

INS studies of the Adsorption of Small Molecules in Metal Organics Frameworks

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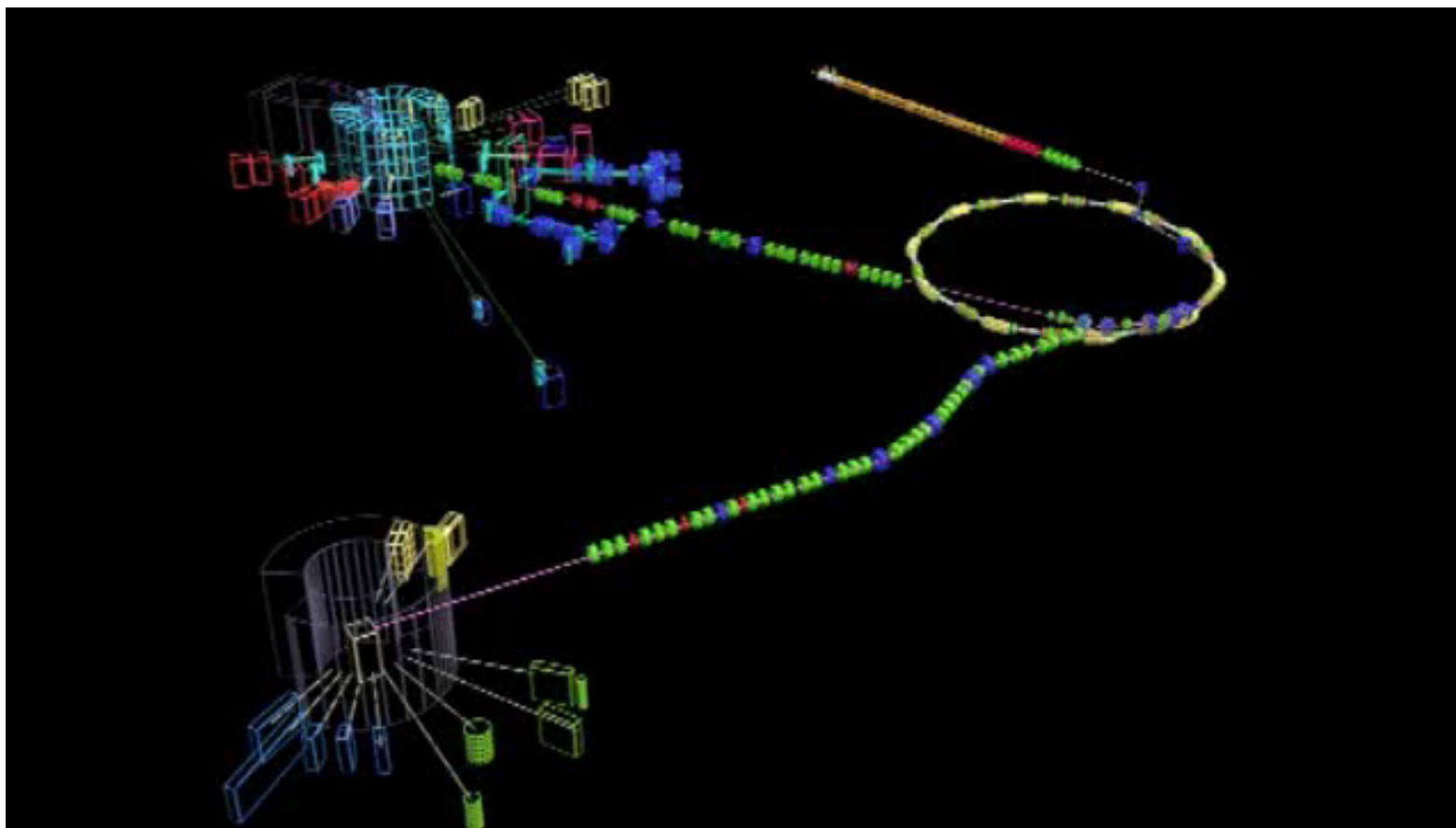


- Diamond (Synchrotron)
- CLF (Central Laser facility)
- ISIS (Neutron and Muon Science facility)

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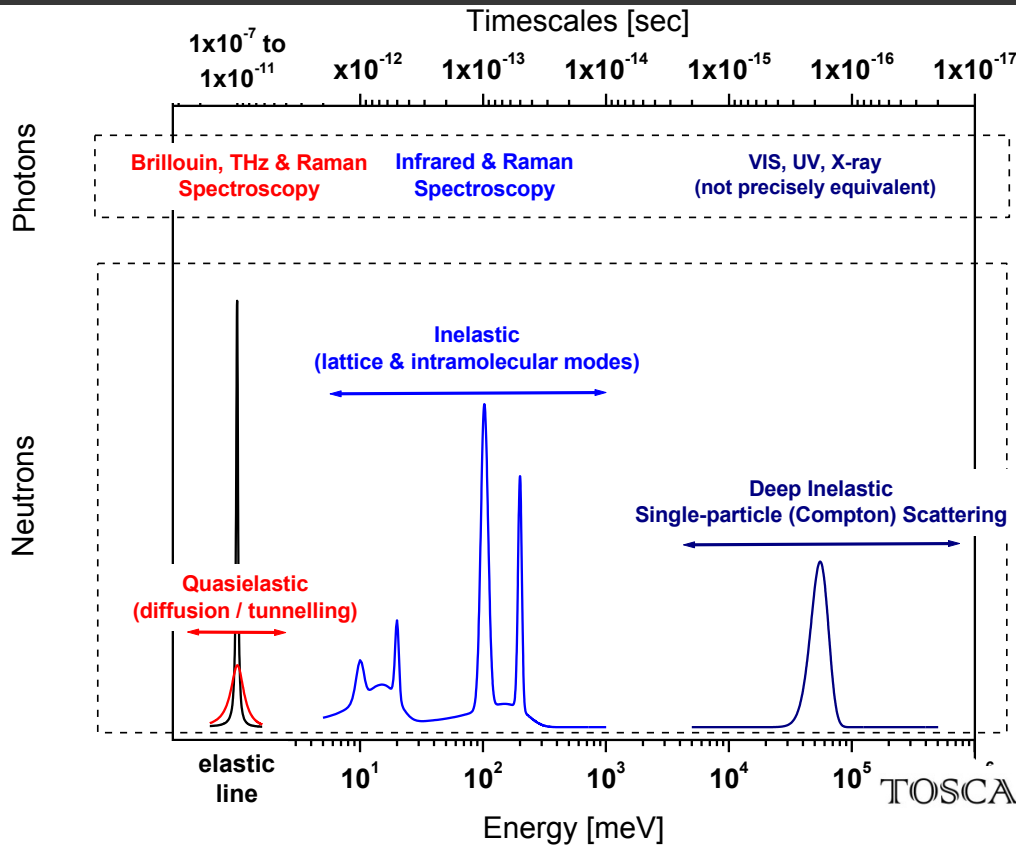


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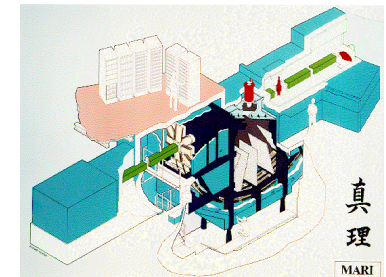
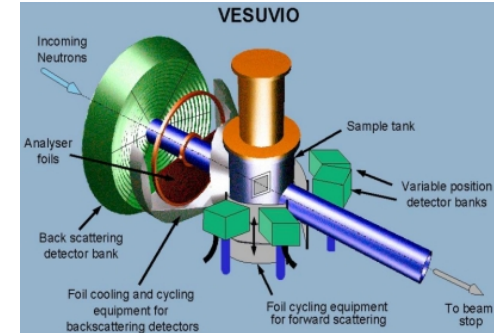


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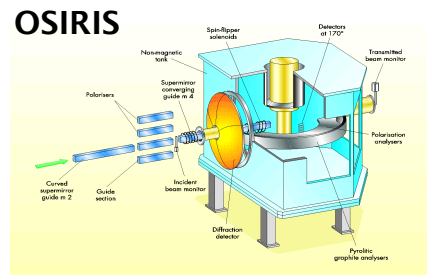
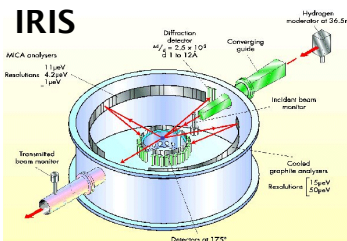
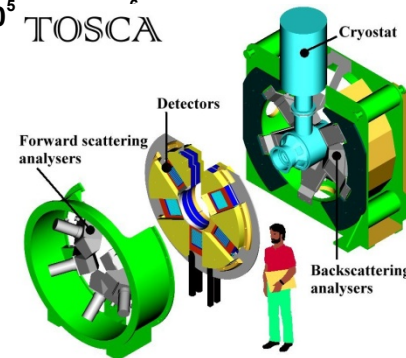
High-resolution Spectroscopy at a Pulsed Neutron Source



High energies (Compton)

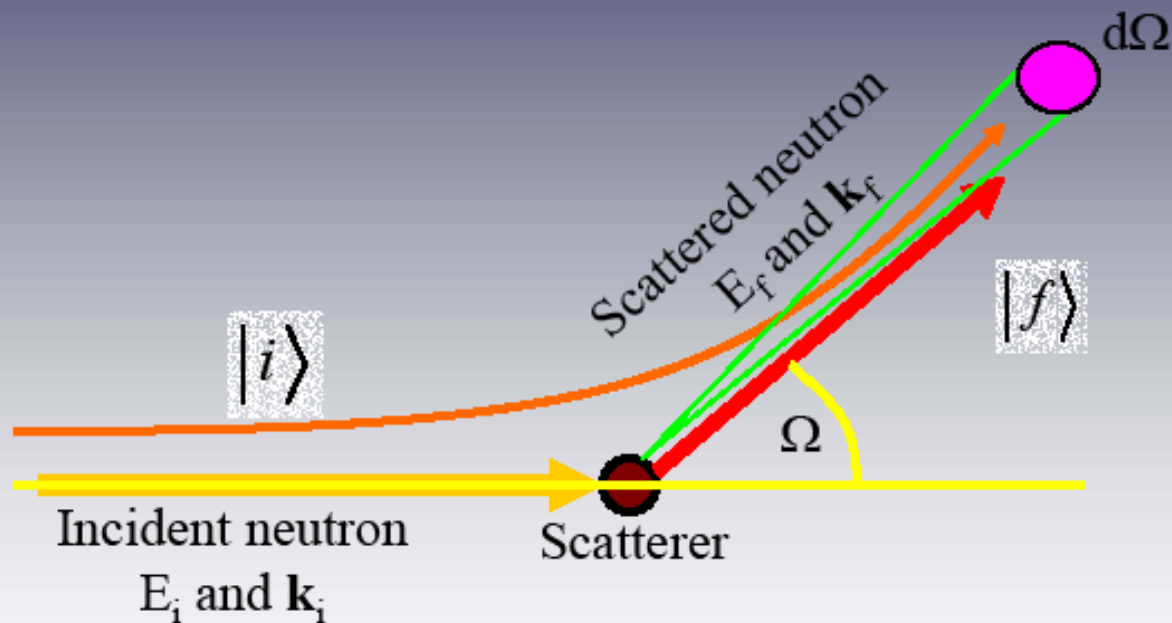


Intermediate energies (Raman-like)

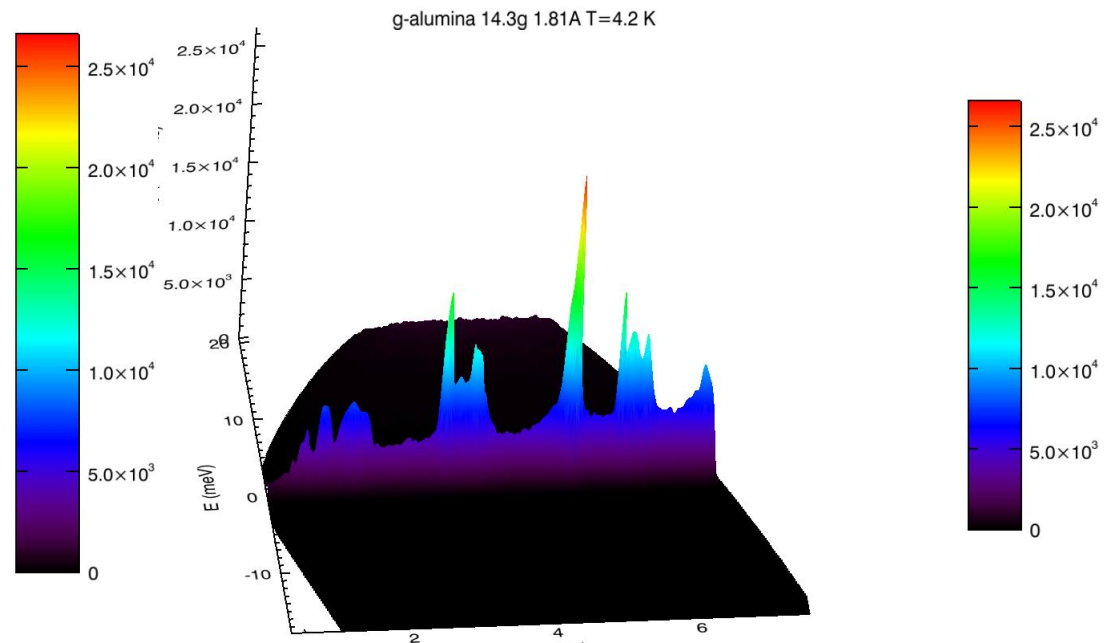
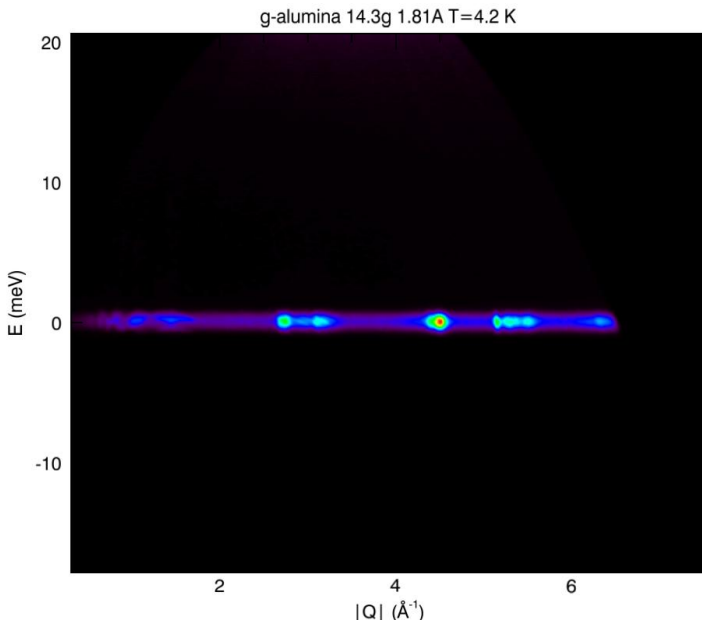


Low energy (THz region)

