Metal-Specific Interactions of H_2 in an Isostructural MOF Series

Outline

Diffuse Reflectance Infrared Spectroscopy

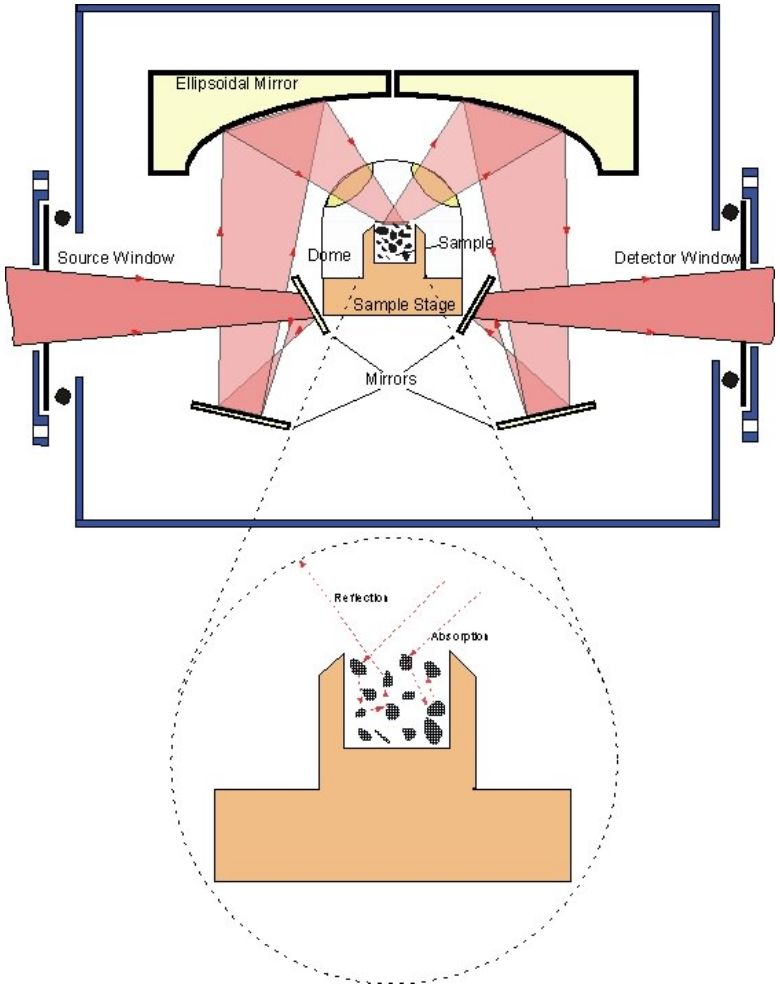
Isostructural series of MOF-74

What is the adsorbed hydrogen doing?

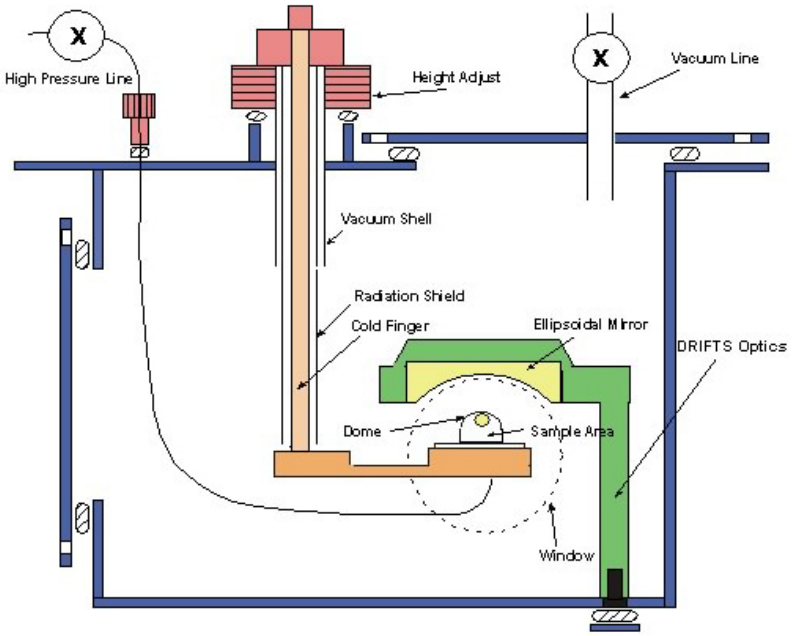
Who cares?

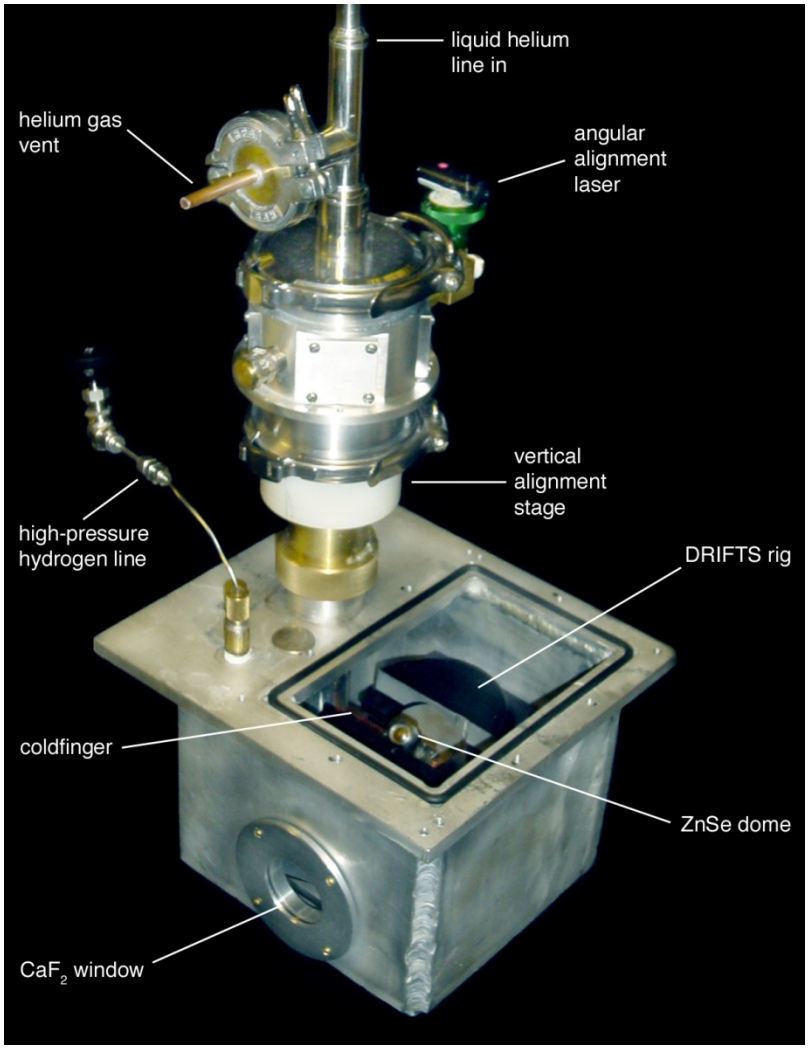
Diffuse Reflectance Spectroscopy

- **H_2 is not IR active**
- Interactions with MOF induce dipole moments
- Need way to increase optical path length
- Use diffuse reflectivity
- Light bounces around within powder sample



