Gas Adsorption in Metal Organic Frameworks : an experiment using the NCNR Disk Chopper Spectrometer

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Overview

- Issues with Energy Storage:
  - The how and the why.
- Applications of Neutron Scattering
  - Locations of molecules
  - Dynamics/binding strengths
- Outlook for this experiment
- Conclusion

Why?

Why alternative fuels?

- Reduce dependence on foreign oil
- New opportunities for agriculture
- Reduce transportation costs
- Harness renewable energy sources
- Clean air in cities
- Reduce greenhouse gas emissions

What are alternative fuels?

- Ethanol (from corn, wood, …)
- Natural gas; 85% of NG used in U.S. is domestic
  (NG; from domestic gas/oil fields, deep-sea methane hydrate fields, landfills, biomass)
- Biodiesel (from soybeans, vegetable oils, …)
- Hydrogen (from NG, water & electricity, coal, …)
- Electricity (from nuclear/hydroelectric/solar/wind power plants)

Why?

Current natural-gas vehicles

- Low emission of
  - hydrocarbons (ozone, smog)
  - NO_x
  - particulate matter
  - Up to 40% reduction of CO_2

- Clean Cities Coalitions:
  - Los Angeles: 1500 CNG buses
  - Kansas City: 200 CNG public utility vehicles
  - U.S.: 130,000 CNG vehicles
  - worldwide: over 5 million CNG vehicles

Alternative fuel systems (BAF Tech.)

In 2006, Gasoline was $2.84 per gallon, diesel was $2.98 per gallon, and CNG was $1.90 per gasoline gallon equivalent !
http://www.eere.energy.gov/afdc/resources/pricereport/price_report.html

Why?



Fuel Storage
Compressed natural gas (CNG) is stored on board vehicles at high-pressure (3,000 psi)

Liquefied natural gas (LNG) must be cooled to –162 ºC.
LNG requires only 30 percent of the space of CNG to store the same amount of energy.

Why?

$1.2 Billion to develop the technology needed for commercially viable hydrogen-powered fuel cells
(2003)

However:

H_2 has 3x energy content by **MASS** c.f. gasoline

Gasoline has 4x energy content by **VOLUME** c.f H_2

Schlapbach and Zuttel (2001) Nature 414: 353-358

Targets

Methane

180 (cc CH_4)/cc 35bar (500 psi)/25K

-achieved using carbonized corncobs
(*Pfeifer, University of Missouri, 2007*)

-IRMOF-6 155 cc/cc
(*Eddaoudi, Science 2002*)

-IRMOF-1 ~115 cc/cc
(*Zhou, in prep.*)

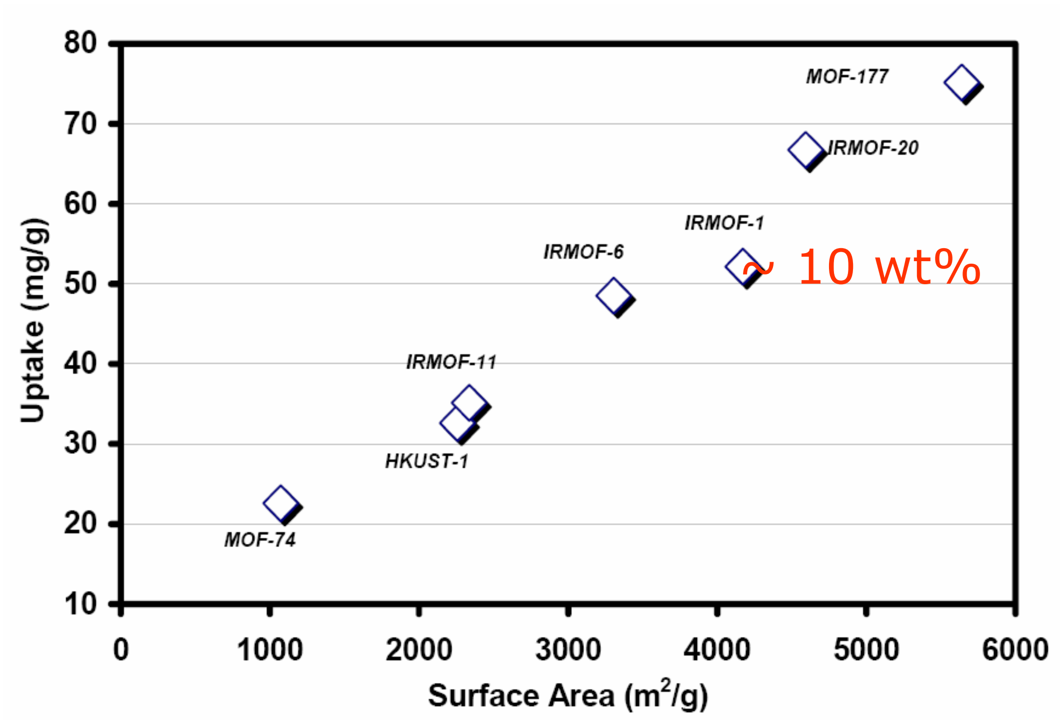
Hydrogen

Parameter	'07	'10
Energy$_{(system)}$ (wt%)	4.5	6
Volumetric (g/L)	36	45
Fuel cost ($ per gge)	3	1.5
Reversible, safe …		

gge: gallon gasoline equivalent

Gravimetric and volumetric of best MOFs @77K
~7 wt%, ~36g/L (e.g. *Dinca, JACS, 2006*) – NOT *SYSTEM*

Hydrogen Storage in MOFs



(Wong-Foy et al. JACS 128, 3494 (2006))

MOF-5 (IRMOF-1) can adsorb ~10 wt% H_2 (<10 K)

(Yildirim et al. PRL 95, 215504 (2005))

Hydrogen Adsorption Enthalpy

HKUST-1	~6.6 kJ/mol [1]
Prussian blue analogus	~7.4 kJ/mol [2]
MOF-74	~8.3 kJ/mol [1]
Zn_3(1,4-benzeneditetrazolate)$_3$	~8.7 kJ/mol [3]
IRMOF-11	~9.1 kJ/mol [1]
$Cu_{1.5}[(Cu4Cl)_3BTT_8]$	~9.4 kJ/mol [4]
PCN-9	~10.1 kJ/mol [5]
$Mn_{1.5}[(Mn_4Cl)_3BTT_8]$	~10.1 kJ/mol [6]

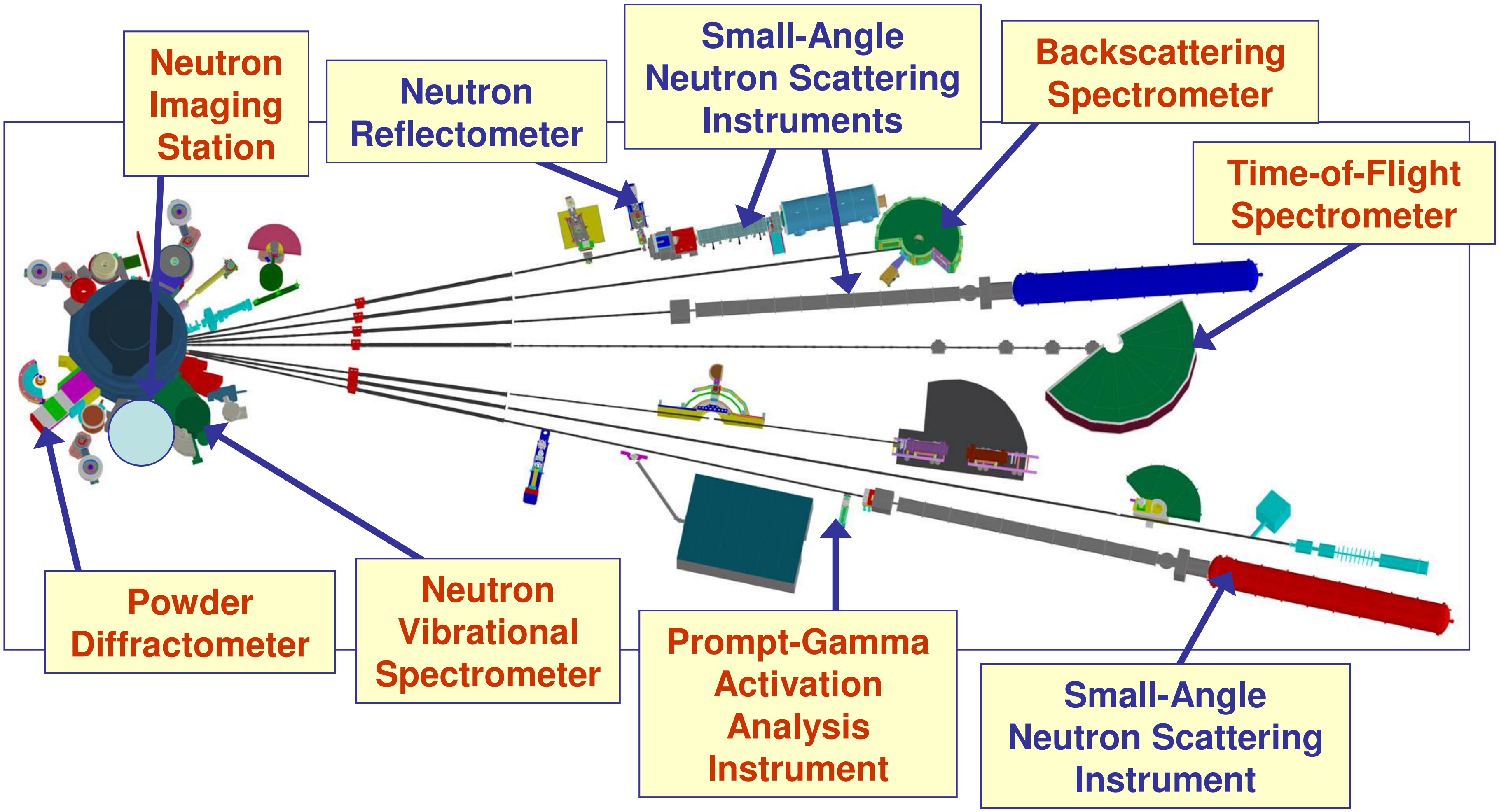
~15 kJ/mol would be ideal for hydrogen storage material working at room temperature.

