex, these domains form a superlattice structure that is difficult to reconcile with the prevailing view of pore-filling as a stochastic process. The visualization of the adsorption process provided by our data, with clear evidence for initial adsorbate aggregation in distinct domains and ordering before an even distribution is finally reached, should help to improve our understanding of this process and may thereby improve our ability to exploit it practically.

Figure 1 shows the three distinct types of interaction in which adsorbates in MOFs can engage: adsorbate molecules can interact with the material's internal surface (regime A); adsorbates can interact among themselves within the confines of a pore (regime B); and adsorbates can interact with each other across pores mediated by the material framework (regime C). Studying the collective adsorbate behaviour in regimes B and C requires porous MOF crystals, with pores that are large enough to enable the organization and behaviour of confined adsorbates to be observed, and with pore walls that are atomically thin and well-defined so as to allow observation of any local perturbations resulting from adsorption. In such systems, we can then use *in situ* small-angle X-ray scattering (SAXS) to detect long-range ordering of adsorbates in multiple pores at precisely controlled temperatures and pressures.

We chose the five mesoporous MOFs with isoreticular structure (IRMOF-74-III, IRMOF-74-IV, IRMOF-74-V, IRMOF-74-V-hex and IRMOF-74-VII) that are based on the crystalline IRMOF-74

structure^{8,23–25}. The robustness of the IRMOF-74 honeycomb-like structure (in projection) is imparted by one-dimensional, rod-shaped magnesium oxide units that run along the pore direction and are held together by organic linkers (Fig. 2a). This rigid oxide unit allows for structural refinements in two dimensions, by keeping constant the structure along the *c* axis of the original MOF structure⁸ (Fig. 2b). Thus, we apply the projected symmetry of the two-dimensional space groups (plane groups) *p3* or *p6* for the unit cell (Fig. 2b, green parallelogram). We therefore need only two variables, *h* and *k*, to specify the reflections with the *h* and *k* indices for the refinement. This allows us to focus on the adsorption region, and stops us from having to deal unnecessarily with the more complicated original symmetry *R3* in IRMOF-74-IV, IRMOF-74-V and IRMOF-74-VII, or *R3* in IRMOF-74-III and IRMOF-74-V-hex (Fig. 2b, red parallelogram).

All of these MOFs exhibit open porosity and have mesopores with sizes of 22 Å, 28 Å, 35 Å and 49 Å (for IRMOF-74-III, IRMOF-74-IV, IRMOF-74-V and IRMOF-74-VII, respectively). IRMOF-74-V-hex, having a pore size of 34 Å, was constructed with a linker functionalized

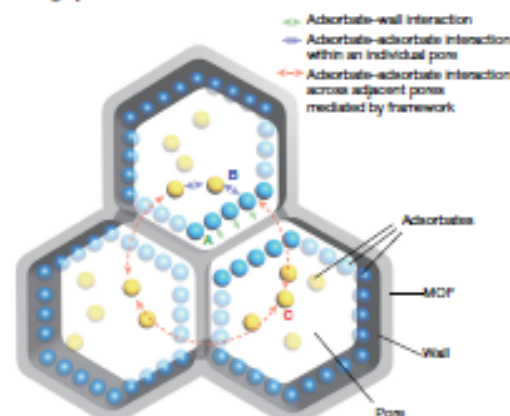


Figure 1 | Three adsorbate-interaction regimes in mesoporous MOFs. In regime A, adsorbed molecules interact (green arrows) with pore walls. In regime B, adsorbates interact amongst each other (blue arrows) within a pore. These two types of interaction and the corresponding regimes have been well studied. Regime C, however, has not been explored; here, adsorbates interact with each other (red arrows) across pore walls, in a way that is mediated by the framework. Light blue, molecules adsorbed onto the internal pore surface; yellow, molecules in the centre of the pores.


¹Graduate School of Energy, Environment, Water and Sustainability, WCU (S21) Plus, WAST, Daejeon 305-701, South Korea. ²Key Laboratory of Biomedical Polymers Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Luotian Road, Wuhan 430072, China. ³The Institute for Advanced Studies, Wuhan University, Wuhan 430072, China. ⁴Department of Chemical and Biochemical Engineering, Rutgers University, 90 Dred Road, Piscataway, New Jersey 08854, USA. ⁵Department of Chemistry, University of California, Materials Science Division at Lawrence Berkeley National Laboratory and Fuel Energy Nanoscience Institute, Berkeley, California 94720, USA. ⁶Riyg Fahd University of Petroleum and Minerals, Dhahran 34464, Saudi Arabia. ⁷

Hydrogen Physisorption on Metal–Organic Framework Linkers and Metalated Linkers: A Computational Study of the Factors That Control Binding Strength

Ehud Tsivion,^{†,§} Jeffrey R. Long,^{†,§} and Martin Head-Gordon^{*,†,§}

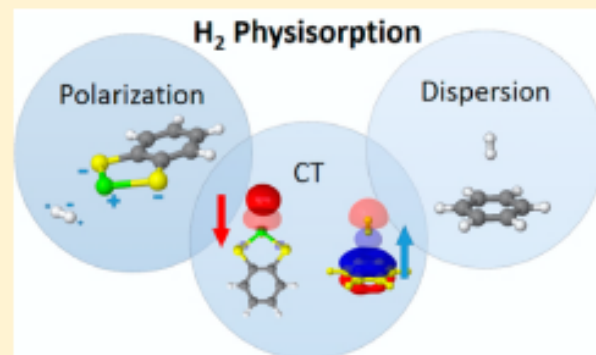
[†]Materials Sciences Division and [‡]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[§]Department of Chemistry, University of California, Berkeley, California 94720, United States

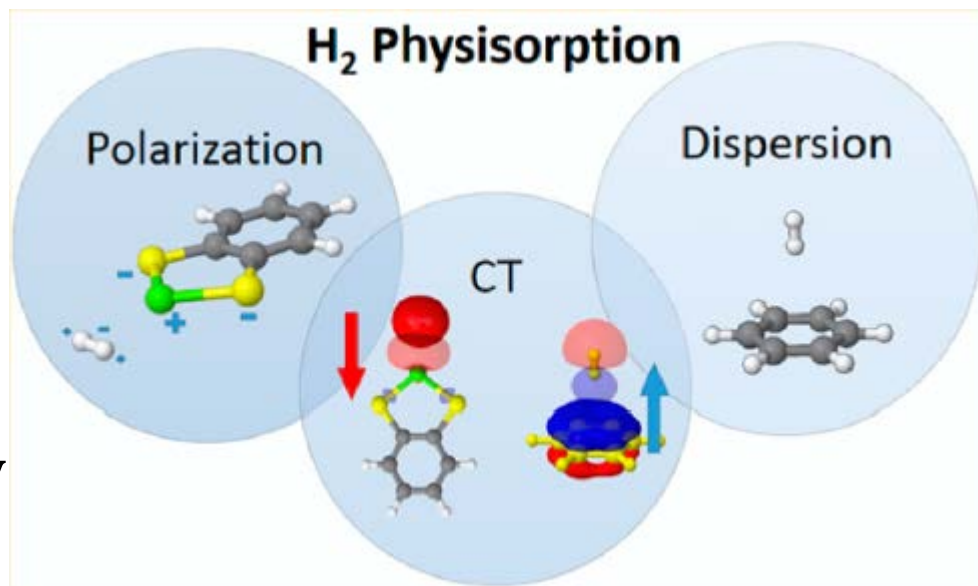
 Supporting Information

ABSTRACT: In order for hydrogen gas to be used as a fuel, it must be stored in sufficient quantity on board the vehicle. Efforts are being made to increase the hydrogen storage capabilities of metal–organic frameworks (MOFs) by introducing unsaturated metal sites into their linking element(s), as hydrogen adsorption centers. In order to devise successful hydrogen storage strategies there is a need for a fundamental understanding of the weak and elusive hydrogen physisorption interaction. Here we report our findings from the investigation of the weak intermolecular interactions of adsorbed hydrogen molecules on MOF-linkers by using cluster models. Since physical interactions such as dispersion and polarization have a major contribution to attraction energy, our approach is to analyze the adsorption interaction using energy decomposition analysis (EDA)

that distinguishes the contribution of the physical interactions from the charge-transfer (CT) “chemical” interaction. Surprisingly, it is found that CT from the adsorbent to the $\sigma^*(\text{H}_2)$ orbital is present in all studied complexes and can contribute up to approximately -2 kJ/mol to the interaction. When metal ions are present, donation from the $\sigma(\text{H}_2) \rightarrow$ metal Rydberg-like orbital, along with the adsorbent $\rightarrow \sigma^*(\text{H}_2)$ contribution, can contribute from -2 to -10 kJ/mol, depending on the coordination mode. To reach a sufficient adsorption enthalpy for practical usage, the hydrogen molecule must be substantially polarized. Ultimately, the ability of the metalated linker to polarize the hydrogen molecule is highly dependent on the geometry of the metal ion coordination site where a strong electrostatic dipole or quadrupole moment is required.



Need Experimental Evidence of Binding Mechanism

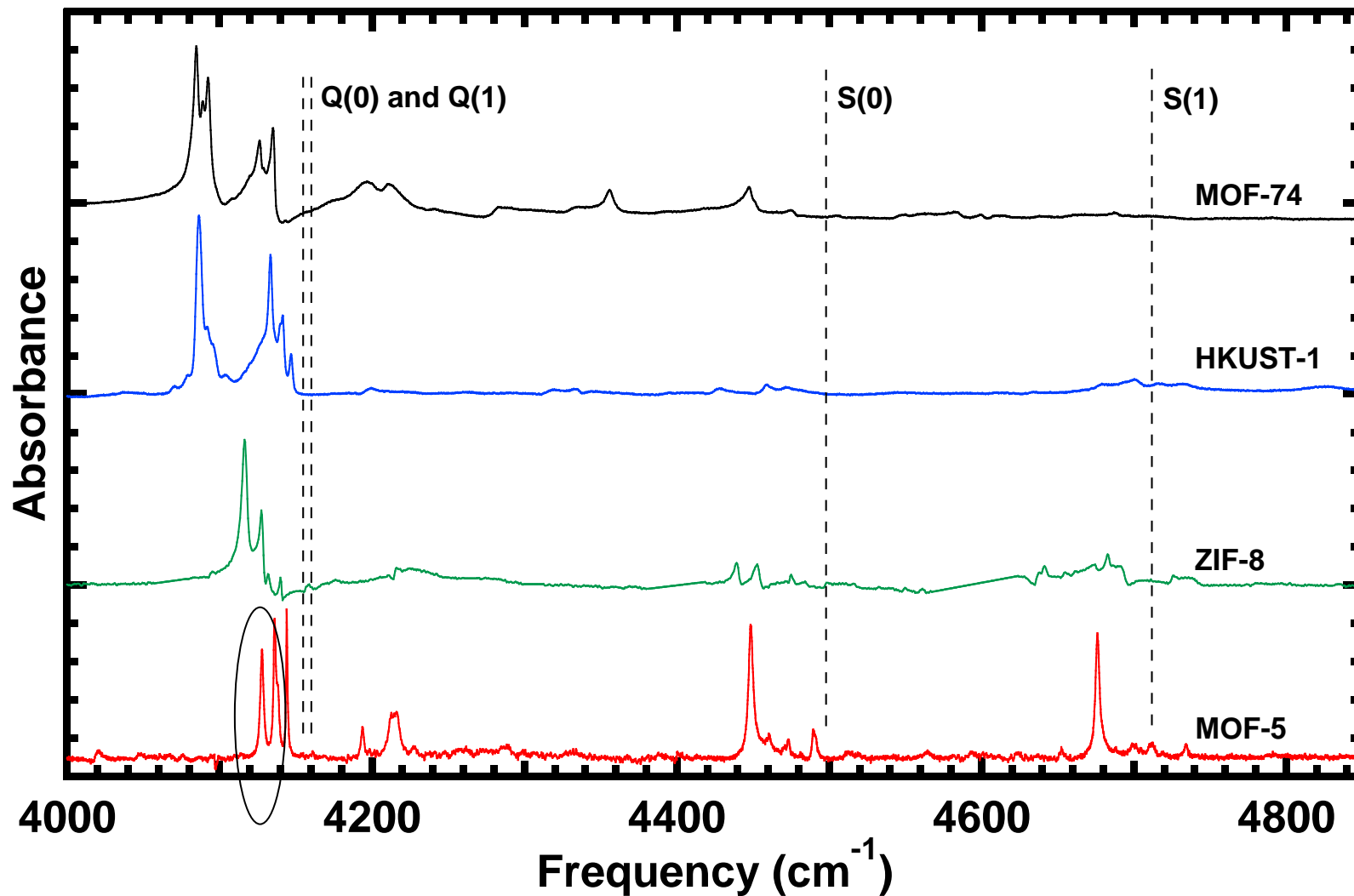


How could we most directly determine the relative contribution of these three mechanisms?

