Infrared Spectroscopy of H_2 in MOFs

1) More than just a characterization technique

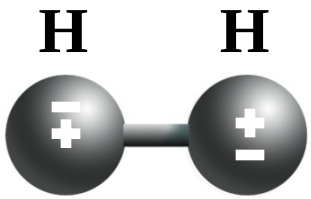
2) Experimental probe of H_2···MOF interactions

3) Requires some specialized equipment

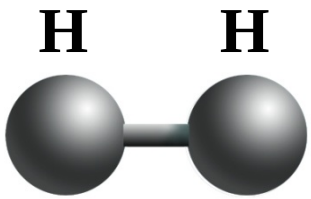
4) Storage, quantum sieving, catalysis

5) CO_2, CH_4, N_2, other gases

Infrared Spectroscopy! Are you crazy?



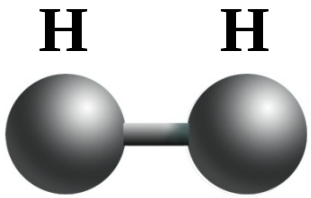
Infrared Spectroscopy! Are you crazy?



The atoms are neutral

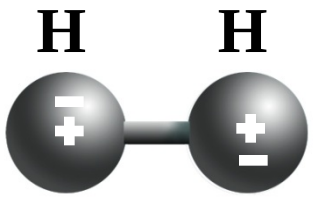
No Dipole moment

Infrared Spectroscopy! Are you crazy?



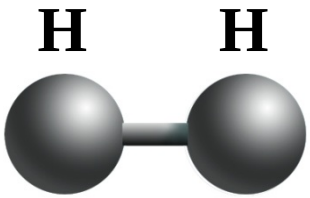
The atoms are neutral

No Dipole moment



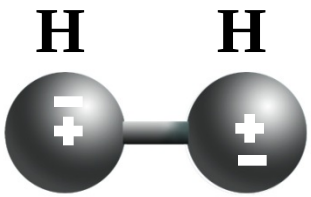
Interactions with MOF can polarize H_2

Infrared Spectroscopy! Are you crazy?



The atoms are neutral

No Dipole moment



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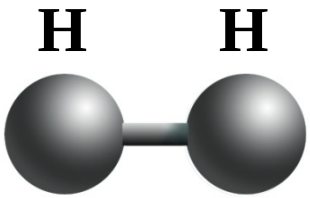

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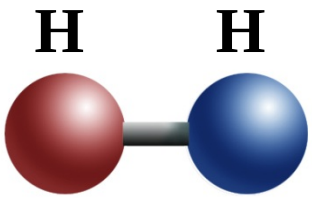
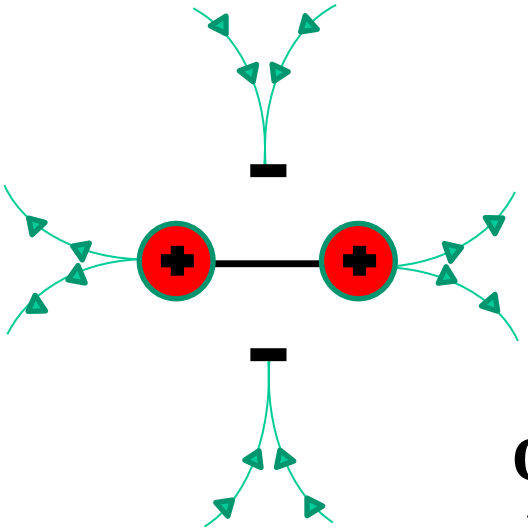


Interactions with MOF can polarize H_2

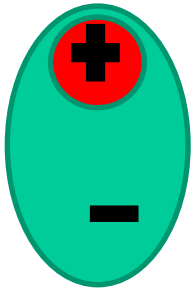
H_2 polarizability is almost isotropic
Mostly activates pure vibrational transitions

H_2 Quadrupole Mechanism



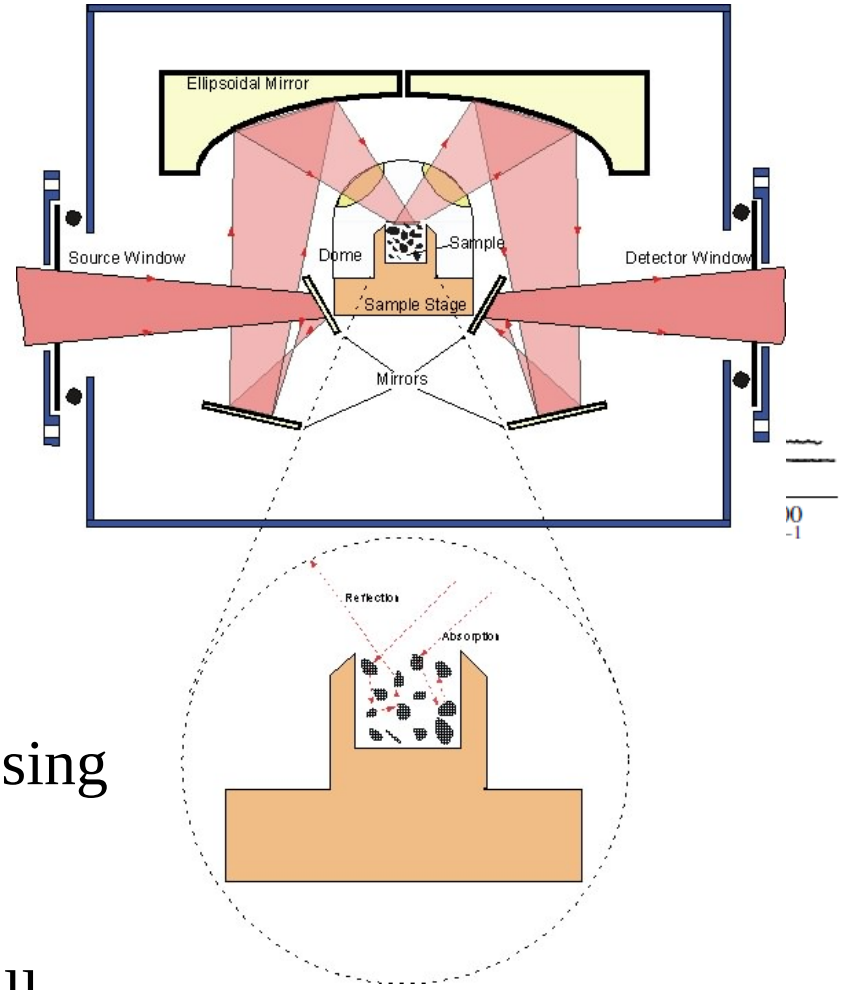
H_2 quadrupole moment can polarize MOF atoms

Quadrupole moment highly anisotropic
Vibrations and Ro-vibrations are activated



Hydrogen polarizes MOF atoms

Diffuse Reflectance Infrared Spectroscopy



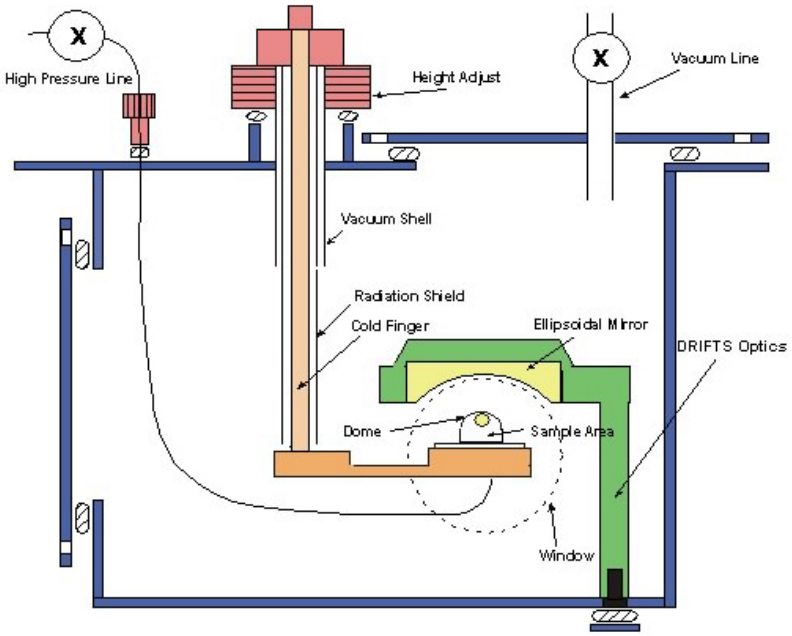
1) Long effective optical path length

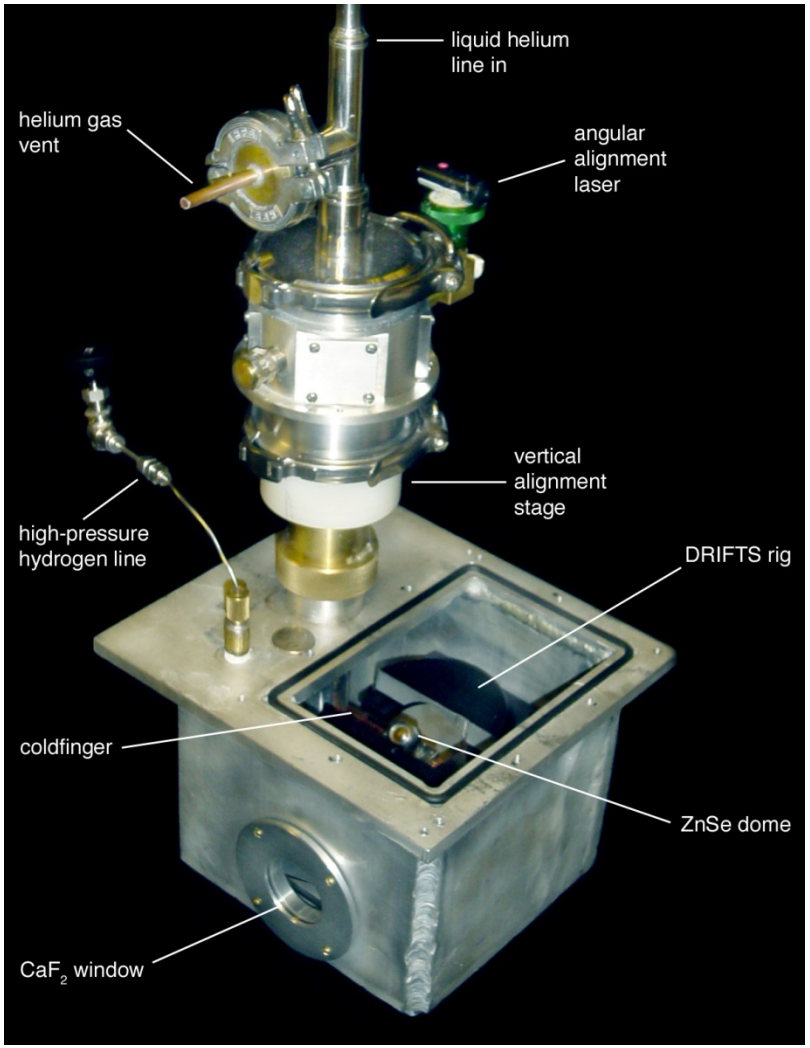
2) Powder sample require no processing

3) Typically use 10 mg of powder

4) Sample chamber can be quite small

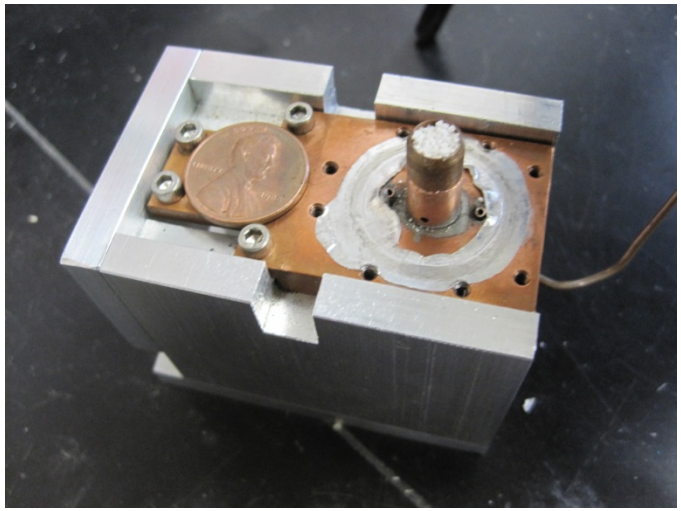
Diffuse Reflectance Spectroscopy: Cryostat Assembly