(S. K. Bhatia, A. L. Myers, *Langmuir* 22, 1688 (2006))

Reference:

1. Rowsell et al., J. Am. Chem. Soc. 128, 1304 (2006)
2. S. S., Kaye et al., J. Am. Chem. Soc. 127, 6506 (2005)
3. M. Dinca et al., J. Am. Chem. Soc. 128, 8904 (2006)
4. M. Dinca et al., Angew. Chem. Int. Ed., in press (2007)
5. S. Ma et al., J. Am. Chem. Soc. 128, 11734 (2006)
6. M. Dinca et al., J. Am. Chem. Soc. 128, 16876 (2006)

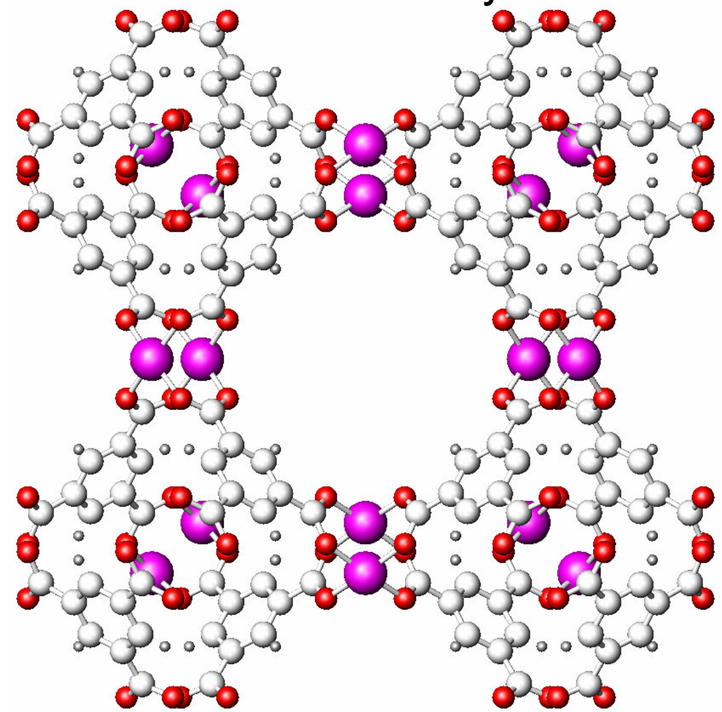
NIST Center for Neutron Research (NCNR)



HKUST-1

Cu_3(1,3,5 benzenetricarboxylate $)_2$

The Cu atoms in the fully dehydrated phase are coordinatively unsaturated



•Desolvated crystals exhibit :

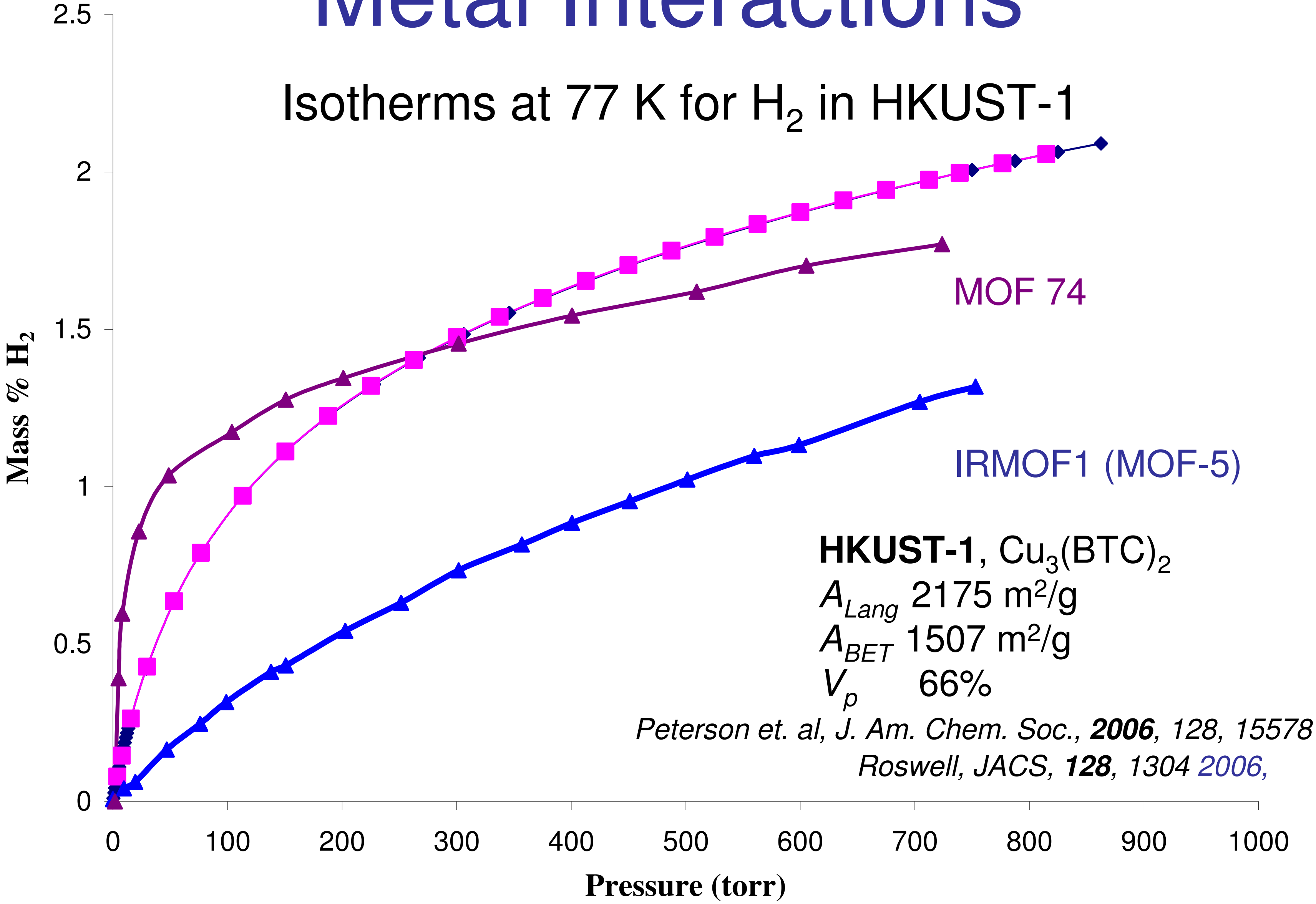
Total H_2 uptake of ~3 wt % at 77 K and 90 bar