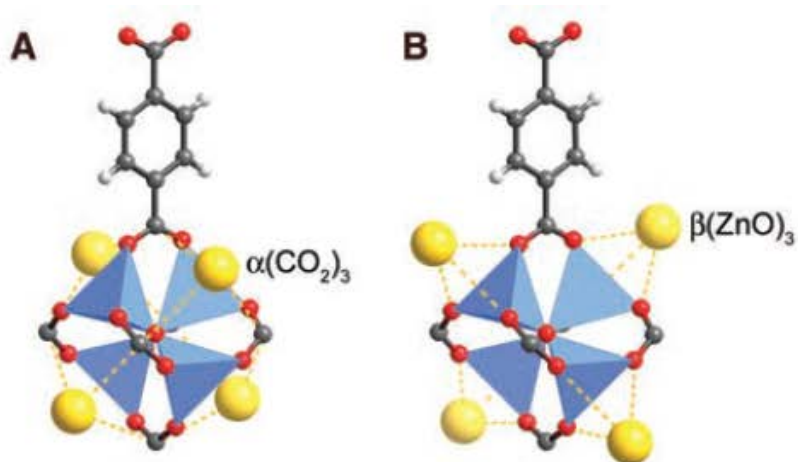
J. Am. Chem. Soc. **136**, 17827 (2014)
Tsvion, Long, and Head-Gordon

“More direct” implies less need for theoretical modelling.

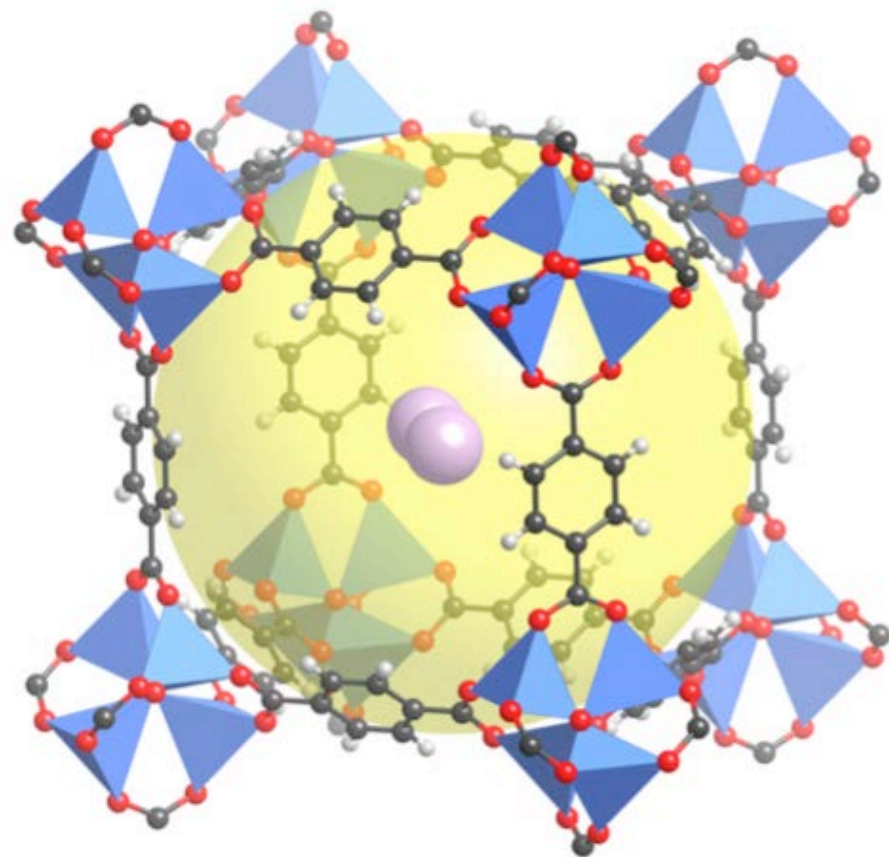
Typical Spectra for H₂ in MOFs at 30 K



Binding Sites in MOF-5

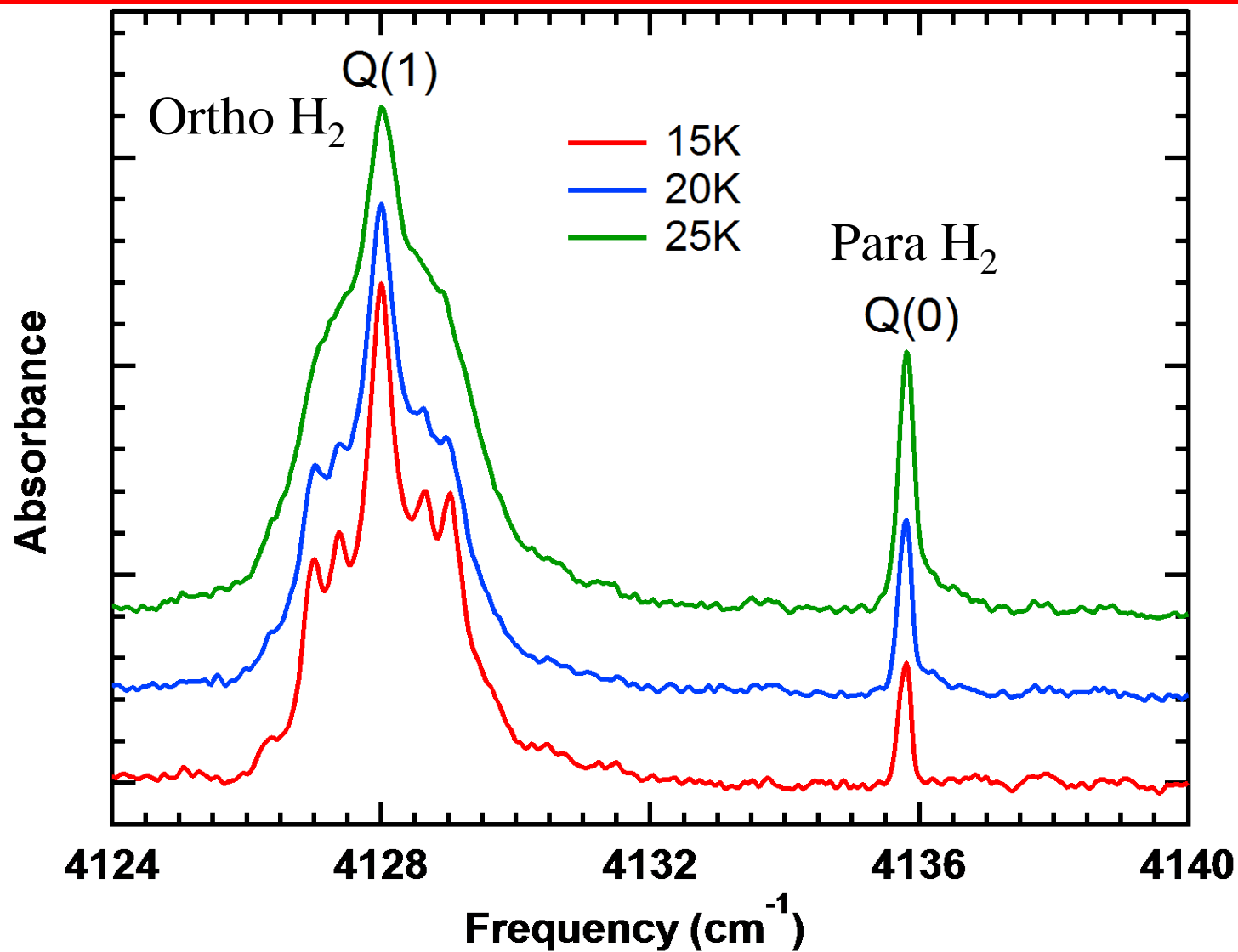


J.L.C. Rowsell, E.C. Spencer, J. Eckert, J. Howard, and O.M. Yaghi, *Science*, **309**, 1350 (2005)