Inelastic Neutron Scattering Spectroscopy



The $S(Q, \omega)$ Map



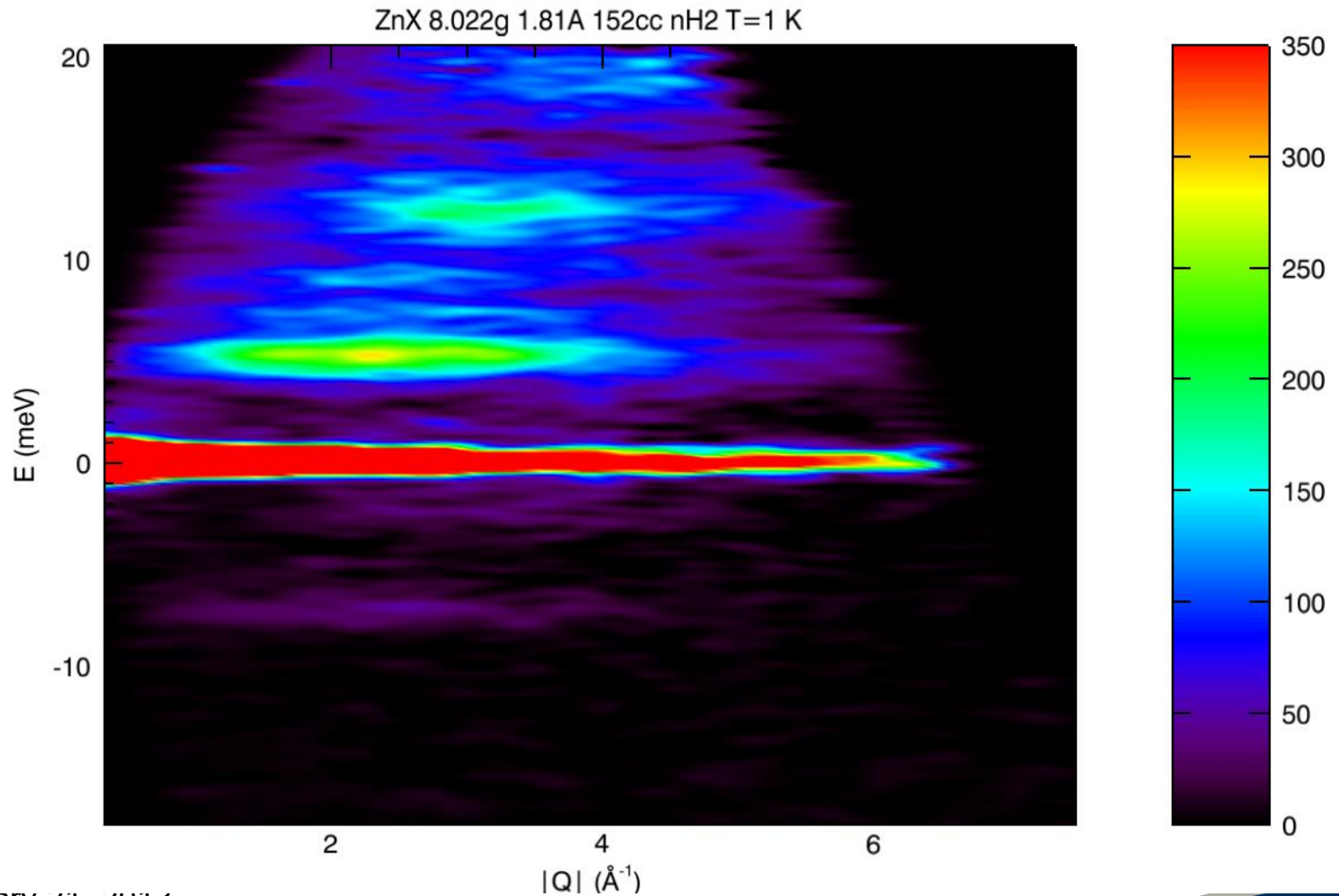
$\omega=0$

Elastic Scattering
Structural Information

Diffraction

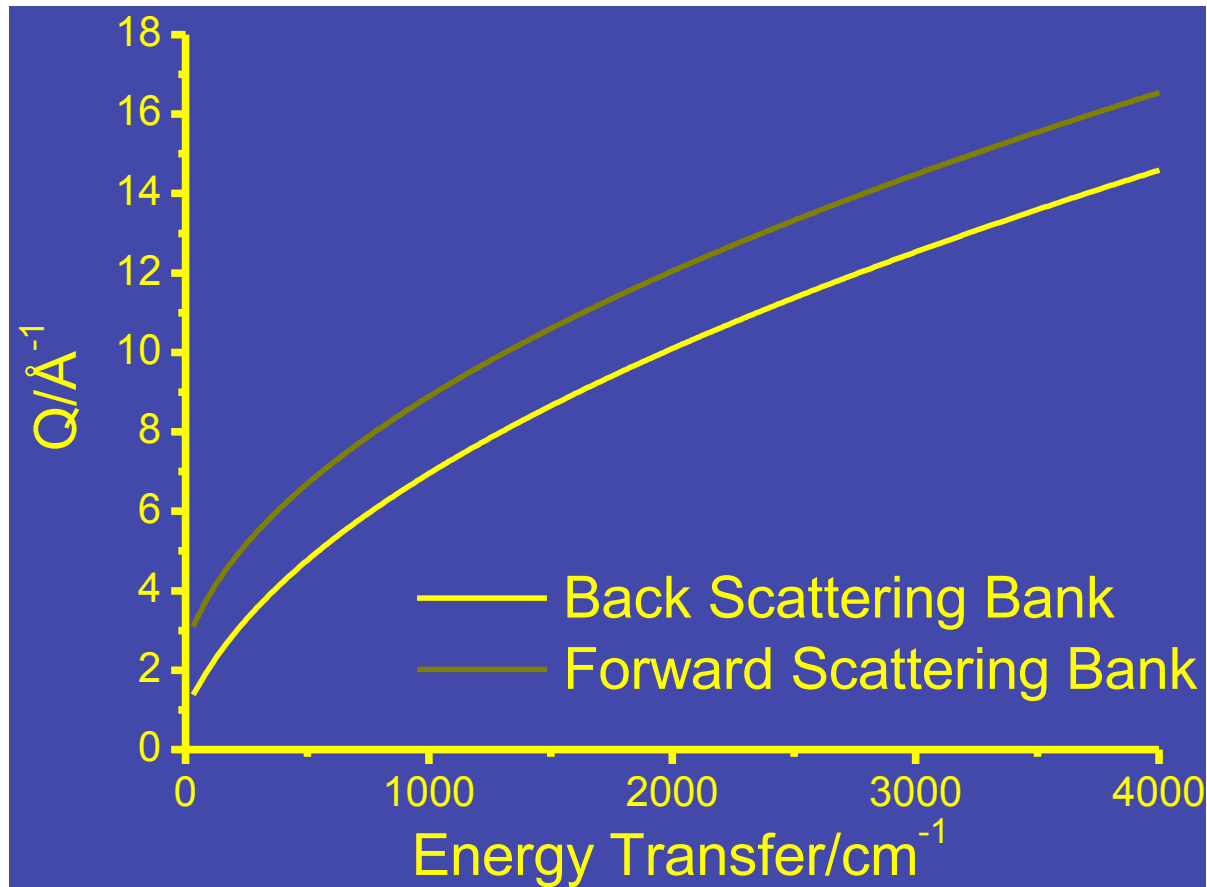
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The $S(Q, \omega)$ Map

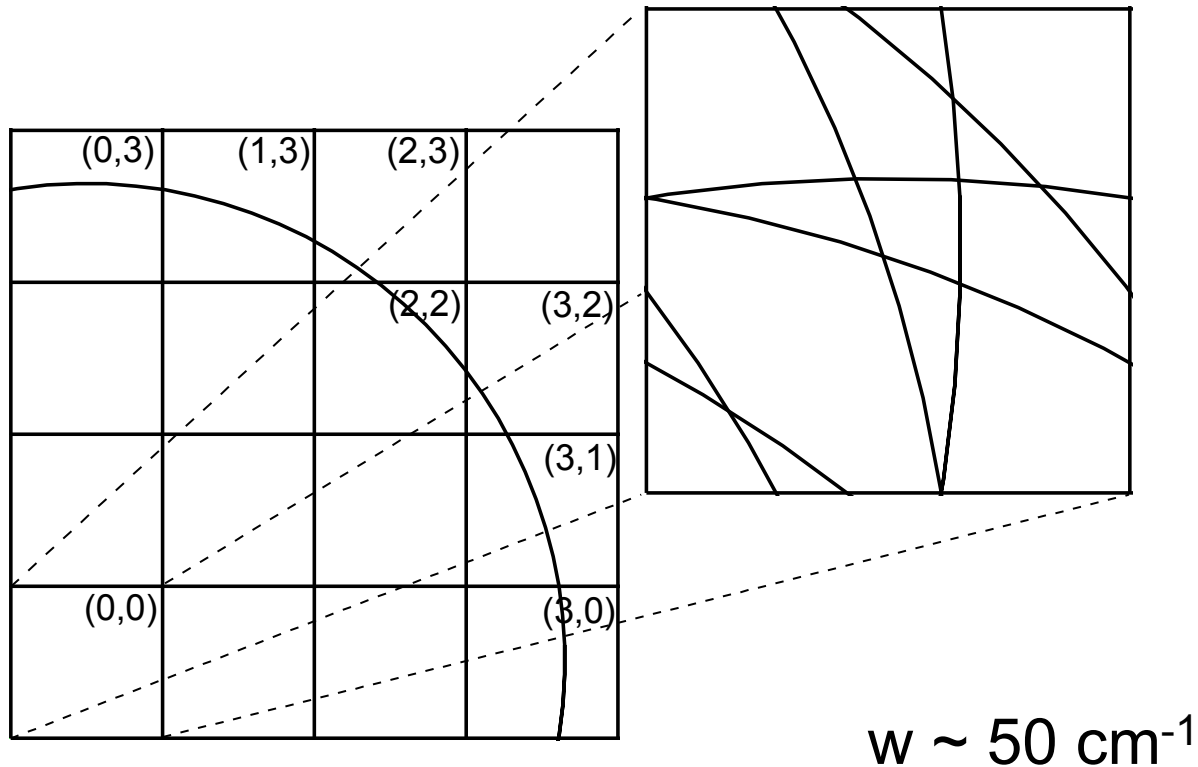


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Trajectory in (Q, ω) space



Powder Average



Uniform sampling of the Brillouin zone

Calculation of INS spectra, the Scattering Law

$$S^{\bullet}(\mathbf{Q}, \omega_{\nu})_l^n = y \sigma_l \frac{\left[(\mathbf{Q} \cdot {}^{\nu} \mathbf{u}_l)^2 \right]^n}{n!} \exp \left(- \left(\mathbf{Q} \cdot \sum_{\nu} {}^{\nu} \mathbf{u}_l \right)^2 \right)$$

a-CLIMAX v.0.0.0 Generalised Problem - D:\Users\Colaborations\Andreas Borgschulte\MgH2-JT-04.aclimax - Last Saved: 16/06/2006 13:50:38

File Windows Advanced Help

g-CLIMAX

Select Your Calculation Options

Transitions 1-10

Intensities

Spectra

Isolated Molecule Calculation

INS Calculation

Perform Smoothing of Wing (for sharp wing shapes)

Extra Calcs

S(Q,w) Map in Q

S(Q,w) Map in Q2

Temperature K

Set Directional Scattering

g-CLIMAX Spectrum Intensity Map

Chart Options

Transitions

0-1

0-2

0-3

0-10

Show Experimental Spectrum

Scales **Min** **Max**

X

Y

Experimental

Experimental Offset

cm-1

Mouse Position
X: - Y: -

Start

Inbox - Microsoft Outlook

Paris Hilton "dará a luz" ...

BBC SPORT | Football | ...

Bill David Proposals

Korea Trip December 2005

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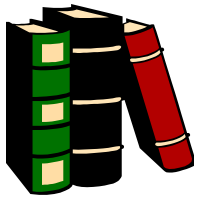
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Di-hydrogen in Porous Materials & Surfaces

**Probing the interactions of H molecules
with the host material**

**Characterization of the interaction
strength**



The Theory



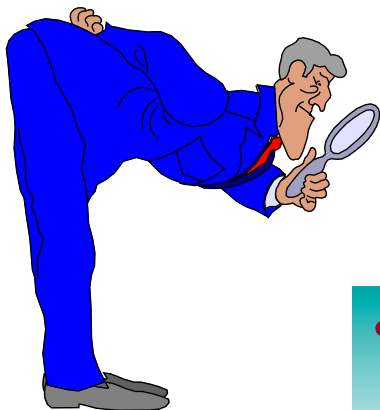
- H_2 ground state ($J=0$) parahydrogen (p- H_2) antisymmetric nuclear spin wavefunction ($\uparrow\downarrow$) and symmetric rotational wavefunction.
- The first rotational state, ($J=1$) orthohydrogen (o- H_2) symmetric nuclear spin wavefunction ($\uparrow\uparrow$) and antisymmetric rotational wavefunction.
- Transitions p- $\text{H}_2 \leftrightarrow$ o- H_2 are detected with neutrons because neutrons exchange spin states with the H_2 molecule.

In solid dihydrogen, H_2 molecules rotate equally freely about all three axes and have the rotational constant B with the same value that in gas phase ($B=59.6 \text{ cm}^{-1}$). Its energy levels are:

$$E_J = J \cdot (J + 1) \cdot B$$

The minimum separation between energy levels is

$$\Delta E = 2B$$



The Interactions

- A hydrogen compound that has a value of $B=29.3 \text{ cm}^{-1}$, H_3 would do the trick, D_2 also works.
- A hindered H_2 rotor constrained to move in two dimensions.