At 27 g H_2/L provides a storage density <40% of that of liquid H_2

A maximum isosteric heat of adsorption of 6.6 kJ/mol

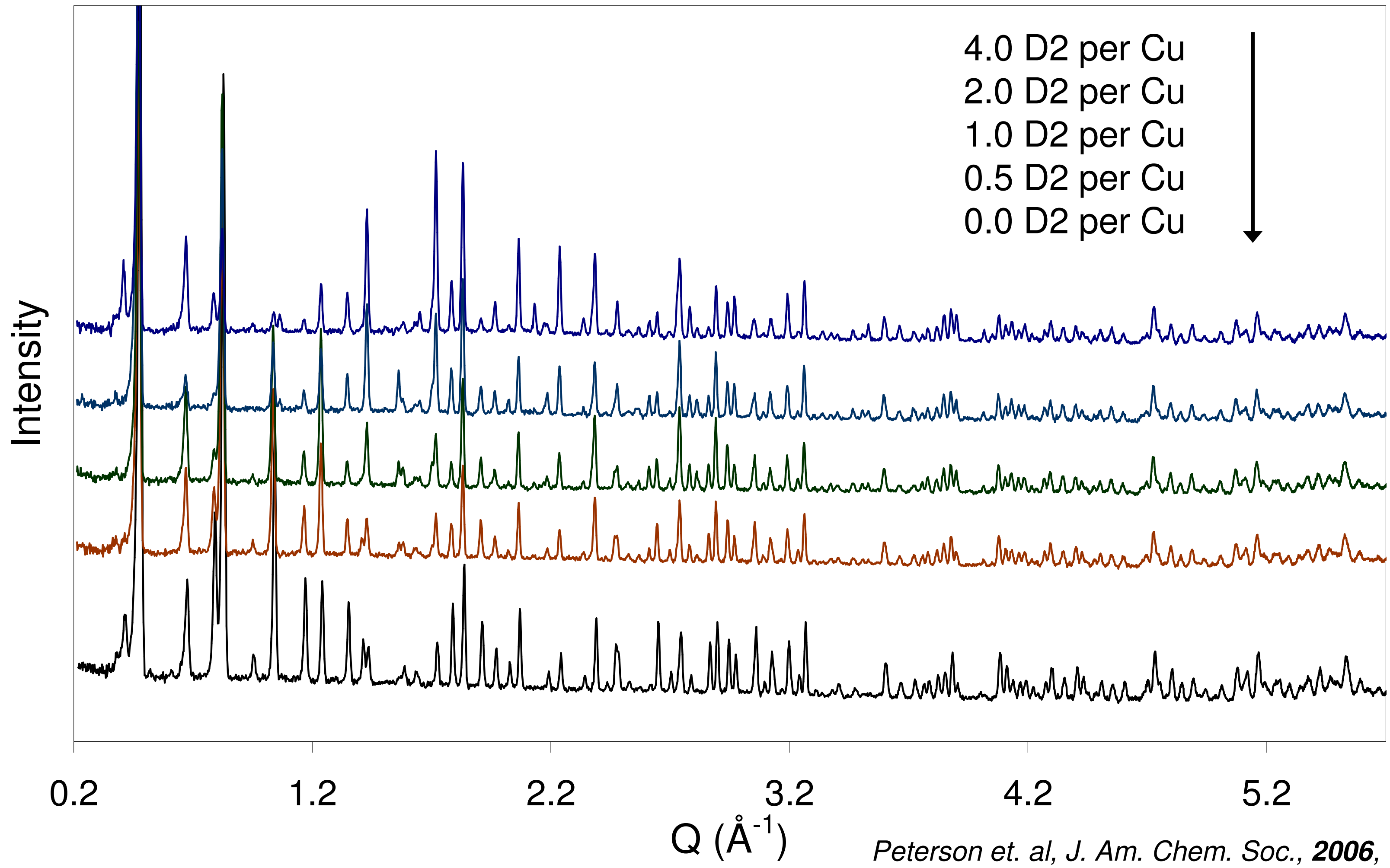
*Chui, Science, **283**, 1148 1999*
*Roswell, JACS, **128**, 1304 2006*
*Wong-Foy, JACS., **128**, 3494 2006*
*Prestipino, Chem. Mater., **18** (5), 1337 2006*

Metal Interactions



Metal Interactions

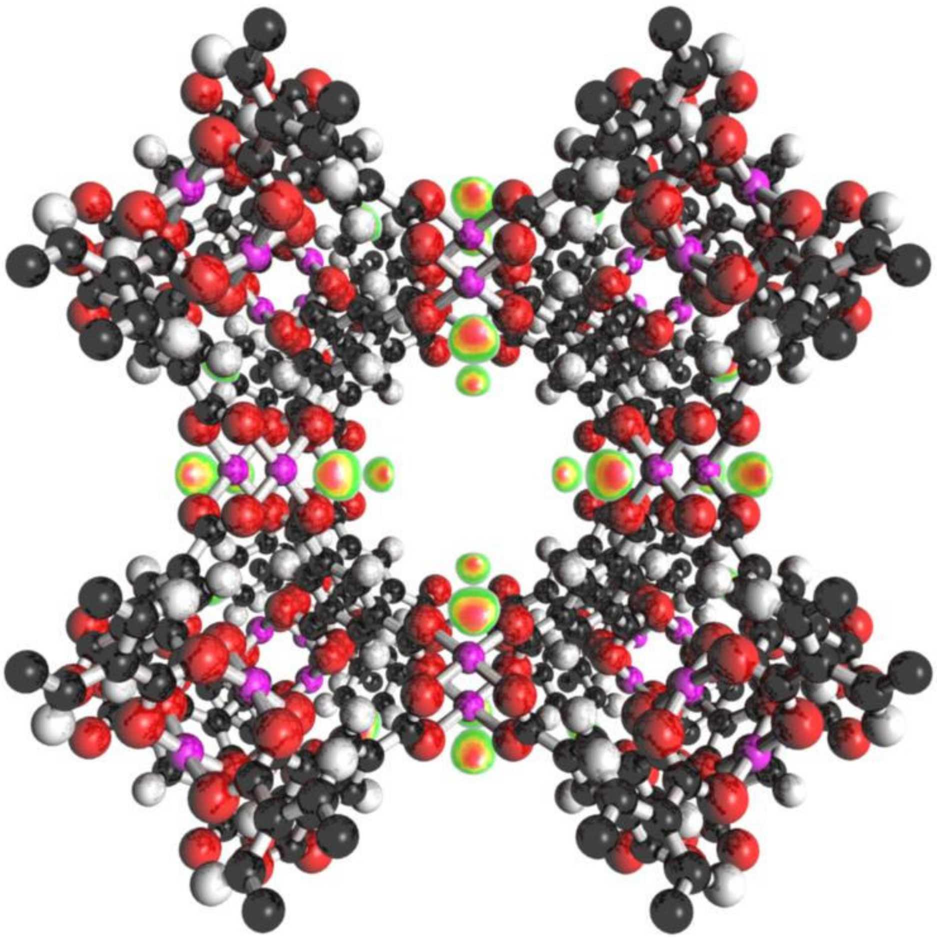
Diffraction patterns for D_2 in HKUST-1

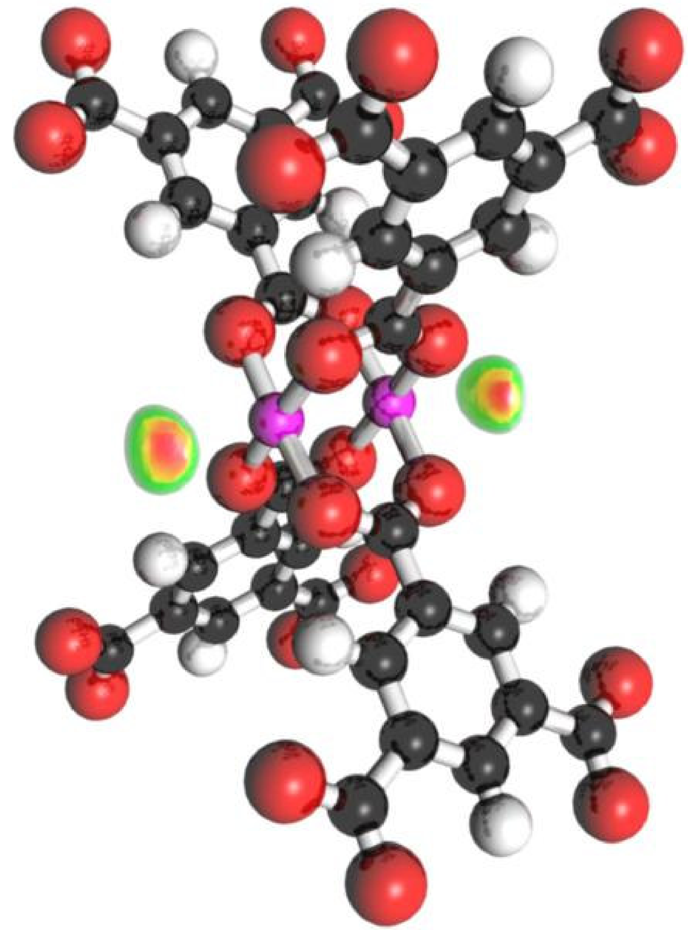


*Peterson et. al, J. Am. Chem. Soc., **2006**, 128, 15578*

Metal Interactions

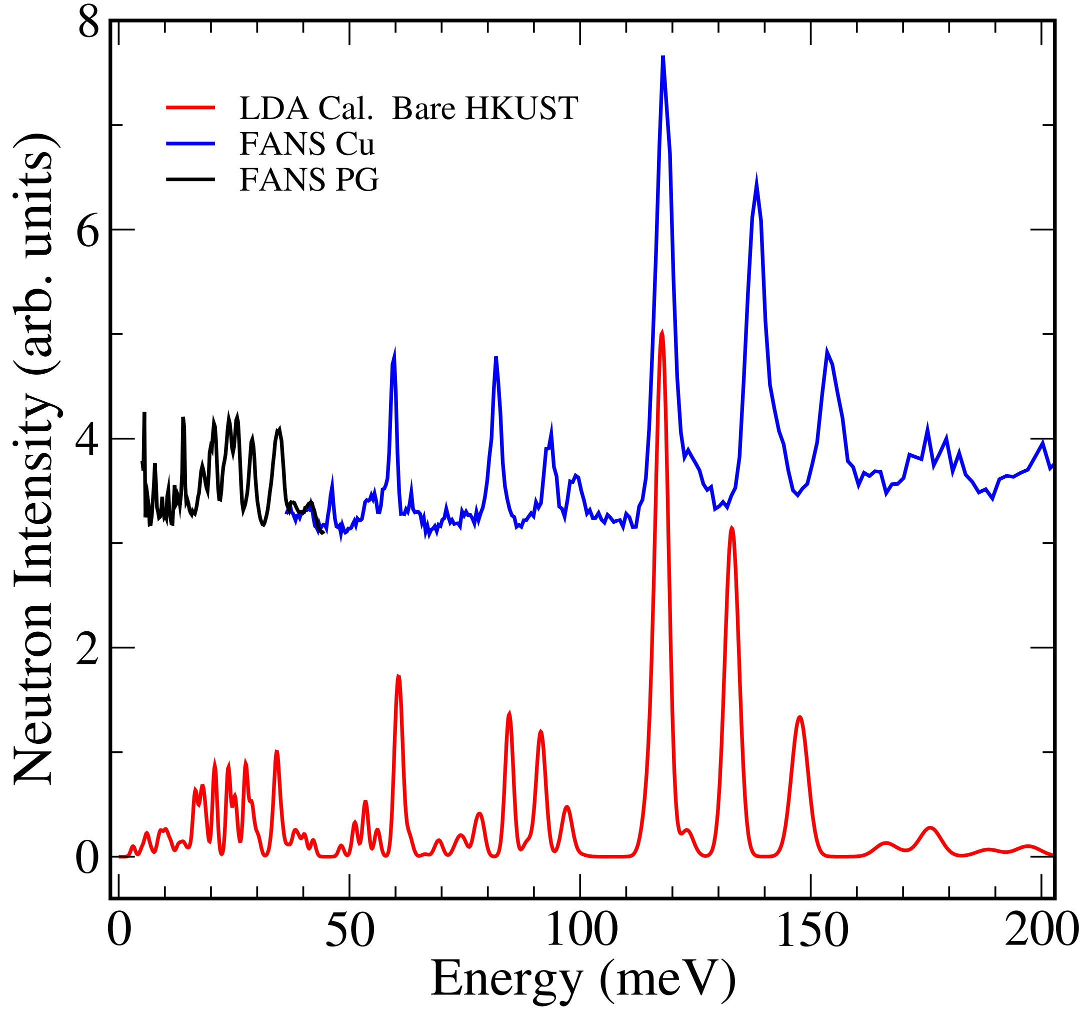
Fourier Difference to locate D_2 in HKUST-1