Diffuse Reflectance Spectroscopy: Cryostat Assembly





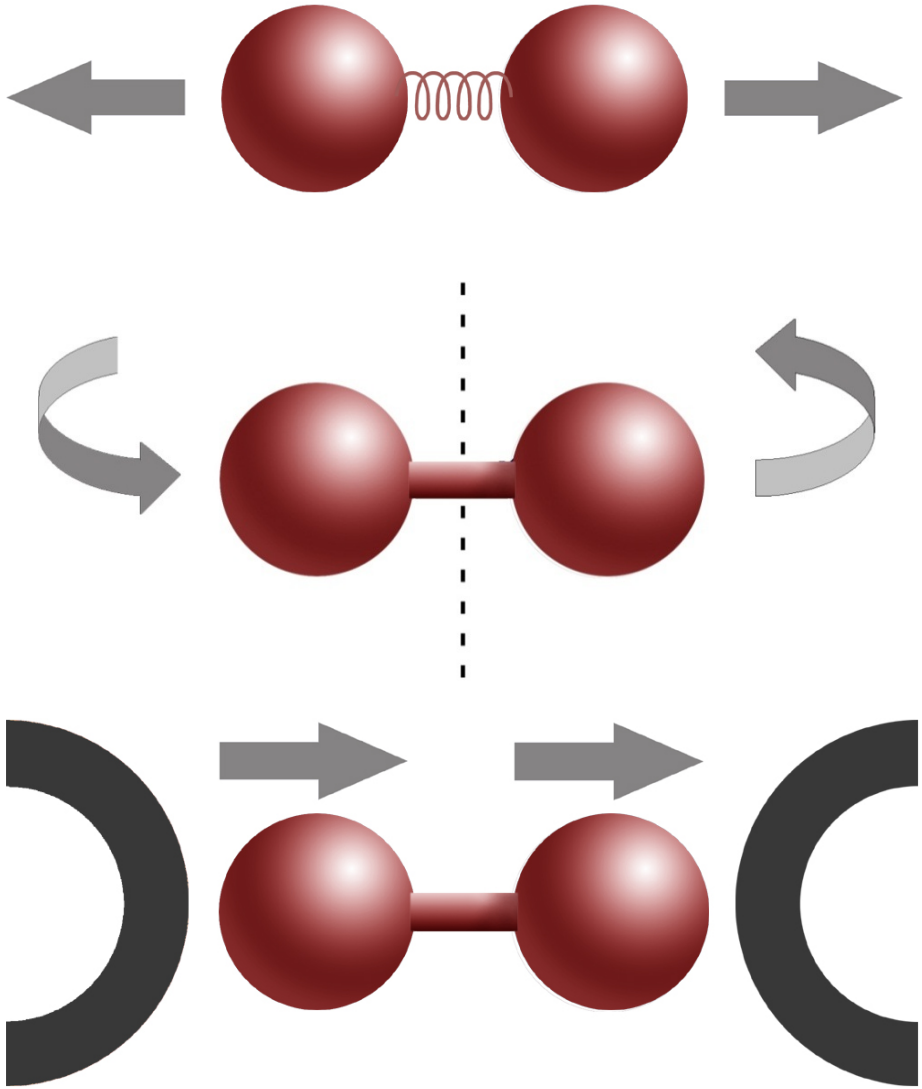
Rev. Sci. Instr. **77**, 093110 (2006)

Quantum Dynamics of Adsorbed H_2

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

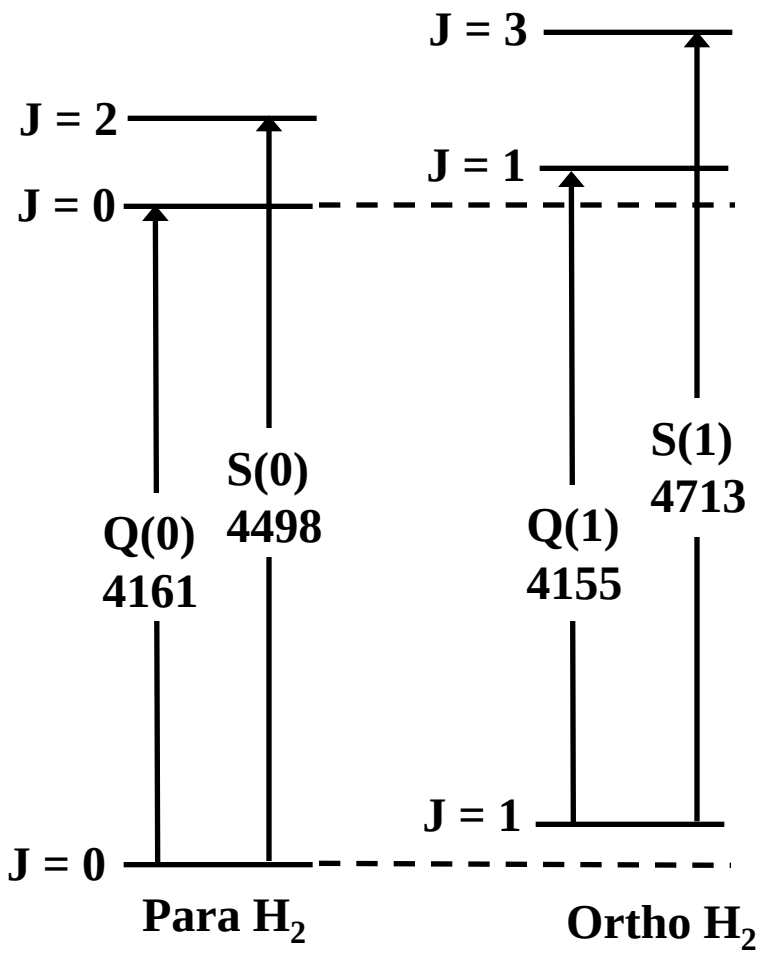
- Rotation
  $E_J = J(J+1)B_0$
  B_0 = 59 cm^{-1} for free H_2