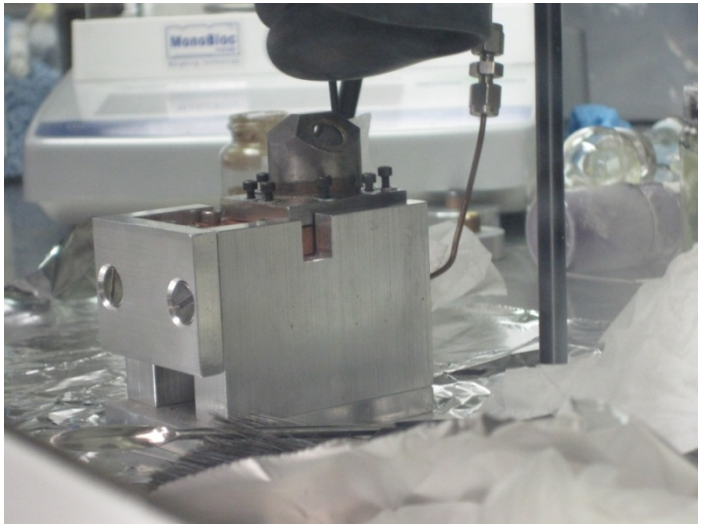


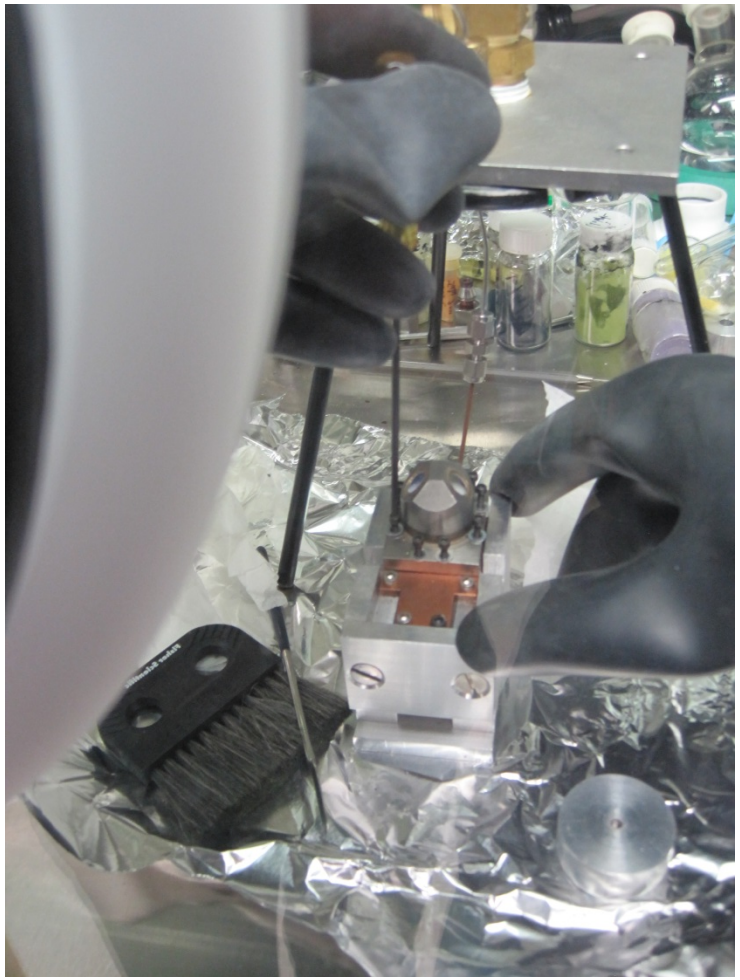


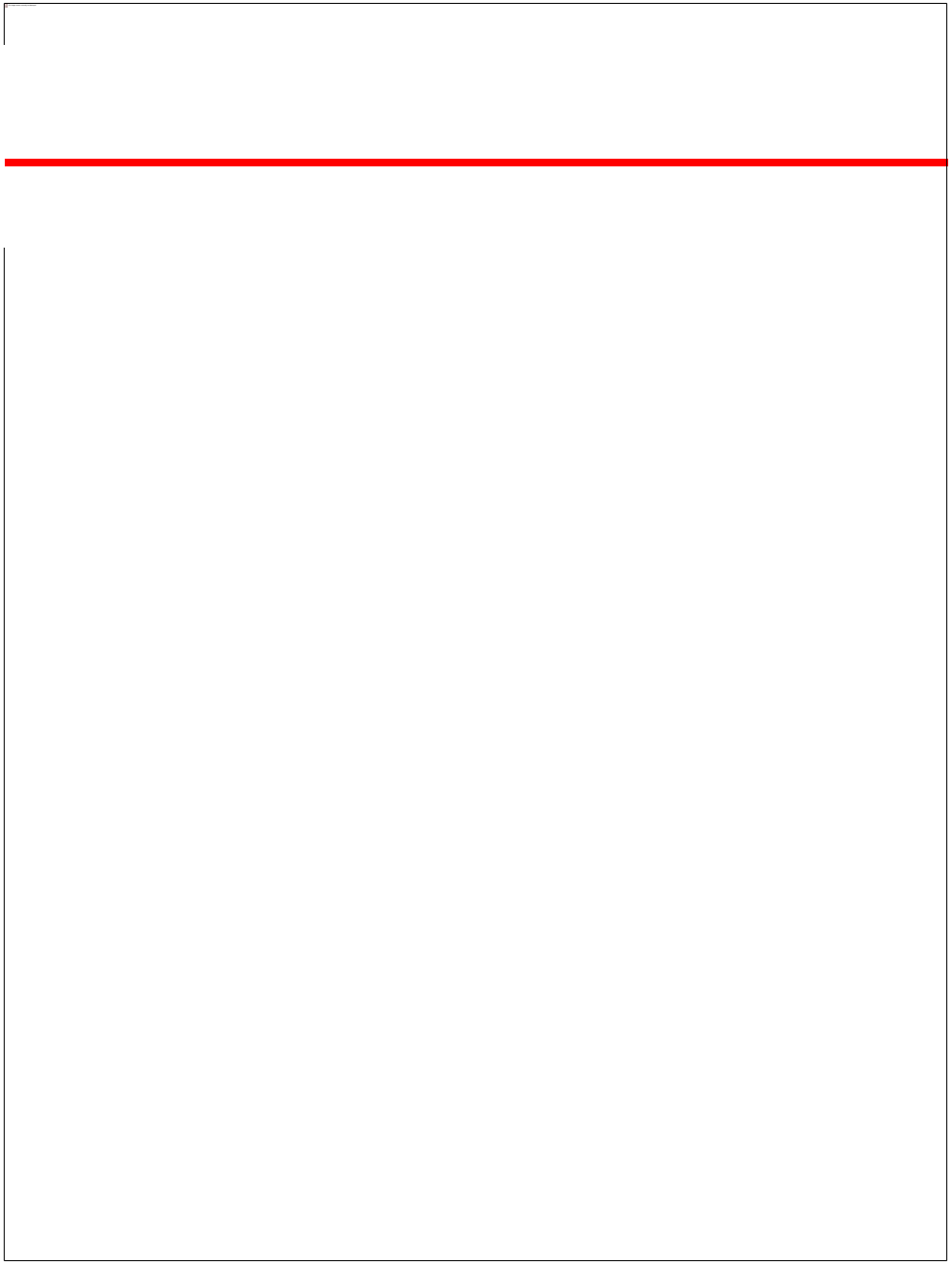
Rev. Sci. Instr. **77**, 093110 (2006)

Samples are mounted in a glove-box







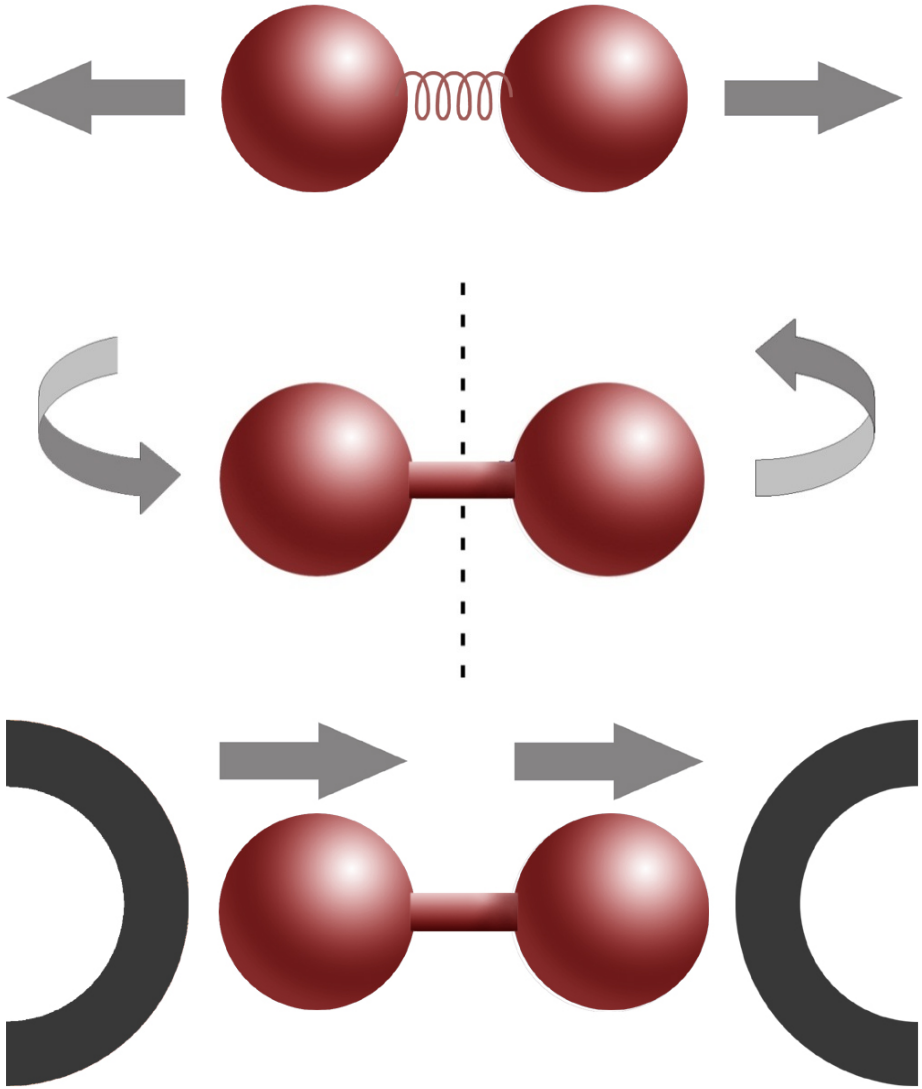


Quantum Dynamics of Adsorbed H_2

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

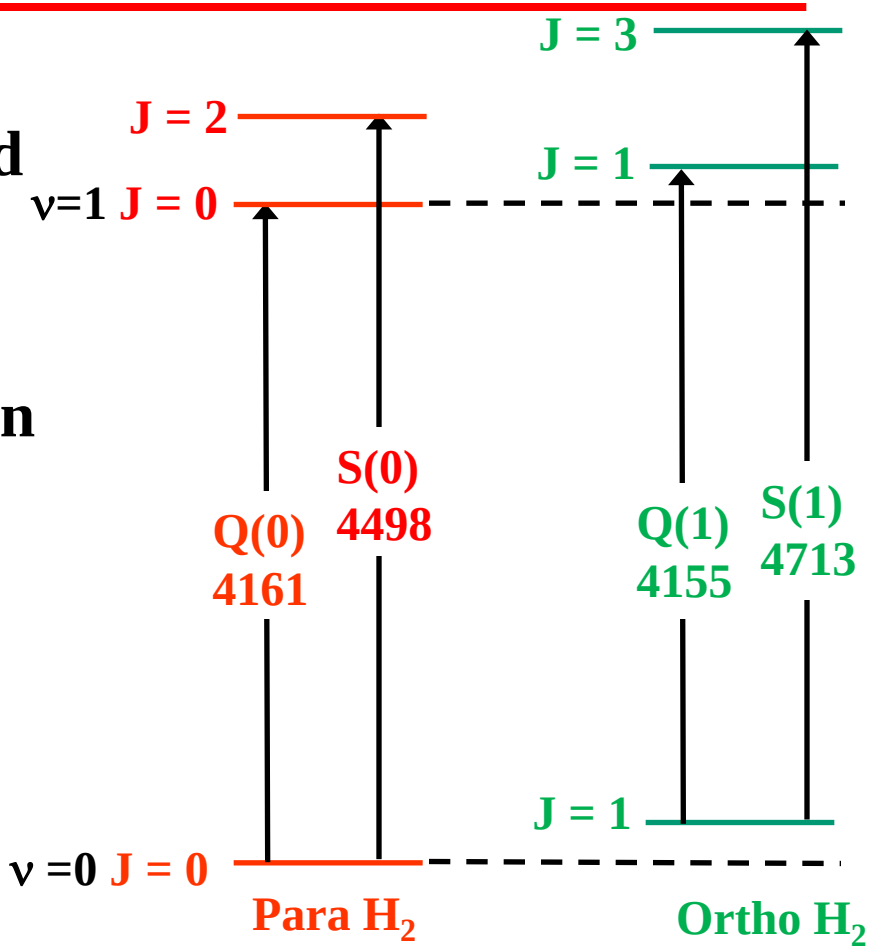
- Rotation
  $E_J = J(J+1)B_0$
  B_0 = 59 cm^{-1} for free H_2

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

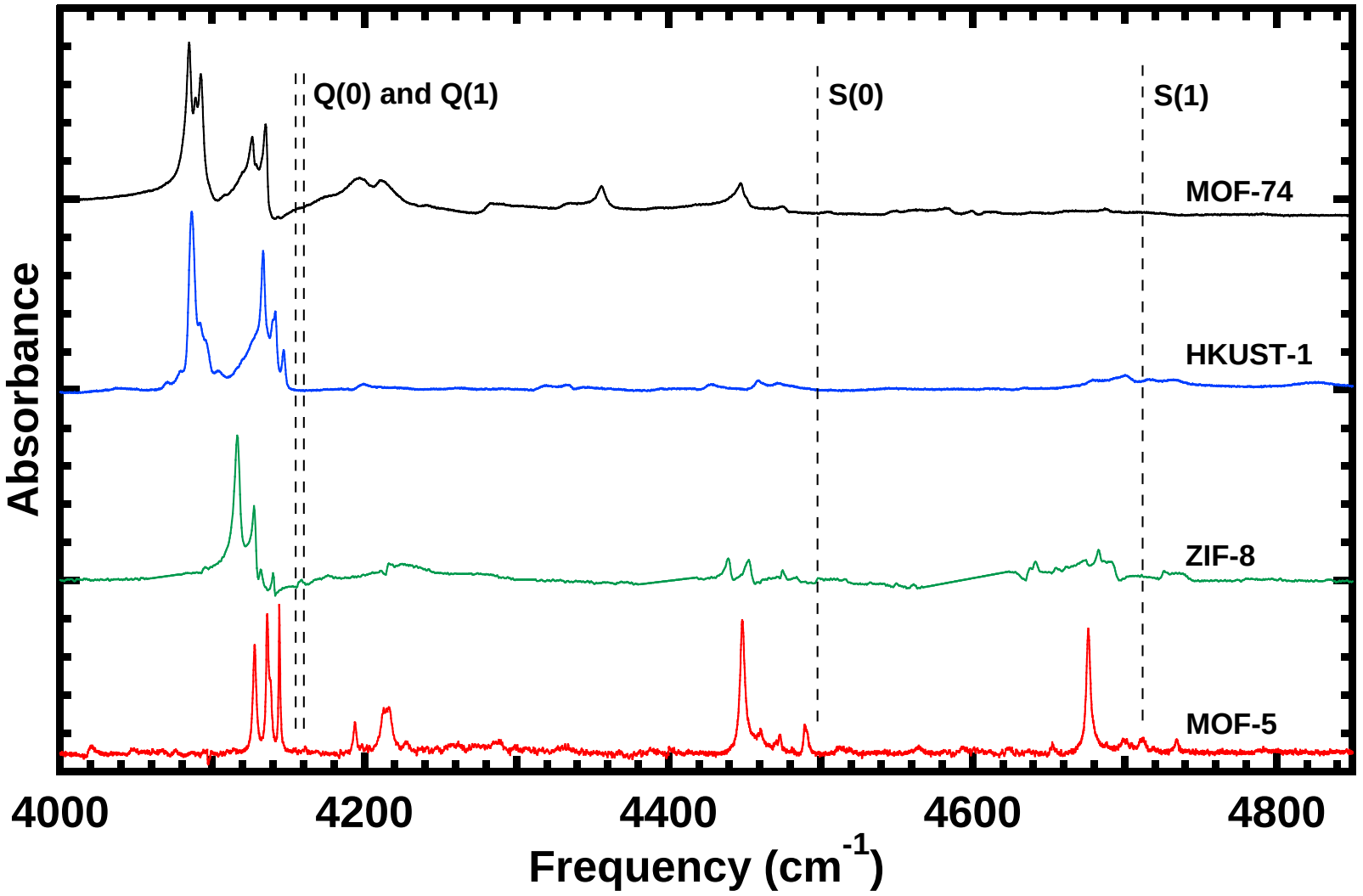


Spectroscopic notation of possible transitions

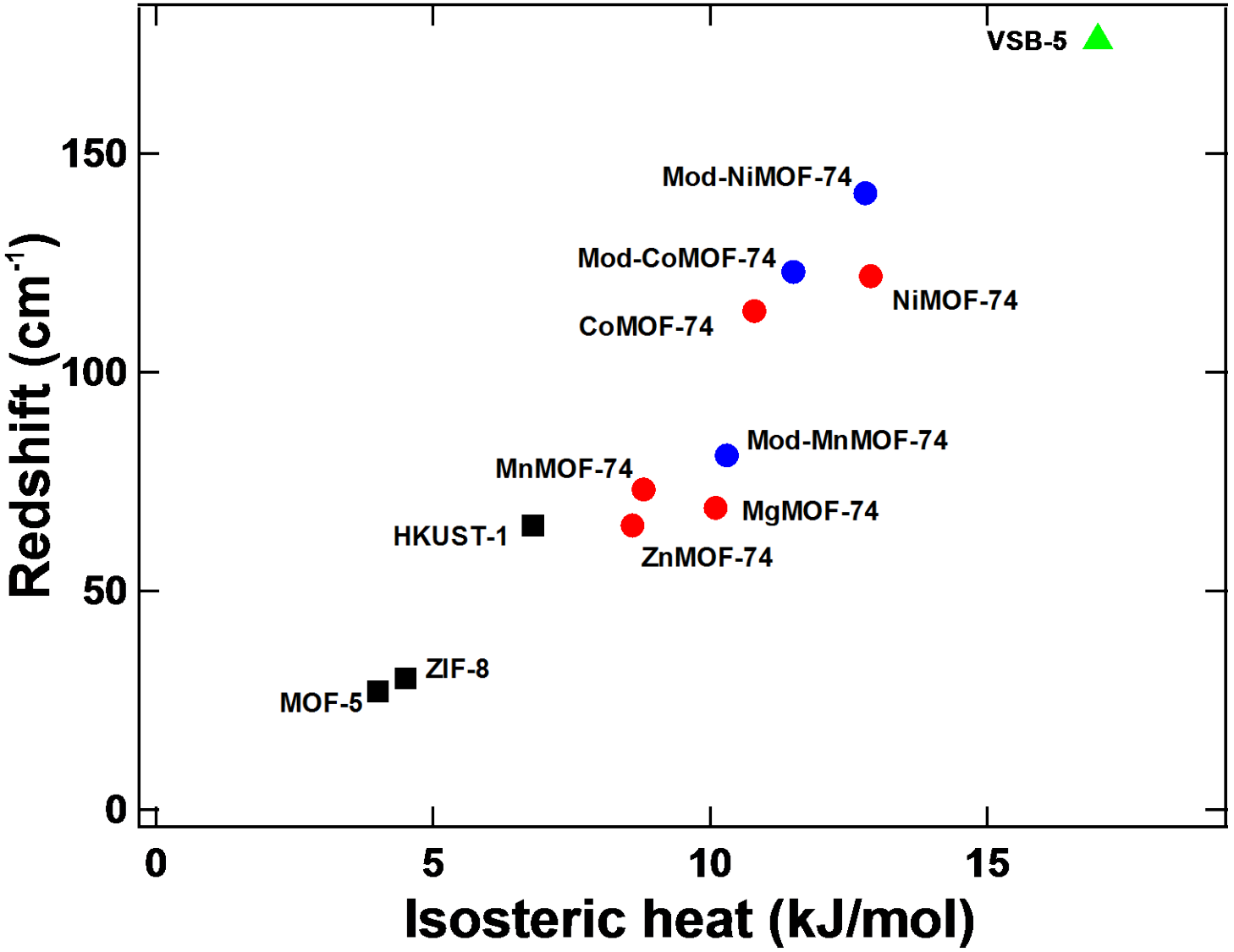
- **Pure Vibrational modes called Q transitions $\Delta J = 0$**
- **Q(0) and Q(1) are very close in energy ~ 6 cm^{-1} apart**
- **Rotational Sidebands called S Transitions $\Delta J = 2$**