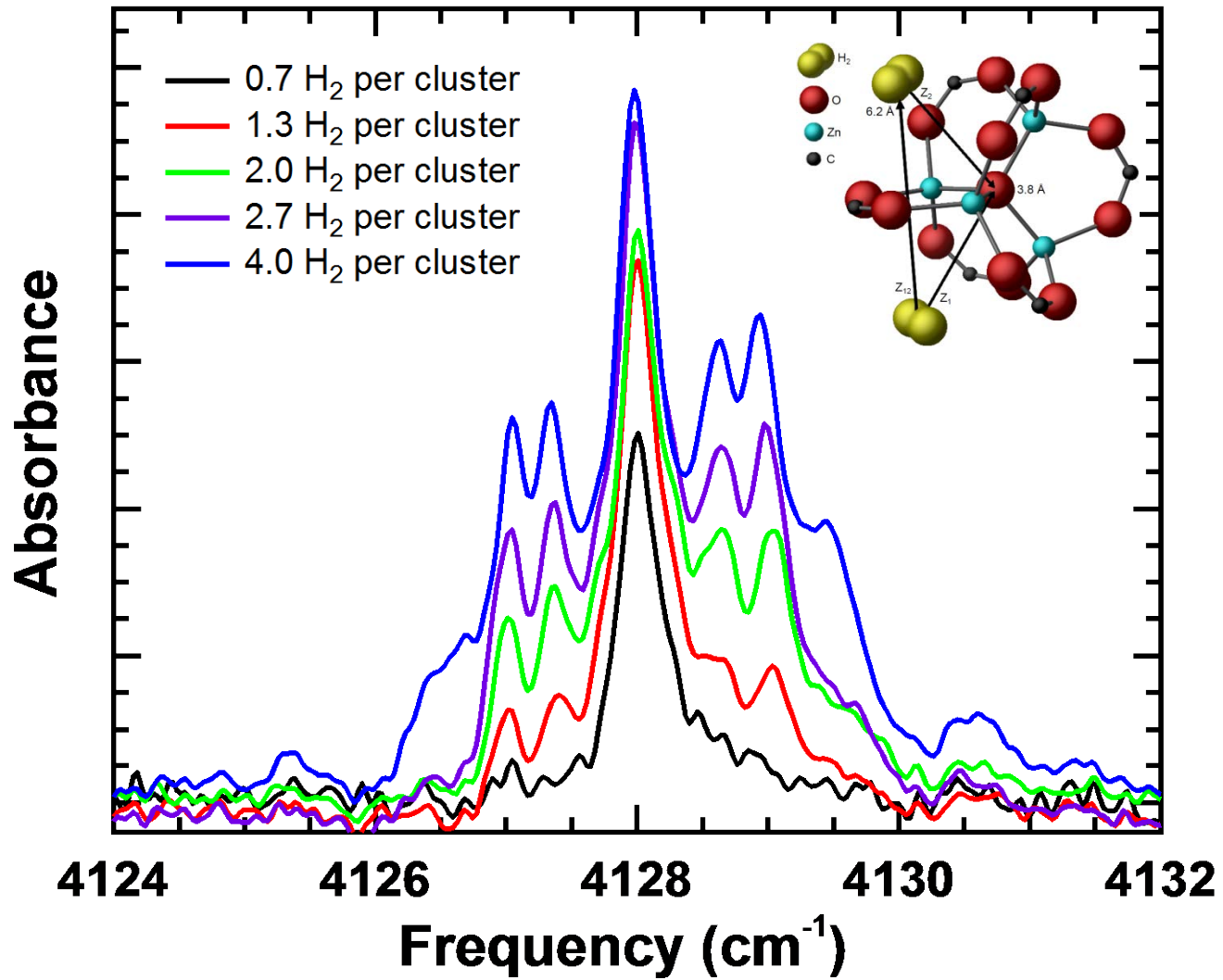


E. Spencer, J. Howard, G. McIntyre, J. L. C. Rowsell, and O. M. Yaghi, *Chem. Commun.* **3**, 278 (2006).

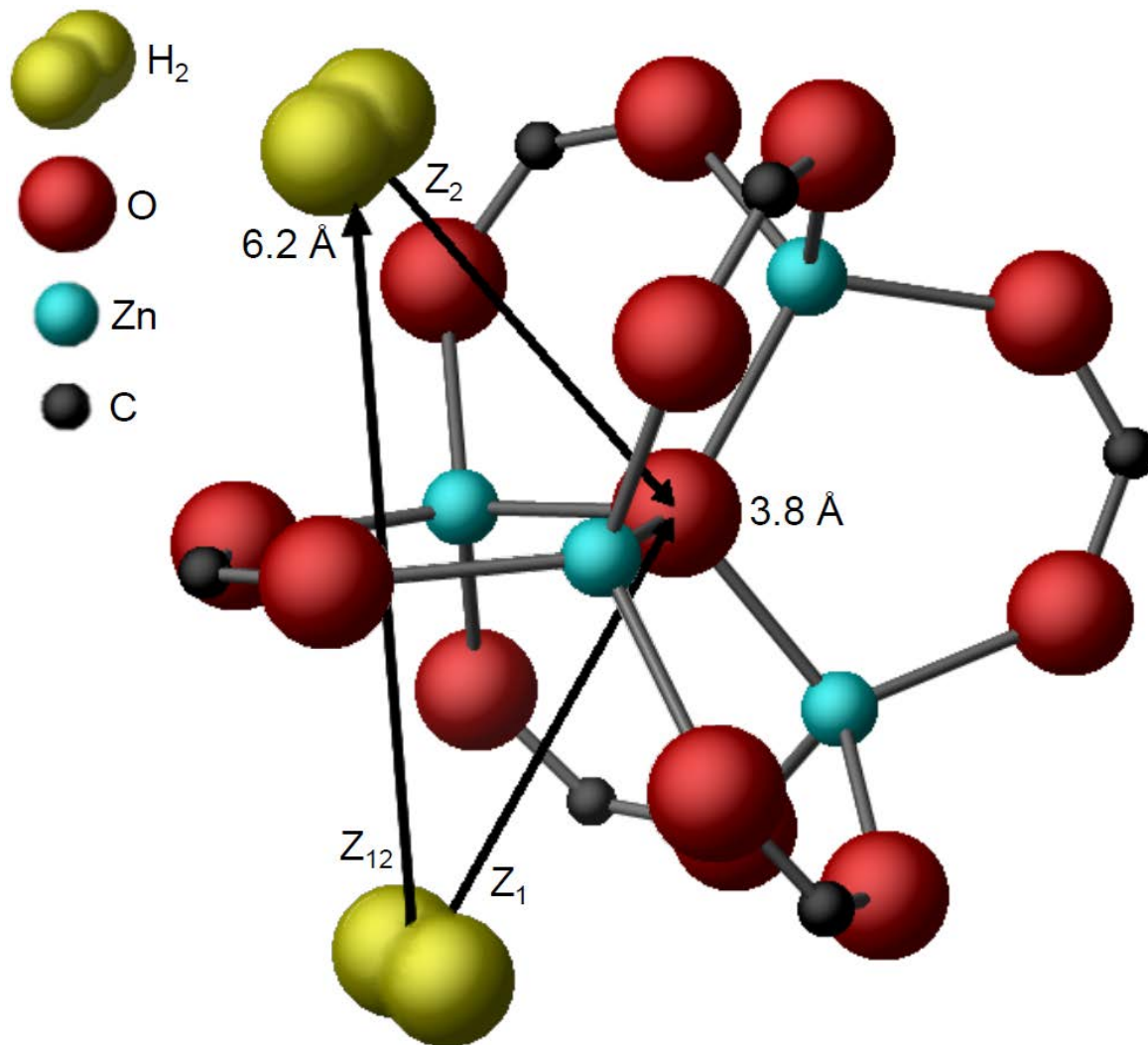
Temperature Dependence of H₂ in MOF-5



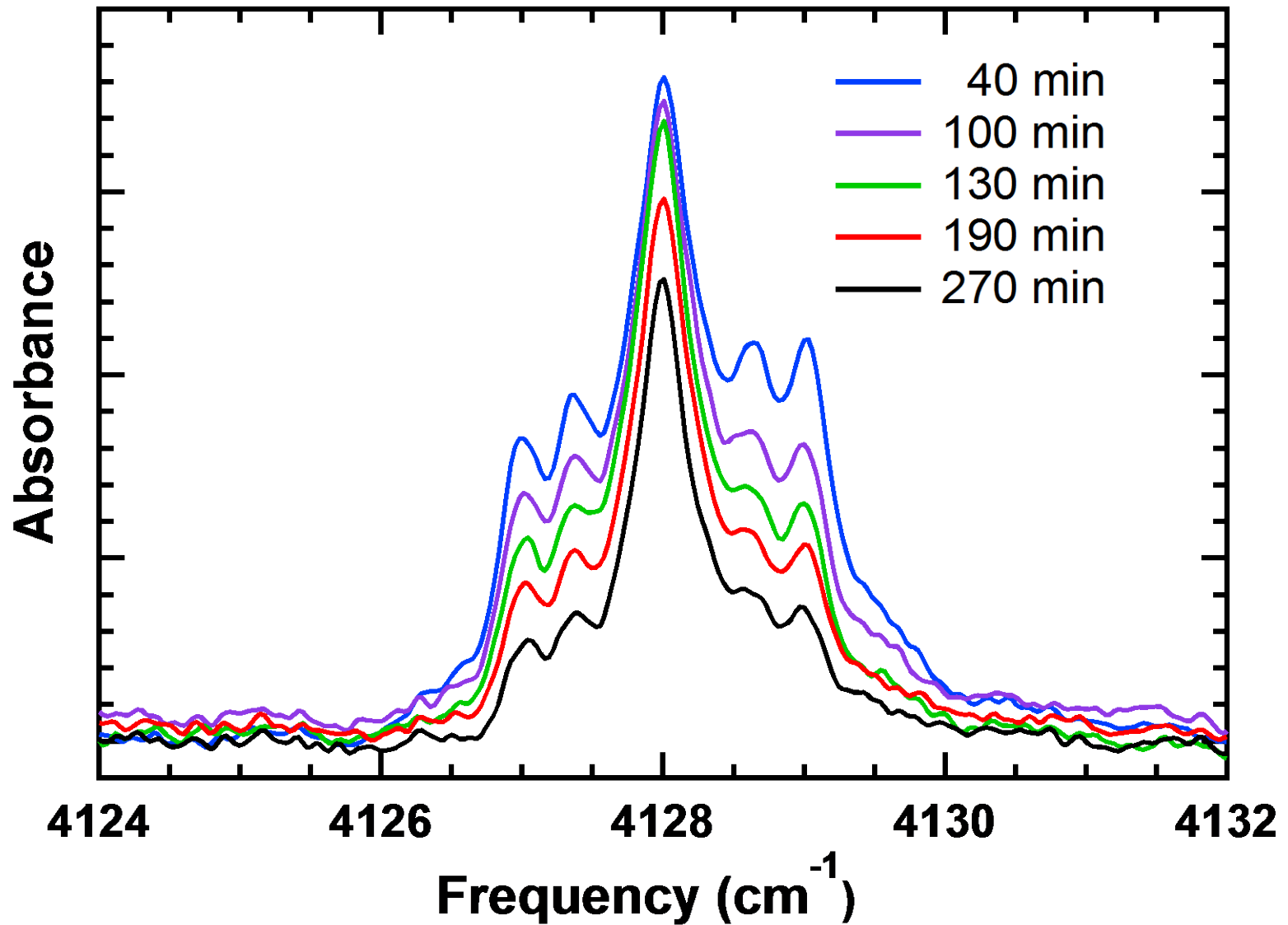
Concentration Dependence



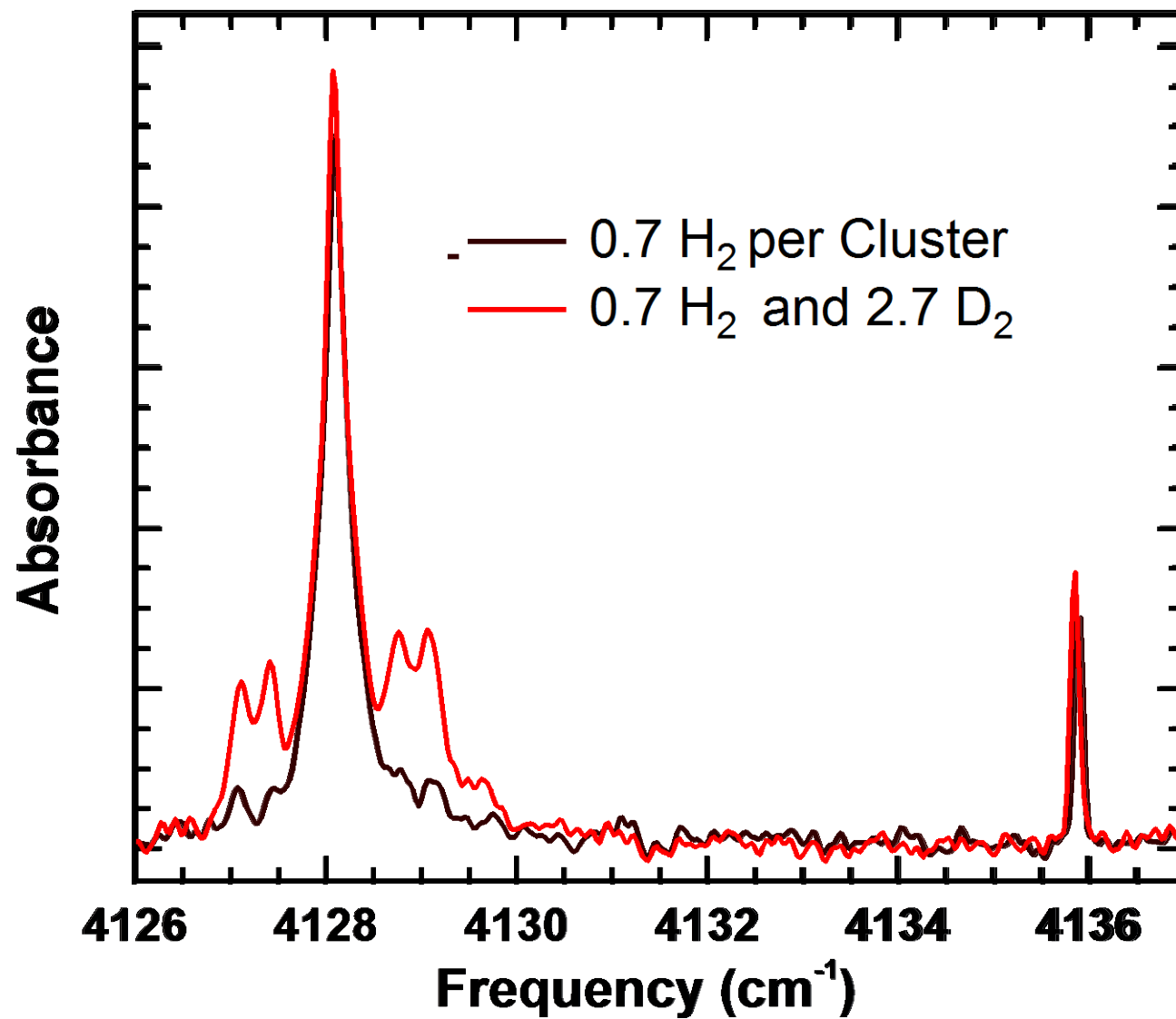