Framework and DFT

Bare HKUST-1 Spectroscopy



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Framework and DFT

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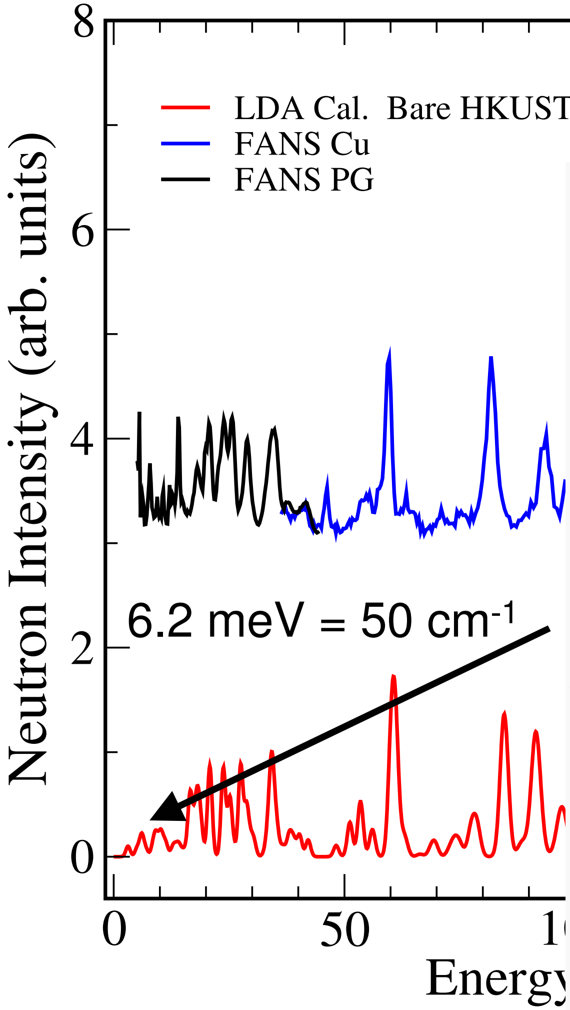

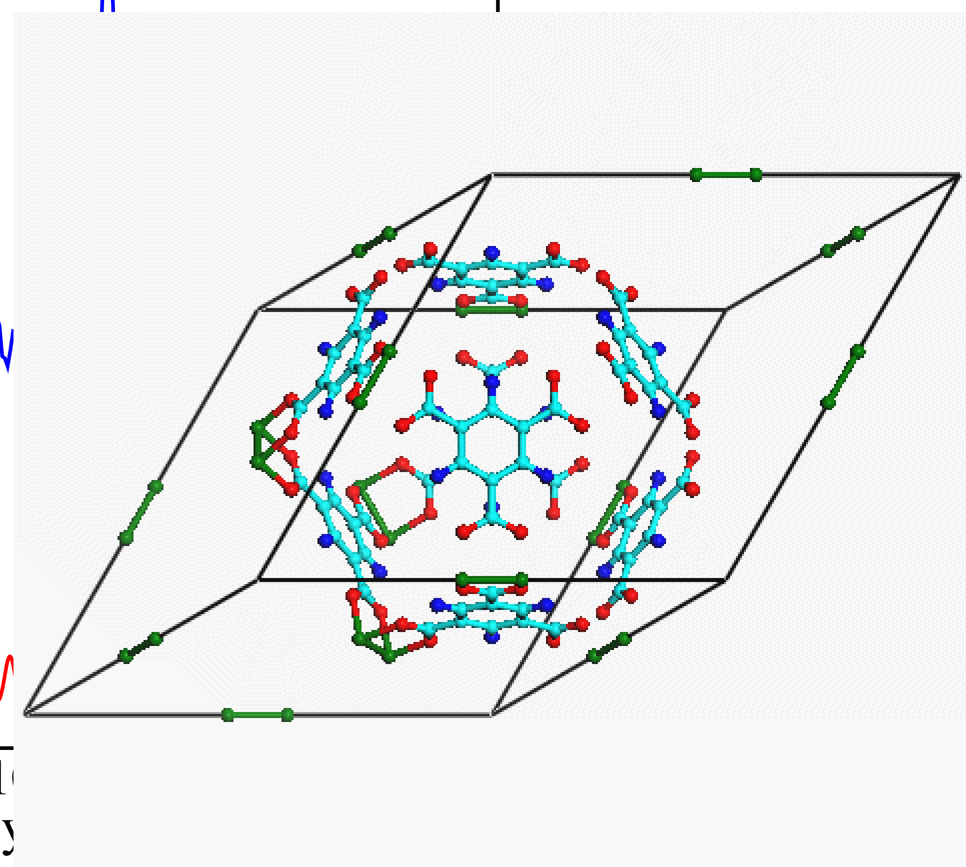

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Framework and DFT

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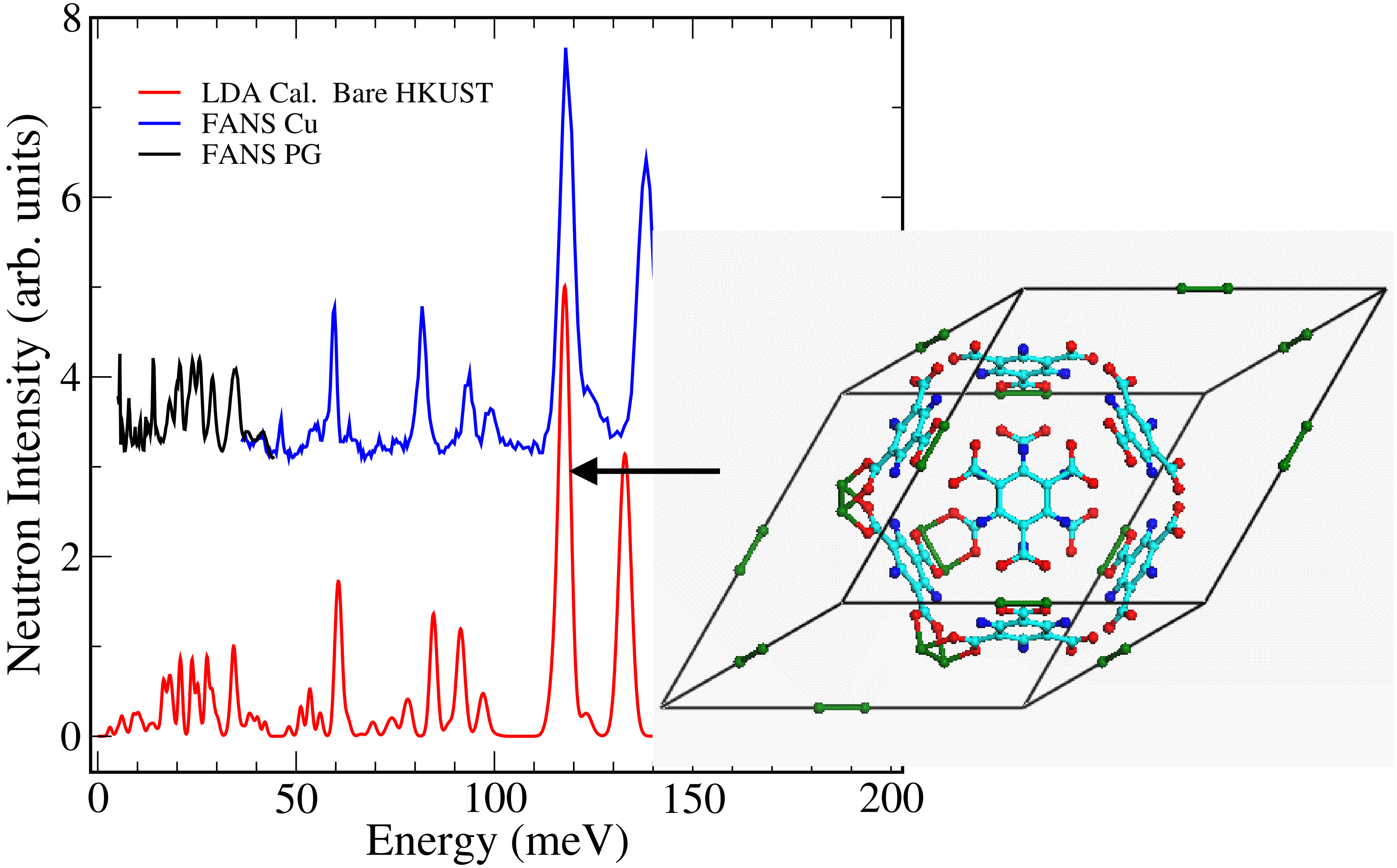