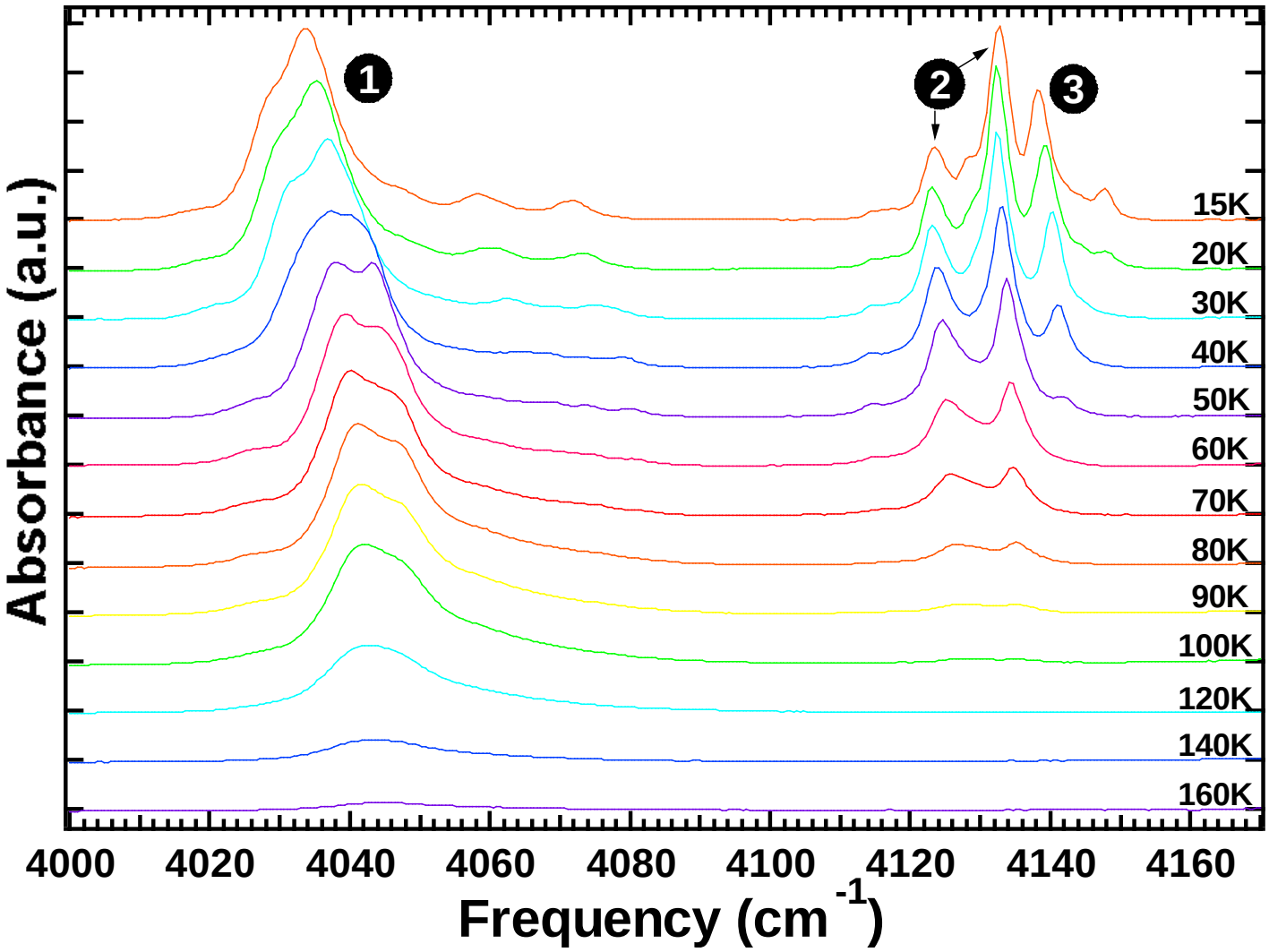
Typical Spectra for H_2 in MOFs at 30 K



Vibrational Redshift as a Function of Binding Energy

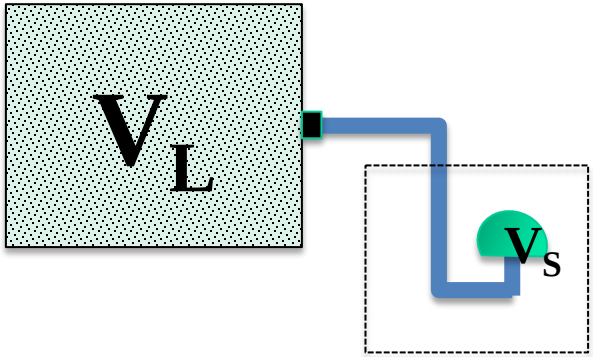


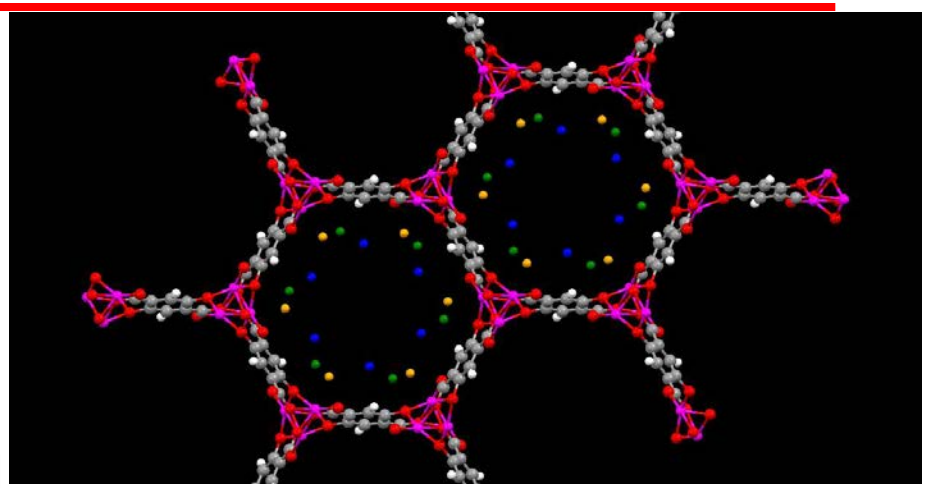
Temperature Dependent Spectra Co-MOF-74

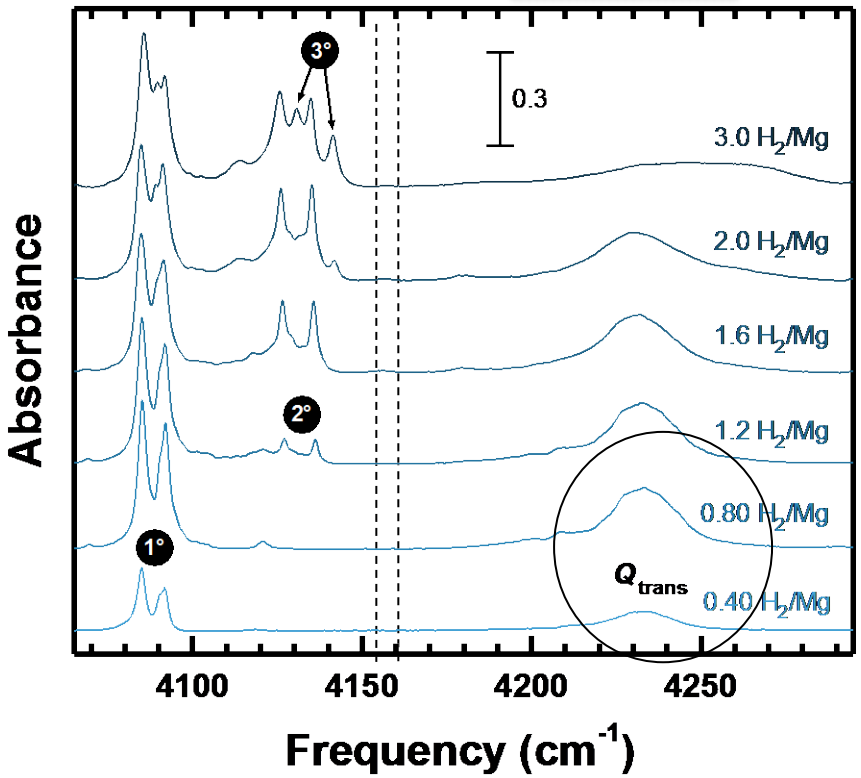


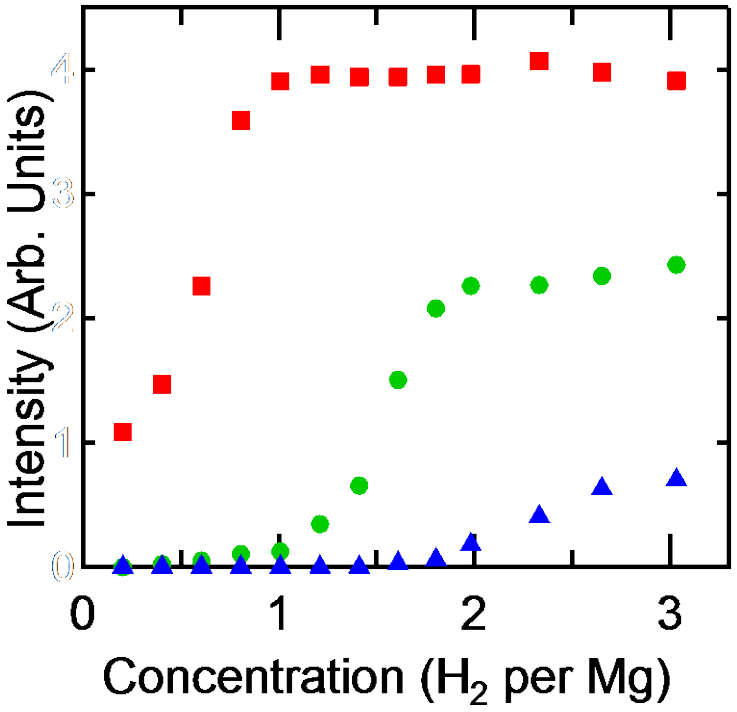
Spectra as a function of concentration (Mg-MOF-74 at 35 K)