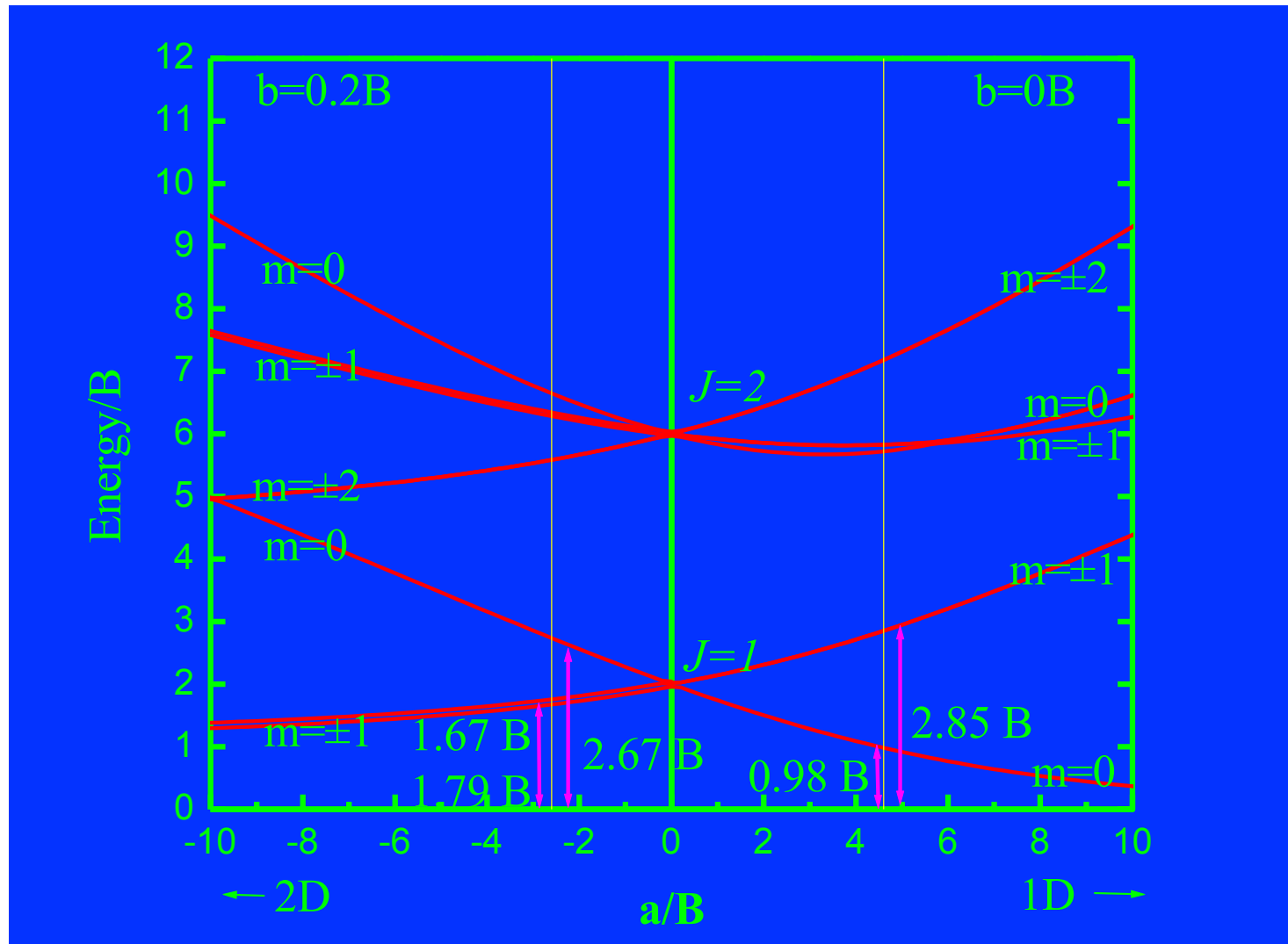
The potential that governs the motion of a H_2 molecule on a surface may be expressed as

$$V(\theta, \phi, z) = K(z - z_0)^2 + \sin^2 \theta \cdot (a + b \cdot \cos \phi)$$

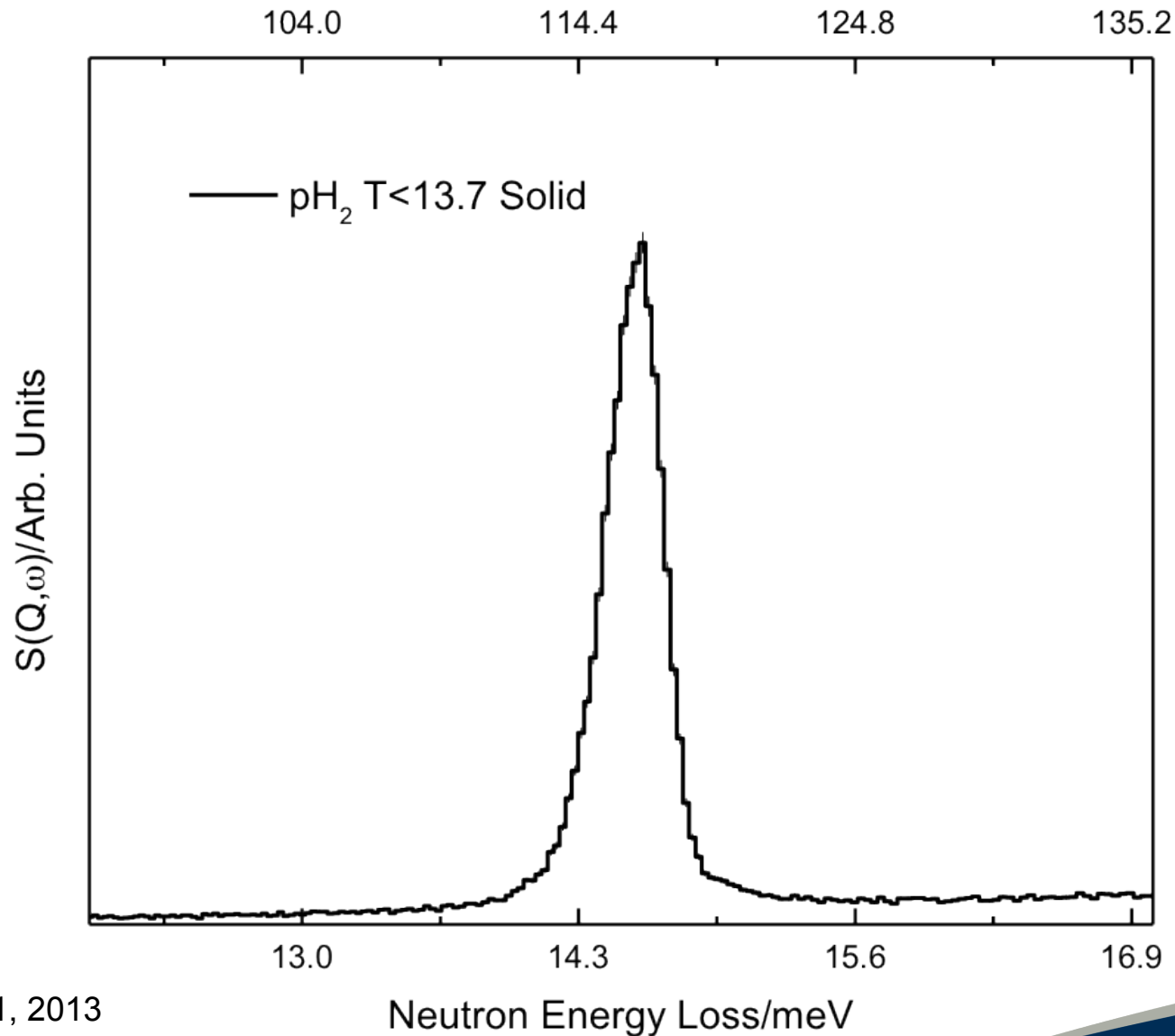
- $a > 0$ the molecule is aligned to an axis (1D case).
- $a < 0$ the molecule is constrained in a plane (2D case)
- The splitting between levels is $1B$ if a is large and negative, because the energy levels are:

$$E_{2D} = J^2 B$$

The Energy Levels

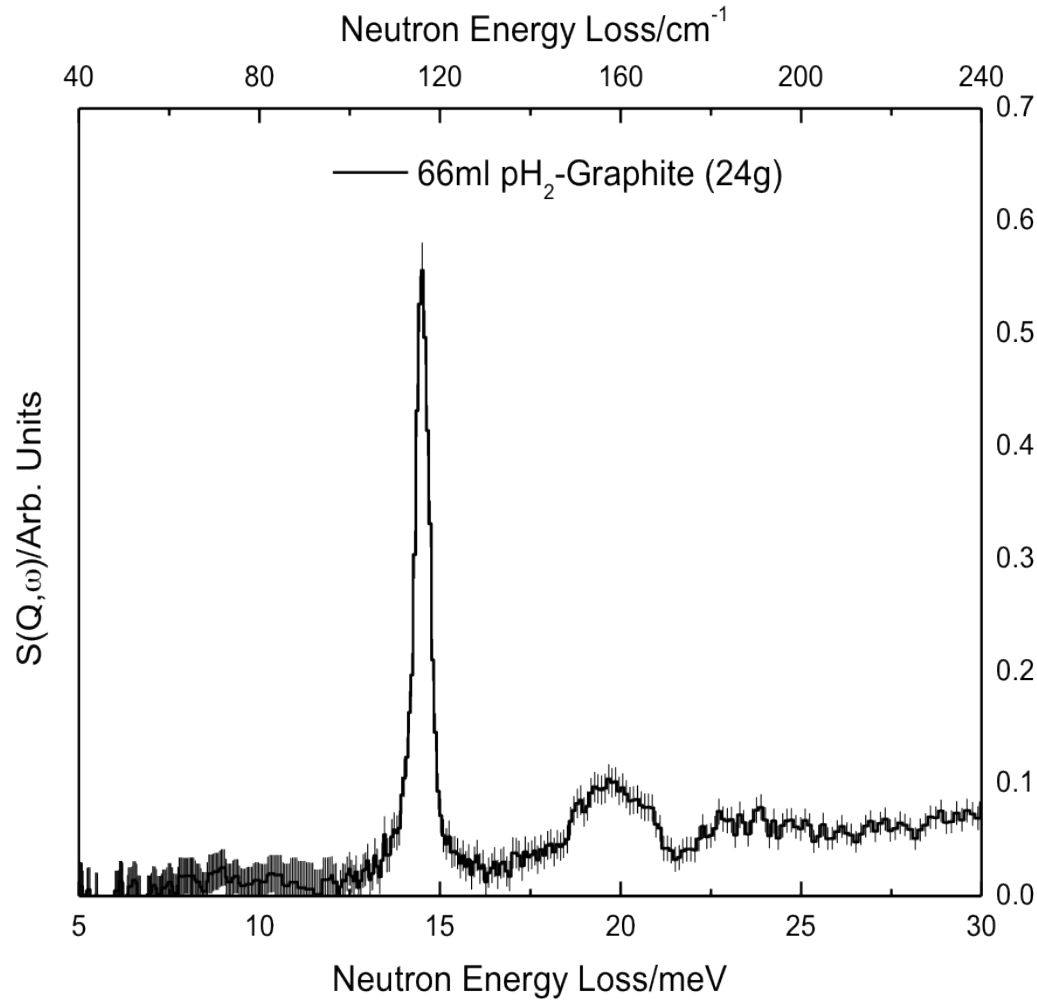


What are we expecting?



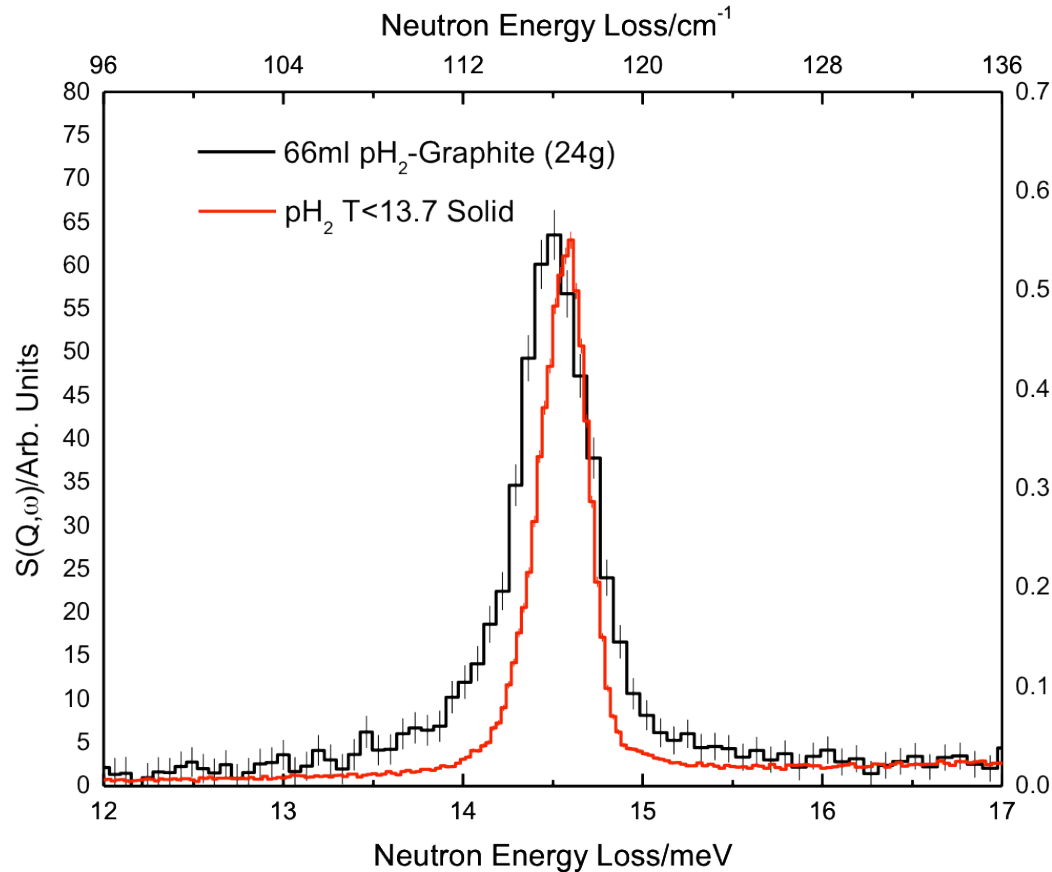
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Interaction of graphite with Hydrogen



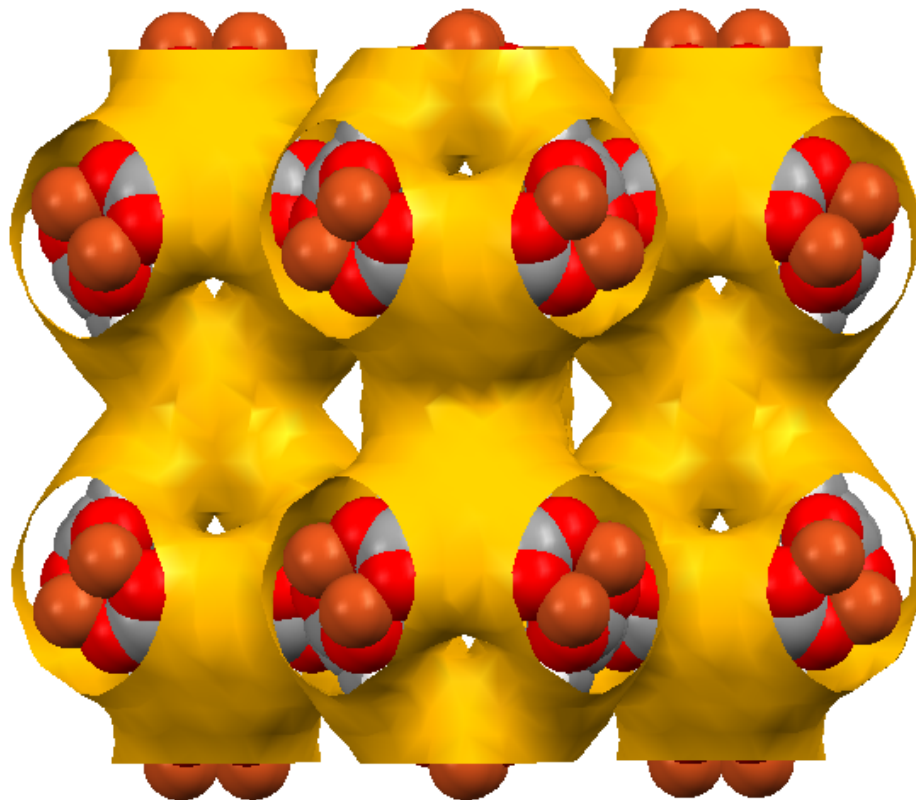
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Interaction of graphite with Hydrogen