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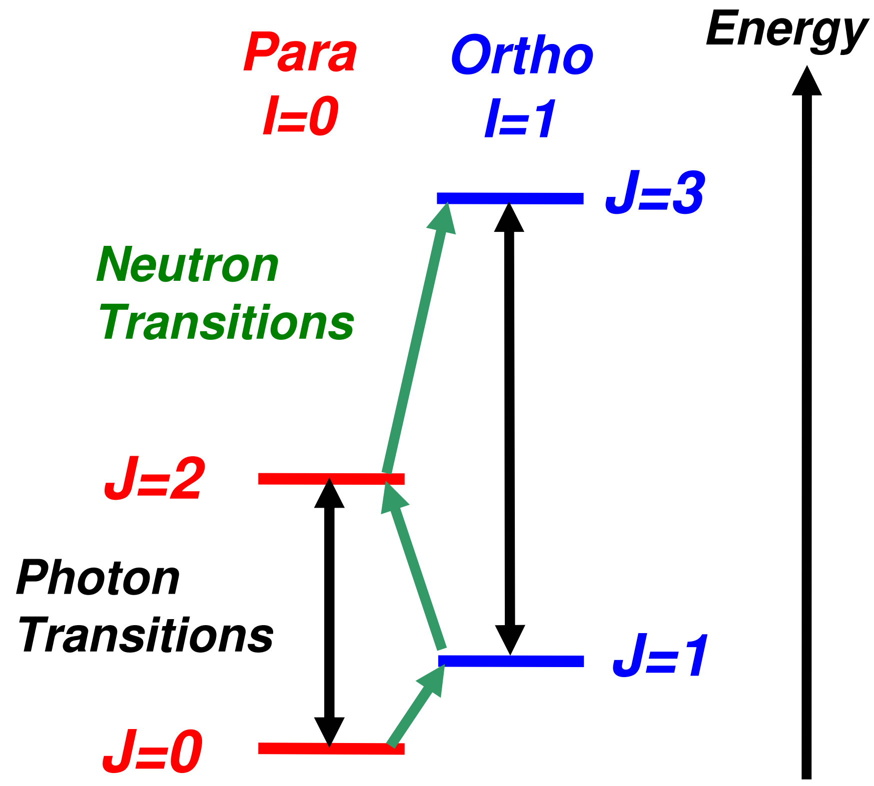
Hydrogen Transitions

Para has a nuclear spin I=0. This constrains J to be even.

Ortho has a nuclear spin I=1. This constrains J to be odd.

Transition between ortho and para species can occur through flipping the nuclear spin.

E_J=B J(J+1), B_{H_2}=7.35 meV

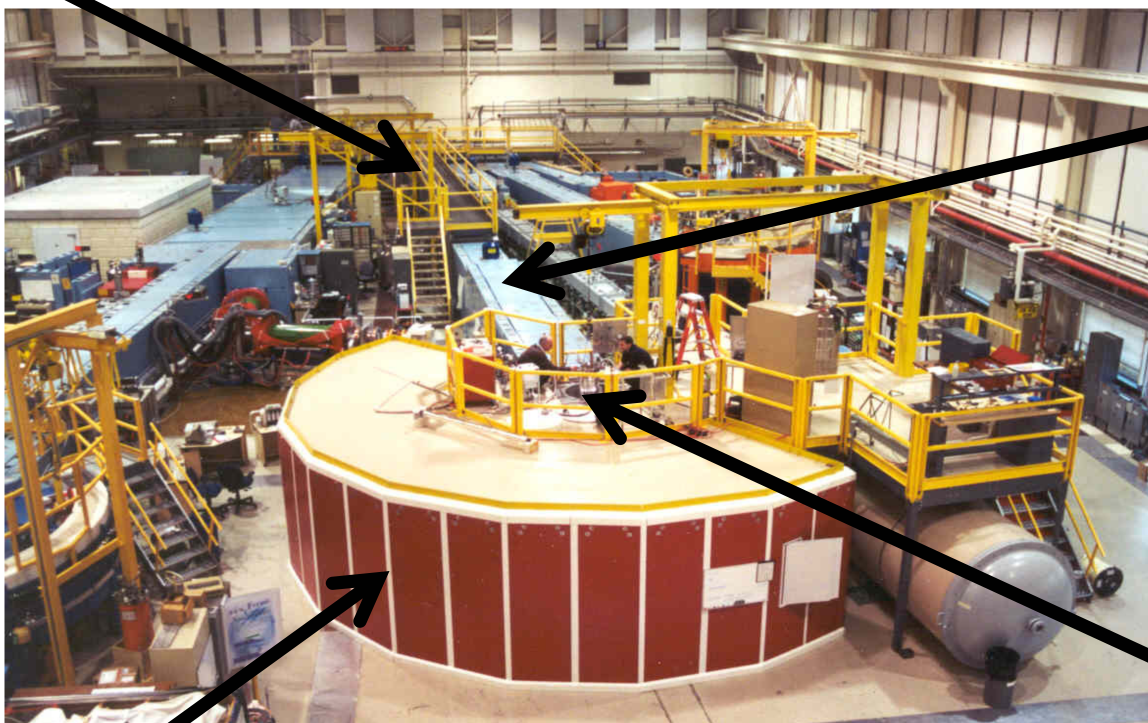


(Neutron energy loss)