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









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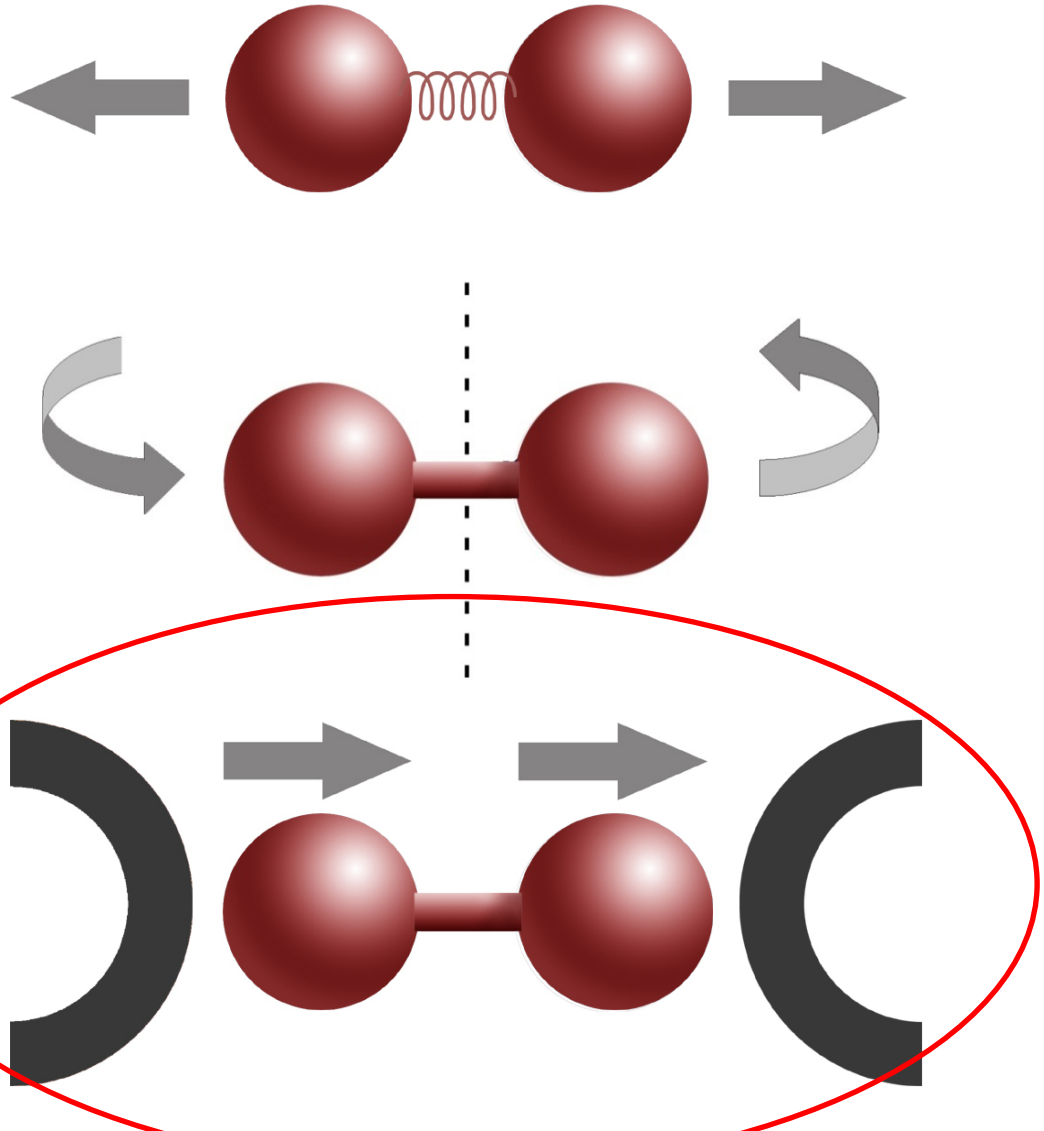
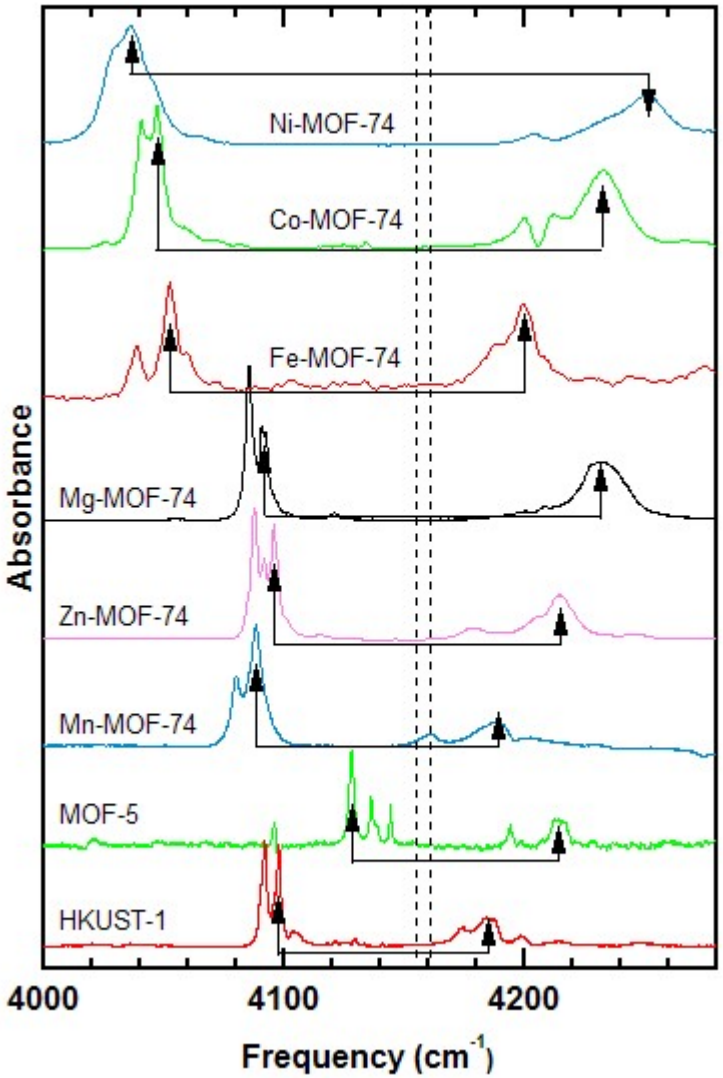
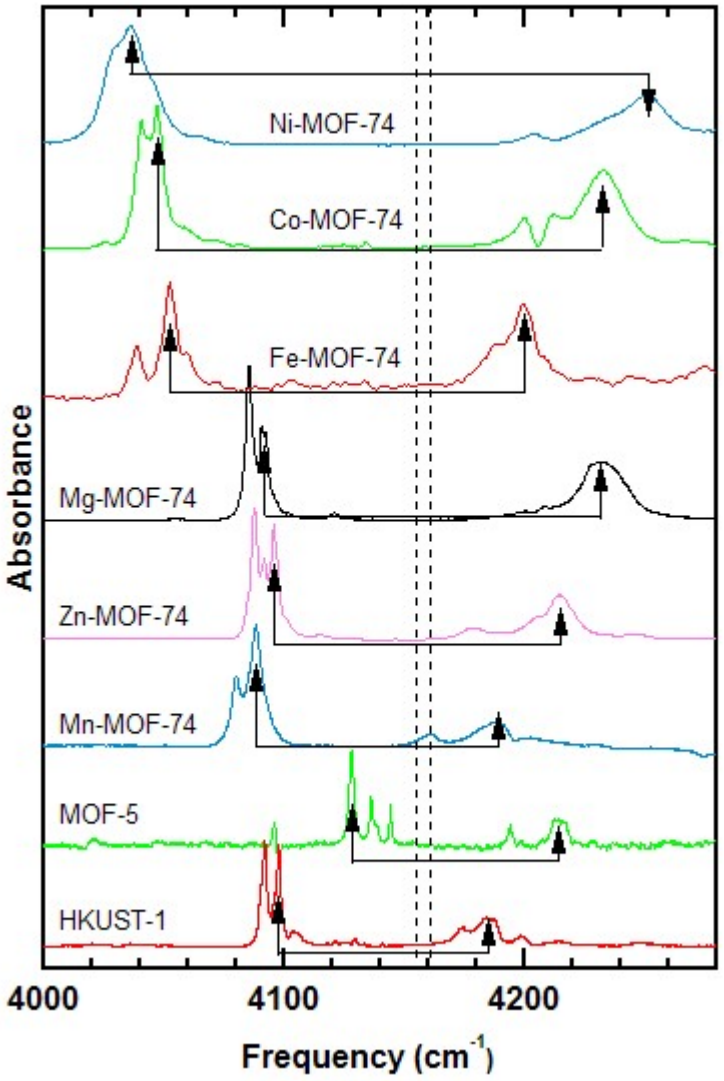


Translational mode energy (quantum sieving?)



Back of the Envelope Calculation



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

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

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

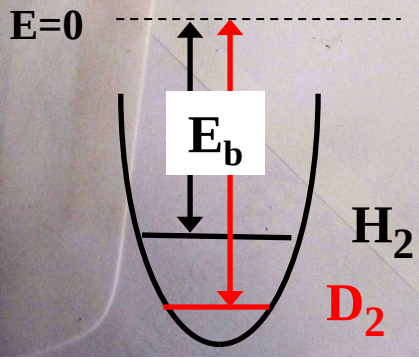
$\omega_{D_2} = 1/\sqrt{2}\ \omega_{H_2}$