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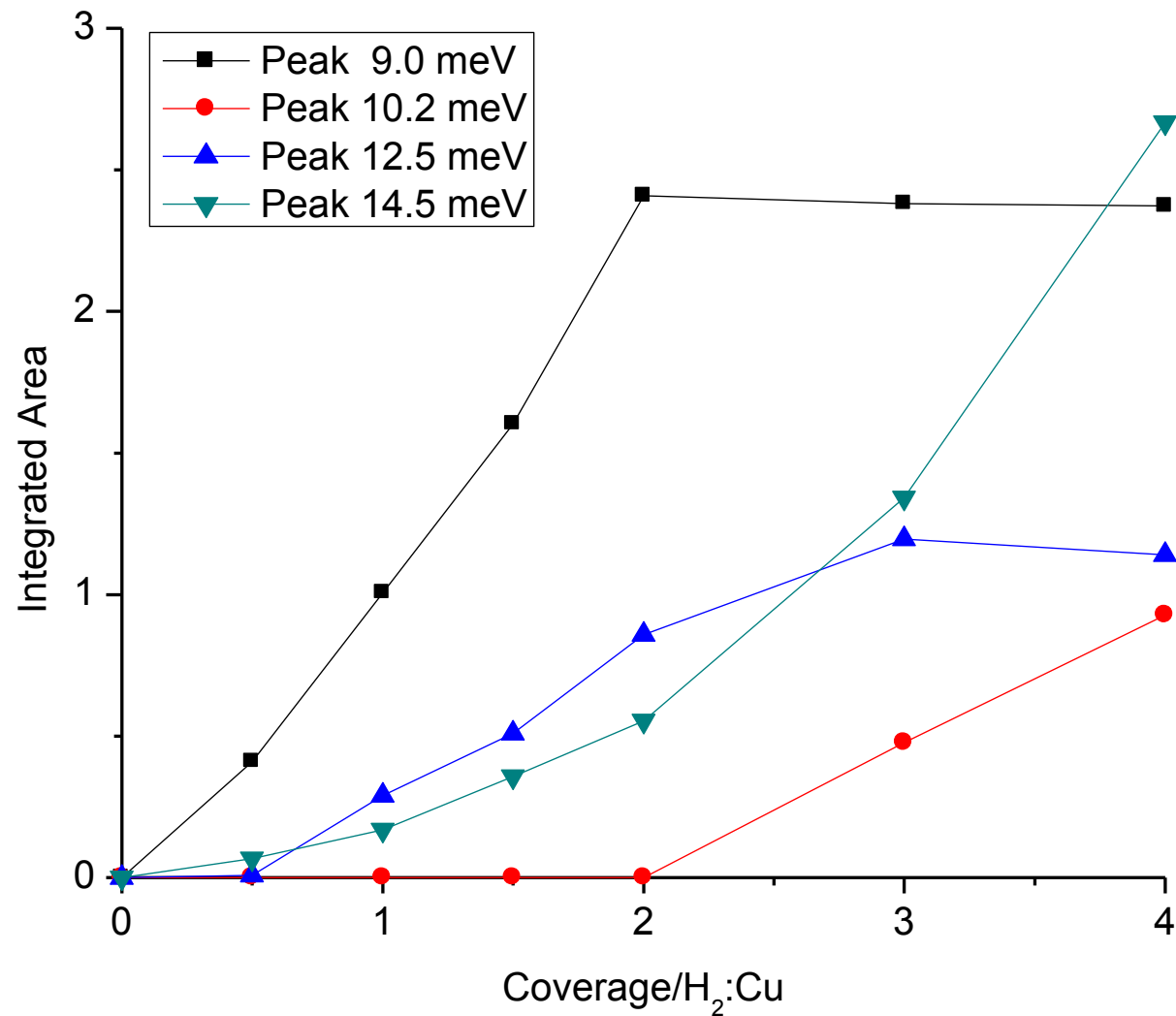
H₂ in Cu-MOF #1



Franck Millange, Sam Callear, Richard Walton, Timmy Ramirez-Cuesta

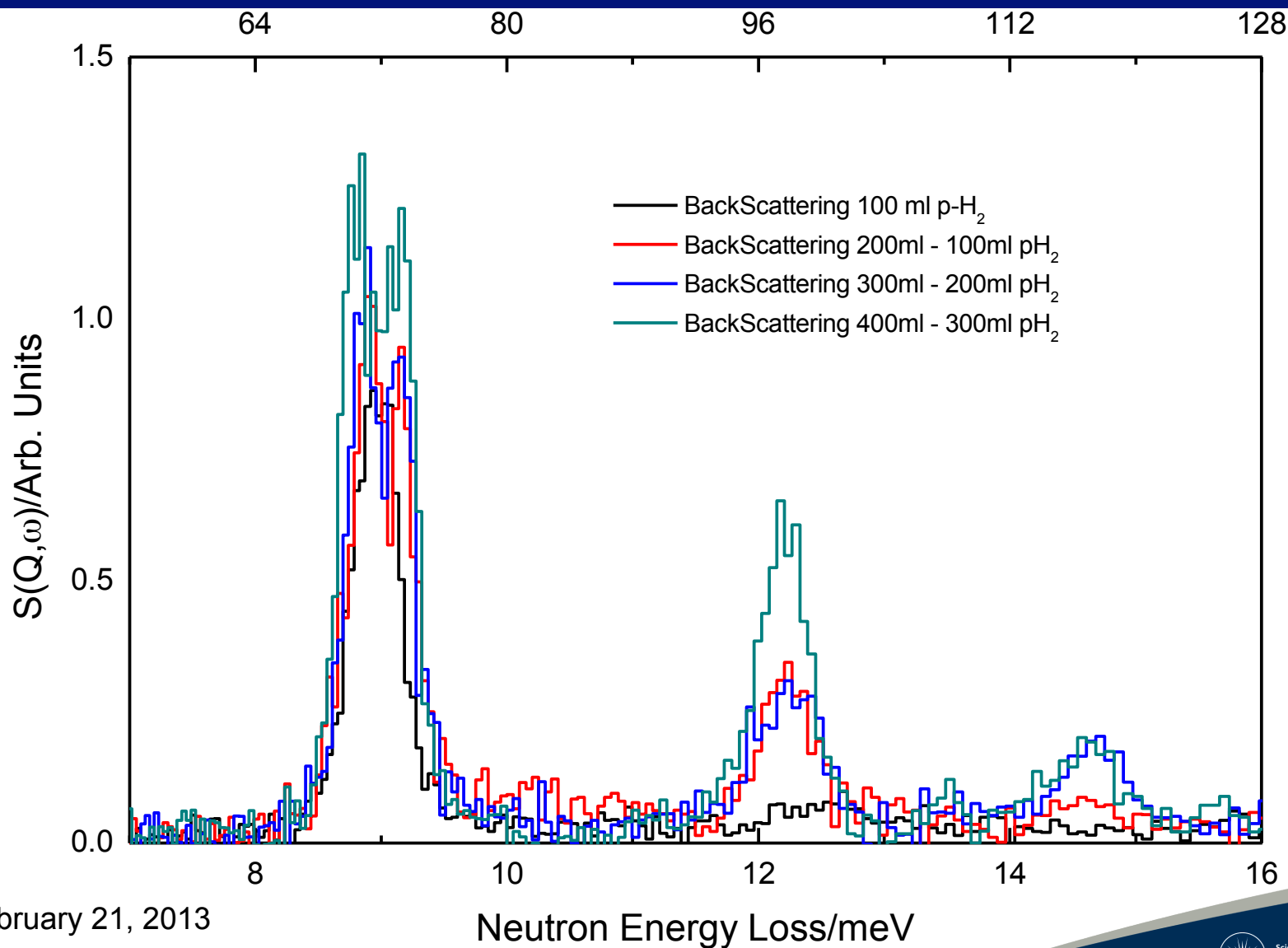
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H₂ in Cu-MOF #1



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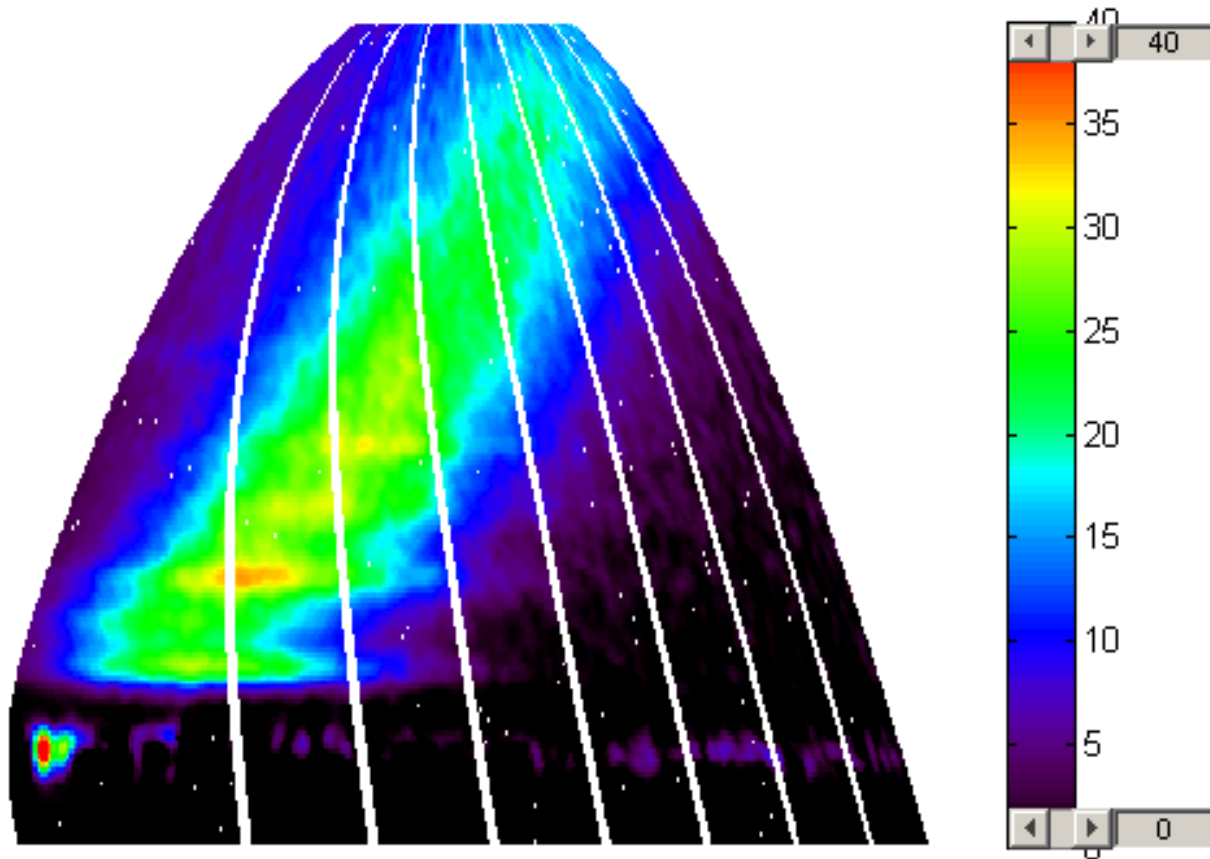
H₂ in Cu-MOF #1



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Neutron Energy Loss/meV

H₂ in Cu-MOF #1

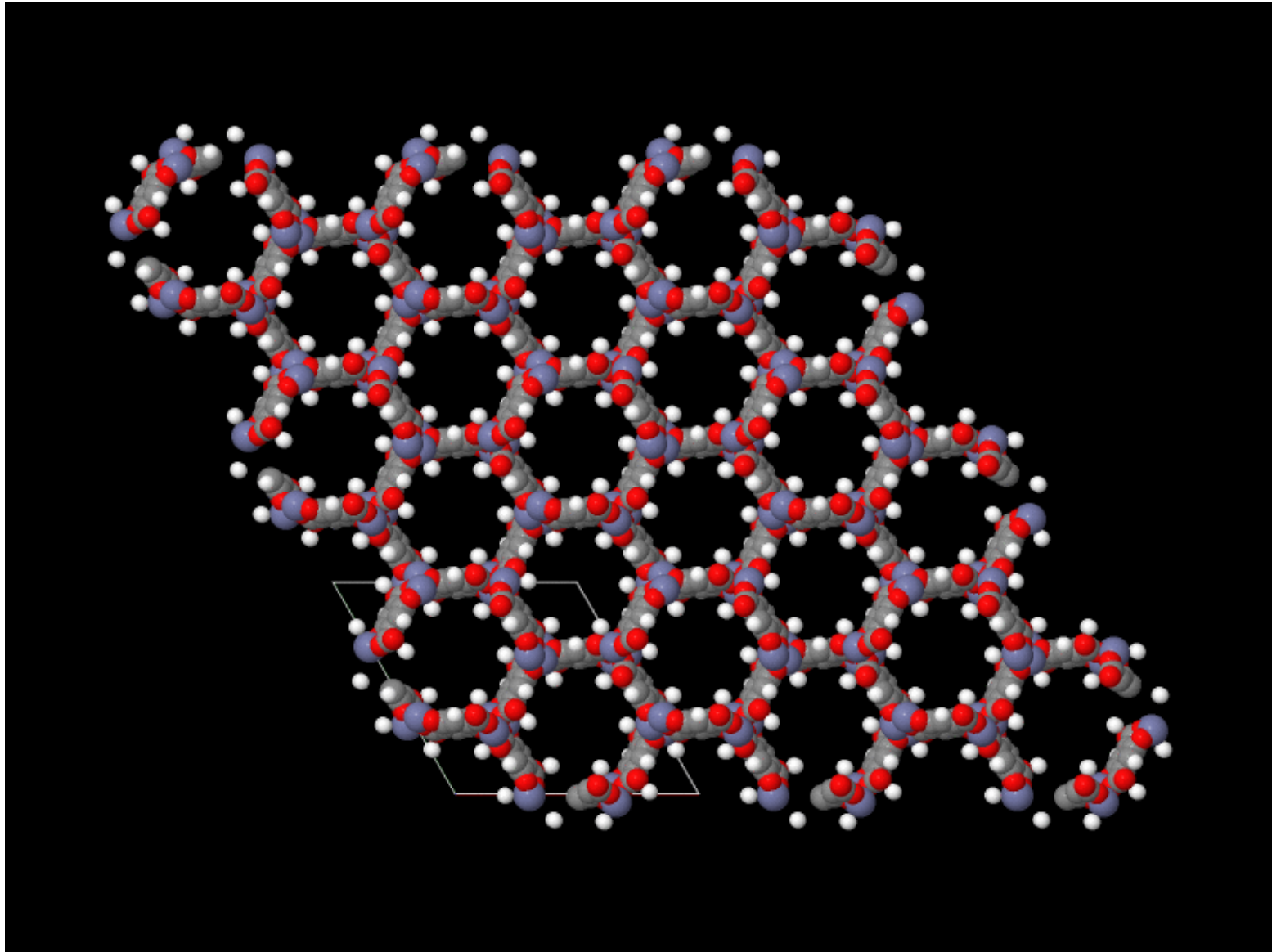


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Character of H₂ adsorbed in a redox-active Fe-containing Metal-Organic Framework