TOF spectroscopy

Disc Chopper Spectrometer

(1) The neutron guide

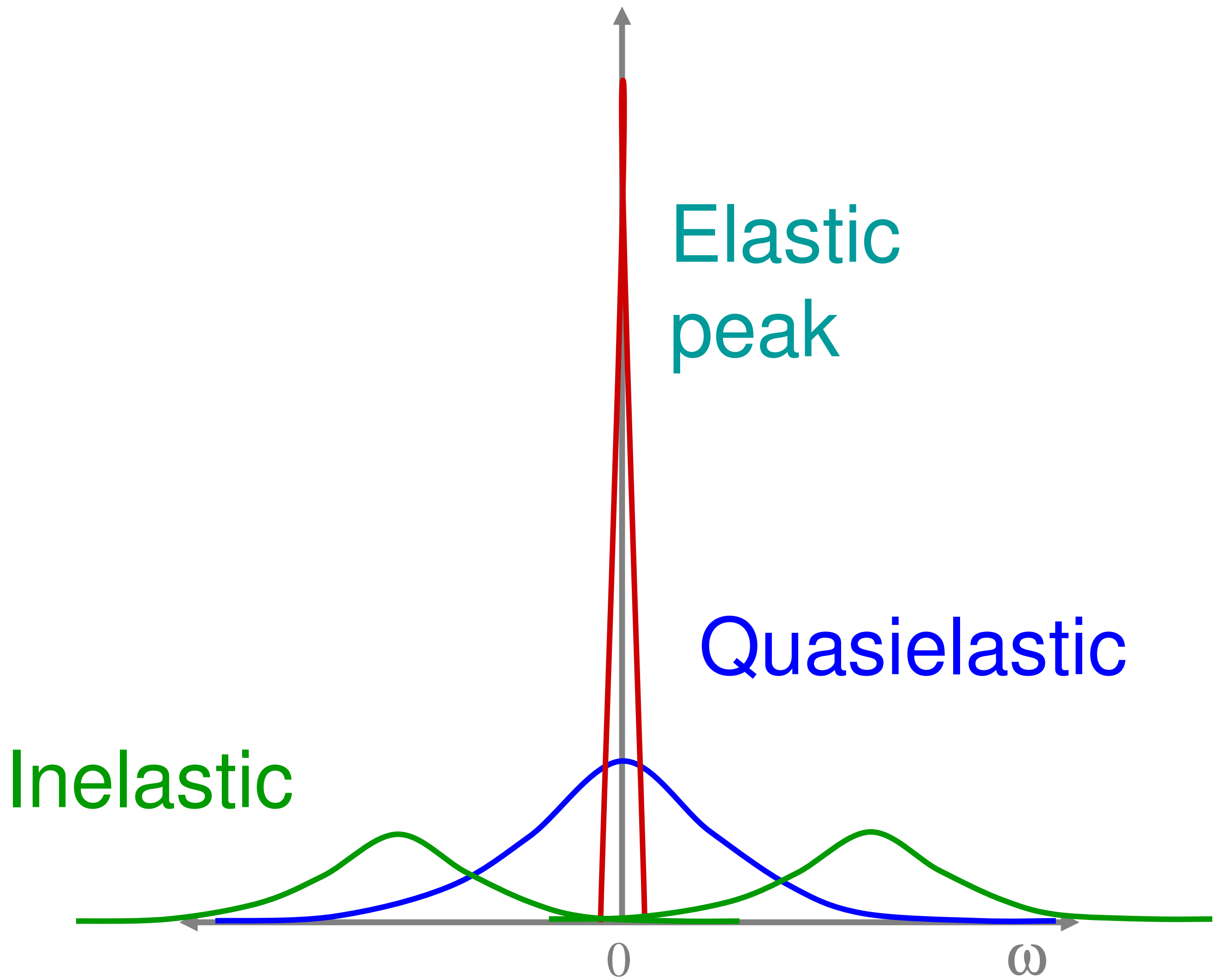


(2) The choppers

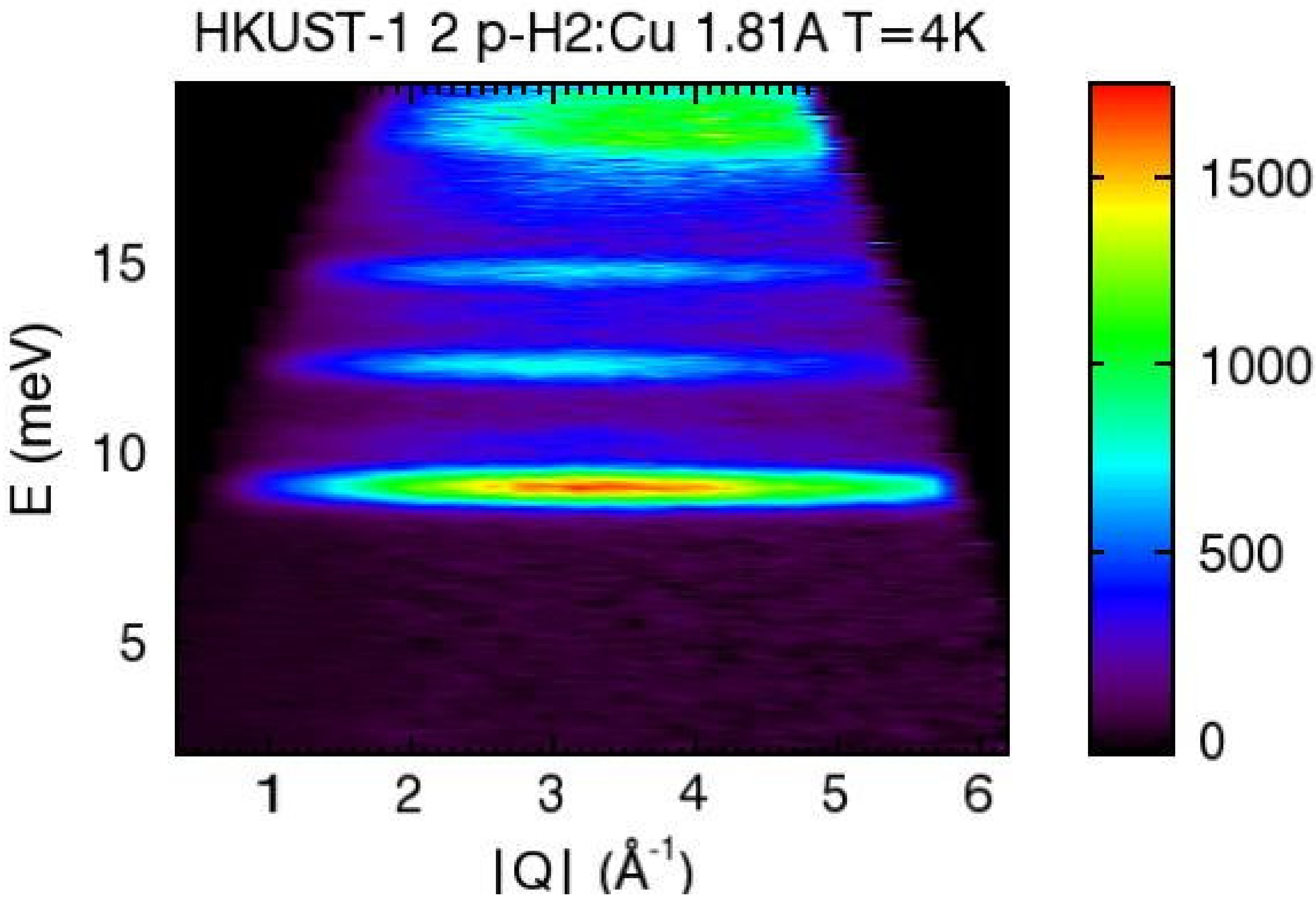
(3) The sample area

(4) The flight chamber and the detectors

Total Scattering



Metal Interactions



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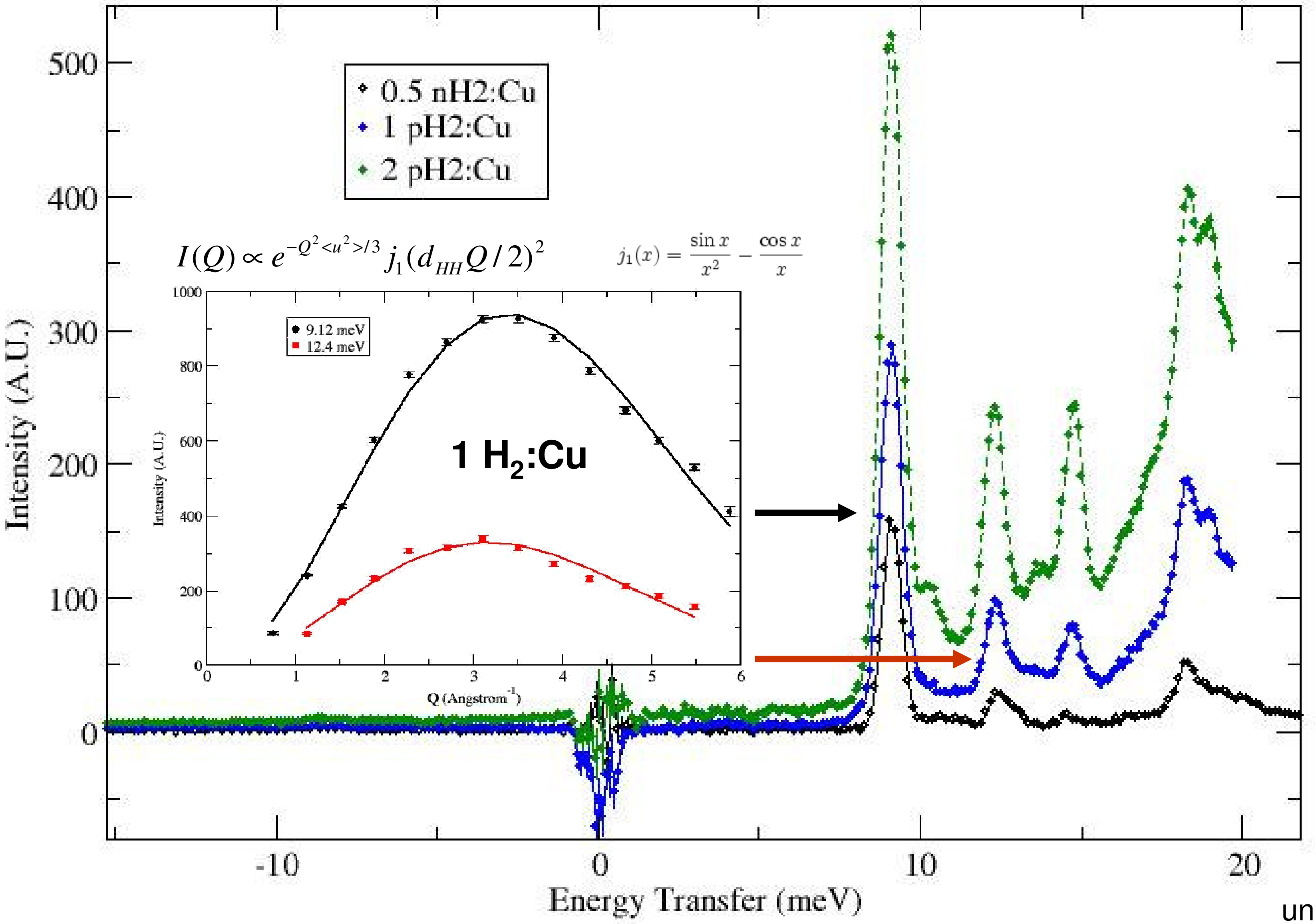
Metal Interactions