MOF-5 with Adsorbed H₂ at Primary Site



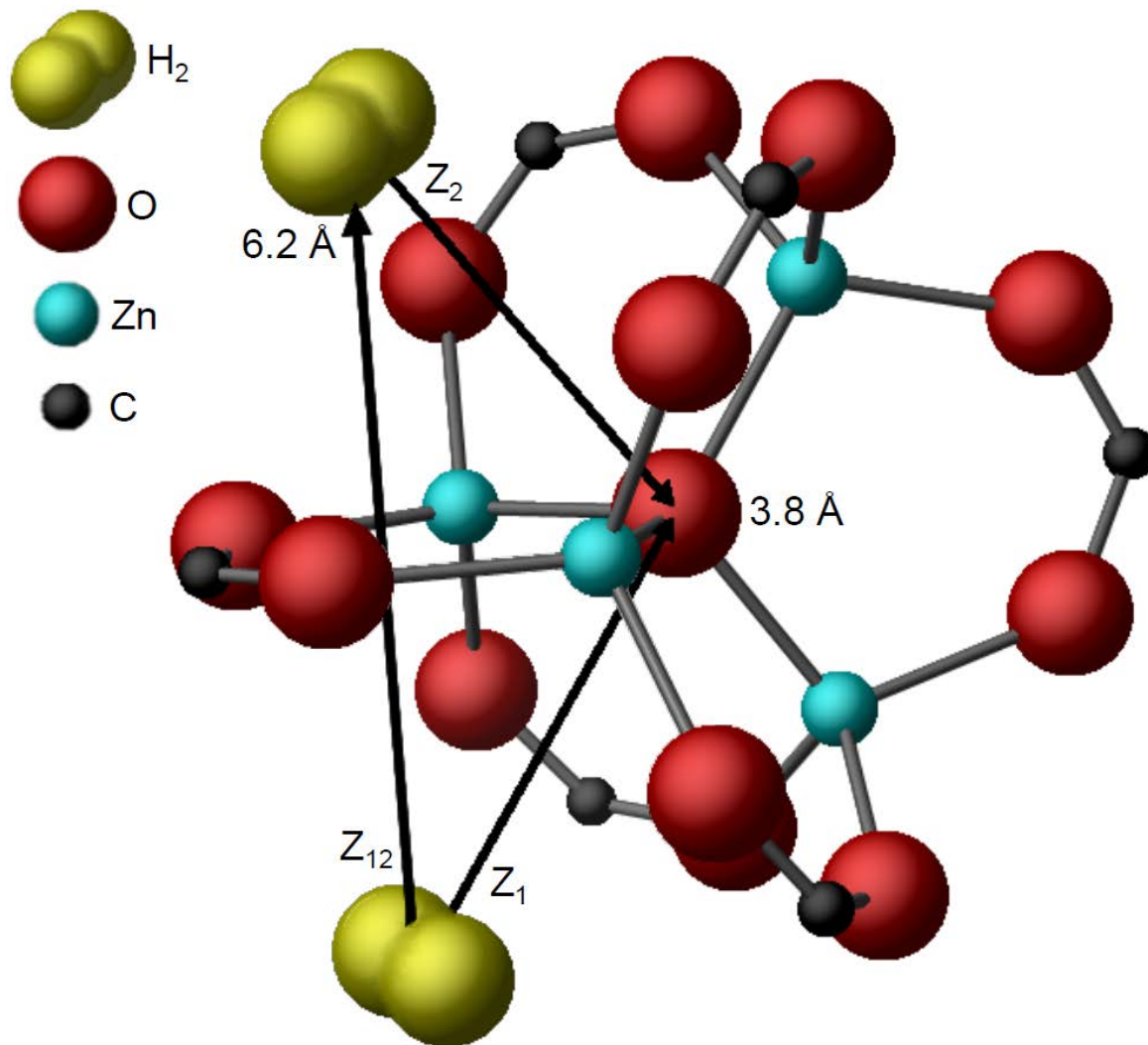
Ortho to Para Conversion with Time



H₂ and D₂ Mixture

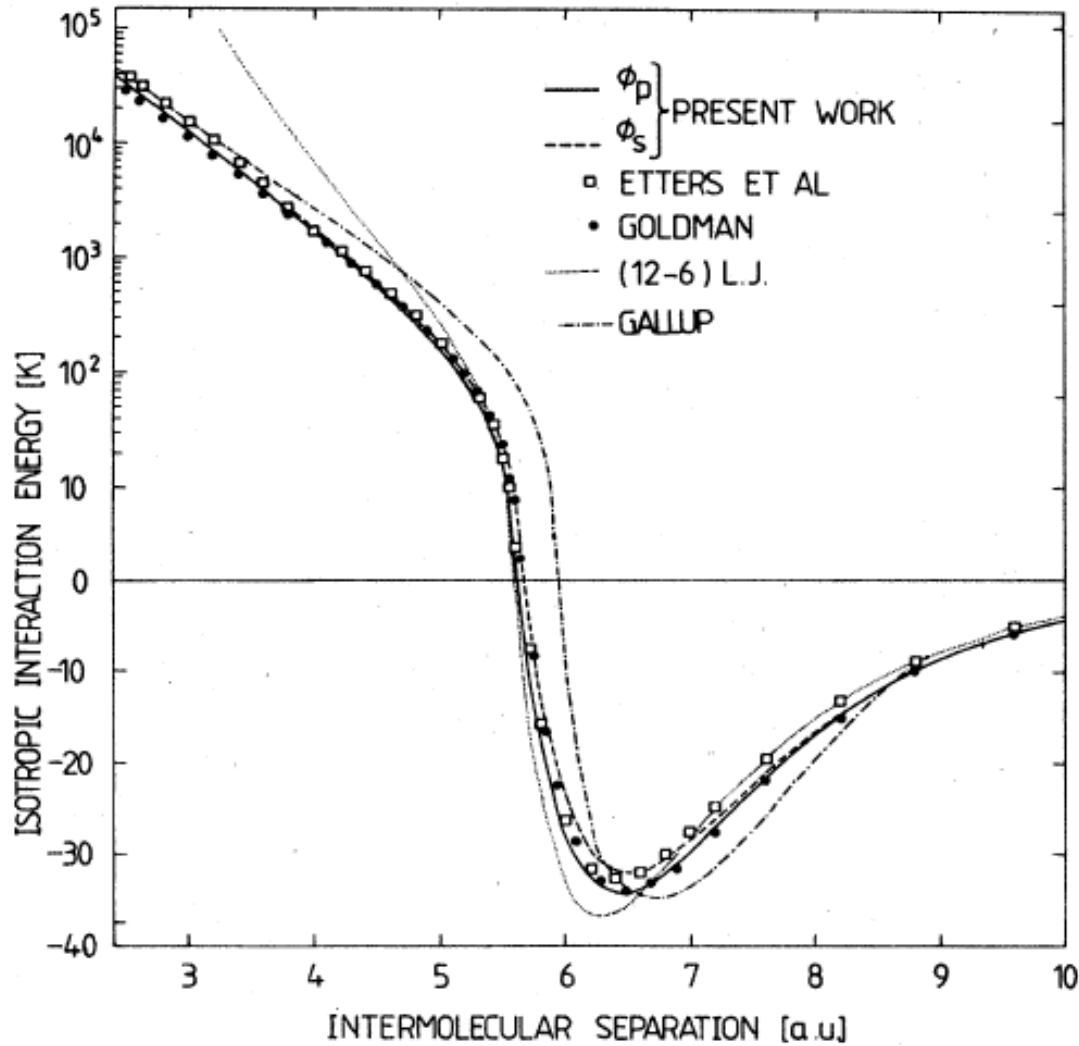


Two H₂ Interacting via Quadrupole-Quadrupole Term

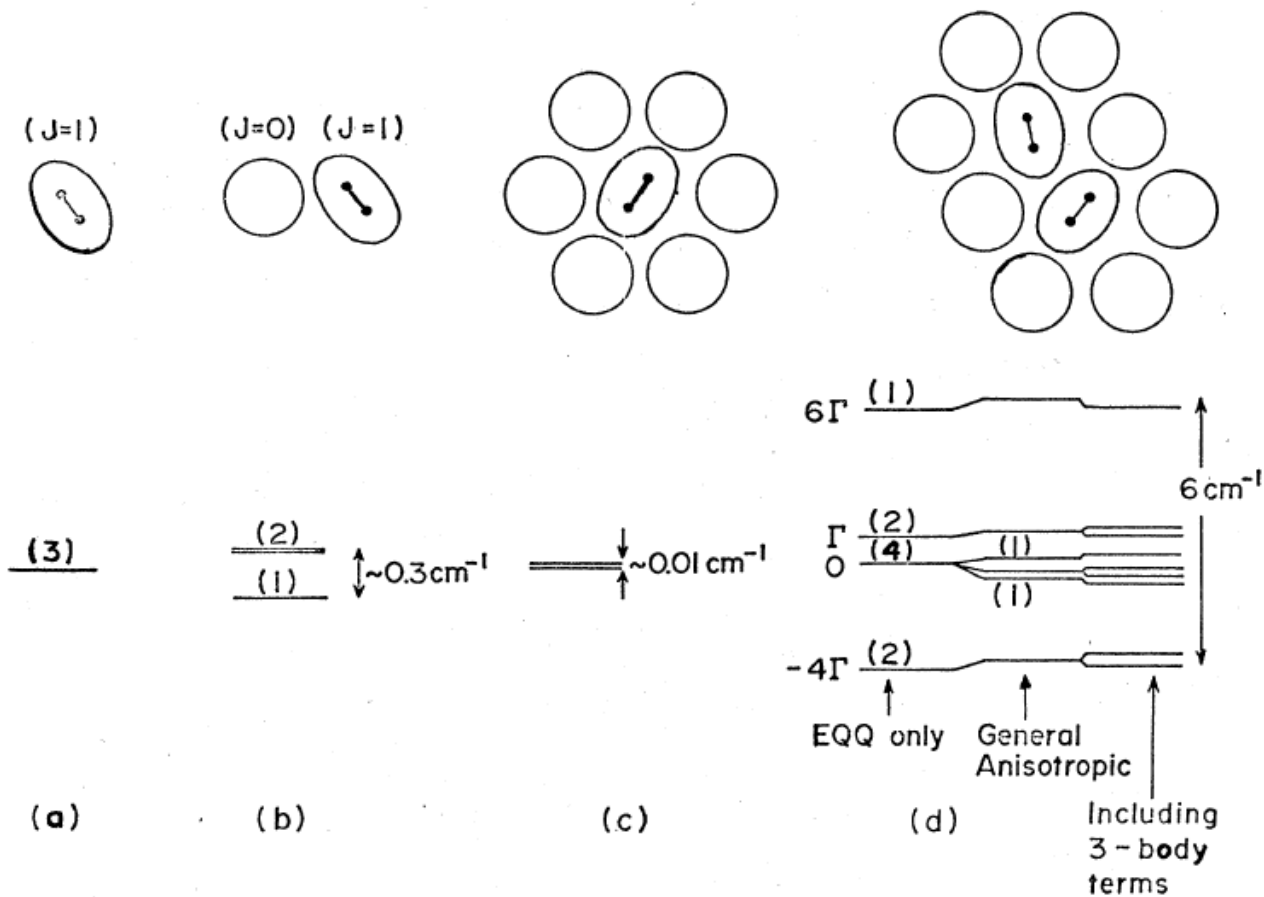


Isotropic $\text{H}_2 \cdots \text{H}_2$ Interaction scales as $1/R^6$