- Translation
  Center-of-mass
  On the order of 150 cm^{-1}

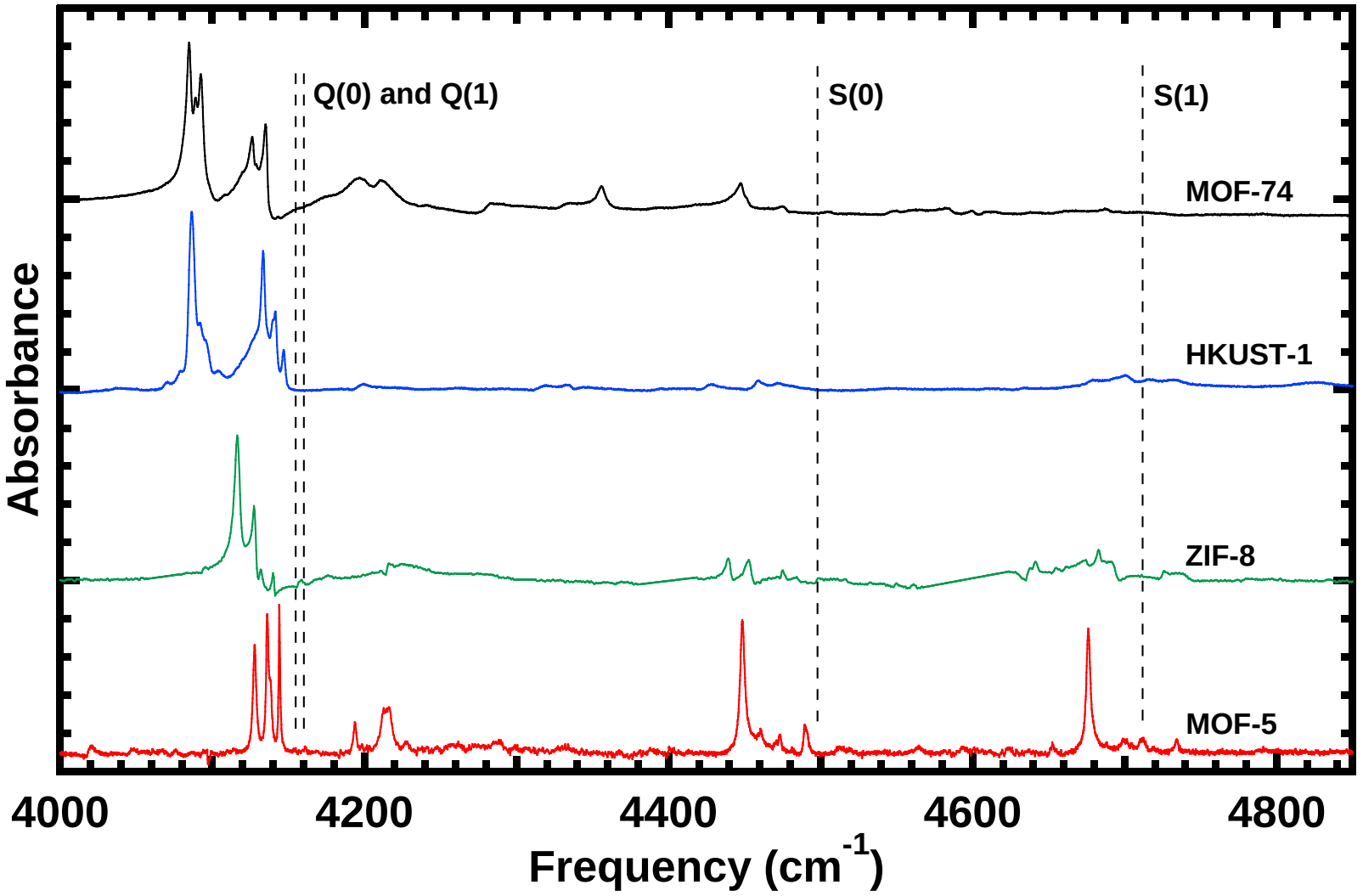


Spectroscopic Notation

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



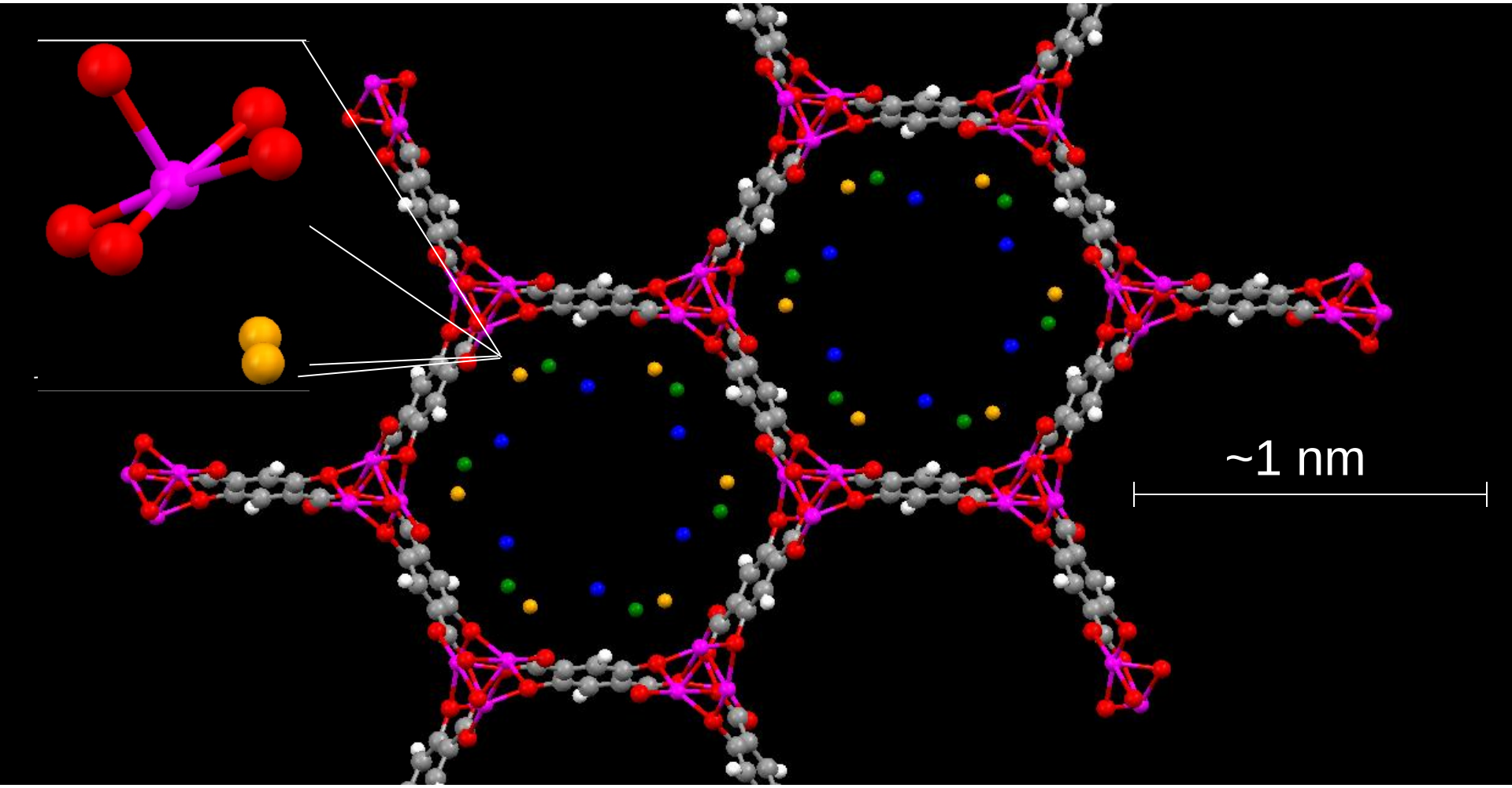
Typical Spectra for H_2 in MOFs at 30 K



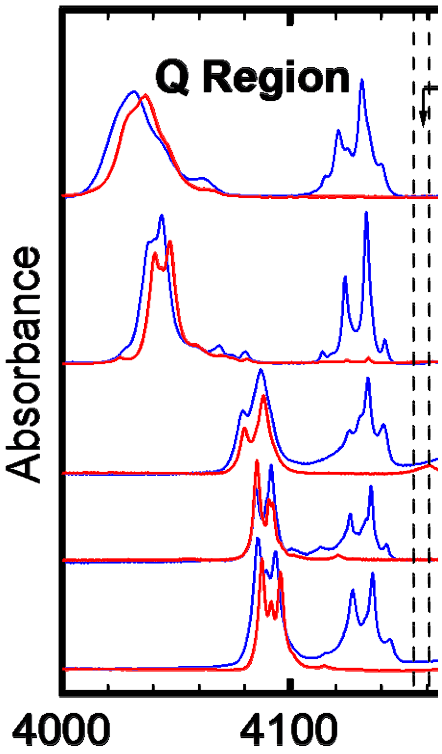
MOF-74 ($M_2C_8H_2O_6$) for M = Mg, Mn, Co, Ni, or Zn

Neutron Diffraction Shows H_2 sited "Coordinatively Unsaturated" Open metal Site"