DCS



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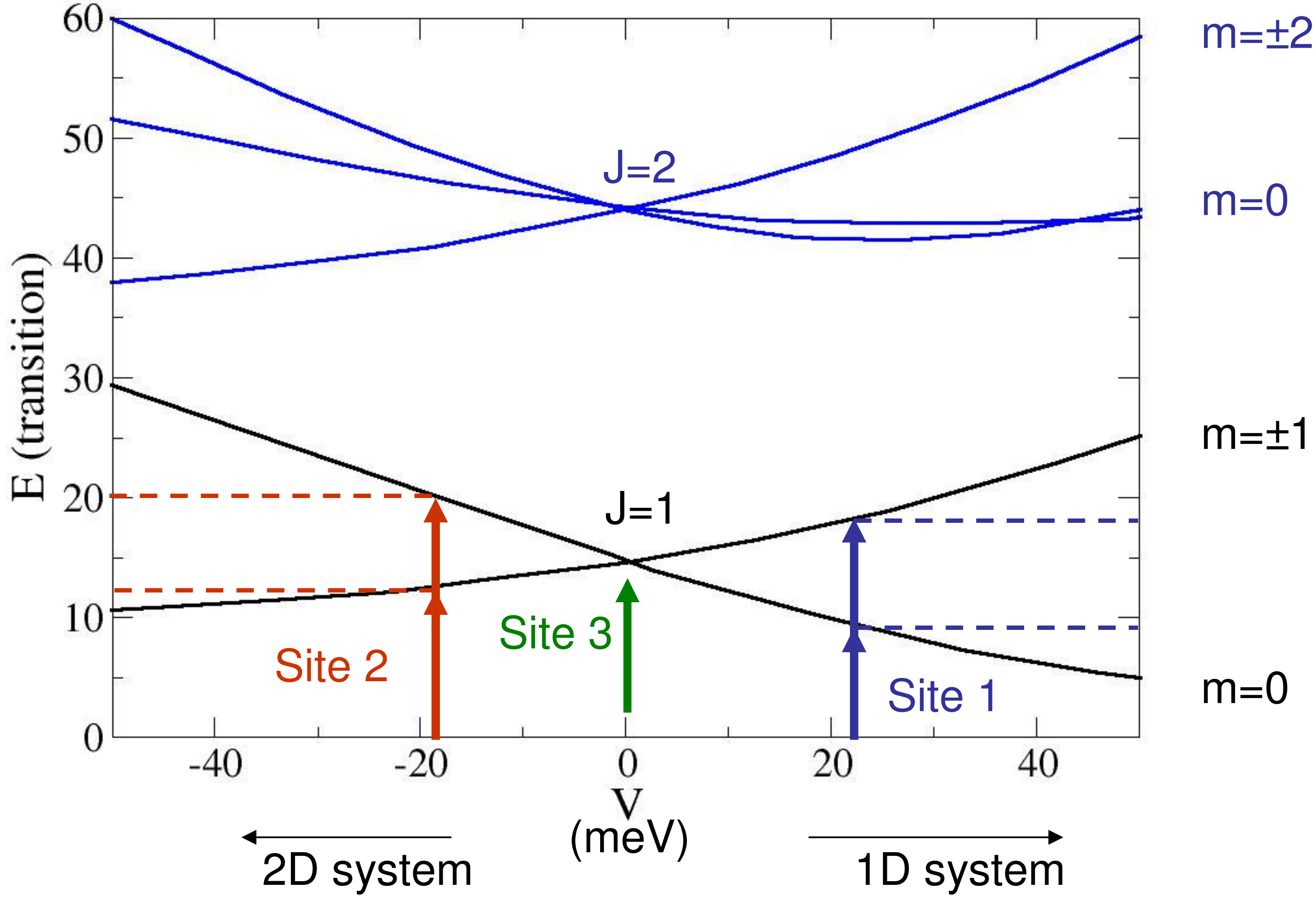
Metal Interactions

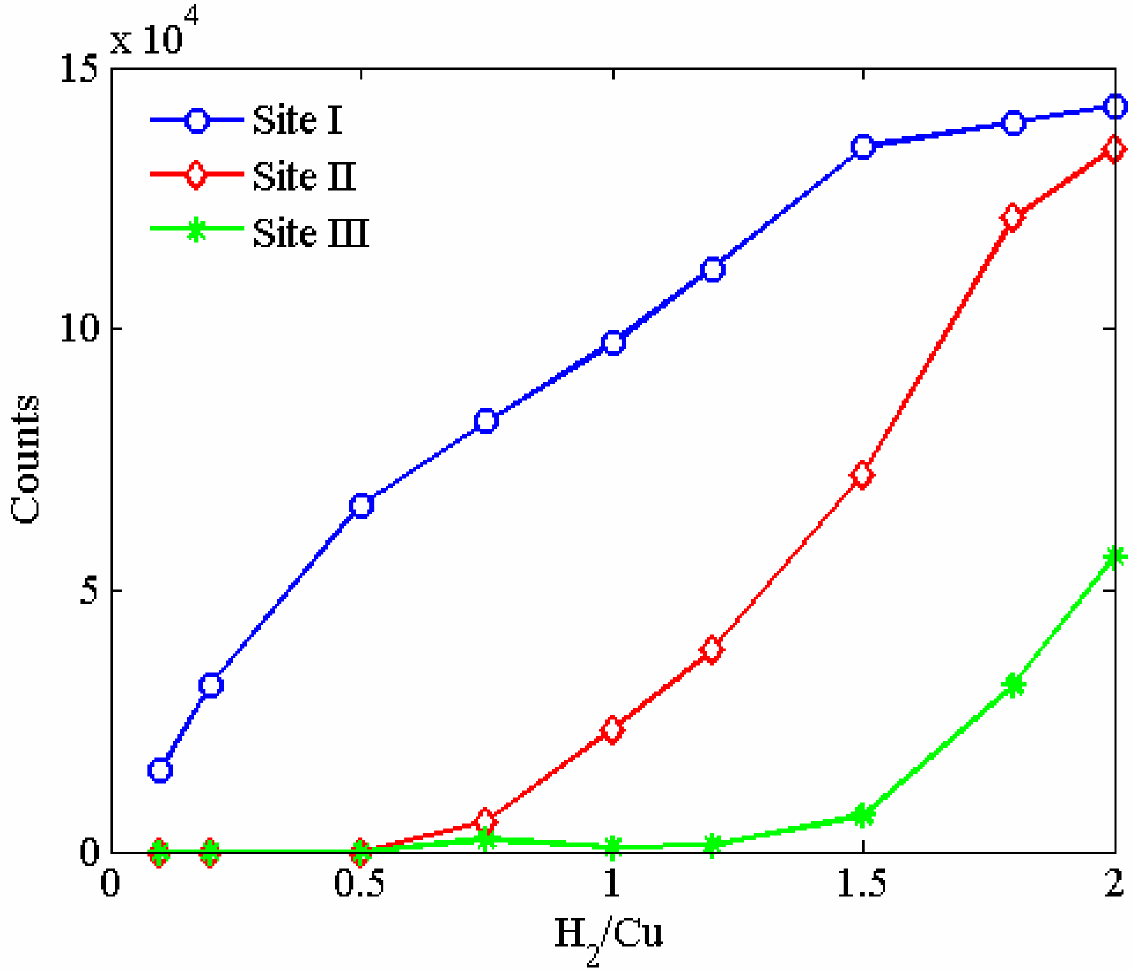
Spectroscopy

The transition tells us about the symmetry and strength of the local potential. A larger rotational barrier *implies* a stronger binding.



Metal Interactions

Extract Intensity as fn of loading…



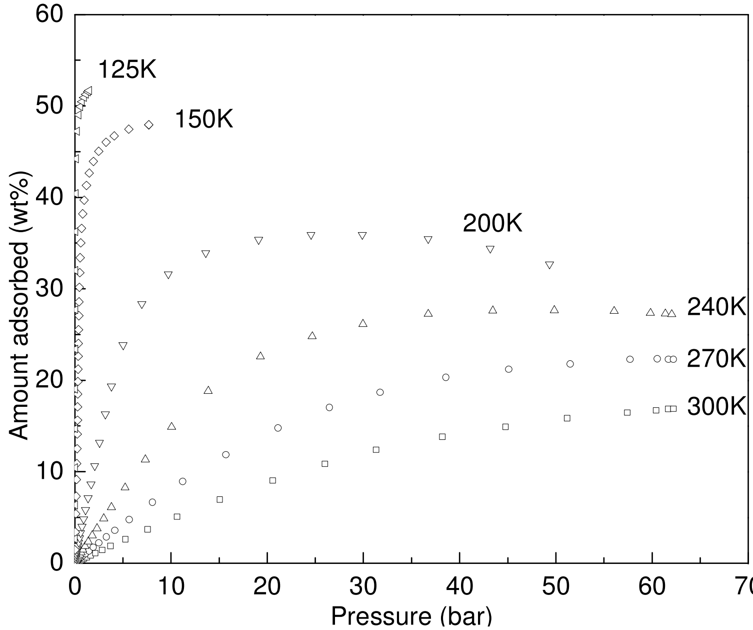
Hydrogen adsorption is complicated!
Do not load just the strongest adsorption sites in order

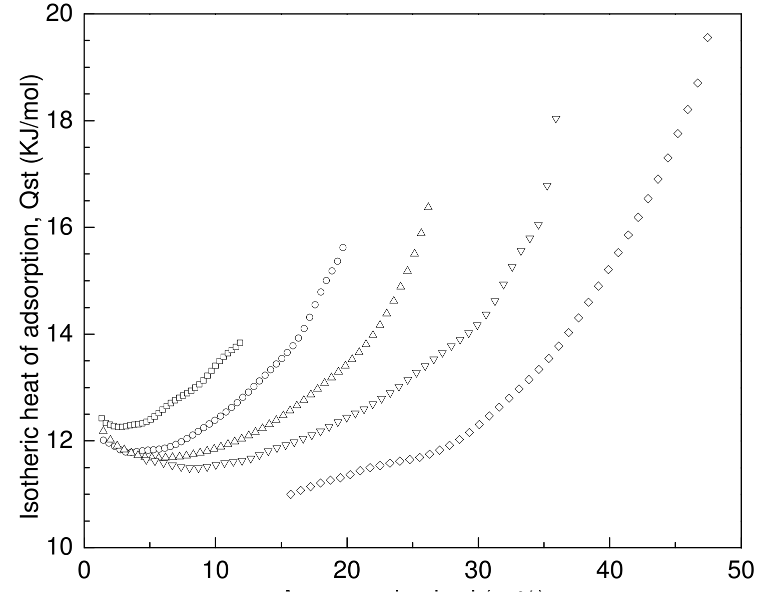
Liu et. al, J. Alloys Compounds

Outlook

- Experience Practical TOF spectroscopy
  - sample choice
  - geometry consideration
- Learn something about the instrument
  - Wavelength / Resolution / Intensity
- Data Reduction
- Data Analysis and Interpretation
  - Tunneling spectroscopy
  - Quasi-elastic spectroscopy
    - spatial and temporal information