Wendy Queen, Craig Brown, Timmy Ramirez-Cuesta

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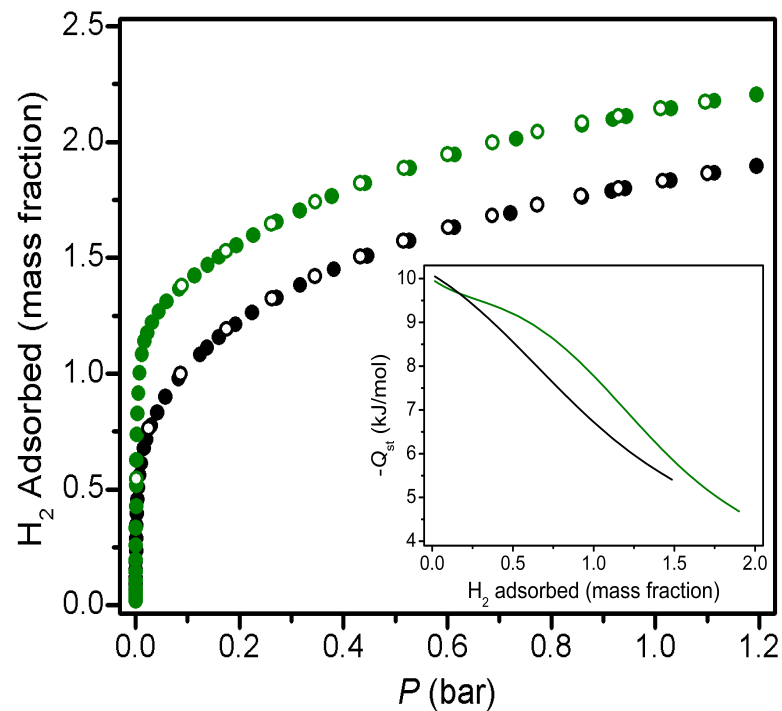
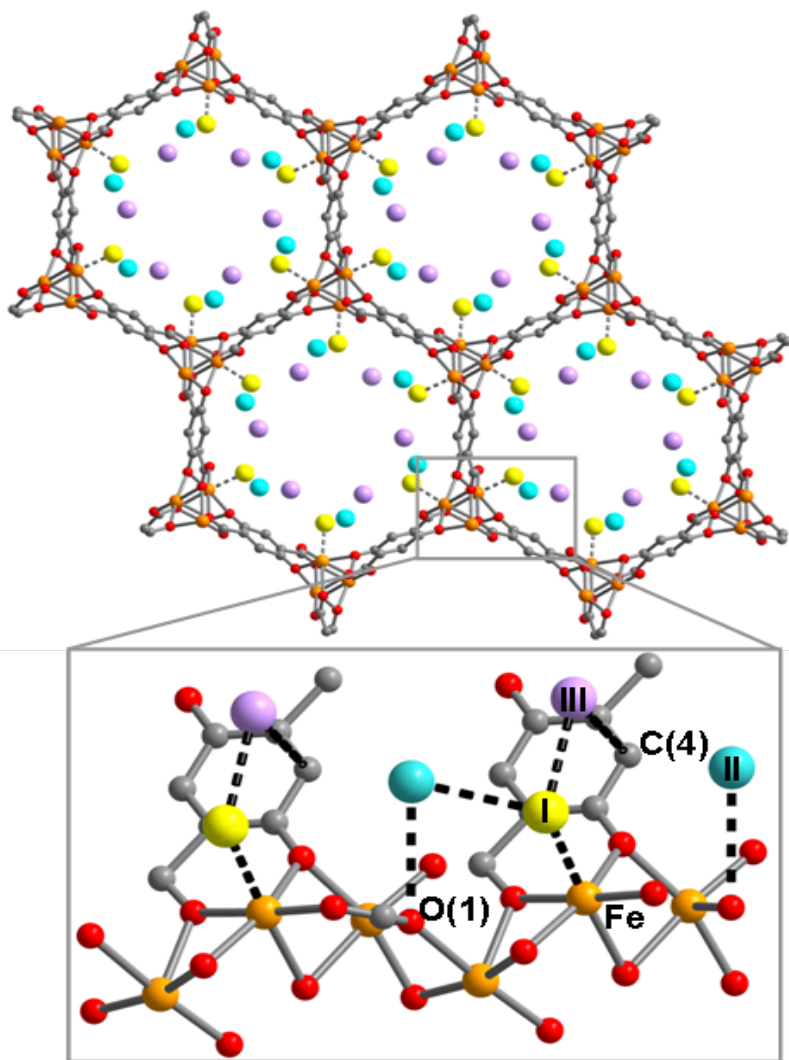


Fig 2 Excess H₂ adsorption isotherms collected for Fe₂(dobdc) (green) and Fe₂(O₂)(dobdc) (black) at 77 K. Filled and open circles represent adsorption and desorption, respectively. Inset: Isosteric heats of adsorption ($-Q_{st}$) plotted as a function of adsorbed H₂ for both Fe₂(dobdc) and the oxidized analog.

Fig 1 [001] view of Fe₂(dobdc) loaded with 2.25 D₂ / Fe²⁺. Orange, gray, red spheres represent Fe, C, and O respectively. The box contains a close up view of the framework wall, showing closest inter D₂ / D₂ and D₂ / framework interactions (drawn as dotted lines) along the channel. Three D₂ sites, determined by powder neutron diffraction, are labeled as I, II, and III in order of binding strength.

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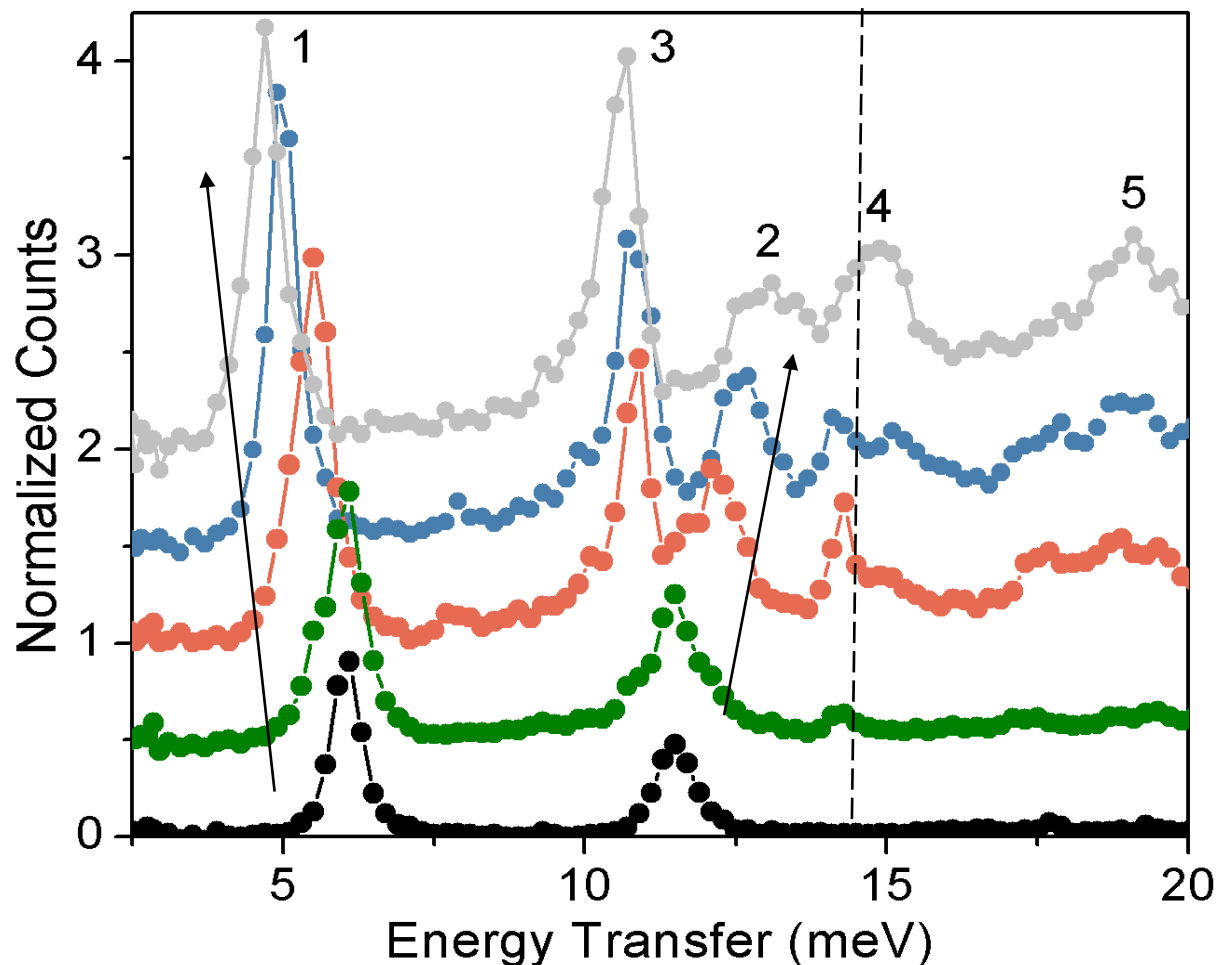
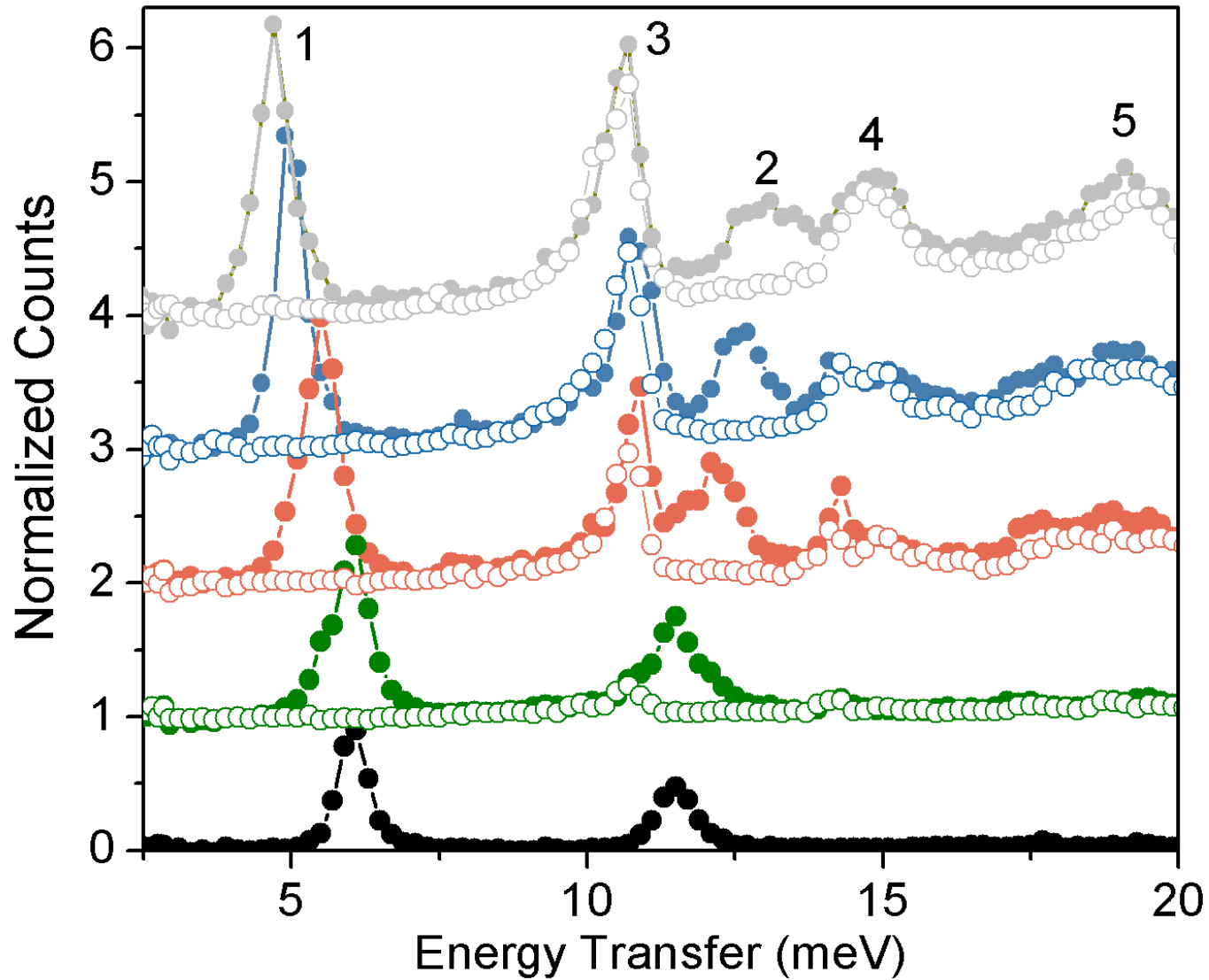


Fig. 3 INS spectra recorded at 20 K for loadings of 0.5 (black), 1.0 (green), 2.25 (orange), 3.0 (blue), and 3.75 (grey) $p\text{-H}_2 / \text{Fe}^{2+}$ in $\text{Fe}_2(\text{dobdc})$. The data were obtained following subtraction of the spectrum of the evacuated framework.

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Thermal Stability of porous structures

AI MIL 53

Collaboration:

Craig Brown, Timmy Ramirez-Cuesta

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Al-MIL 53 opening

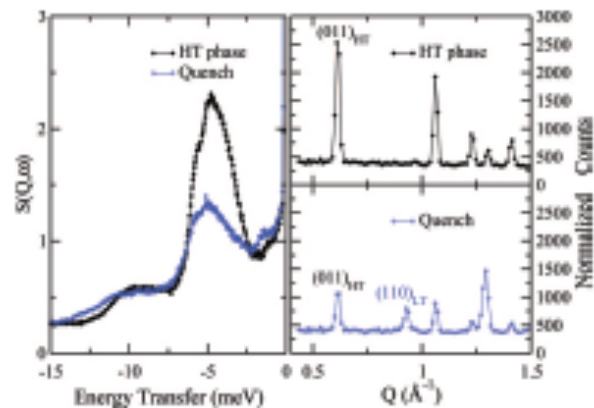
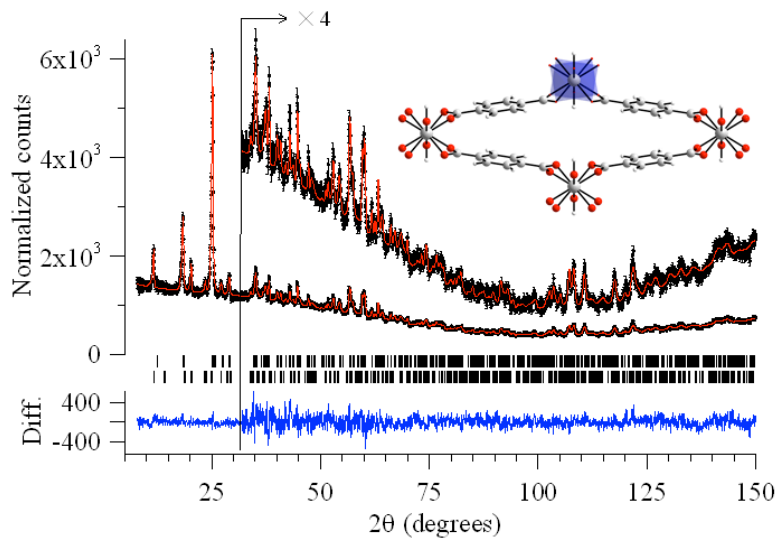
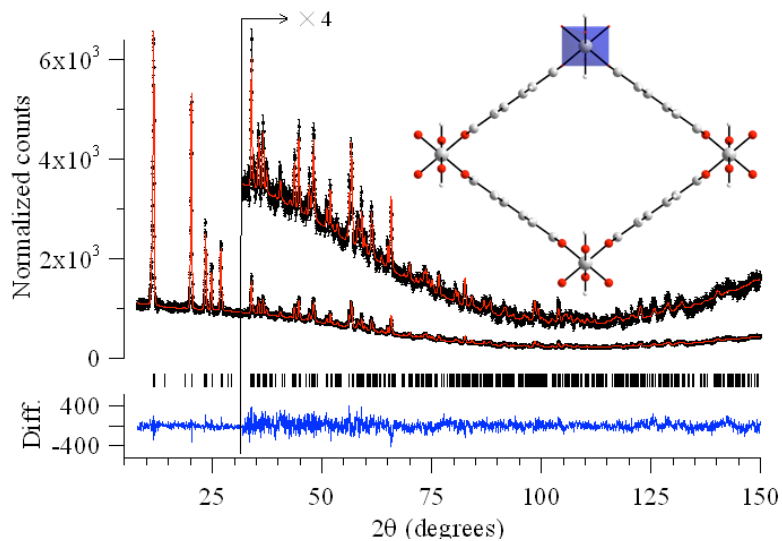
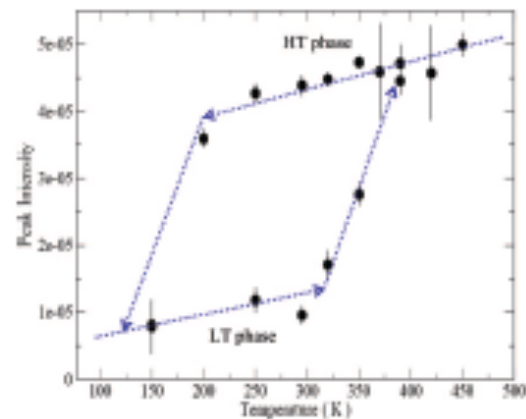
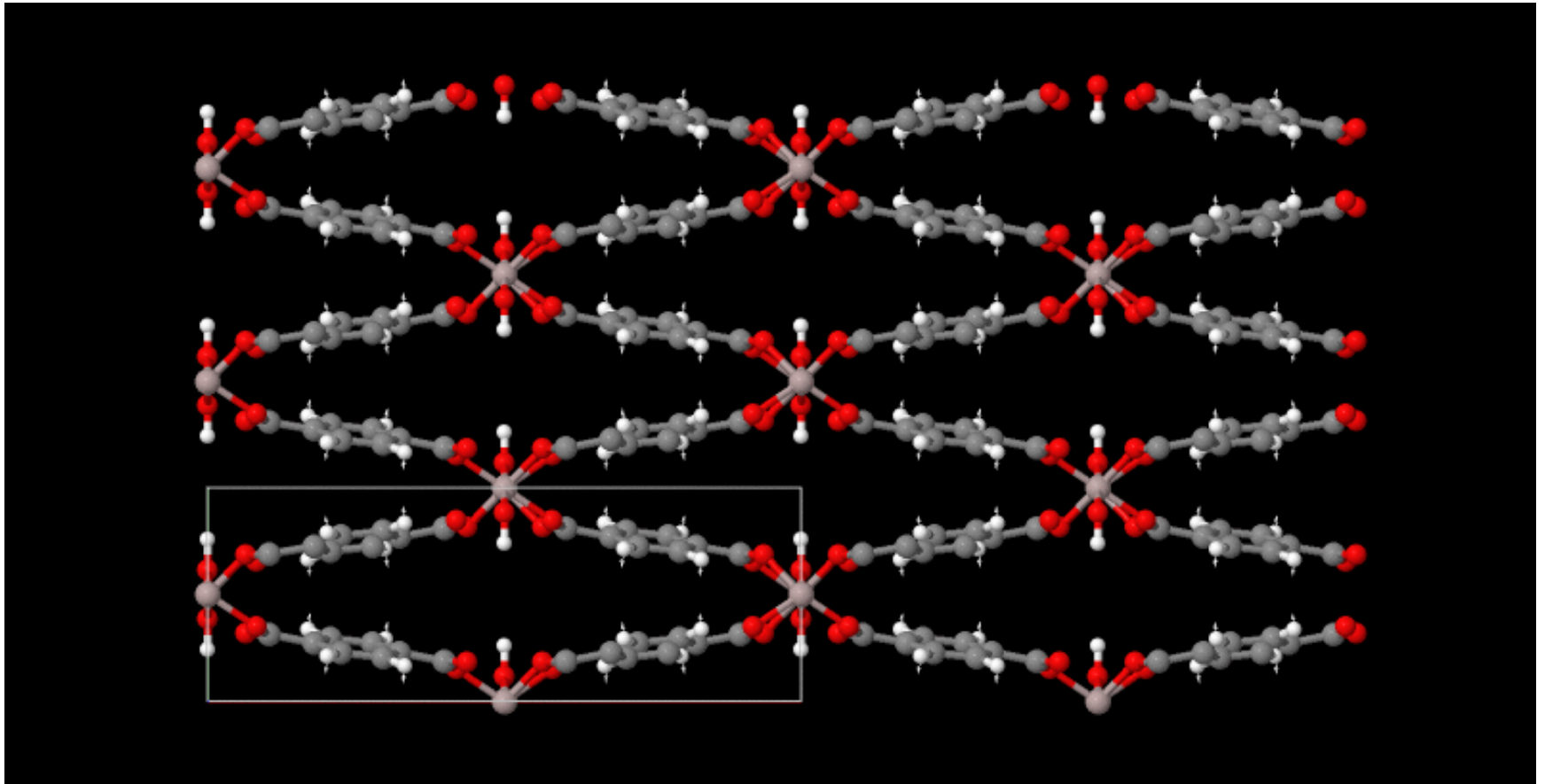


FIGURE 2. (Left panel) Inelastic neutron scattering spectra of MIL-53(Al) measured at room temperature for the HT phase (solid circles) and the predominantly LT phase (open circles, labeled "Quench"). (Right panel) Simultaneously measured diffraction patterns of the HT and LT phases with the largest d -spacing reflections noted for each phase. Error bars indicate one standard deviation of the counting statistics.



MIL-53 AL, closed structure



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INS of MIL-53 AL

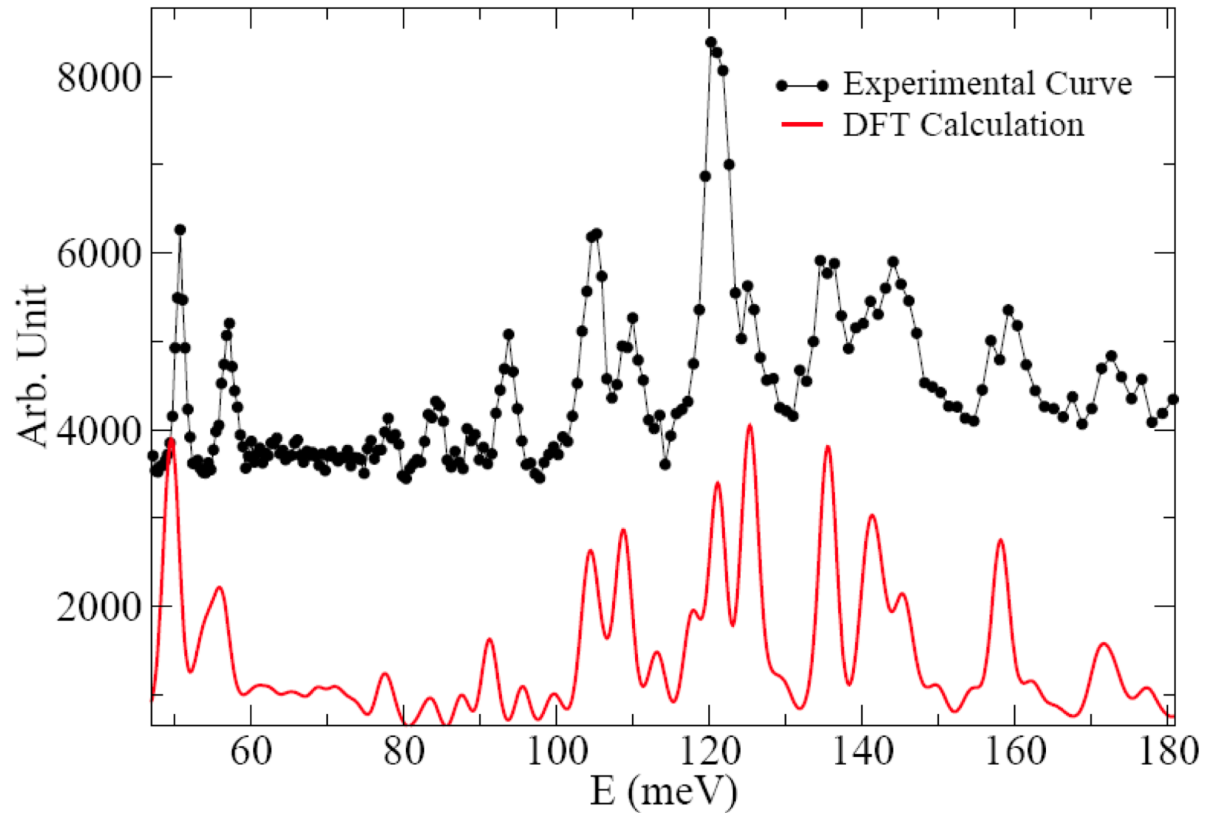
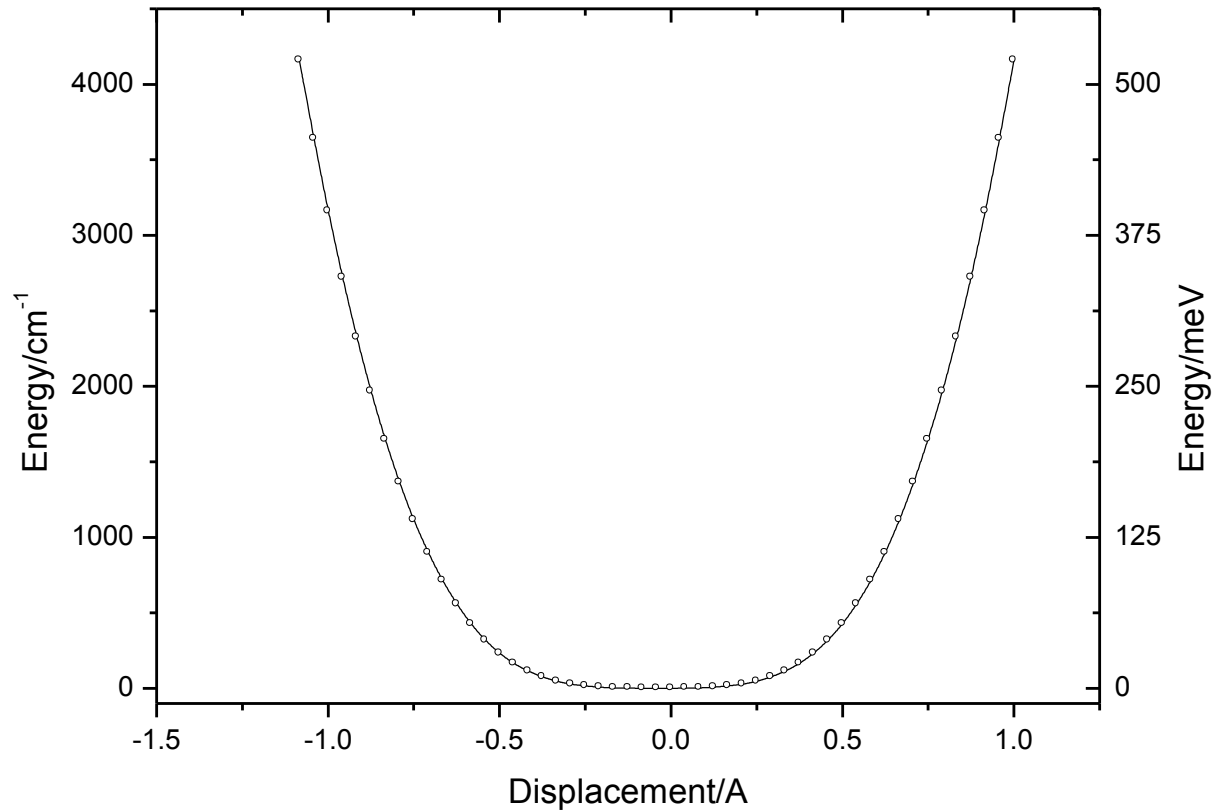


Figure 5. The comparison of the vibration frequency of MIL-53 at the LT phase obtained by the DFT calculation and the neutron scattering experiments. The solid cycle represent the results measured by an inelastic neutron scattering instrument, and the thick line is obtained with the DFT calculation.

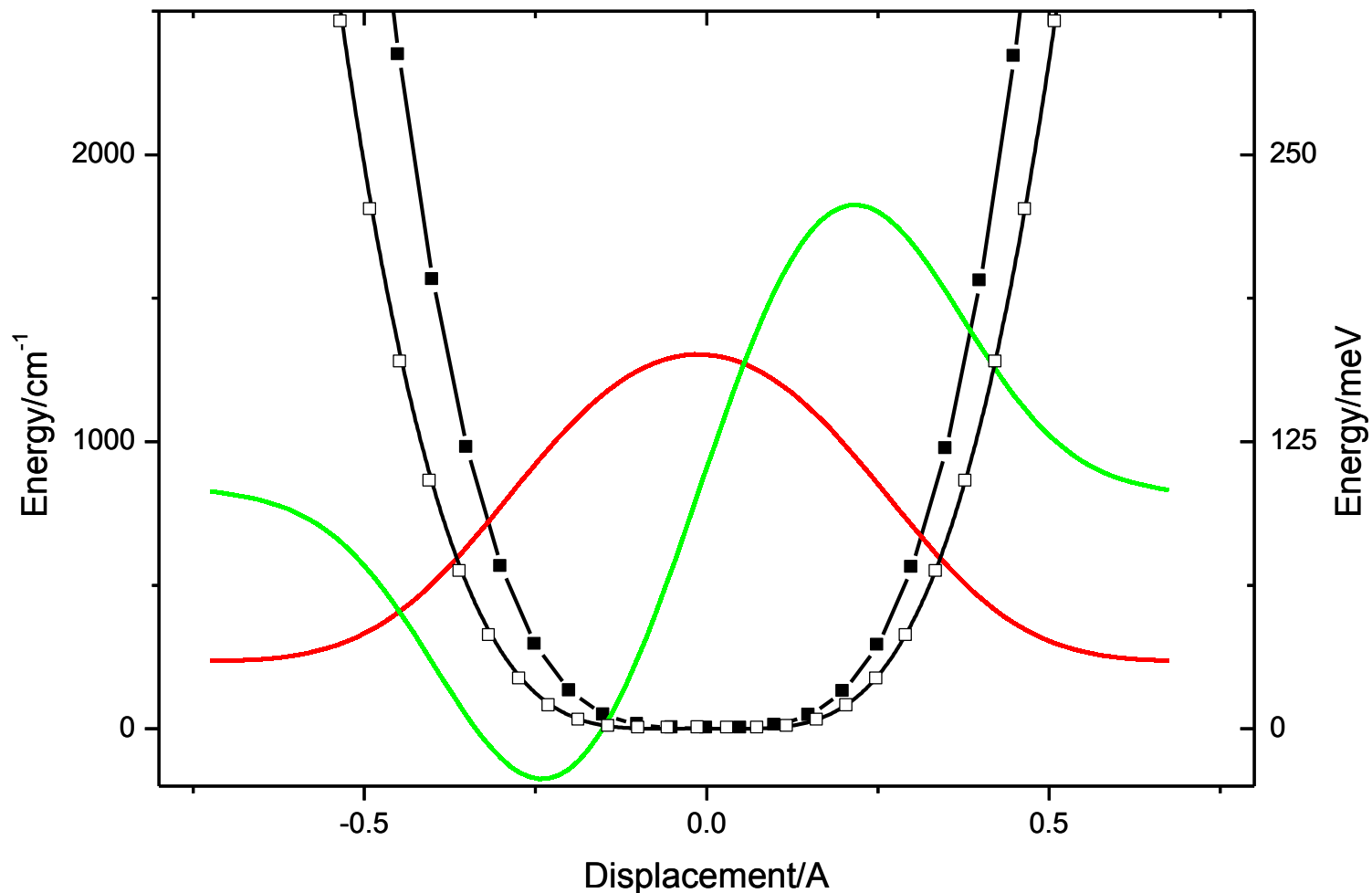
What drives the phase transition?