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

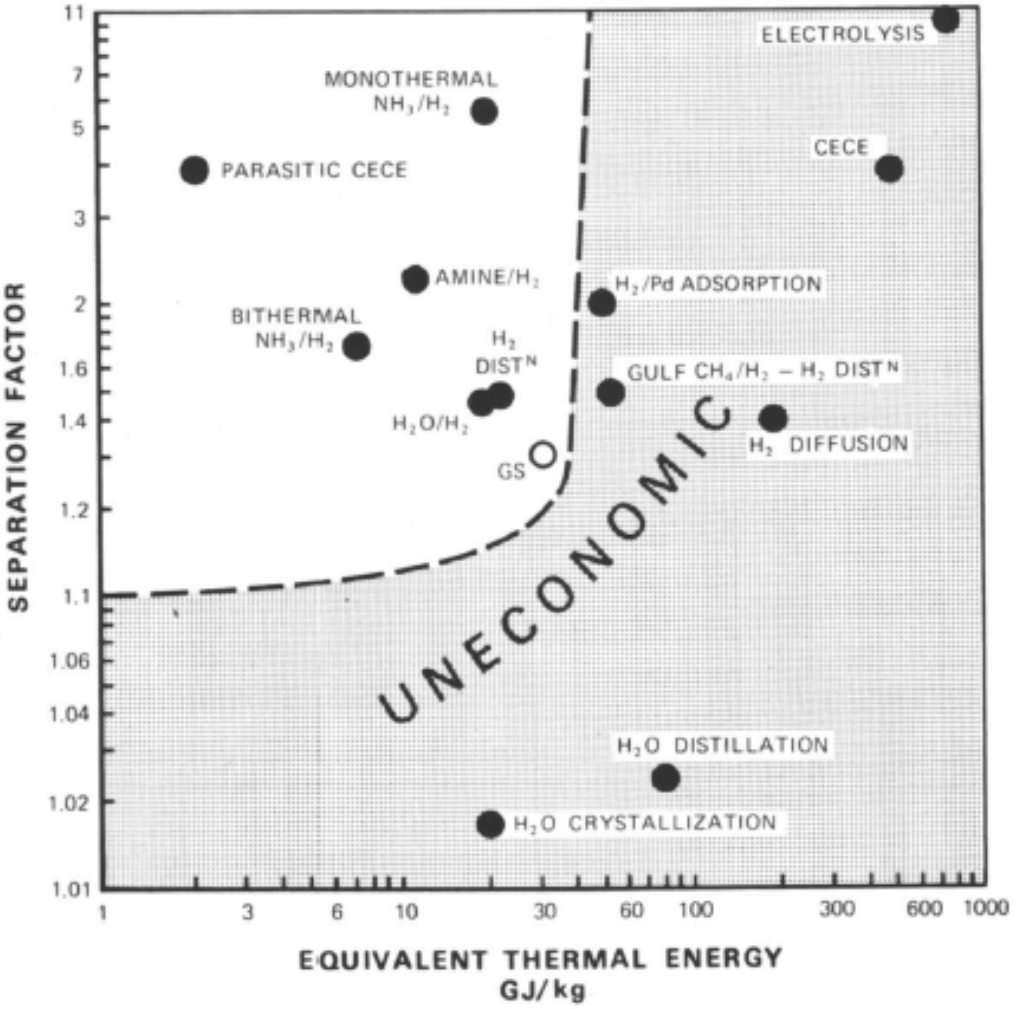
$\Delta ZPE = 120K$

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

$e^{120/77} = 4.75$

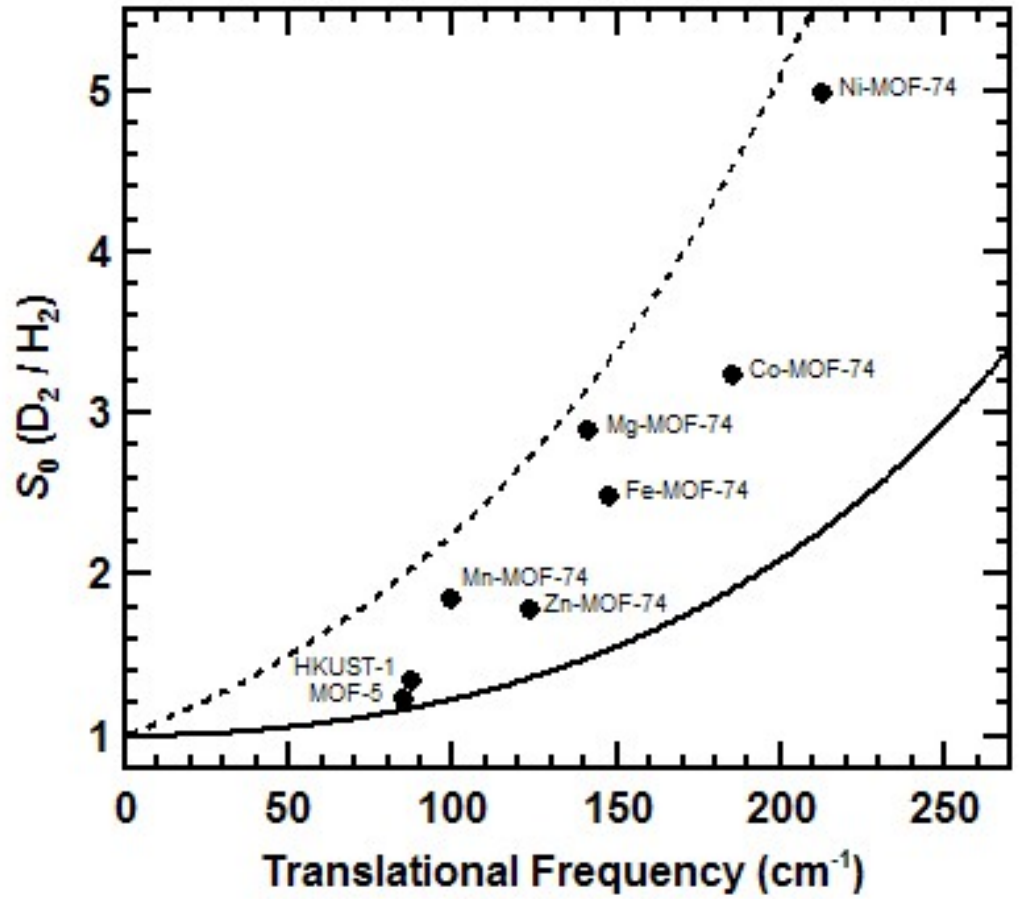


Standard Separation Techniques



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

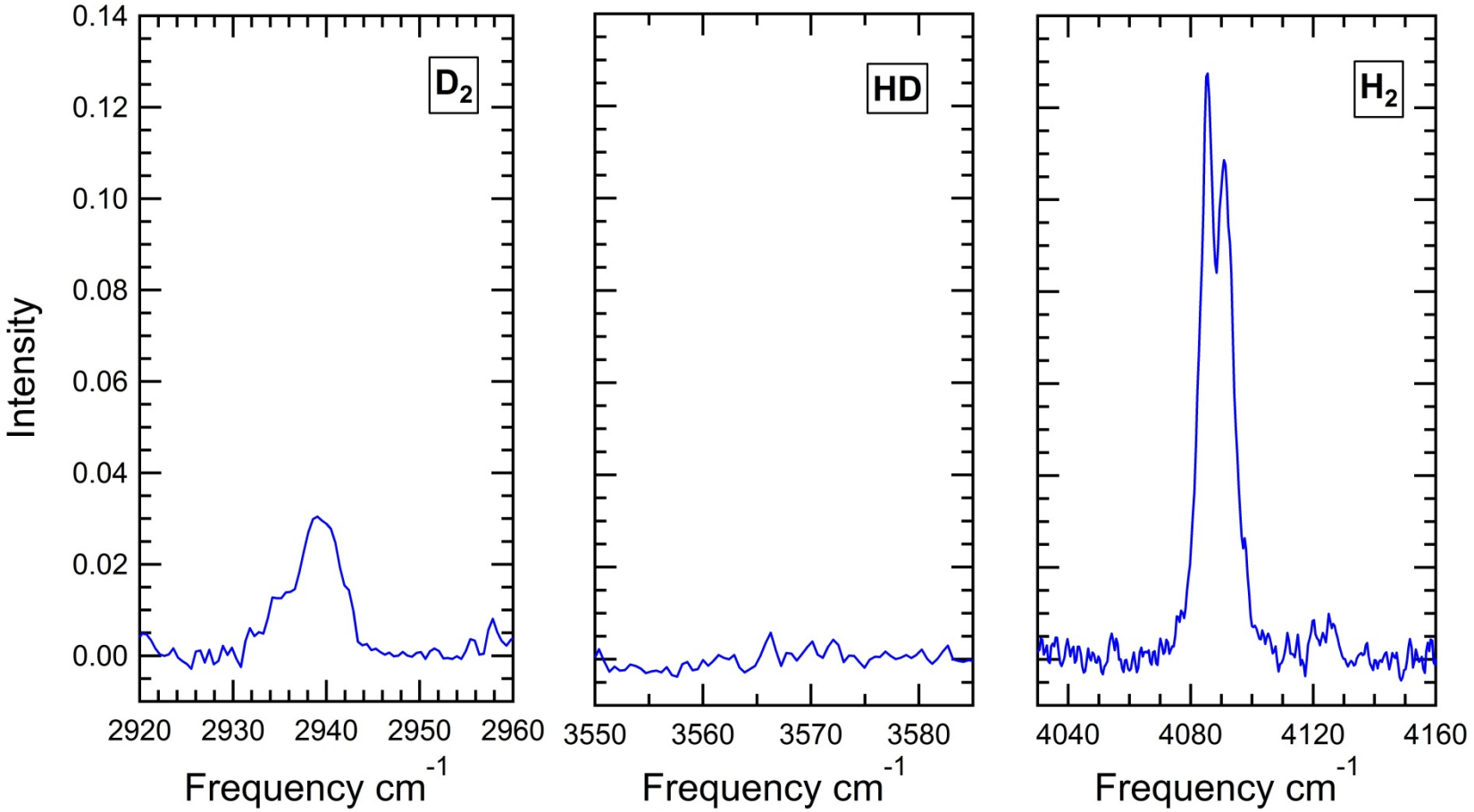
Selectivity vs Translational Frequency



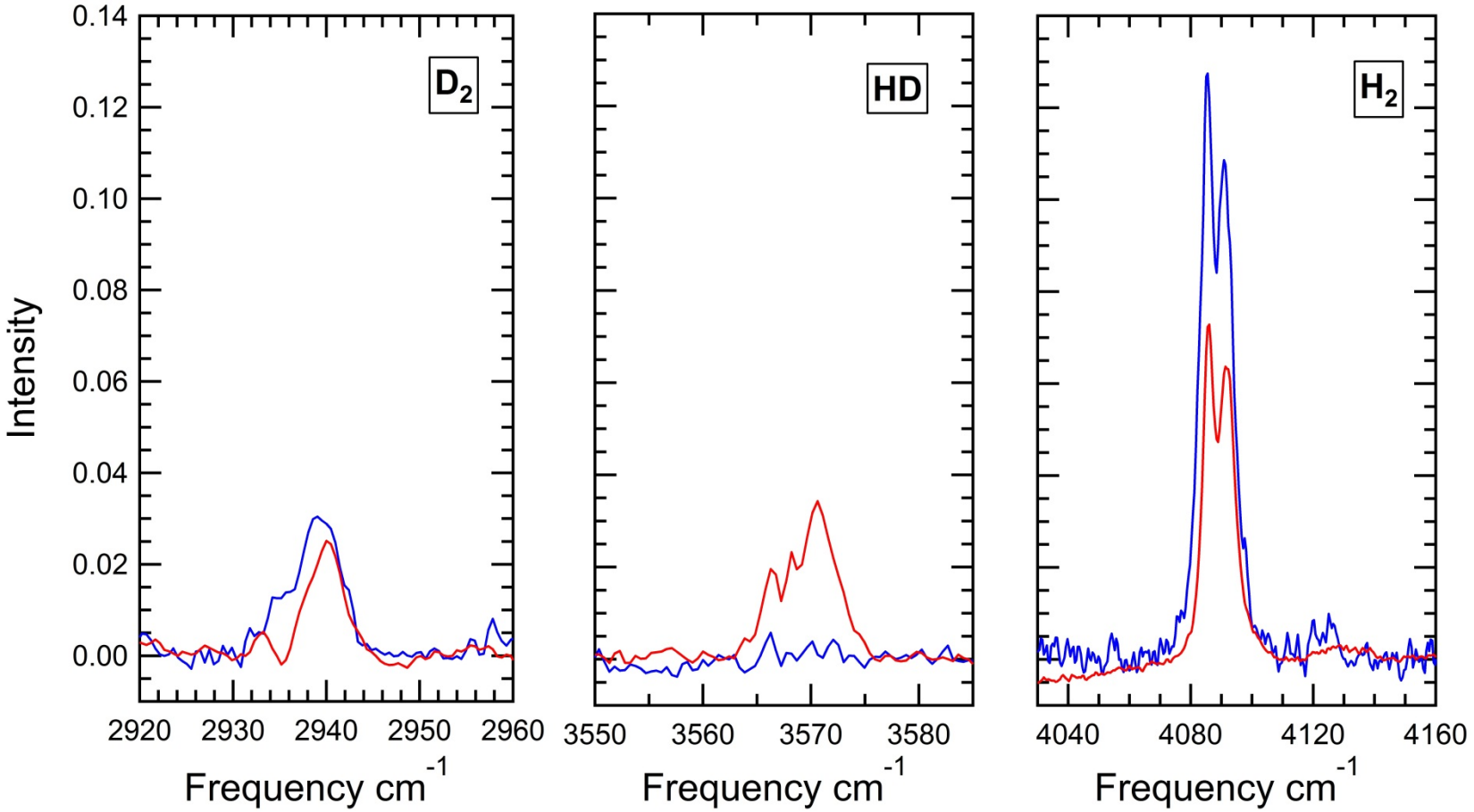
J. Am. Chem. Soc.
2013, 135, 9458−9464

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

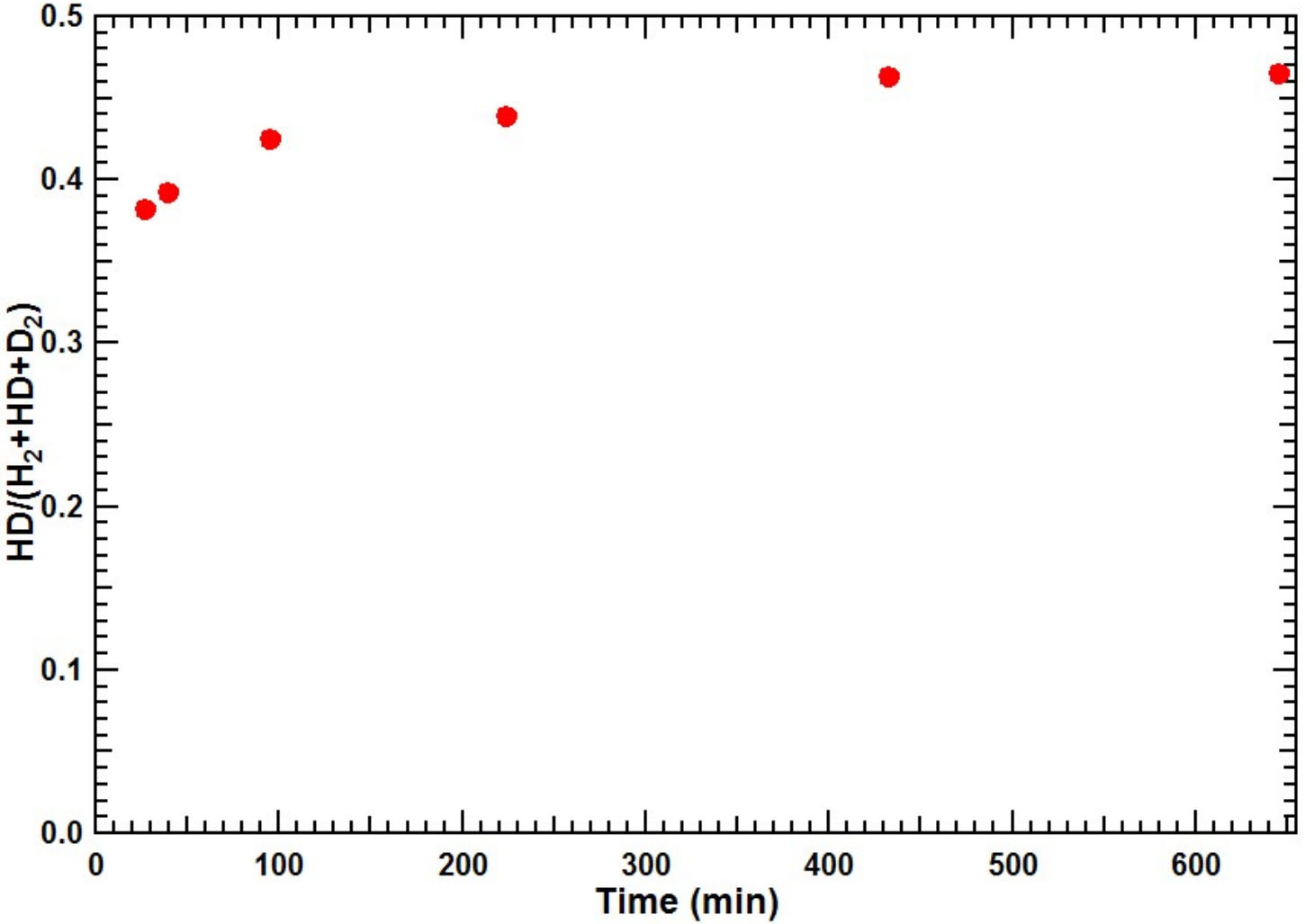
H_2 and D_2 Mixtures in Mg-MOF-74



H_2 and D_2 Mixtures (After sitting at room temperature)



Mass Spectroscopy HD formation at room temperature



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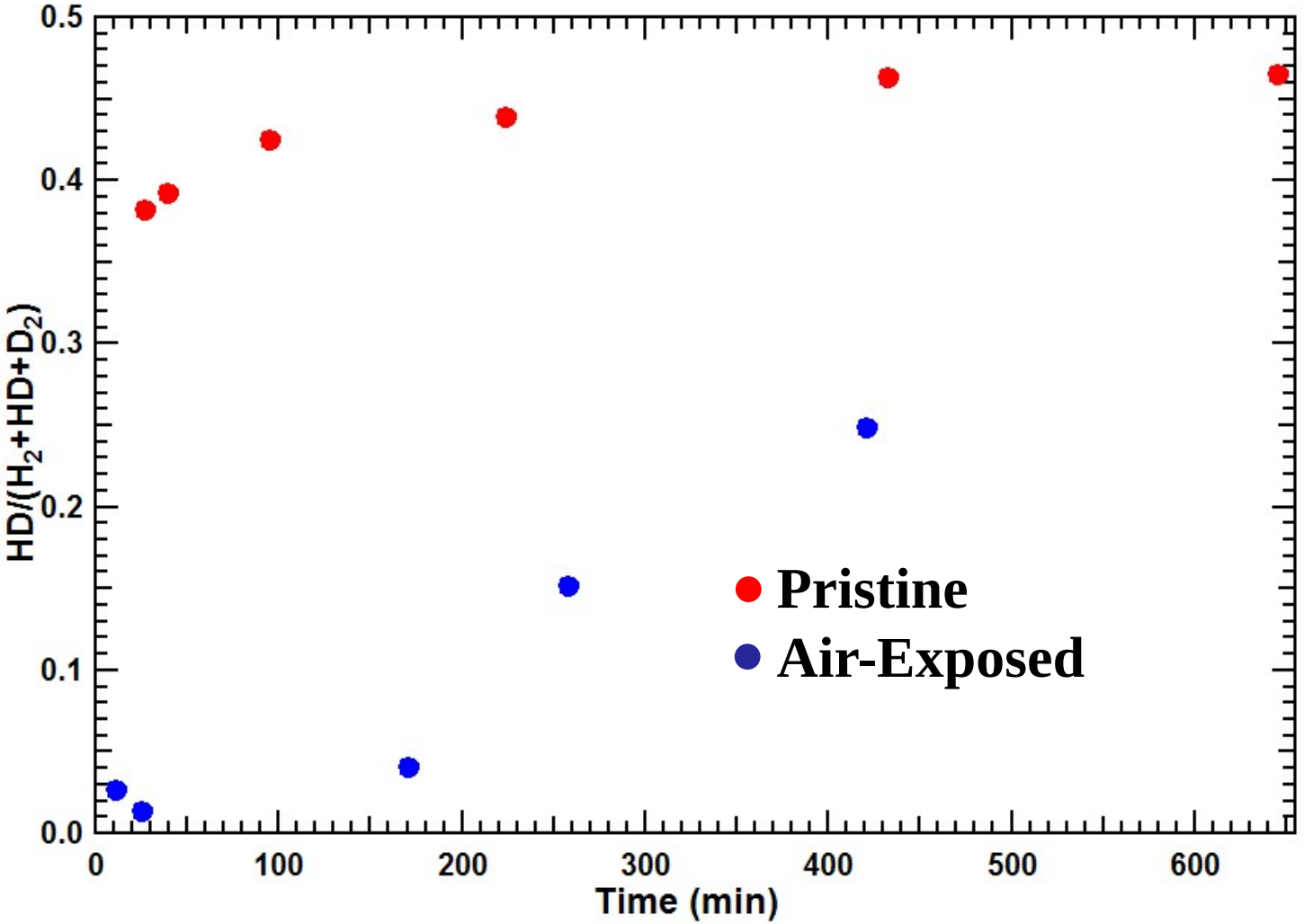

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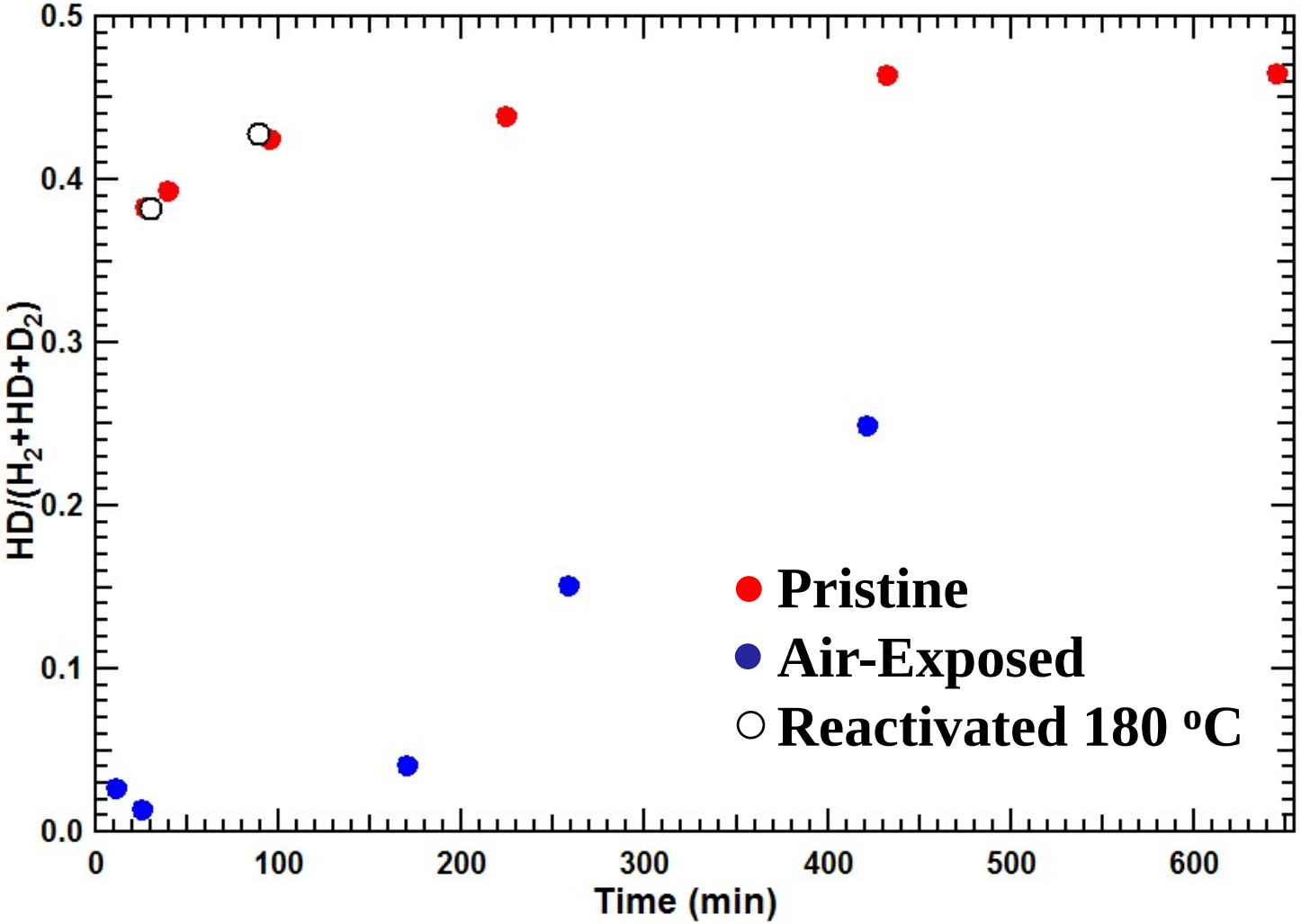
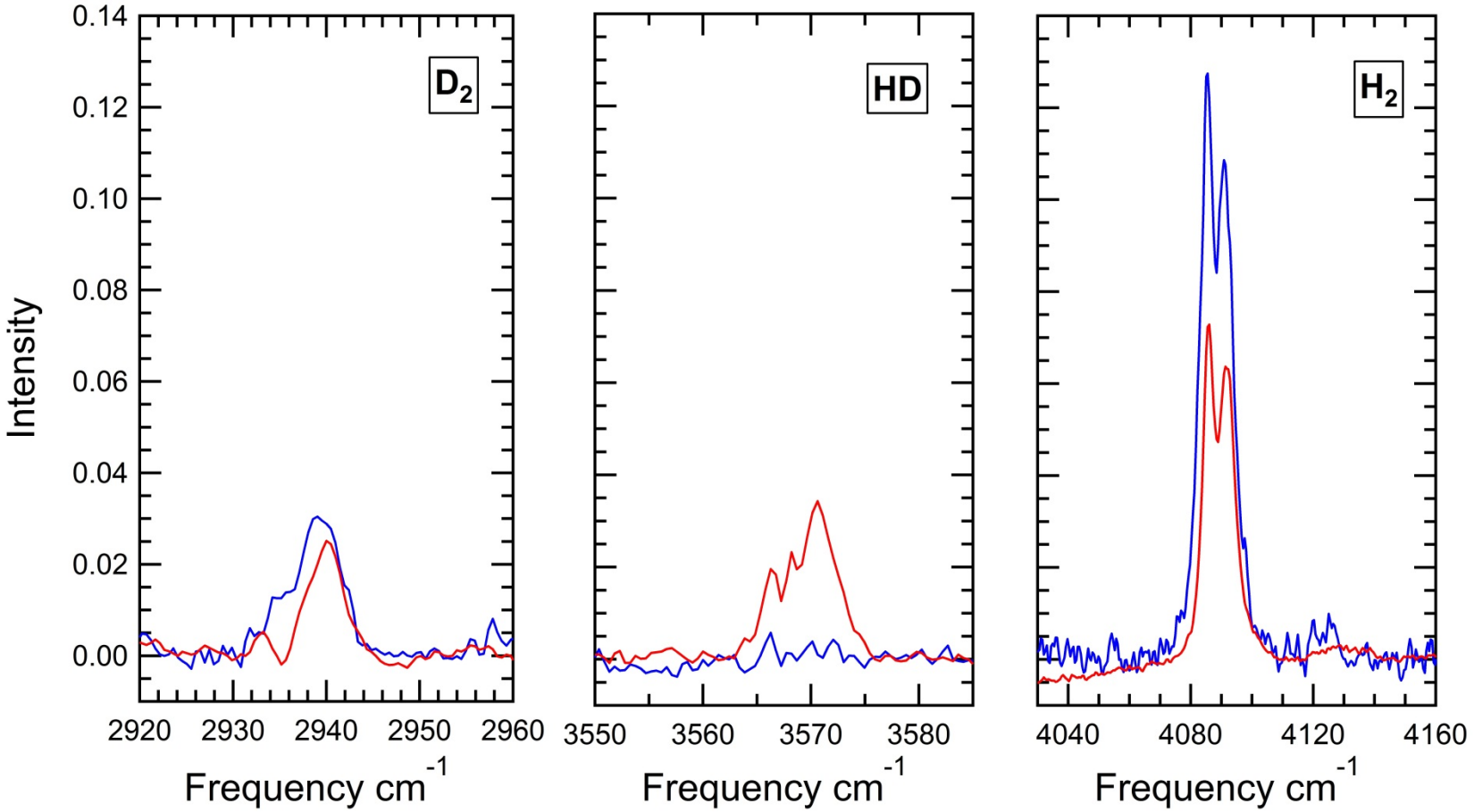