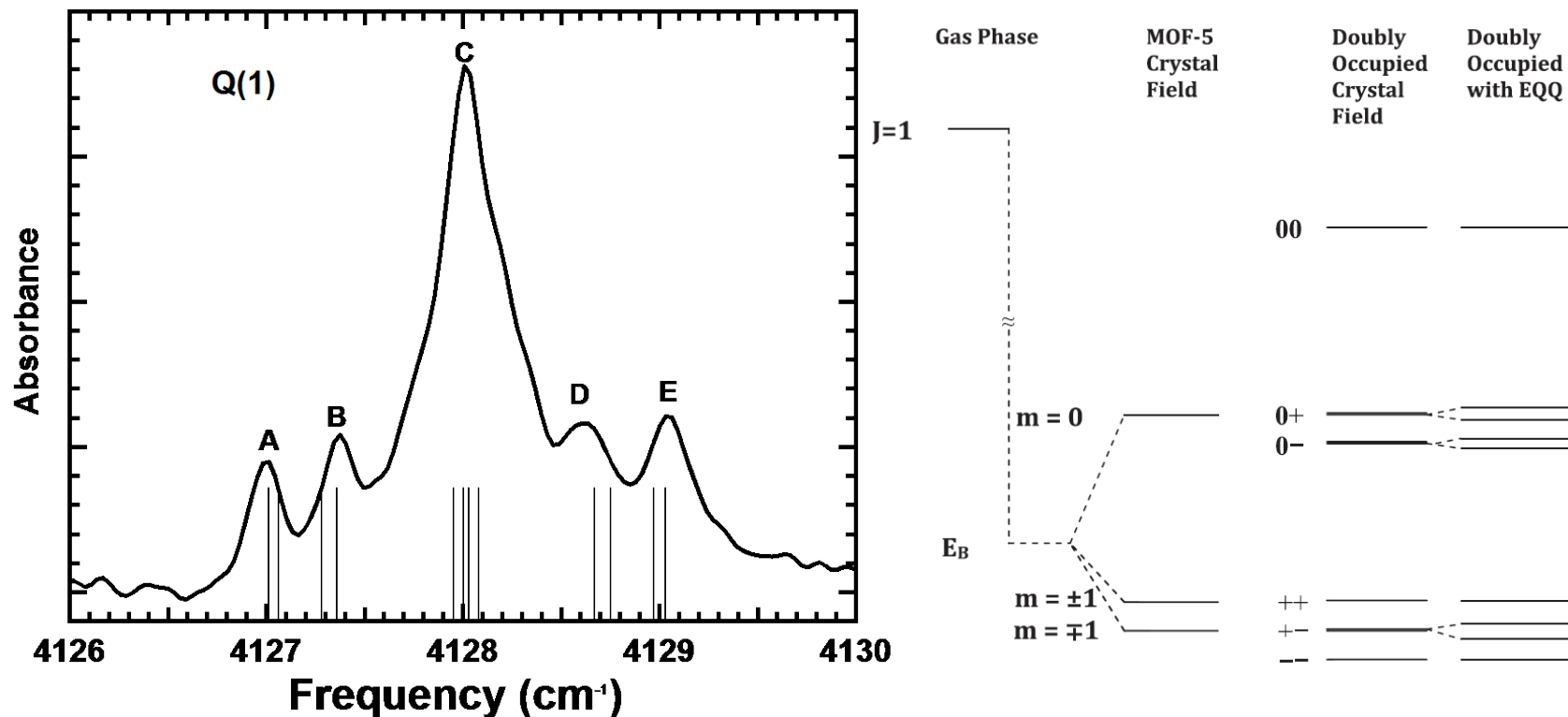
Silvera, Rev. Mod. Phys. **52**, 393 (1980)



Quadrupole···Quadrupole Interaction Scales as $1/R^4$



Stick Spectrum for Interacting *ortho*-H₂ Pairs



Phys. Rev. B **93**, 134304 (2015)

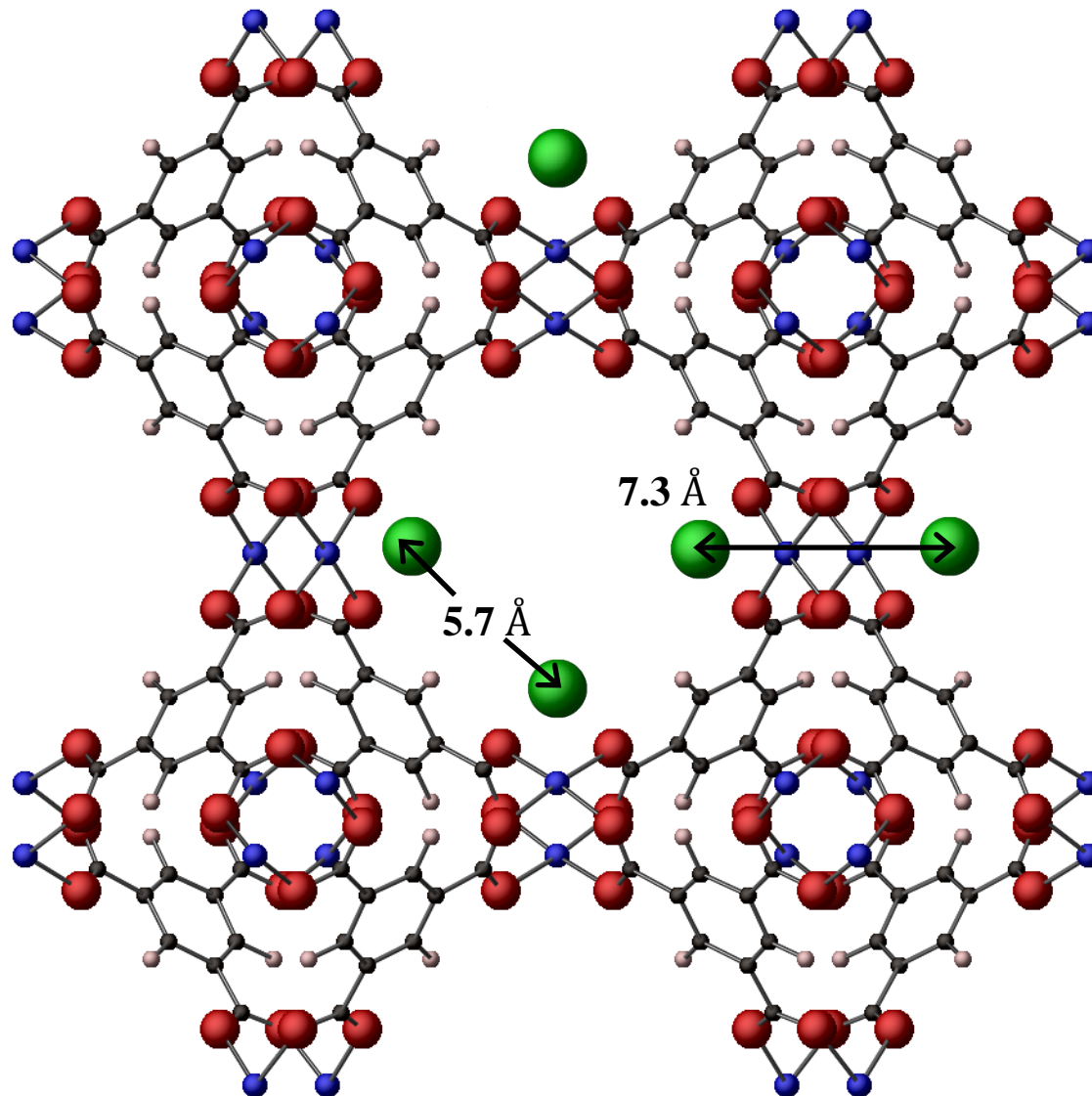
Extracted crystal field splitting between $m \pm 1 = 0.8 \text{ cm}^{-1}$