J. Am. Chem. Soc., 130, 10166-10772 (2008).

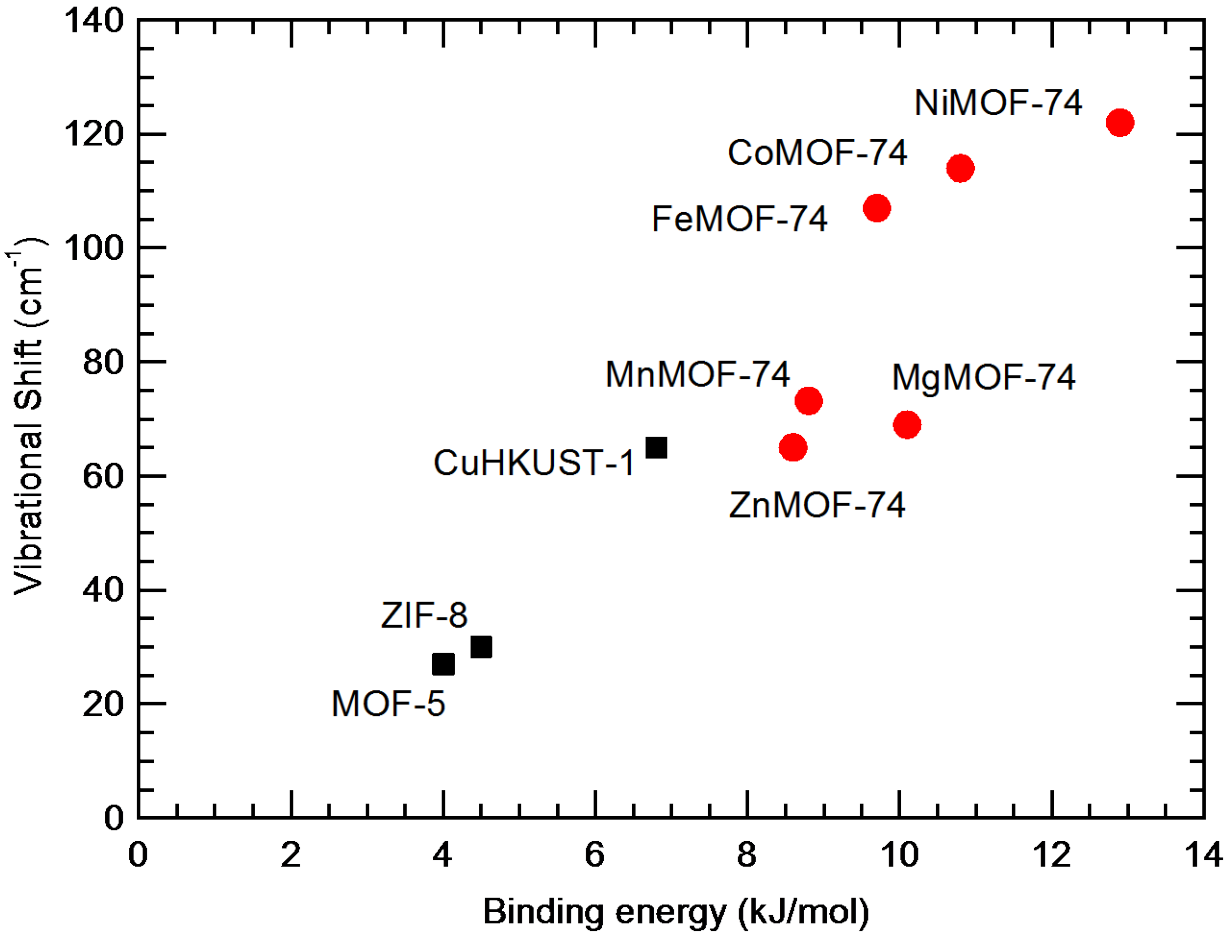


Spectra for H_2 in MOF-74 at 35 K



Red spectrum

Blue spectrum



Hydrogen-Hydrogen Interactions?

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Spectroscopic Evidence for the Influence of the Benzene Sites on Tightly Bound H_2 in Metal–Organic Frameworks with Unsaturated Metal Centers: MOF-74-Cobalt