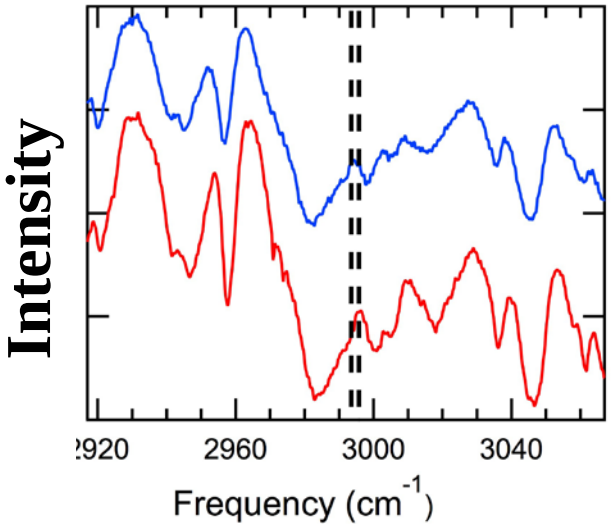
H_2 and D_2 Mixtures (After sitting at room temperature)



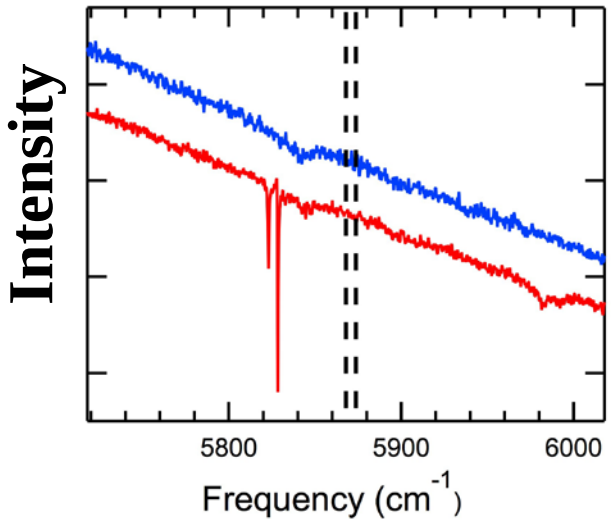
Deuterium in MOF-5

Pure MOF-5

MOF-5 with D_2



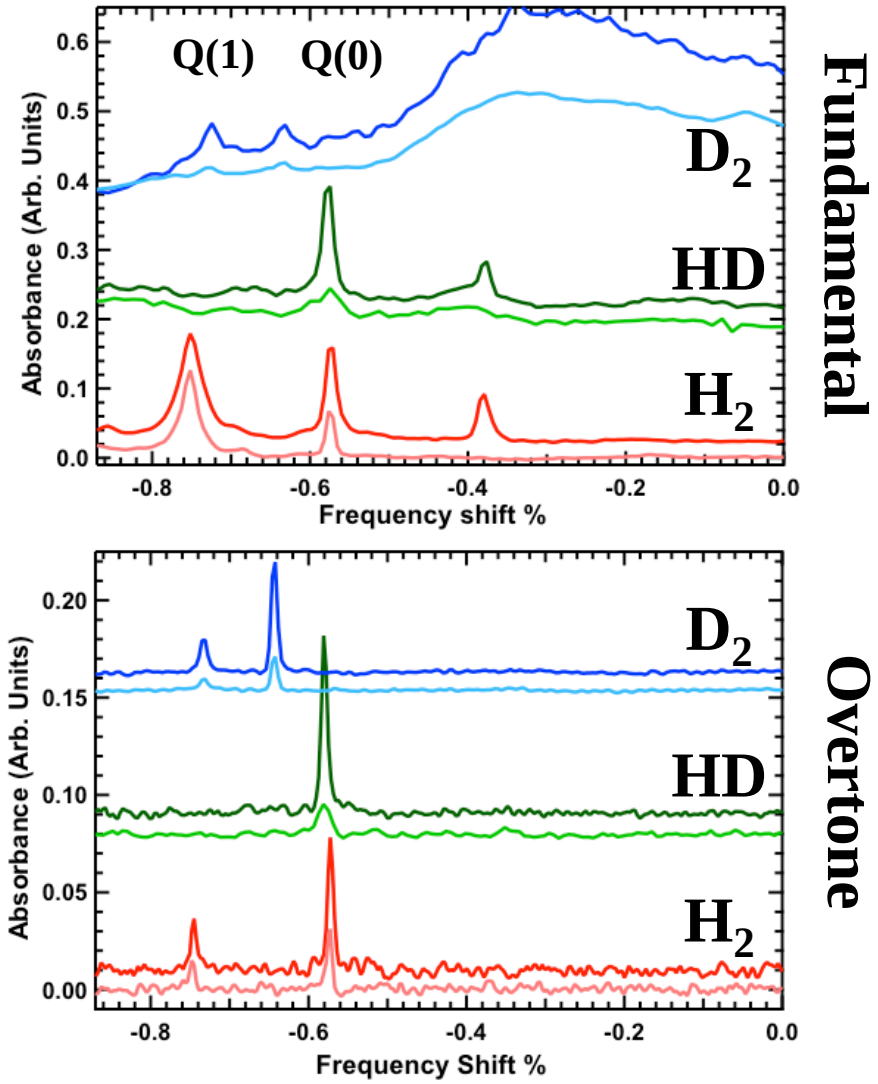
Fundamental



Overtone

Frequency Shift Fundamental versus Overtone

J. Mol. Spect. 2015, 307, 20-26



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Article

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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

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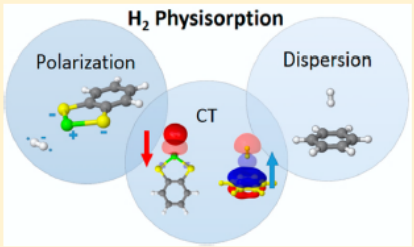
Supporting Information

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 $\sigma^*(H_2)$ 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 $\sigma(H_2) \rightarrow$ metal Rydberg-like orbital, along with the adsorbent $\rightarrow \sigma^*(H_2)$ 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.



INTRODUCTION

Hydrogen (H_2) gas is a promising candidate for future use as an energy carrier for mobile applications such as vehicles and aircrafts. Hydrogen has almost three times higher gravimetric energy content than gasoline, and its combustion or utilization in a fuel cell is a "zero emission" process that results in the formation of water without emitting any compounds that pollute the environment or disrupt the climate. Since H_2 is an extremely volatile gas under standard conditions, the energy available per unit volume (volumetric energy density) is too low for practical application, requiring its storage at high pressures or as a liquid at cryogenic temperatures on board a vehicle. An efficient method for the storage of H_2 is therefore a necessary technology for its effective use as a fuel. The 2017 DoE target values for an onboard hydrogen storage system for light-duty fuel cell vehicles are a gravimetric capacity of 5.5 wt % (kg H_2/kg) and a volumetric capacity of 4.0 vol % (kg H_2/L) at an operating temperature of −40 to 60 °C. To the best of our knowledge, these targets have yet to be met by any known material upon incorporation into a storage system.

Metal–organic frameworks (MOFs) are a family of compounds consisting of metal ions or clusters coordinated to organic ligands (linkers), which form extended network structures. These materials have attracted attention for their potential use as gas-storage media:[1] MOF structures often have sizable pores that can be filled with guest molecules, many of which are adsorbed to the internal surfaces. Moreover, the MOF composition and structure can be modified and tuned for many purposes,[2] such as catalysis[3] and chemical separations.[1,4]

A reversible mechanism for adsorption and release of H_2 from its storage material is needed for any practical storage application. In this respect, the weak physisorption of H_2 in MOFs is advantageous, since H_2 can reversibly adsorb to pore surfaces within the MOF and be easily released when needed. However, the weak adsorption enthalpy (H_{ads}) of H_2 to most known MOFs poses a challenge. At ambient temperatures, an adsorption enthalpy of −15 to −20 kJ mol^{-1} is needed for optimum hydrogen storage–delivery cycles depending upon

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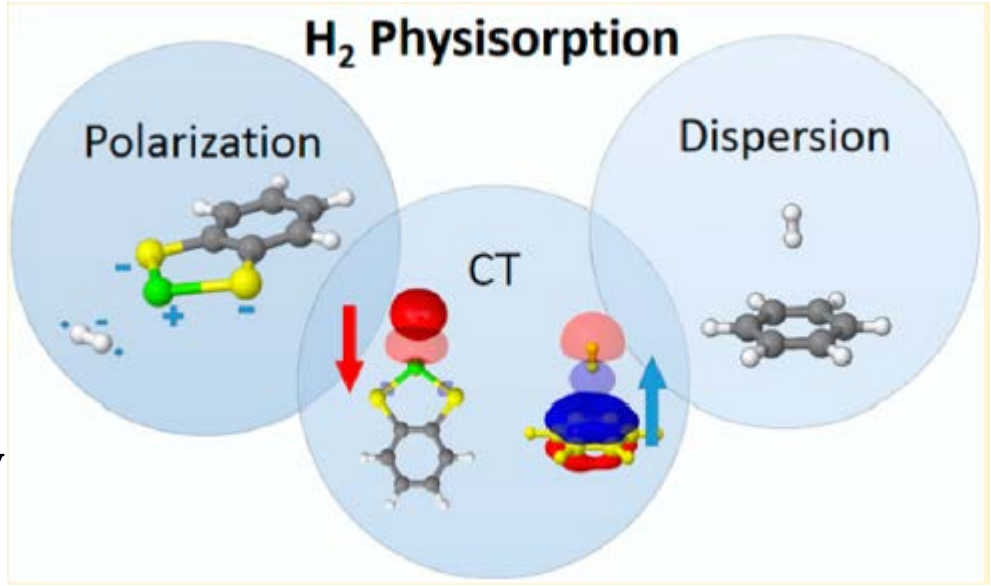
Direct Experimental Evidence of Binding Mechanism?

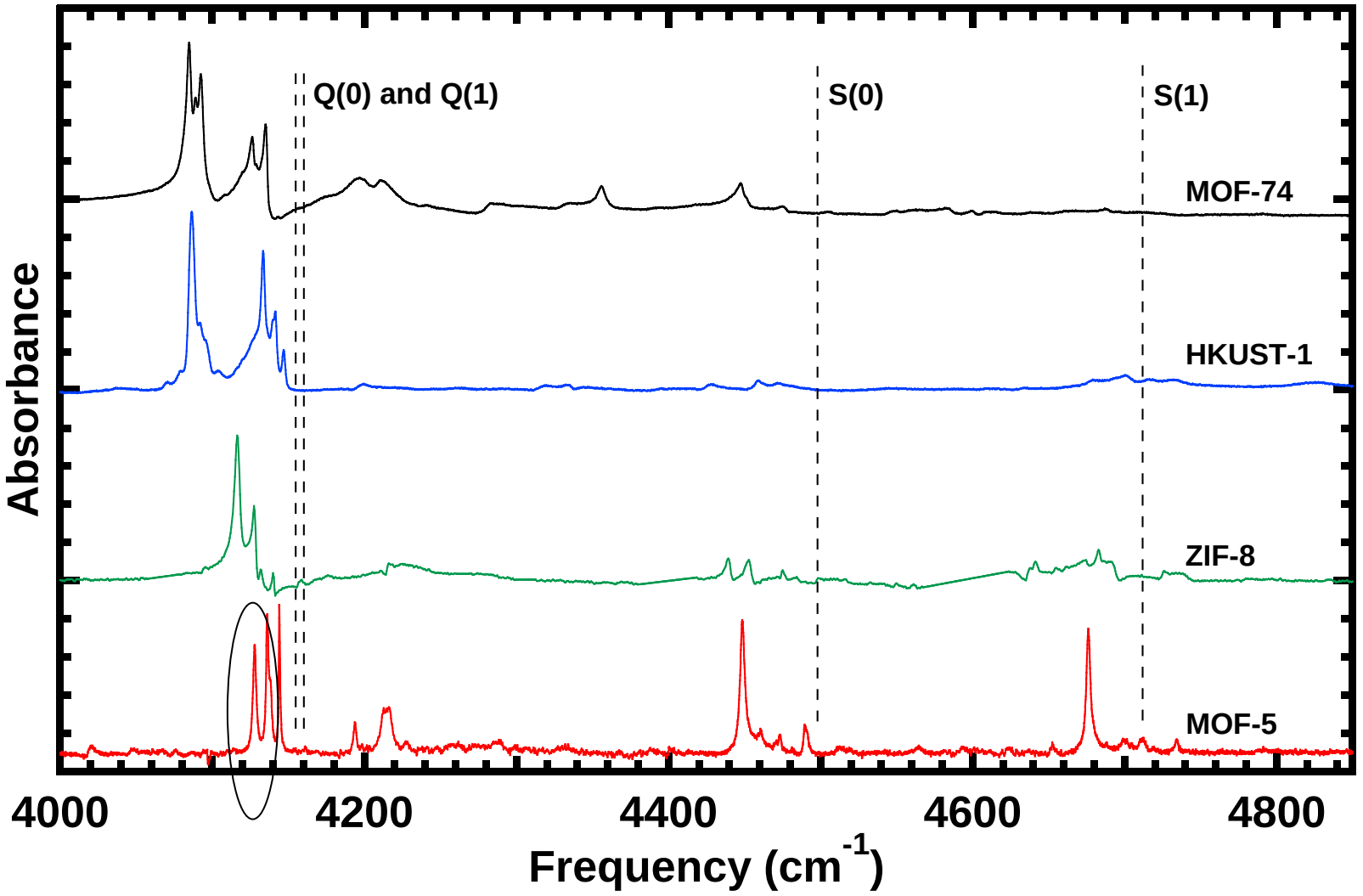


How could we most directly determine the relative contribution of these three mechanisms?