This compares with prediction by Kong *et al.* $= 0.5 \text{ cm}^{-1}$

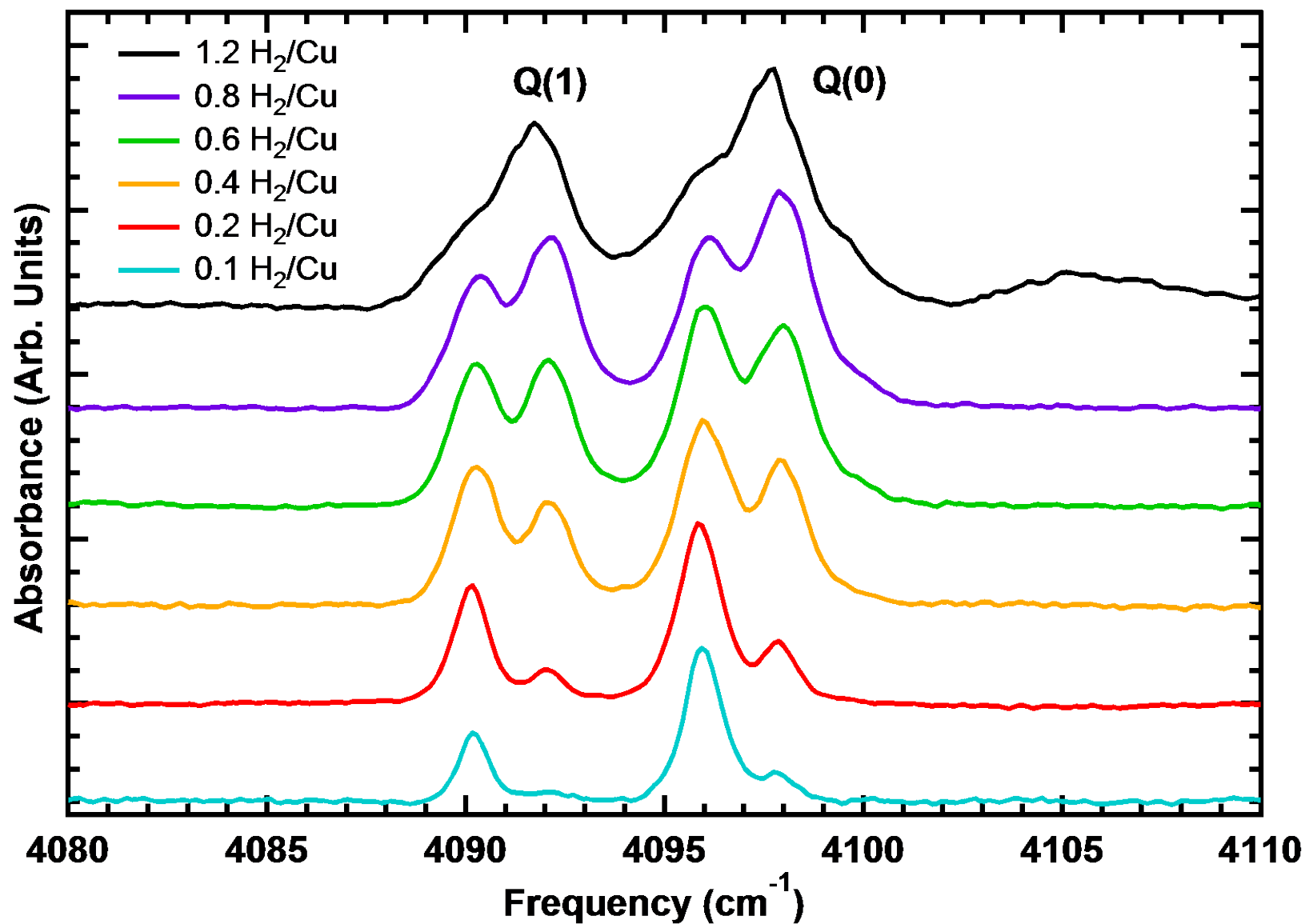
Phys. Rev. B **83**, 121402 (2011)

Double Paddle Wheel Structure: Open Metal Sites

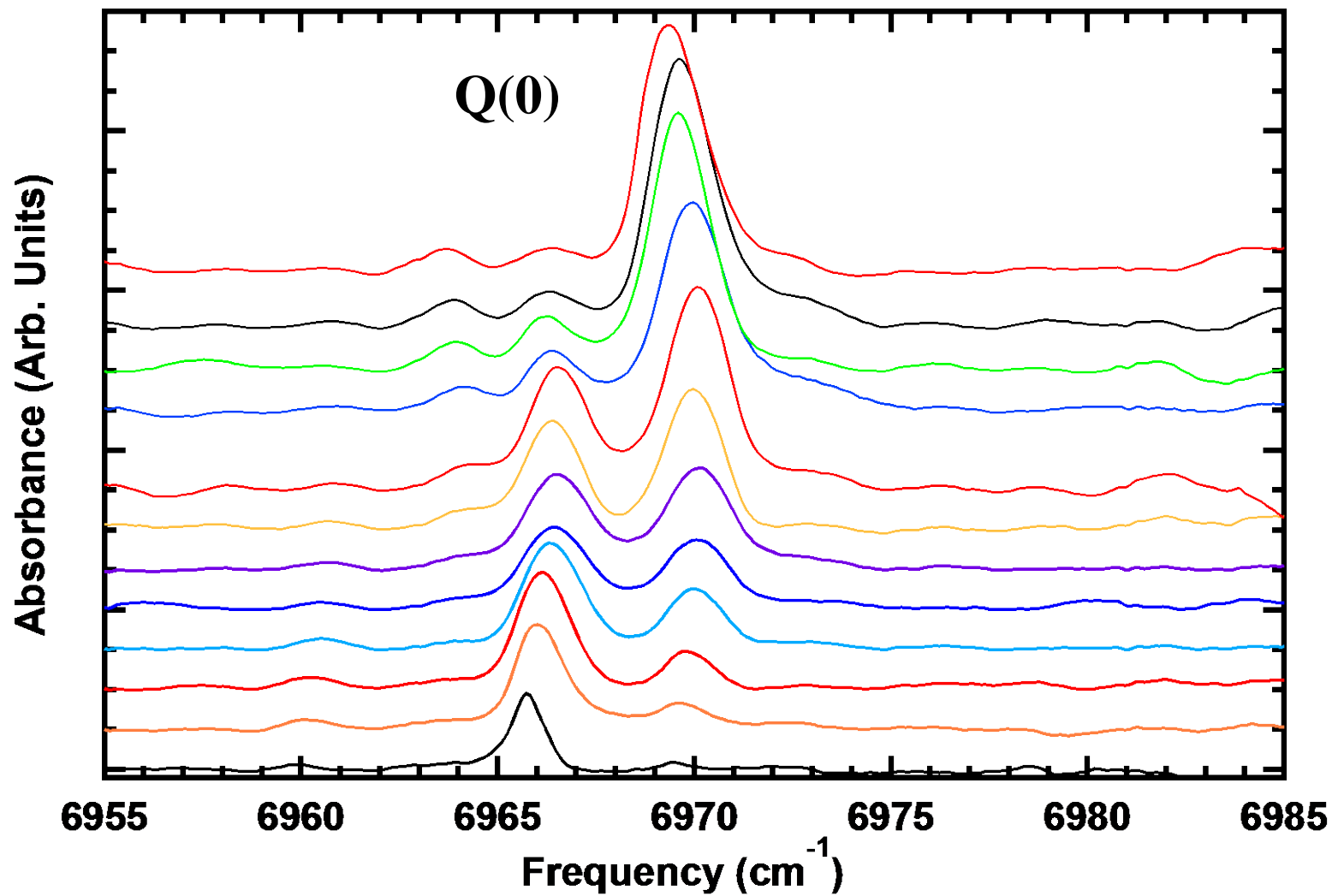
HKUST-1



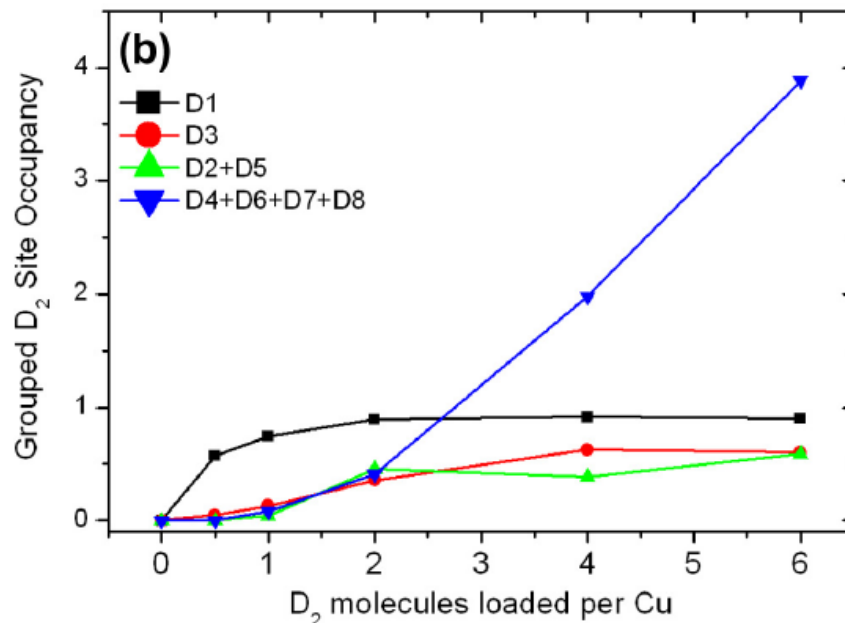
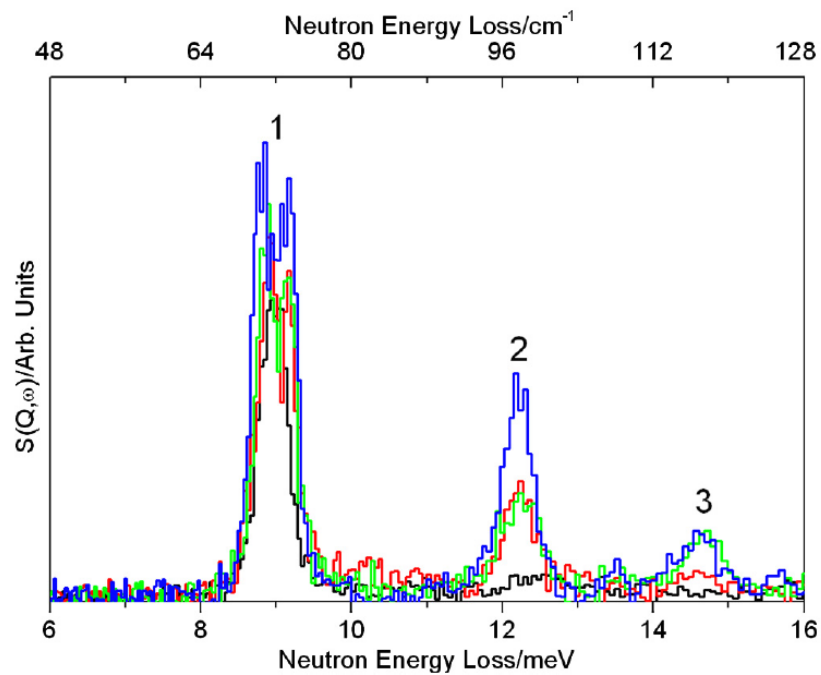
Adsorbed H₂ Vibration in HKUST-1 at 15 K