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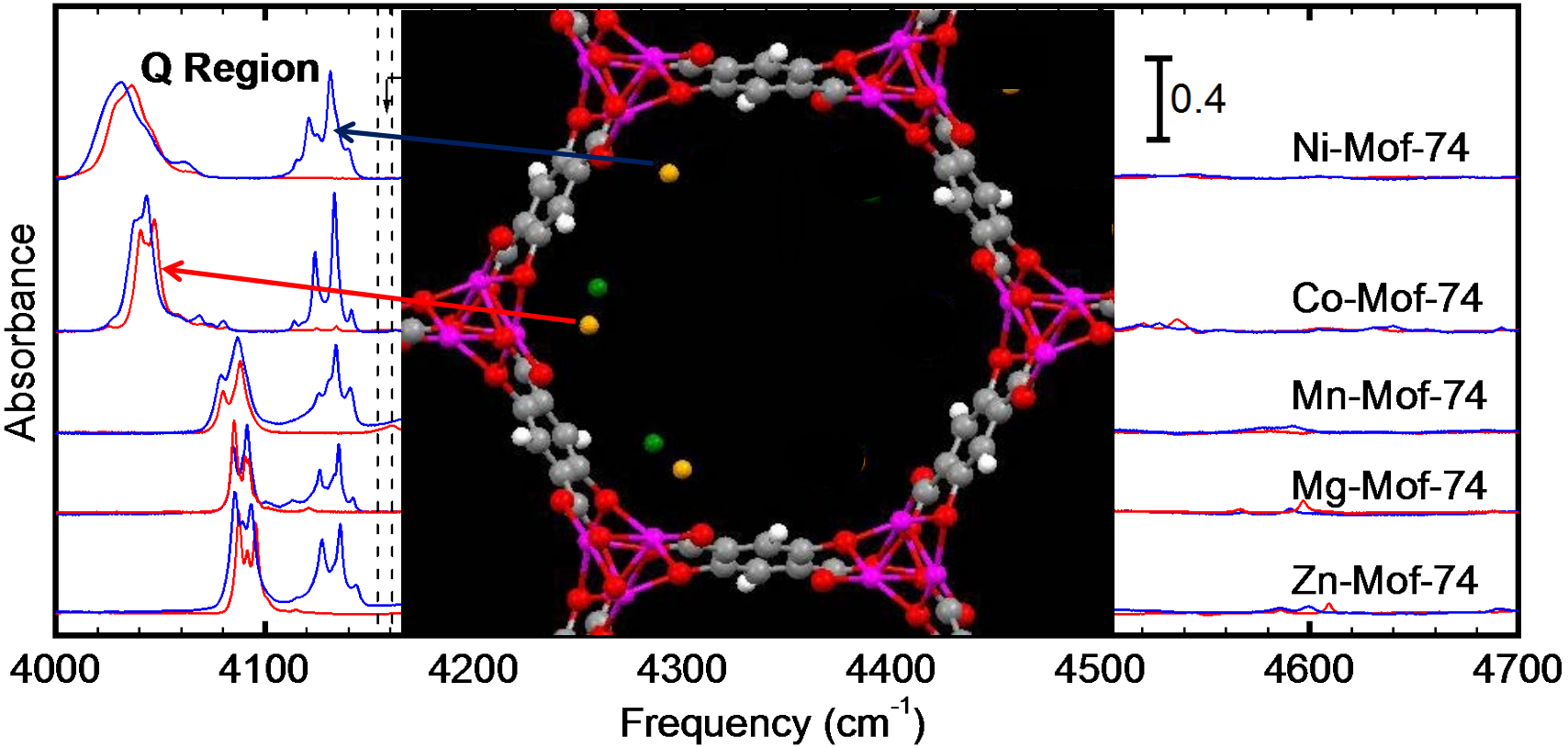
Molecular Hydrogen "Pairing" Interaction in a Metal Organic Framework System with Unsaturated Metal Centers (MOF-74)

Nour Nijem,[†] Jean-François Veyan,[†] Lingzhu Kong,[‡] Haohan Wu,[§] Yonggang Zhao,[§] Jing Li,[§] David C. Langreth,[‡] and Yves J. Chabal*[,†]

Spectra for H_2 in MOF-74 at 35 K



Claims

Weakly shifted peaks due to isolated H_2 at open metal site

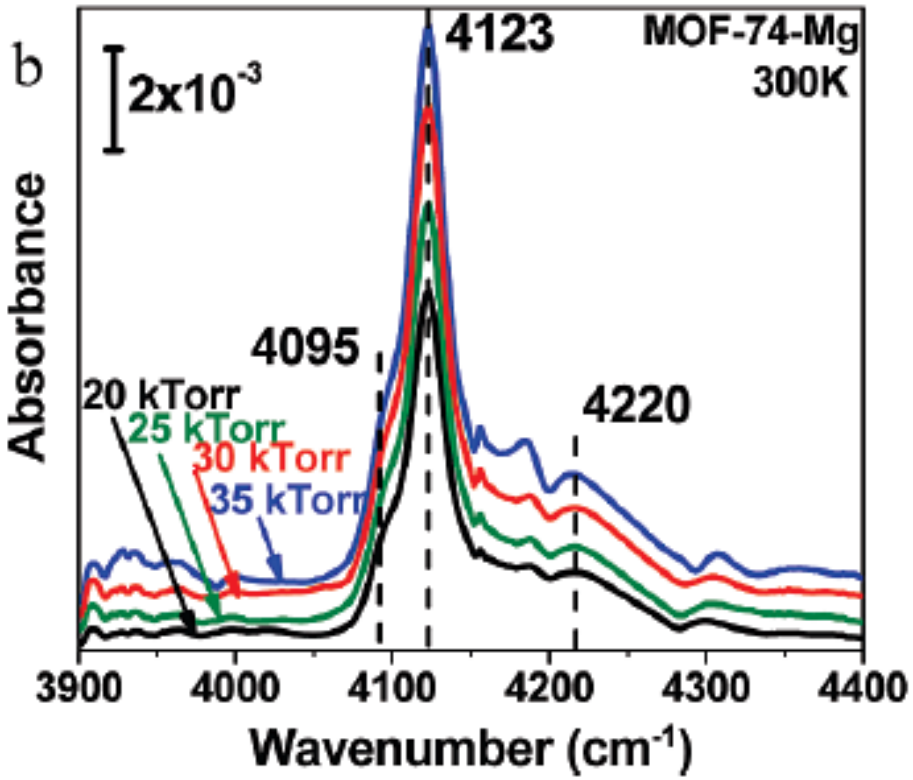
Strongly shifted peaks due to $H_2 \cdots H_2$ pair interactions

Who Cares?

If claims are true then:

- $H_2 \cdots H_2$ interactions can actually dominate
- Use of Variable Temperature Infrared Spectroscopy now in doubt
- D_2 and H_2 exhibit radically different behavior
- Success of “van der Waals DFT” calculations

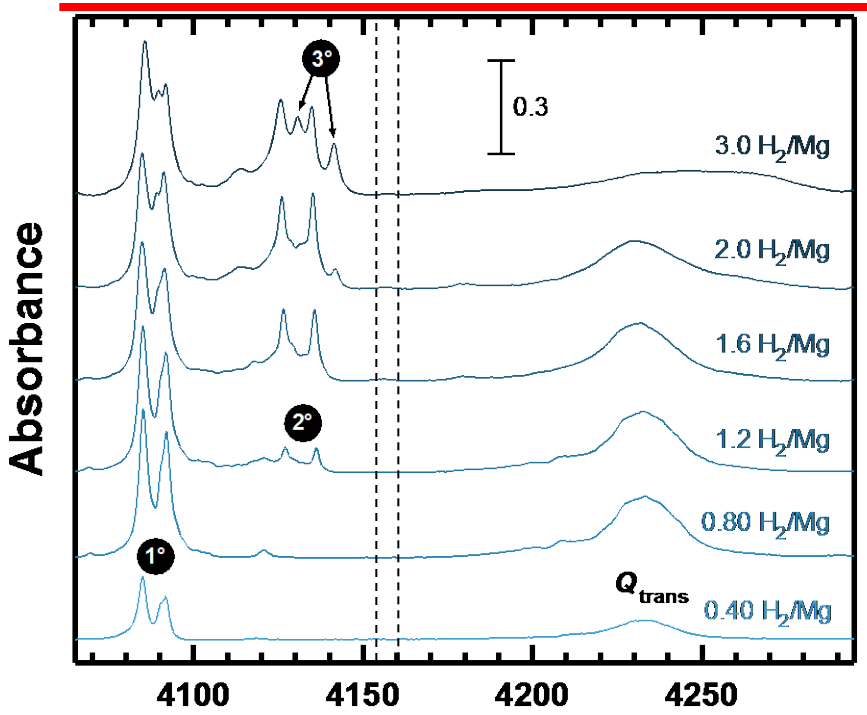
Room Temperature Data J. Am, Chem. Soc. **2010** 132, 14834