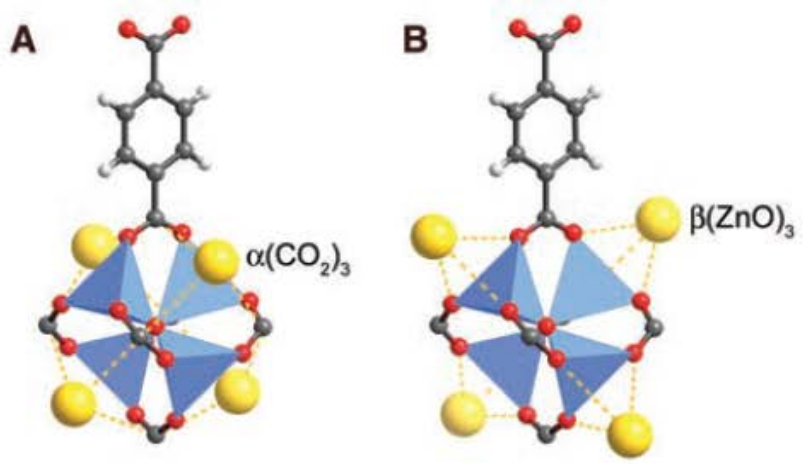
J. Am. Chem. Soc. **136**, 17827 (2014)
Tsivion, Long, and Head-Gordon

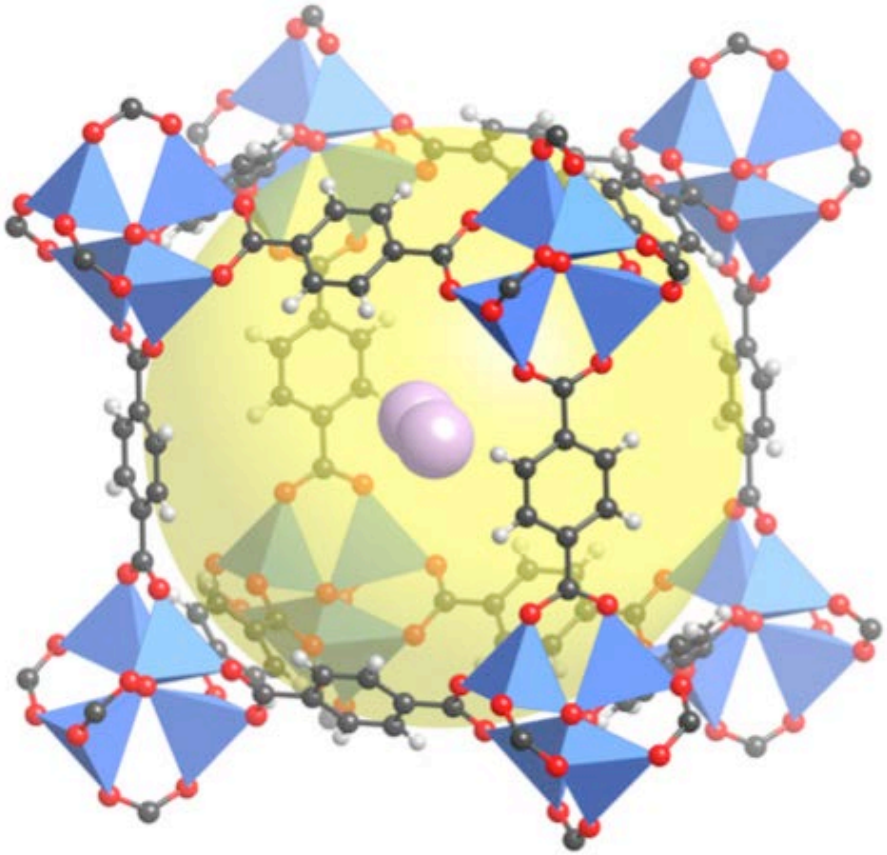
“More direct” implies less need for theoretical modelling.

Typical Spectra for H_2 in MOFs at 30 K



Binding Sites in MOF-5

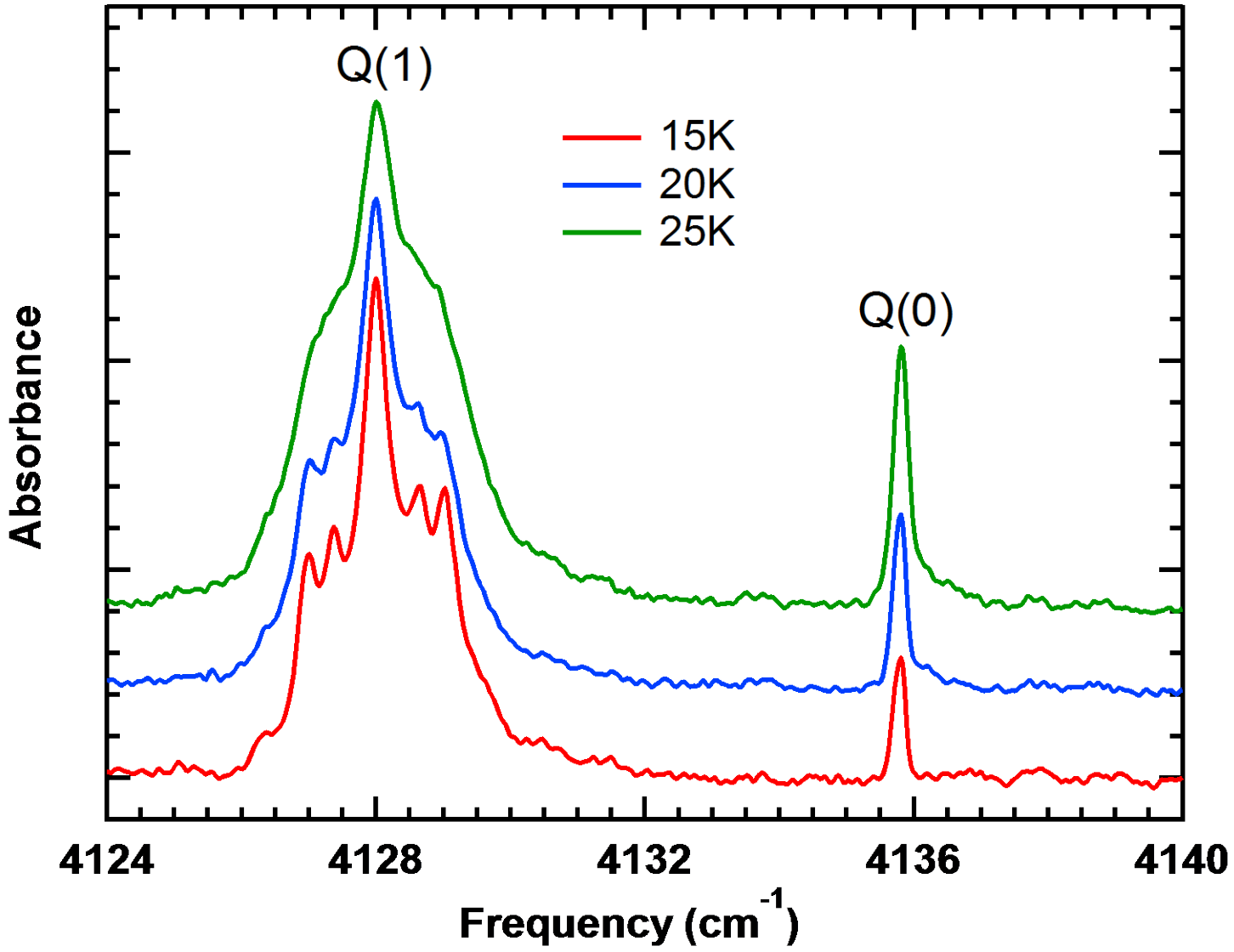




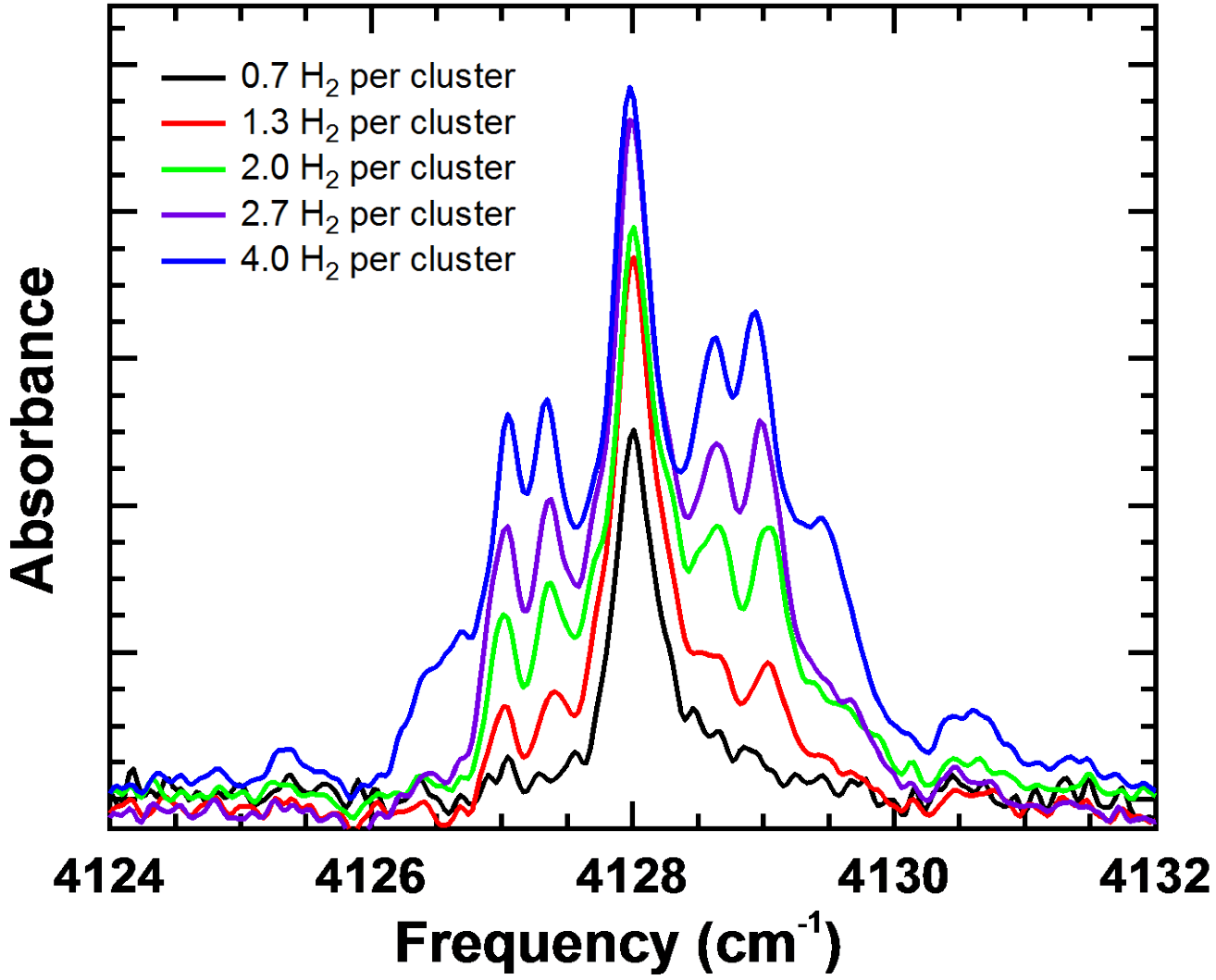
J.L.C. Rowsell, E.C. Spencer, J. Eckert, J. Howard, and O.M. Yaghi, Science, **309**, 1350 (2005)