Adsorbed HD Vibration Overtone in HKUST-1

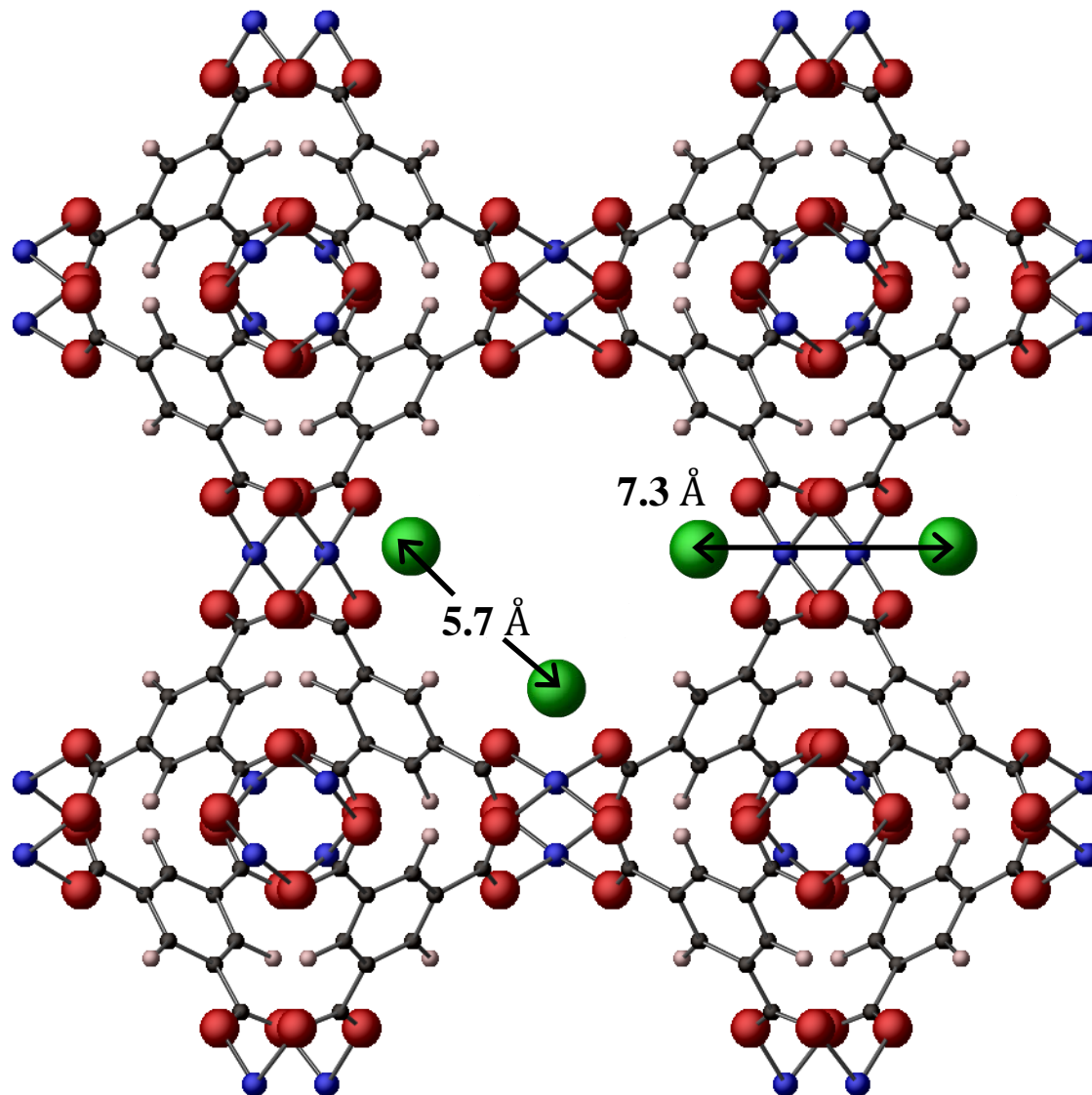


Neutron Scattering

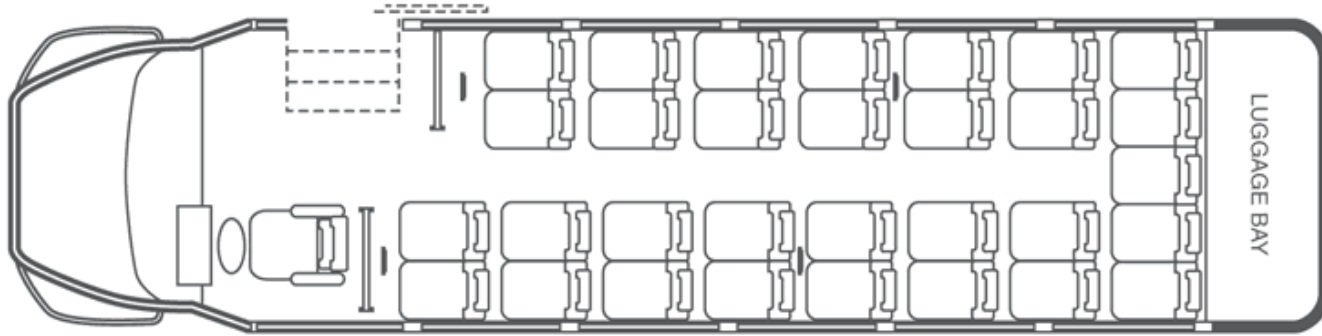


S.K. Callear *et al.* Chem. Phys. **427**, 9 (2013)

HKUST-1 Structure

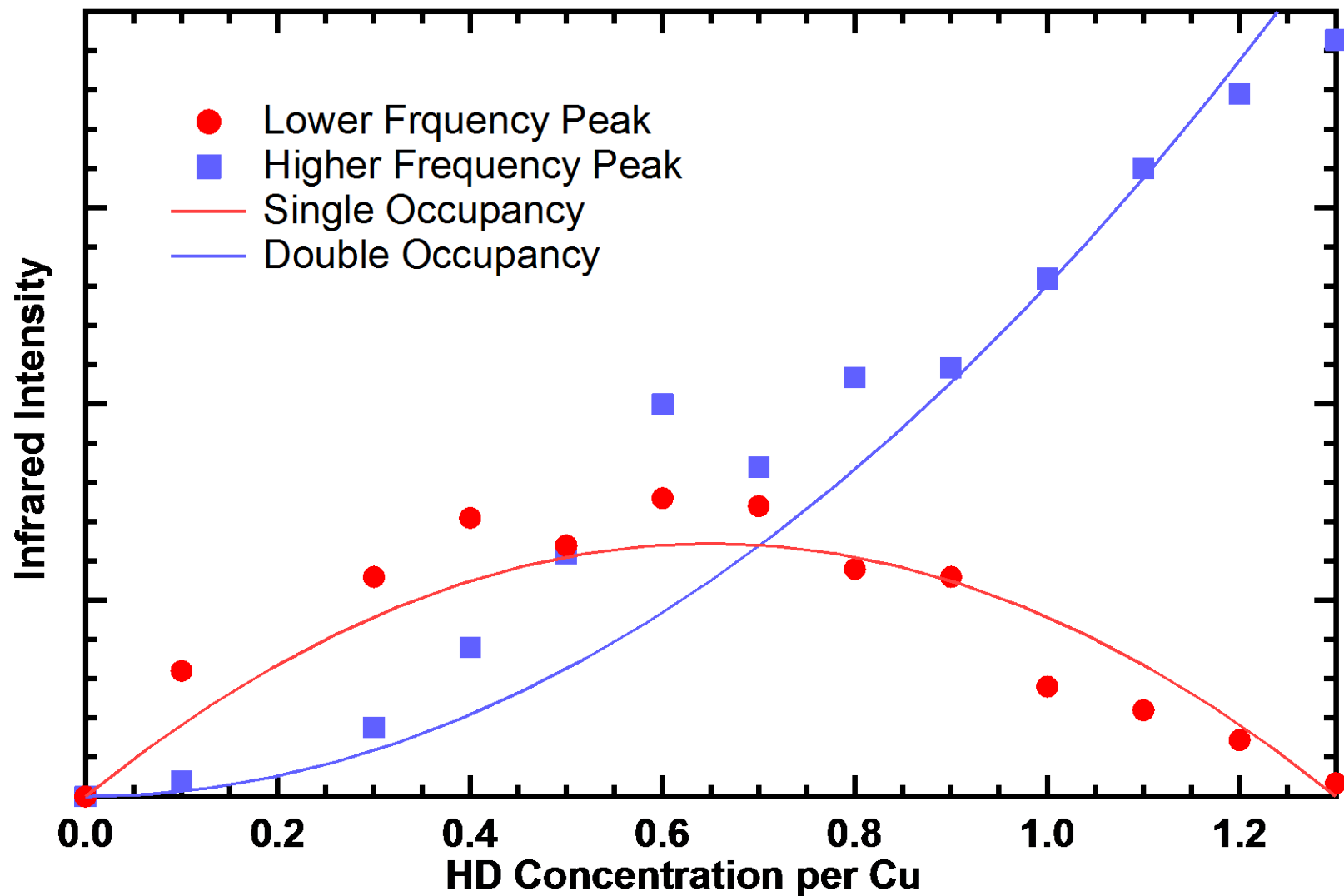


School Bus Sitting: Friends or Loners?

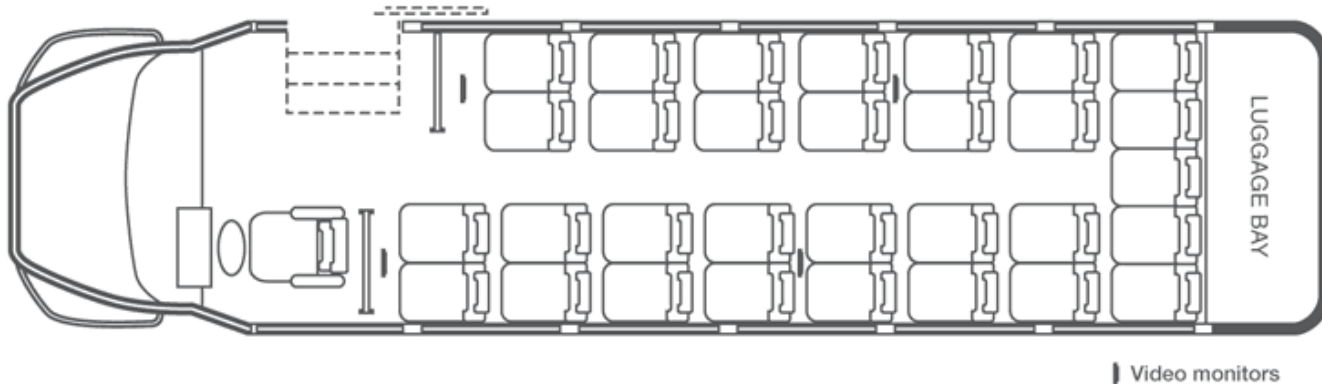


Video monitors

Infrared Intensity and Random Metal-site Filling



School Bus Sitting: Friends or Loners?