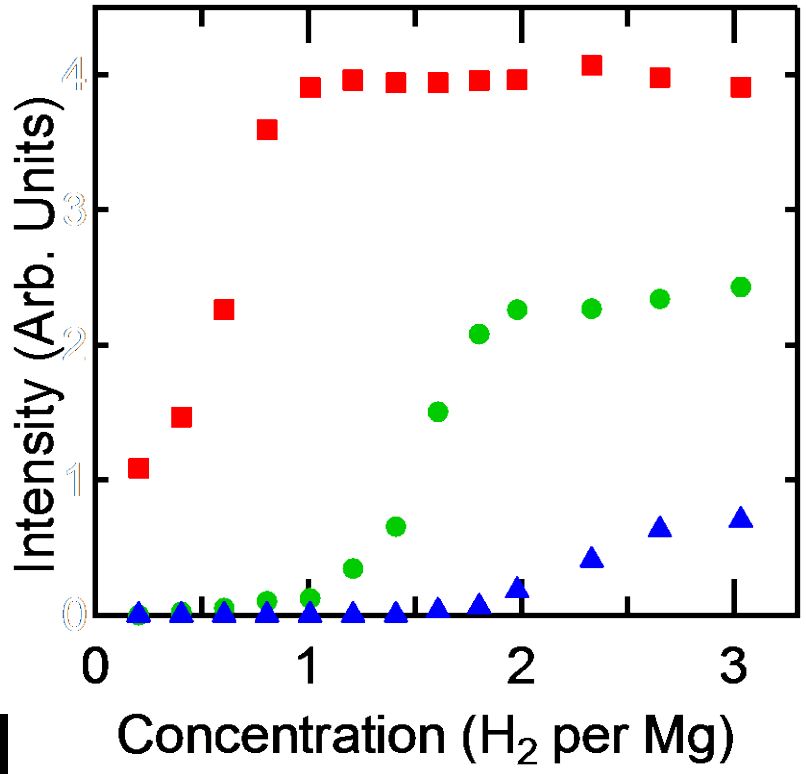


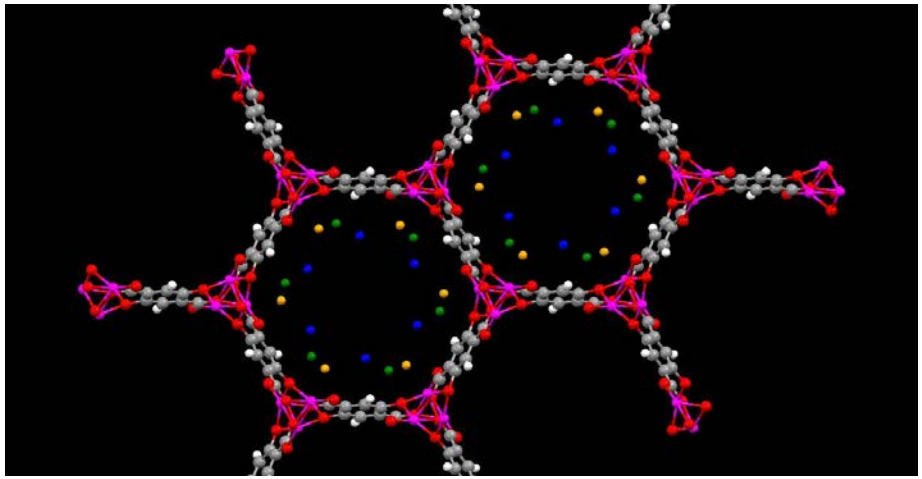
Spectra show weakly shifted (secondary site) peak dominating

Claim thermal barriers are a big concern

Spectra at 35 K after loading and cooling from 150 K

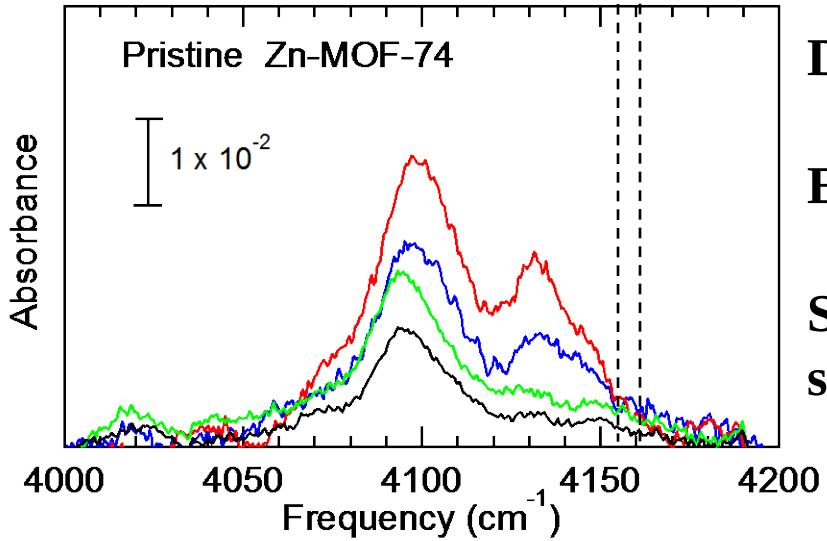






Strongly shifted peaks saturate at 1 H_2 per metal

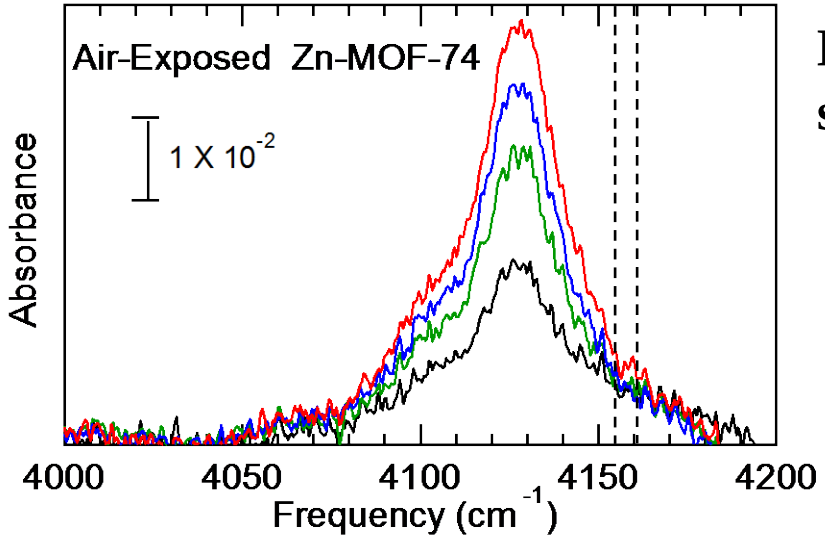
Room Temperature Spectra Pressures up to 100 bar