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

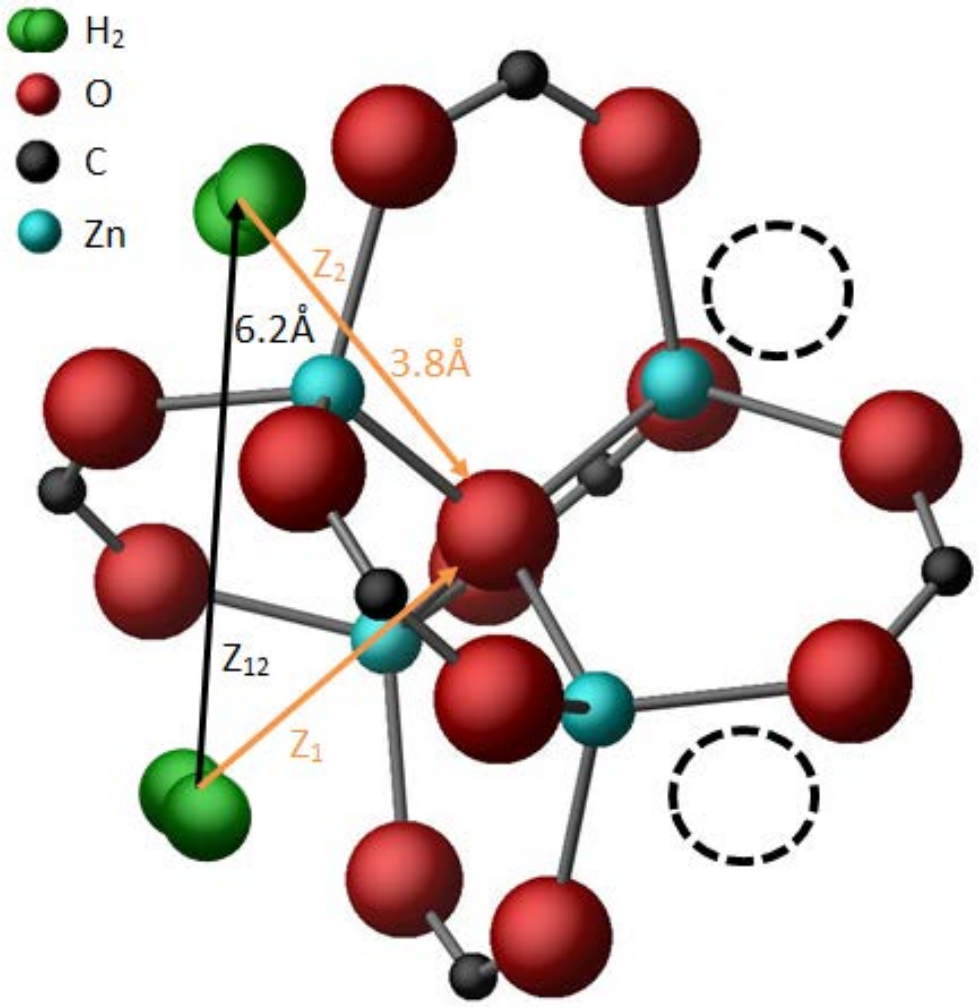
MOF-5 Temperature Dependence



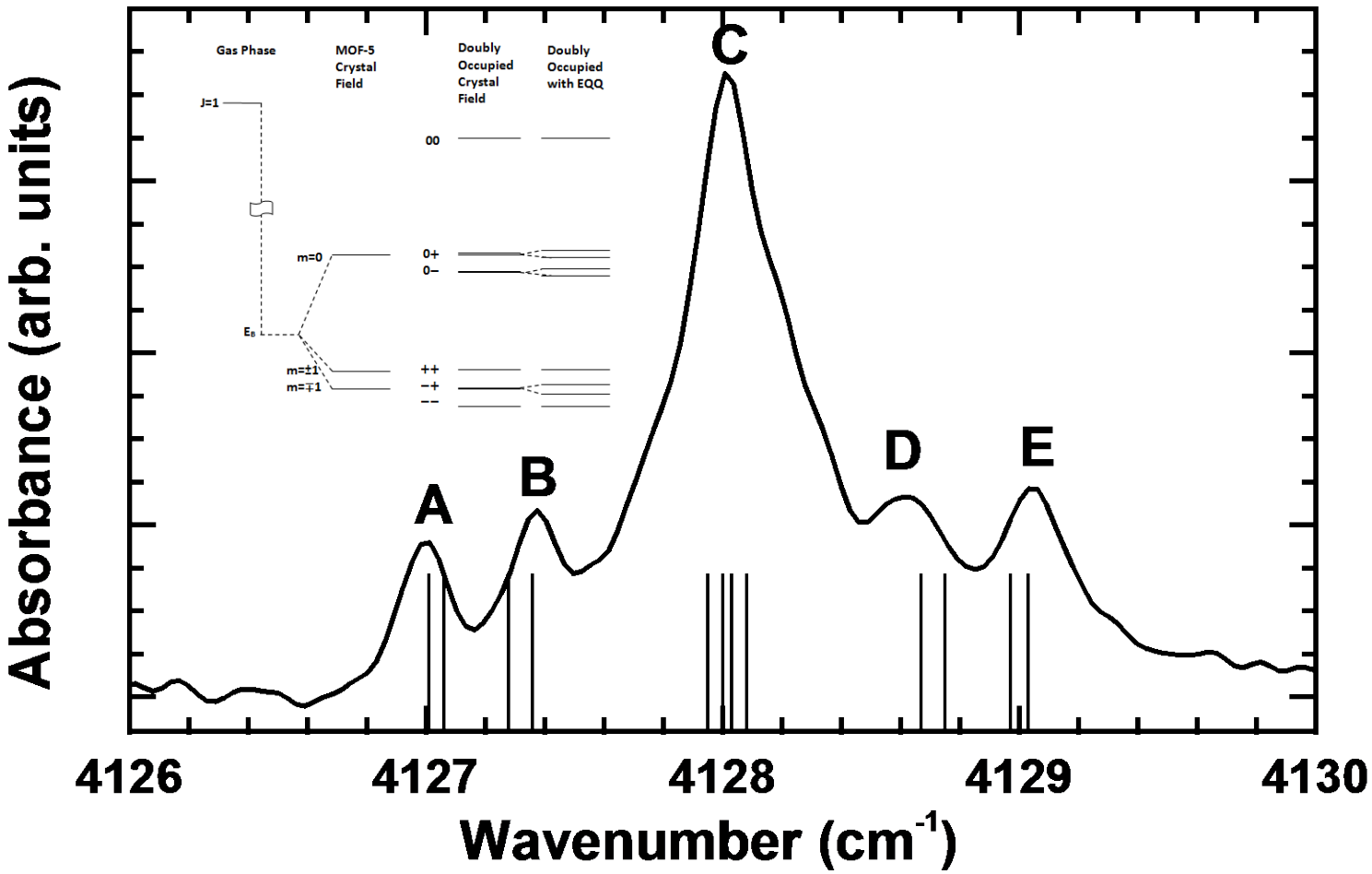
Concentration Dependence



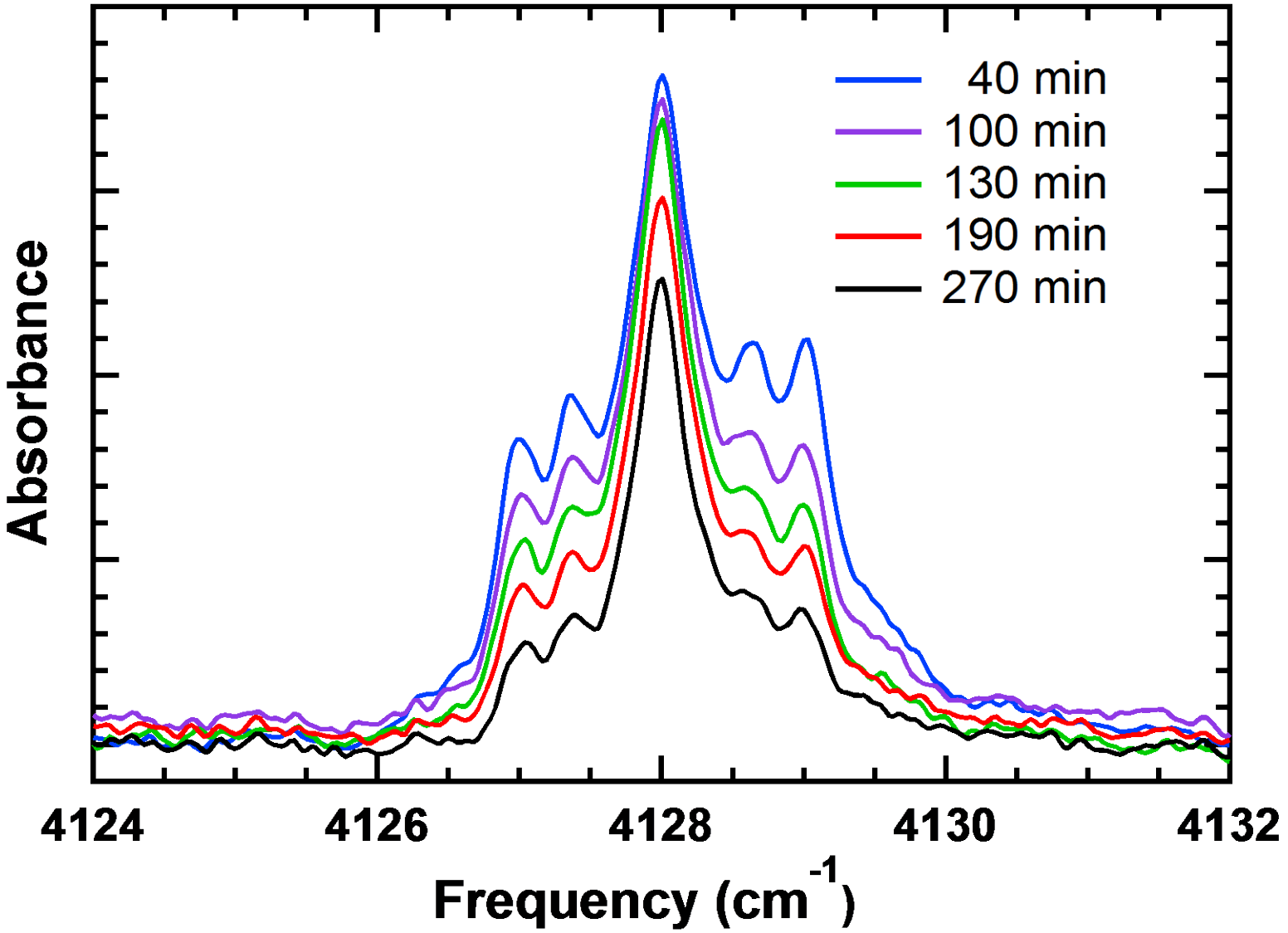
MOF-5 with H_2 Molecules at Primary Site



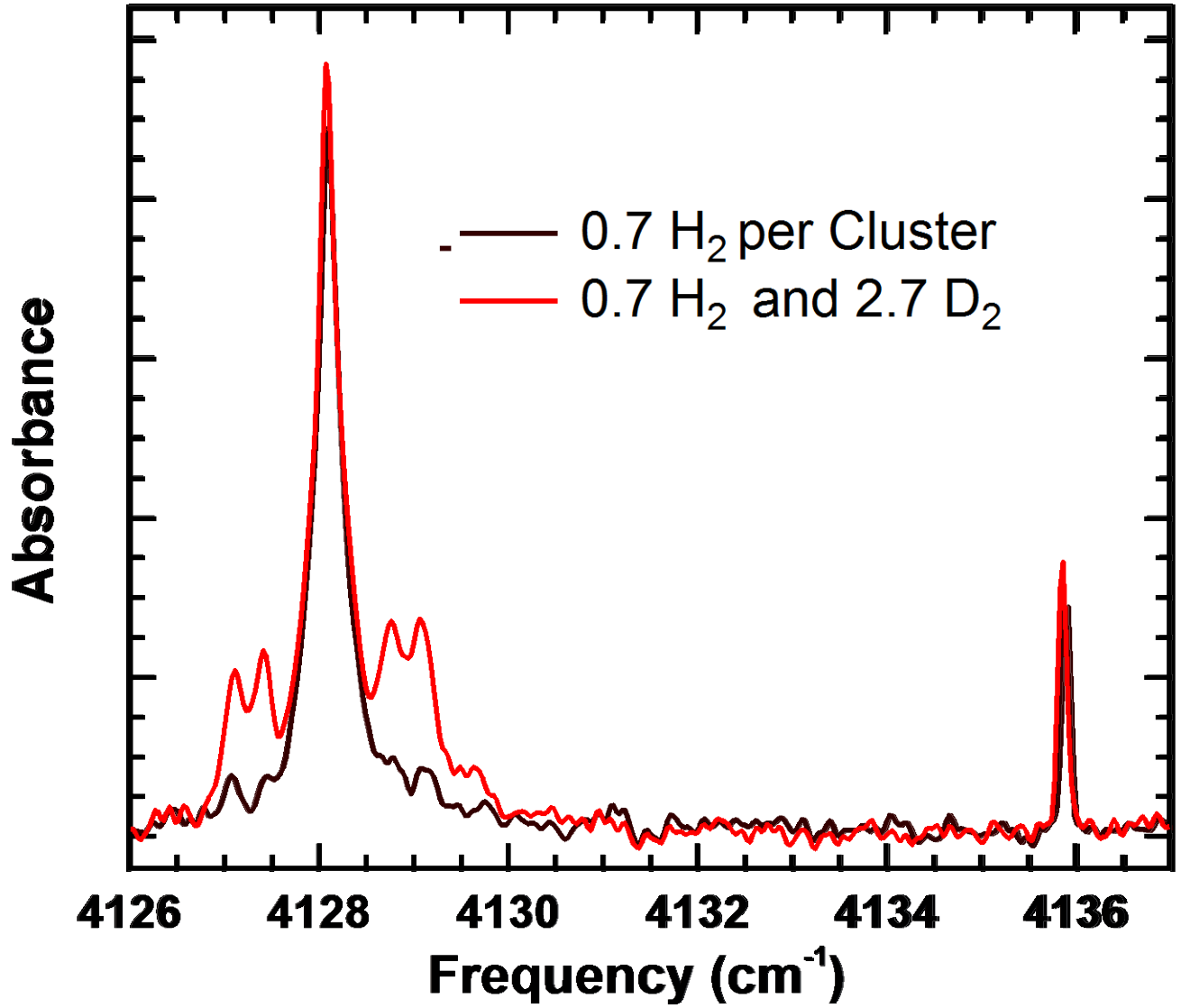
Stick Spectrum for Interacting *ortho*-H_2 Pairs



Ortho to Para Conversion with Time

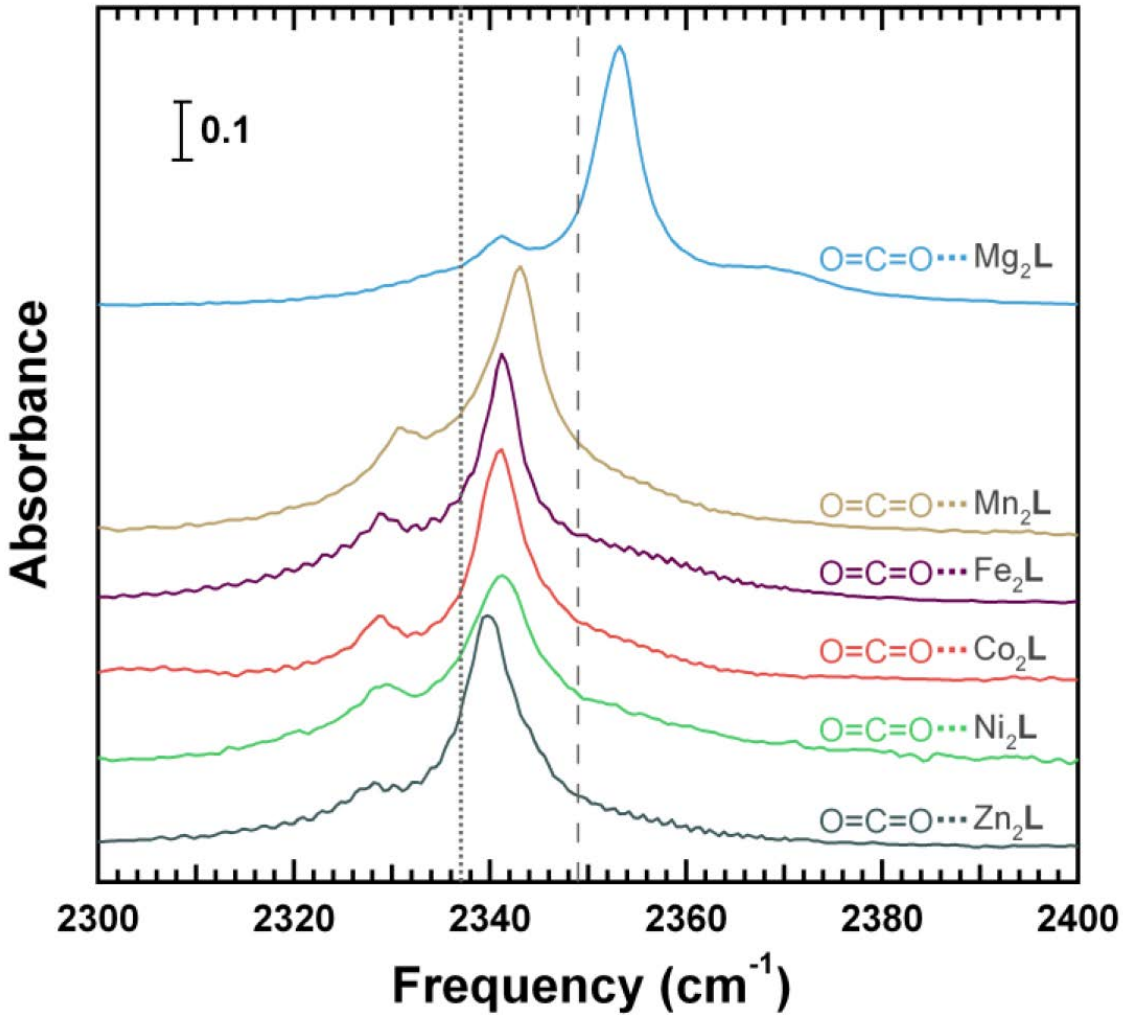


H_2 and D_2 Mixture



CO_2 in Different Metal MOF-74

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



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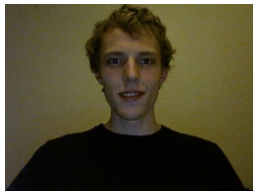

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