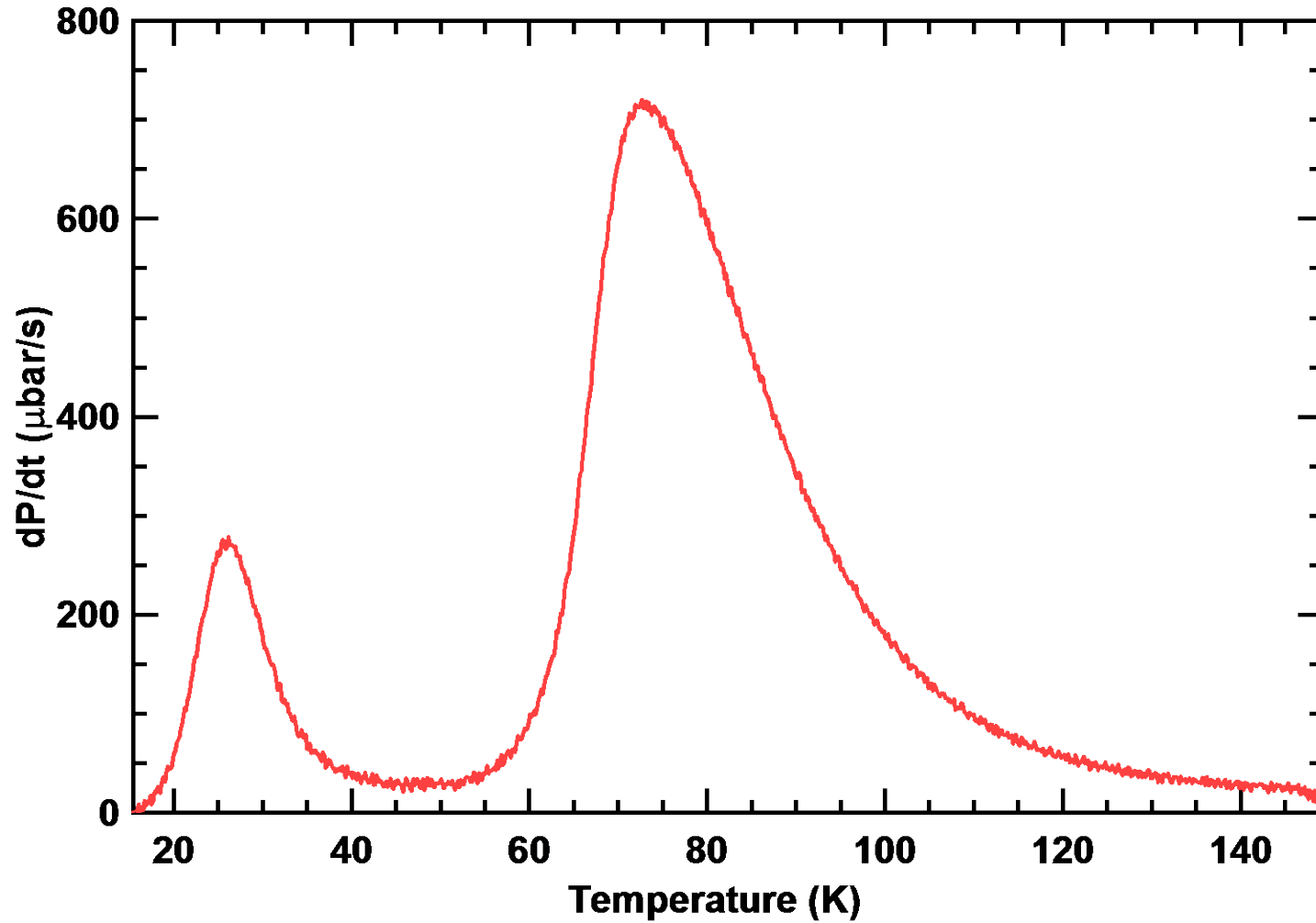
Is there anywhere else the kids can sit?

What happens if the teacher yells “Everybody sit down”?

Thermal equilibrium and site mobility.

At what temperature is mobility frozen out?

Outgas Rate for H₂ and He in HKUST-1



Conclusion

- 1. IR spectroscopy reveals adsorbate information on a site by site basis (best when combined with diffraction)**
- 2. MOF \cdots H₂ interaction energy can be extracted**
- 3. H₂ \cdots H₂ interactions emerge**
- 4. Working on determining the state of the adsorbed H₂**

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**Jesse
Hopkins**
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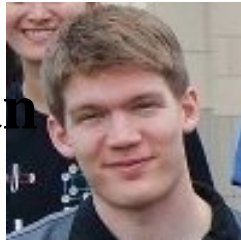
**Brian
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**Elizabeth
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Cal. Tech*



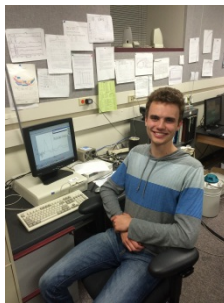
**Yorgos
Strangas**
*U. Michigan
Beth Israel MD*



**Kai
Shinbrough**
Still at Oberlin



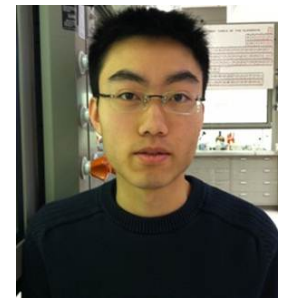
**Chris
Eckdahl**
Still at Oberlin

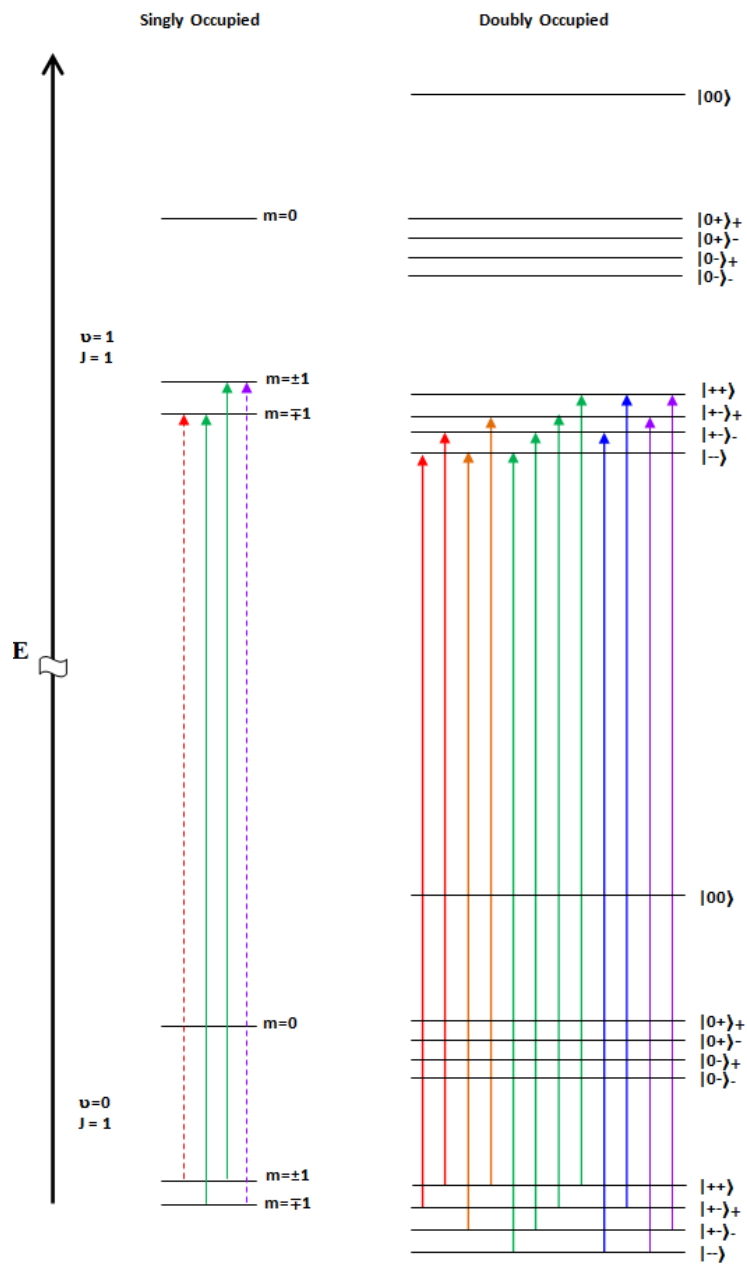


**Cooper
McDonald**
Just graduated

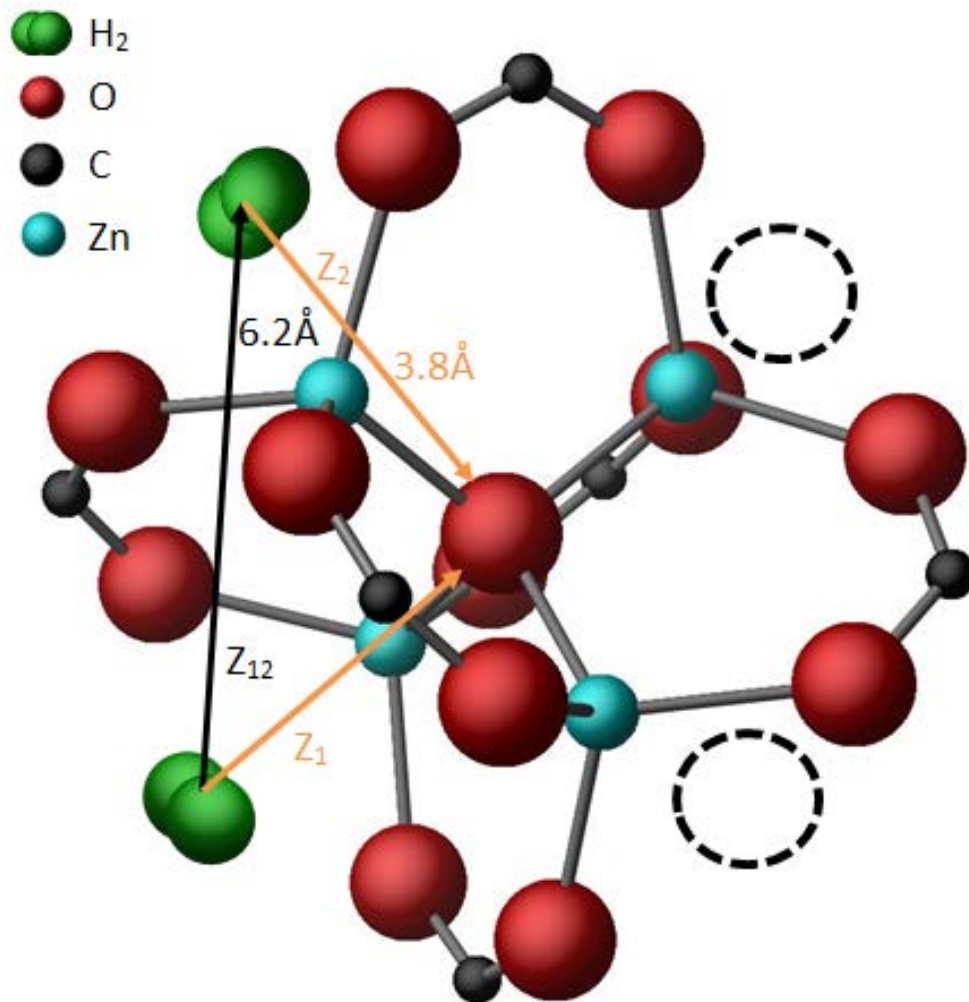


**Holden
Lai**
Berkeley U.



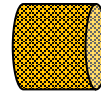


MOF-5 with H₂ Molecules at Primary Site



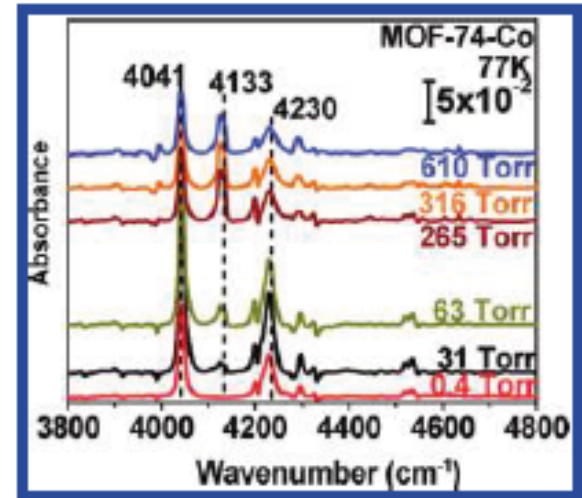
Possible Infrared Techniques for H₂

a) Transmission through
KBr/sample compact



e.g. Chabal group

J. Am. Chem. Soc. 2011, **133**, 4782



b) Transmission through
thin pressed pellet



e.g. Bordiga group

Phys. Chem. Chem. Phys., 2007, **9**, 2676