Data consistent with low temp spectra

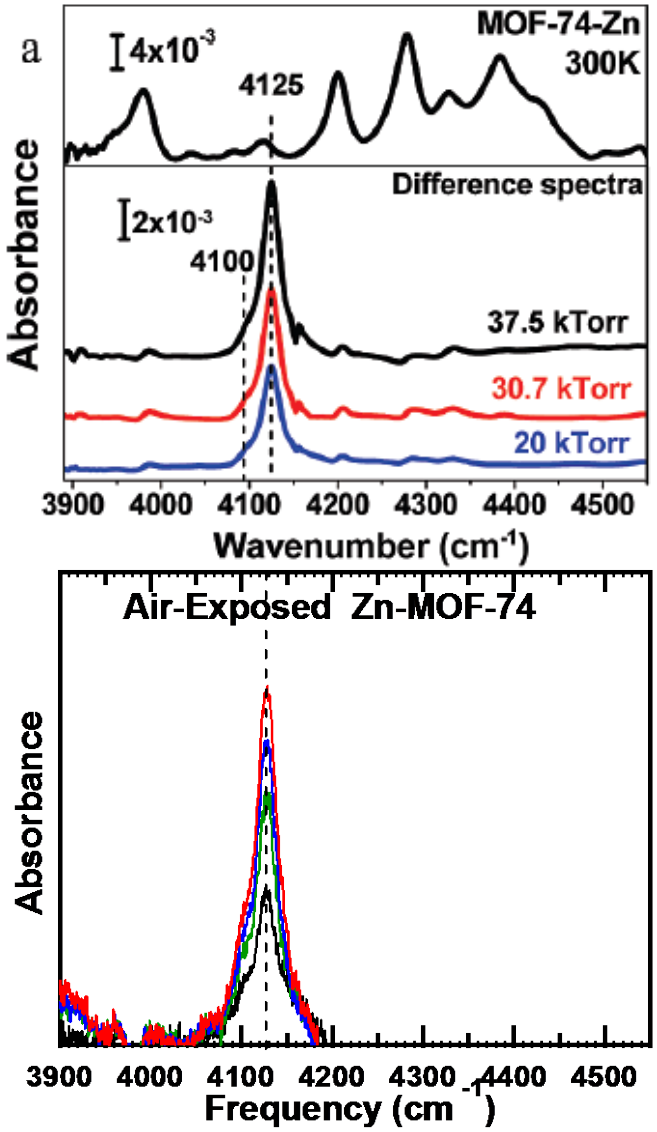
Exposed-metal site fills first

Secondary sites occupy before saturation of primary



Exposure to air significantly alters spectrum

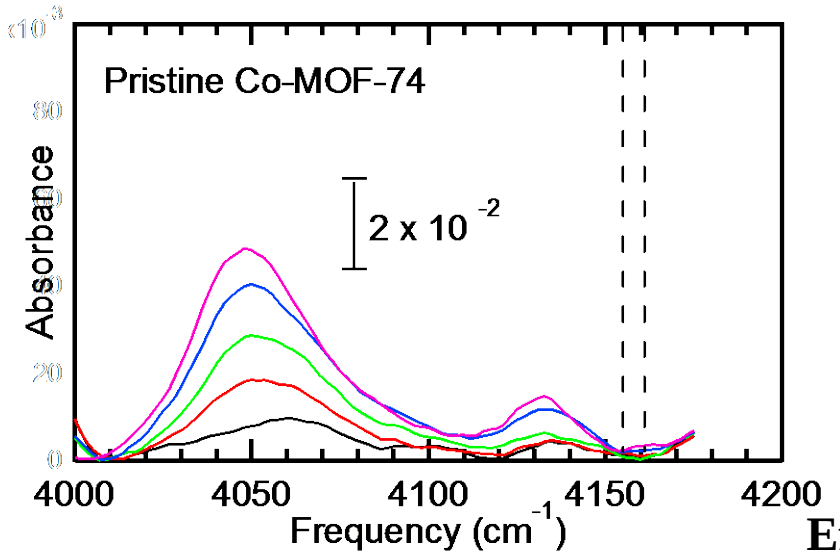
Room Temperature Spectra



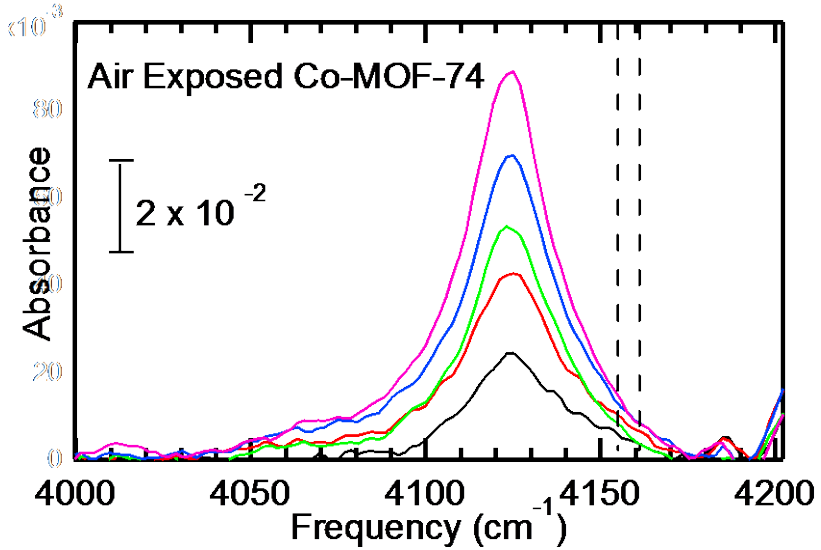
Spectra from:
J. Am, Chem. Soc. **2010,** 132, 14834.