Adsorption isotherms





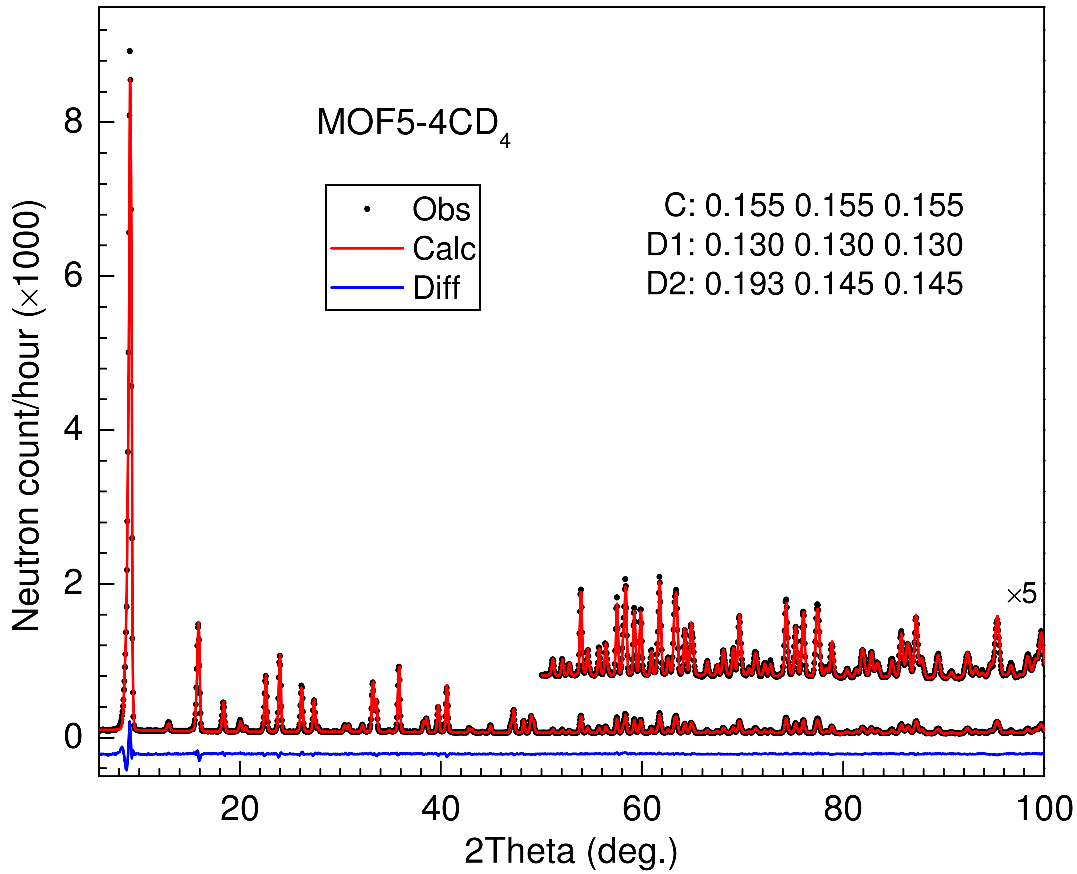
The maximal excess adsorption capacity of CH_4 in MOF-5
51.7 wt%, or 24 CH_4 per MOF-5 formula (i.e., 4Zn).
This is reduced to ~15 wt% (115 cc/cc) at room temperature, 35bar.

The excess isosteric heat of adsorption (calculated using the Clausius-Clapeyron equation) for the initial CH_4 adsorption in MOF-5 is ~12.2 KJ/mol. At high concentration, Qst increases with increasing amount adsorbed, indicating the importance of the interactions between adsorbed CH_4 molecules.

(*Zhou, in prep.*)

Where are the methane molecules?

The adsorption sites were directly determined from the difference-Fourier analysis of neutron powder diffraction data. Initial adsorption occurs at the MOF5 "cup site" with a well defined CH_4 orientation. We did not see any well-defined sites for additional adsorption.

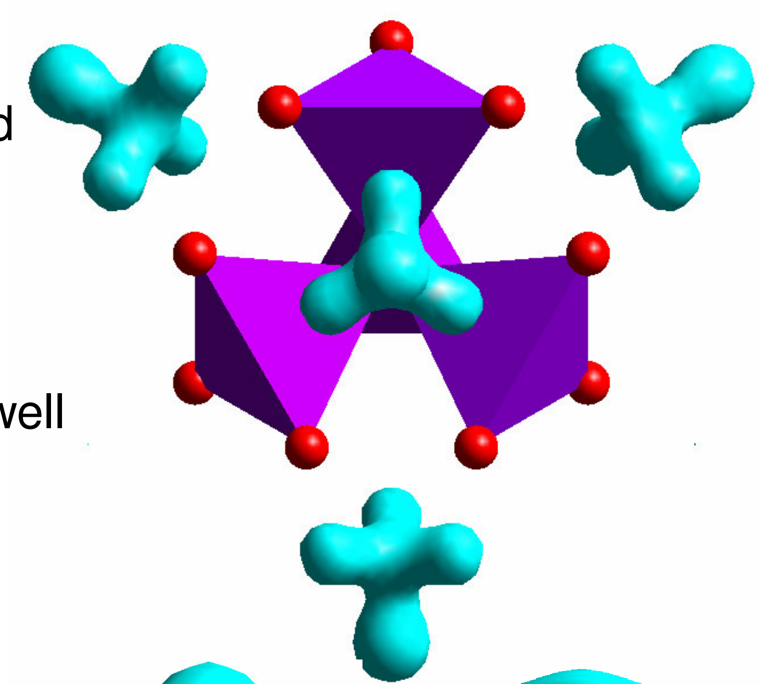


The neutron powder diffraction pattern of MOF-5:$4CD_4$ at 4 K with the Rietveld refinement.

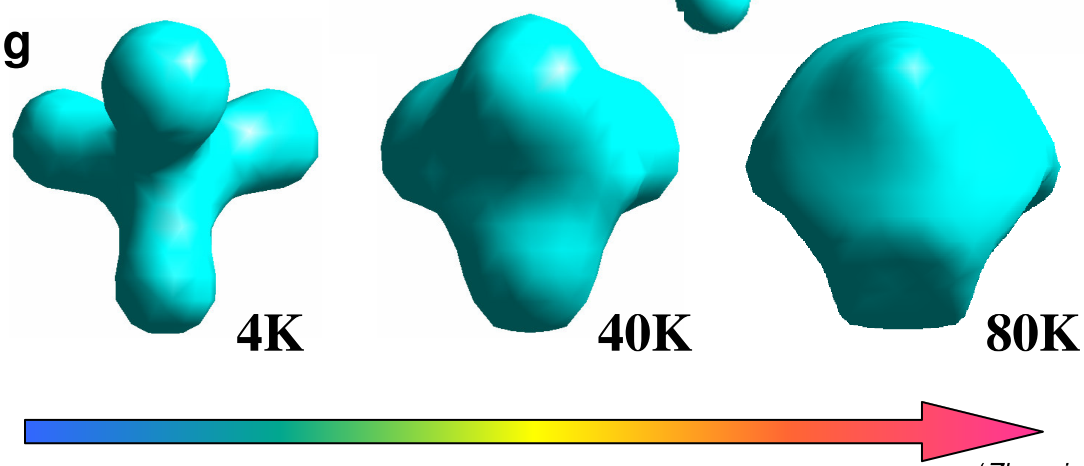
(*Zhou, in prep.*)

Where are the methane molecules?

The isosurface of the difference-Fourier (DF) neutron scattering-length density superimposed with the ZnO_4 clusters of the MOF-5 host structure, indicating the location of the first methane adsorption sites. This is a “direct measurement” (like taking a picture) of the methane molecules packed in the solid with a well defined orientation.



T-dependent neutron scattering is further used to visualize the methane orientational dynamics with increasing temperature.



(*Zhou, in prep.*)

Types of Experiments

- Translational and rotational diffusion processes, where scattering experiments provide information about time scales, length scales and geometrical constraints; the ability to access a wide range of wave vector transfers, with good energy resolution, is key to the success of such investigations
- Low energy vibrational and magnetic excitations and densities of states
- Tunneling phenomena

- **Chemistry ---** e.g. clathrates, molecular crystals, fullerenes
- **Polymers ---** bound polymers, glass phenomenon, confinement effects
- **Biological systems ---** protein folding, protein preservation, water dynamics in membranes
- **Physics** --- adsorbate dynamics in mesoporous systems (zeolites and clays) and in confined geometries, metal-hydrogen systems, glasses, magnetic systems
- **Materials ---** negative thermal expansion materials, low conductivity materials, thermo-electrics, hydration of cement, carbon nanotubes, proton conductors, metal hydrides

Conclusions

- Neutrons can tell us where atoms are located.
- Neutrons can tell us how a lattice vibrates->
  -very sensitive to the local potential
- Neutrons can tell us adsorbate-framework interaction strengths