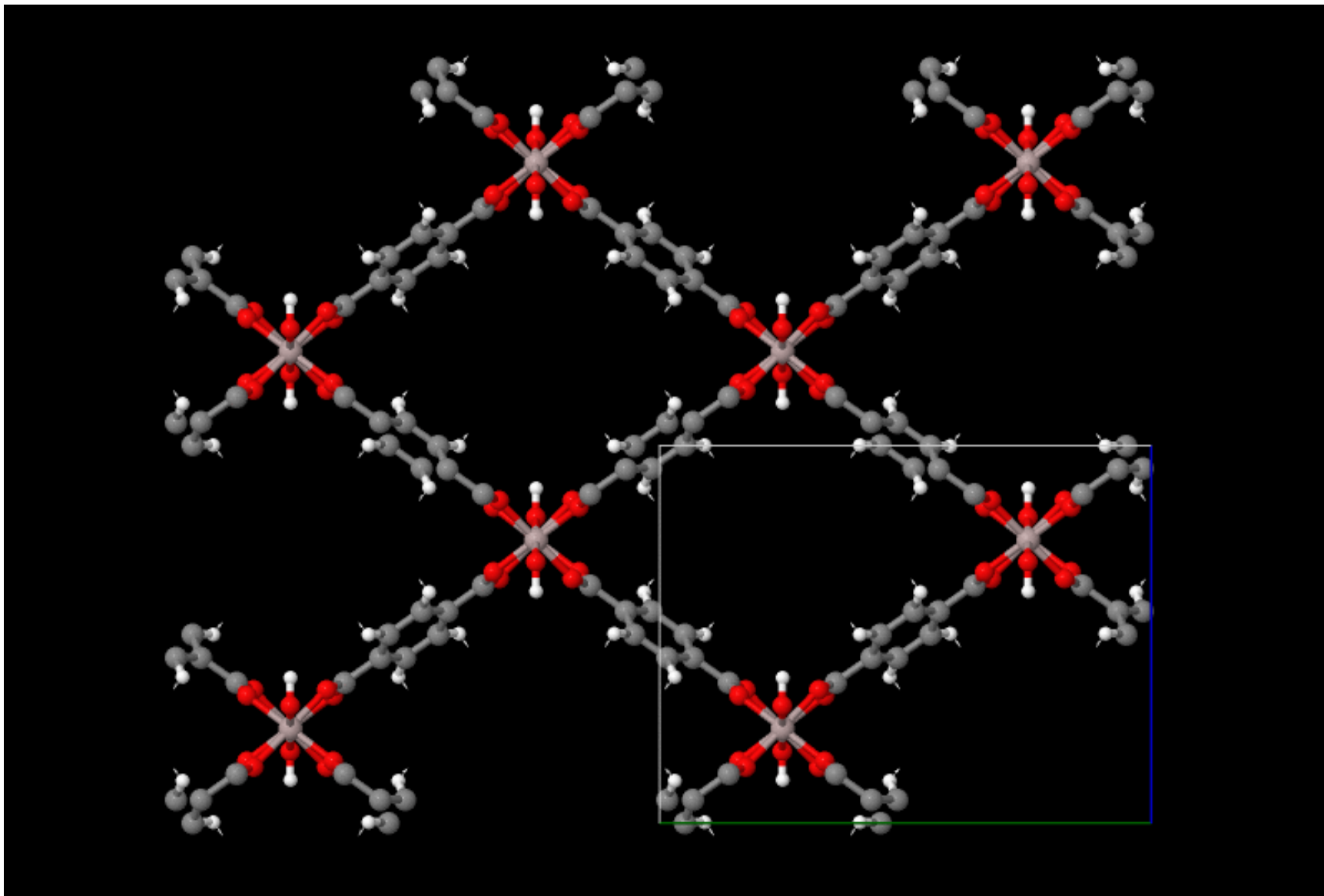
- Look at all the modes in the solid (Gamma point)
- Found the most anharmonic
- Solution of the Schrödinger equation
- Negative modes
- Also seen in Cu BTC (Angewandte Chemie International Edition, 49 (2010) 585)

PES for the anharmonic mode Closed Structure



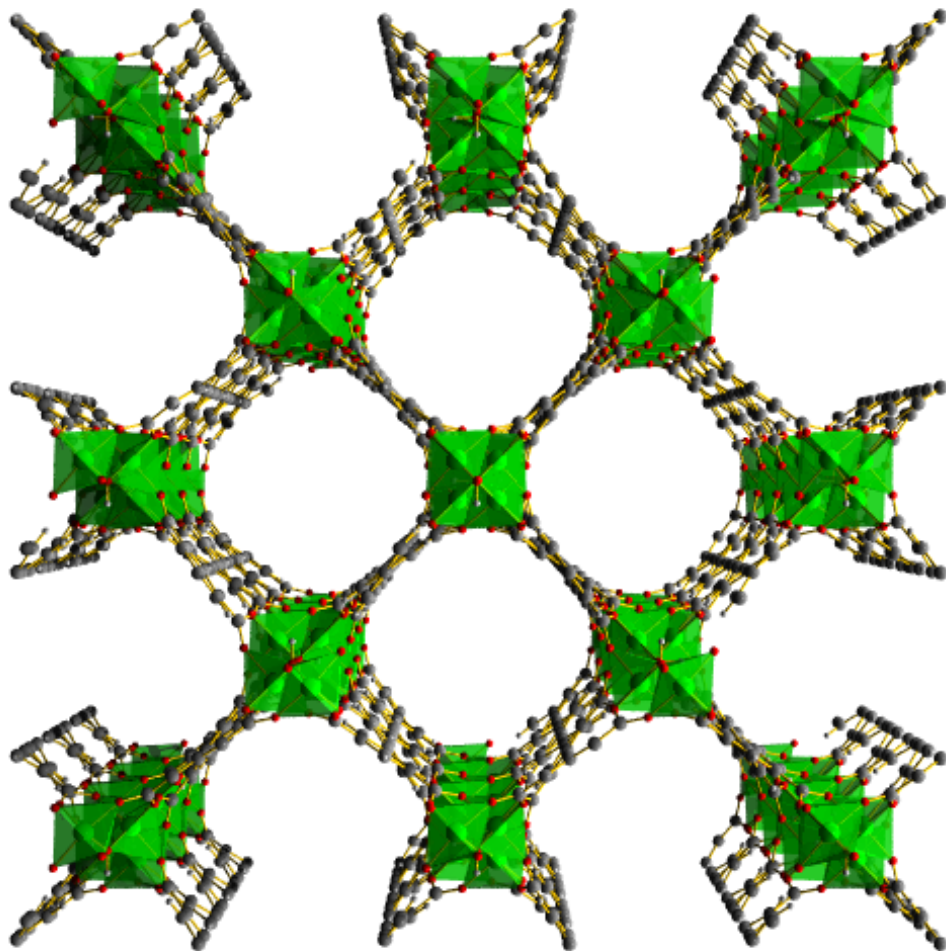
Energy Levels for the anharmonic modes Open Structure





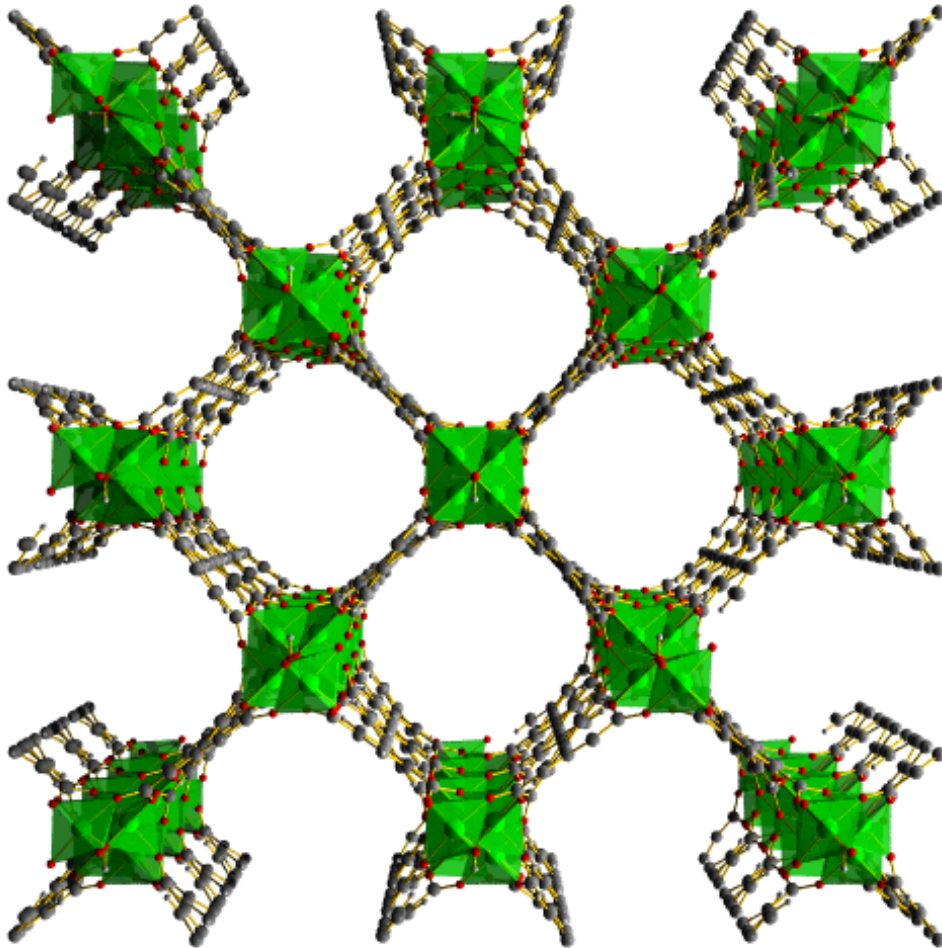
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Microporous Al-MOF NOTT-300