Our Spectra on Air-Exposed Zn MOF-74

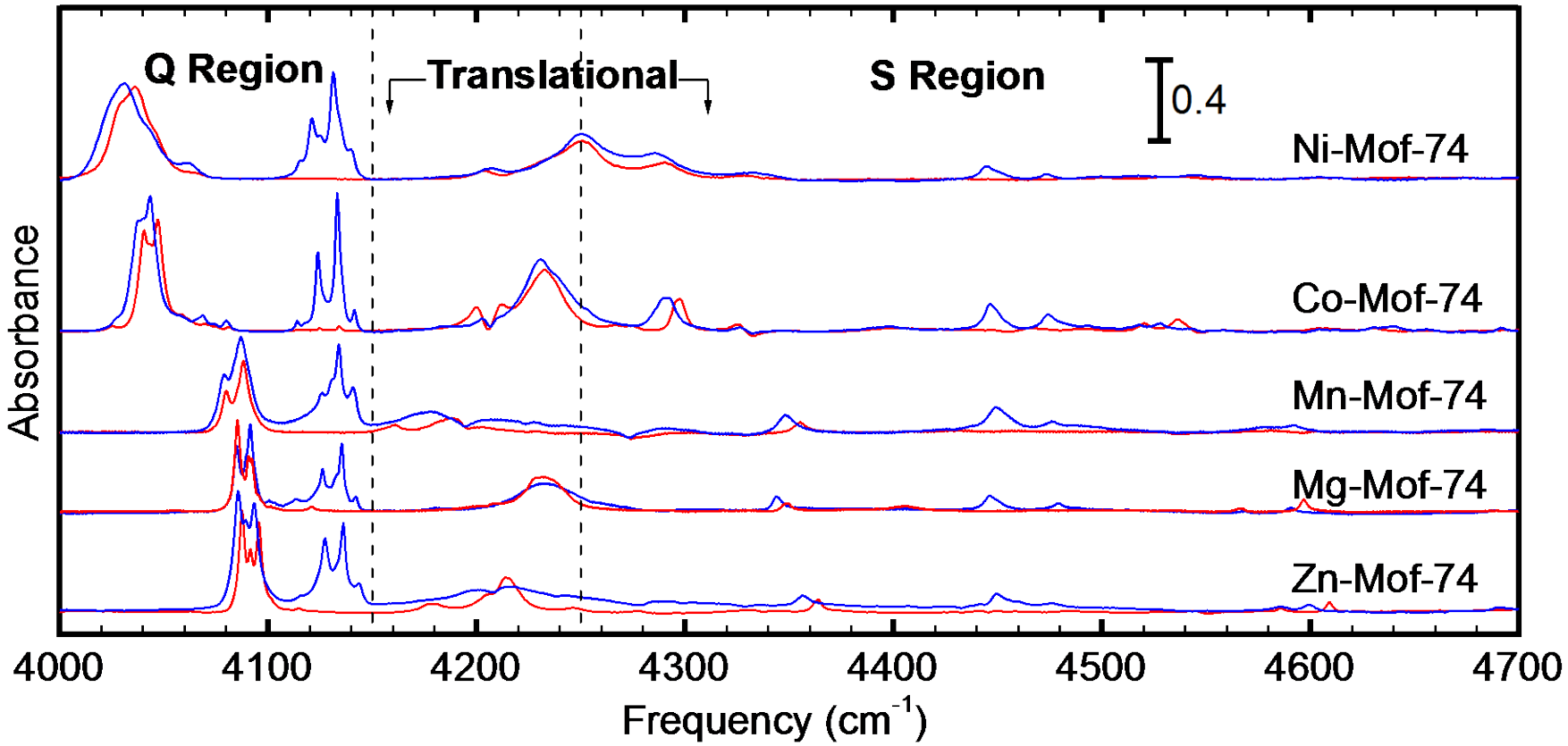
Room Temperature Spectra



Effect even more pronounced for Co-MOF-74

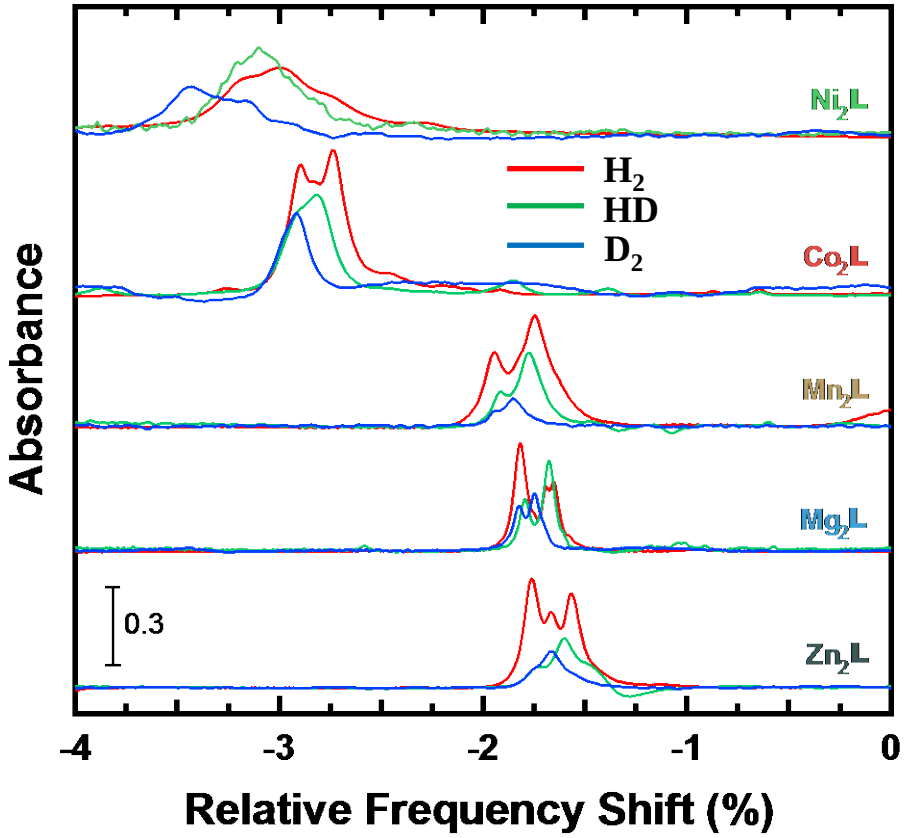


$H_2 - H_2$ Interactions



Shift most notable in S(0) bands, maximum of ~ 6 cm^{-1}

Isotope Effects: H_2, HD, and D_2



Buckingham Model

$\Delta\nu/\nu_{free}$ = constant

Deviations from Buckingham model most likely due to vibrational translational coupling

Conclusion

- **Infrared Spectroscopy is a very powerful tool**
- **Great for parameterizing theoretical models**
- **We see no evidence for large H_2 – H_2 induced shifts**
- **Air-exposure is a real concern with MOFs**

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

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Metal-Specific Interactions of H_2 Adsorbed within Isostructural Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Diffuse reflectance infrared (IR) spectroscopy performed over a wide temperature range (35–298 K) is used

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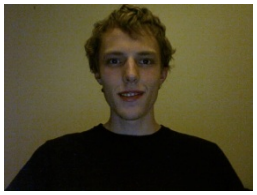

Jennifer Schloss