Martin Schroeder,
Sihai Yang,
Sam Callear
Timmy Ramirez-Cuesta

Microporous Al-MOF NOTT-300



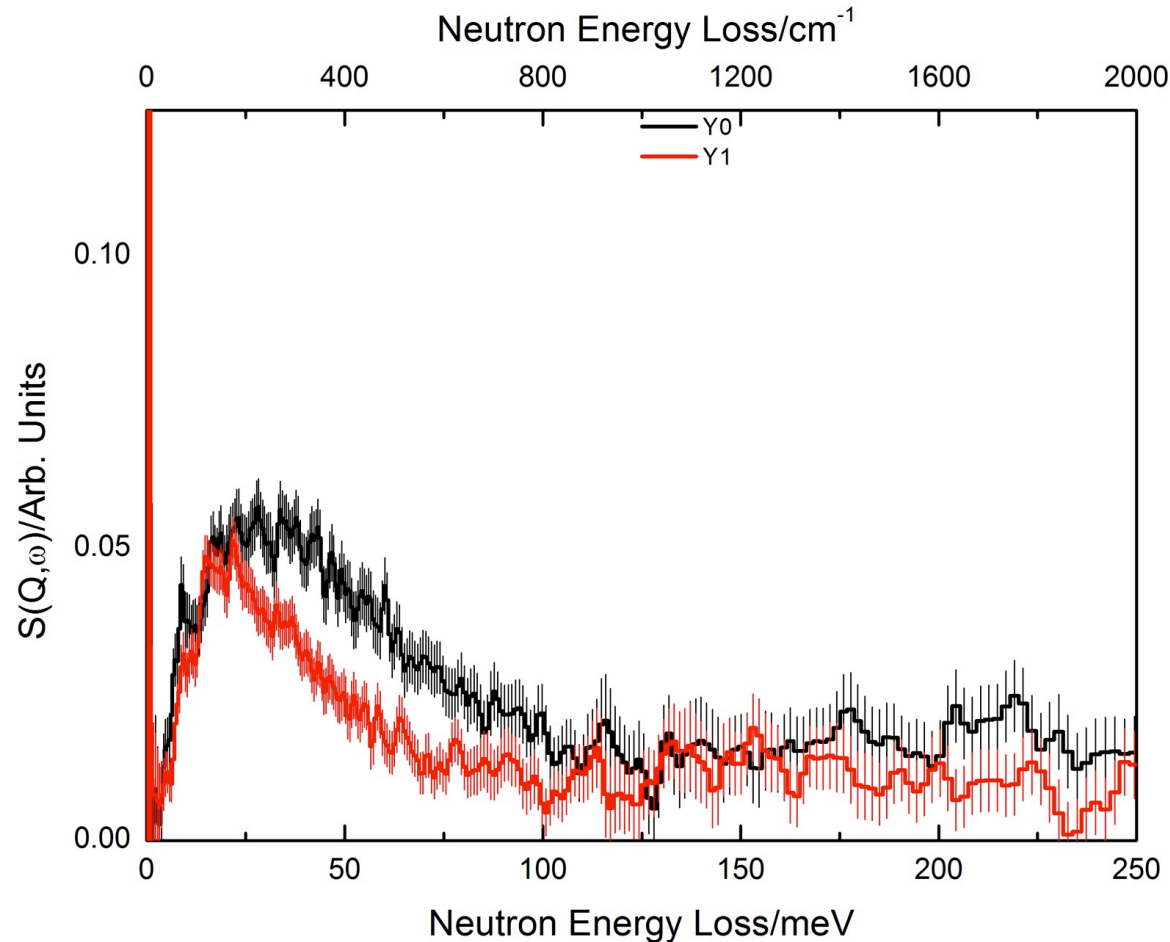
1D pore channels

Pore size $6.5 \times 6.5 \text{ \AA}^2$

Pore volume 0.40 cc/g

Specific surface area
 $1800 \text{ m}^2/\text{g}$

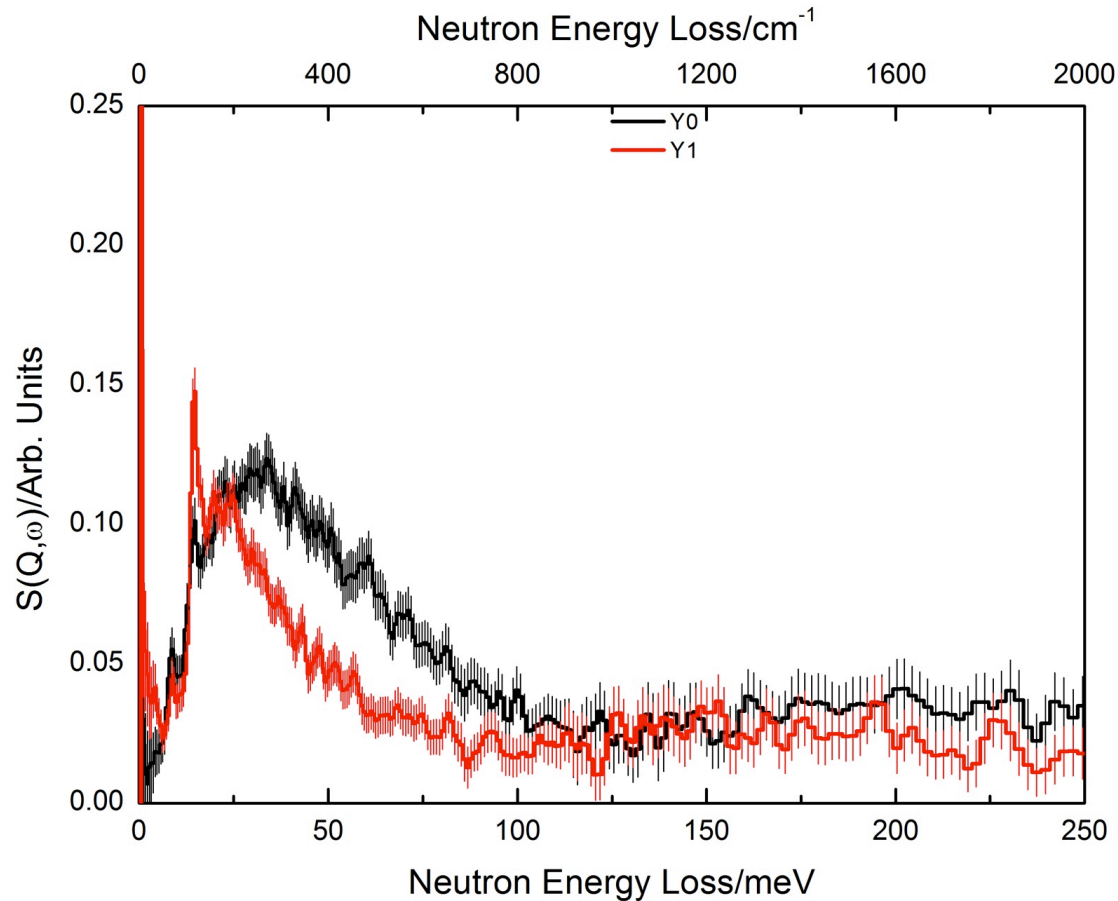
H₂ in NOTT-300



H₂ needs 17 K to go into the MOF at all

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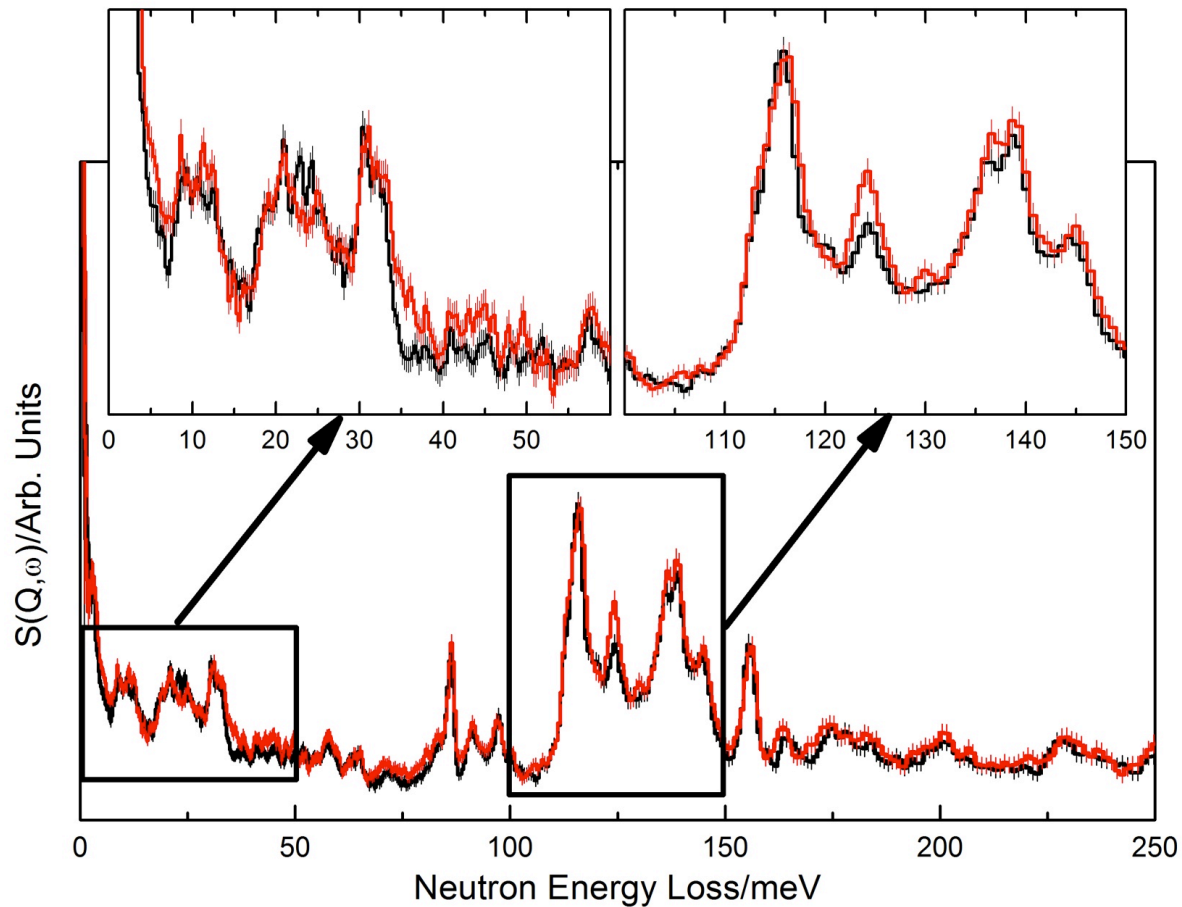
H₂ in NOTT-300



H₂ does not interact with OH groups

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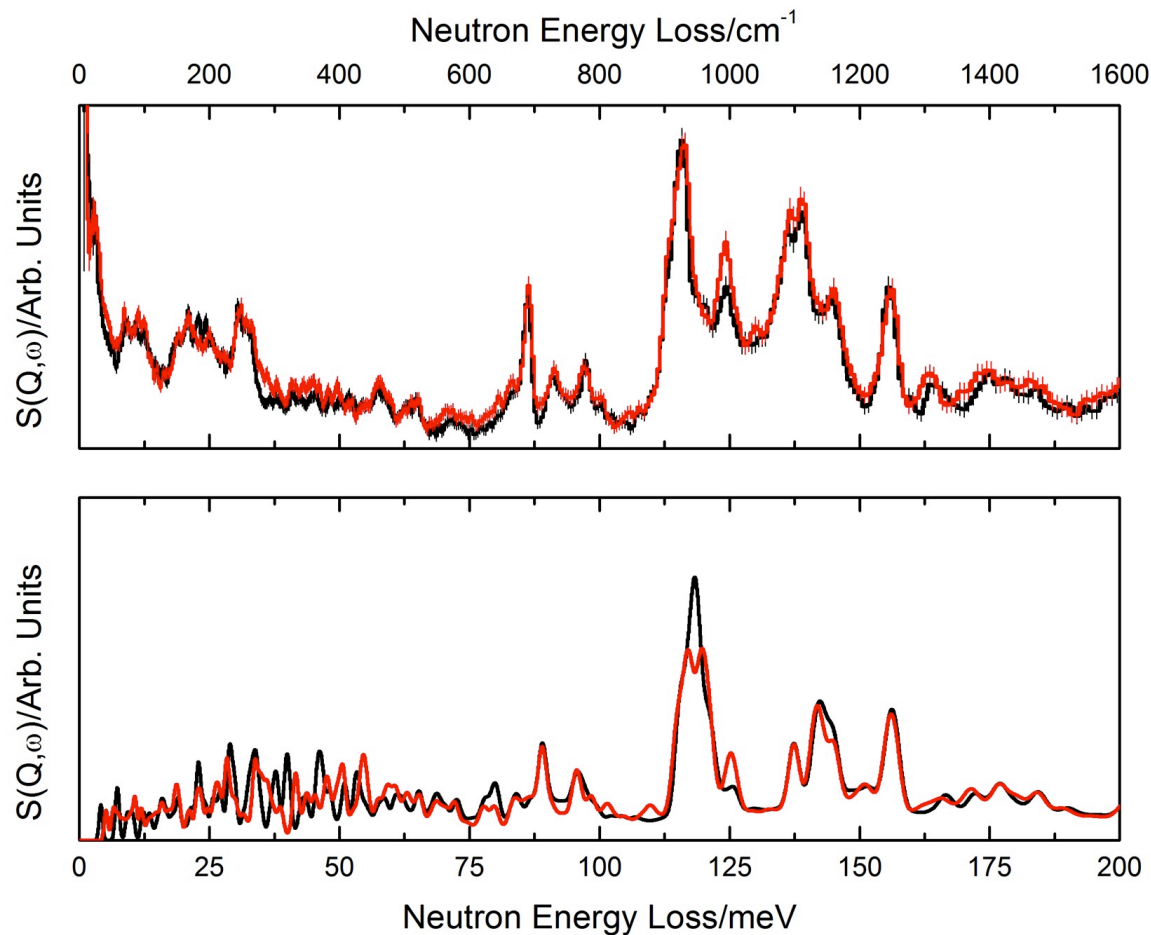
CO₂ in NOTT-300



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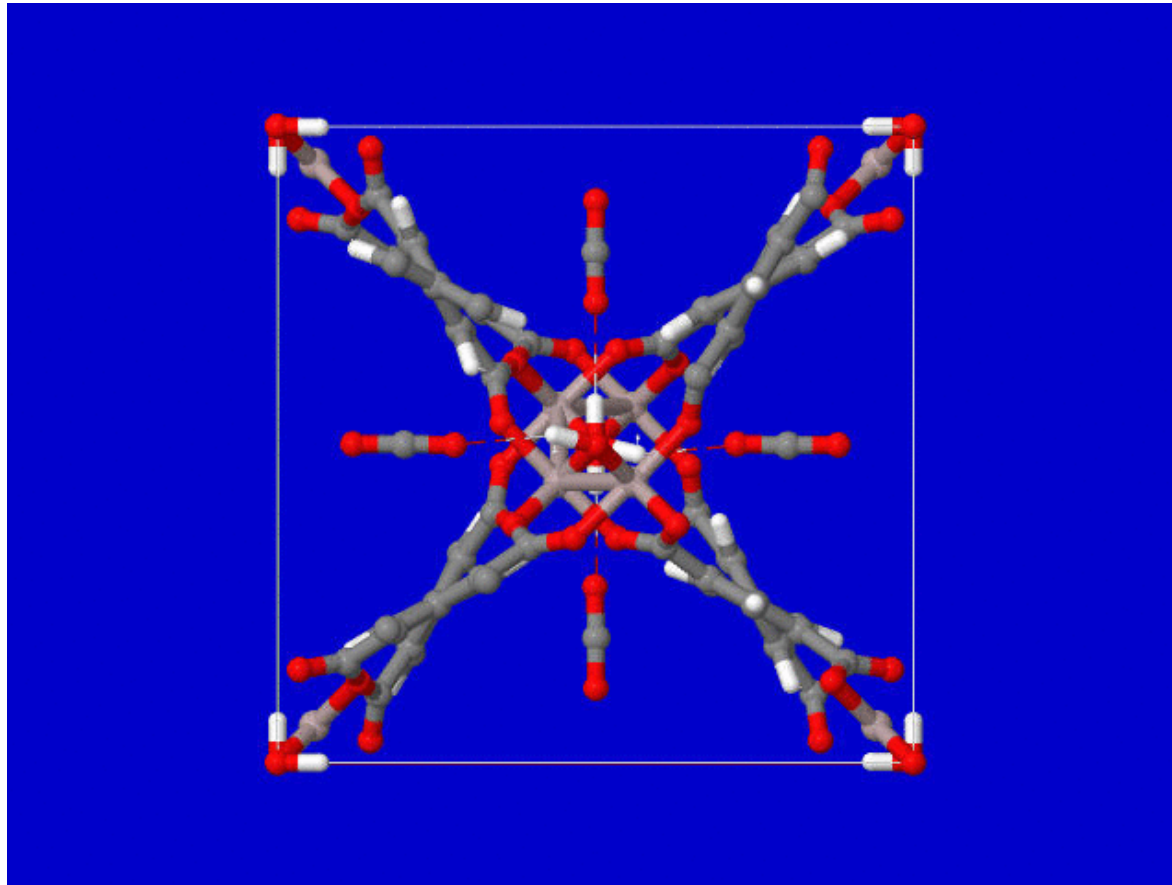
Strong affinity to CO₂ and SO₂
But not to N₂ and O₂

CO₂ in NOTT-300 Modelling



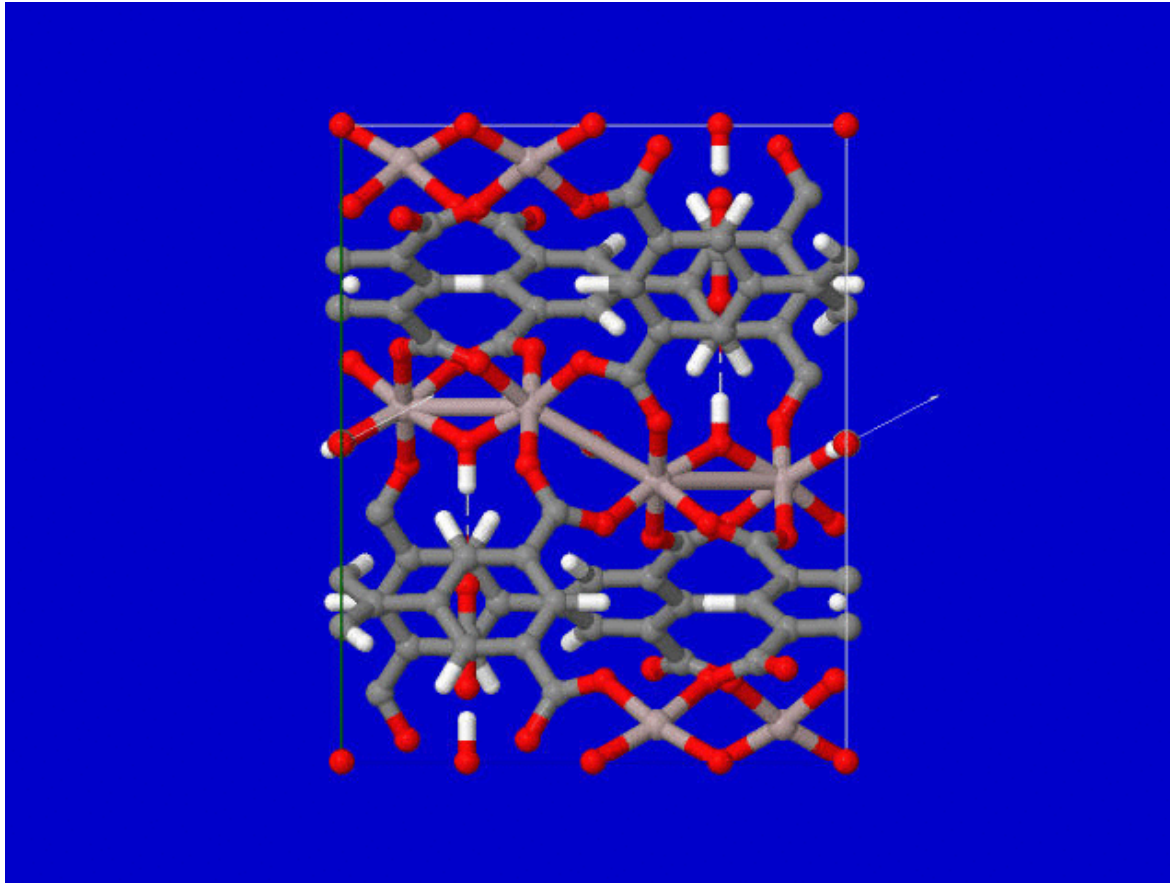
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CO₂ in NOTT-300 Modelling



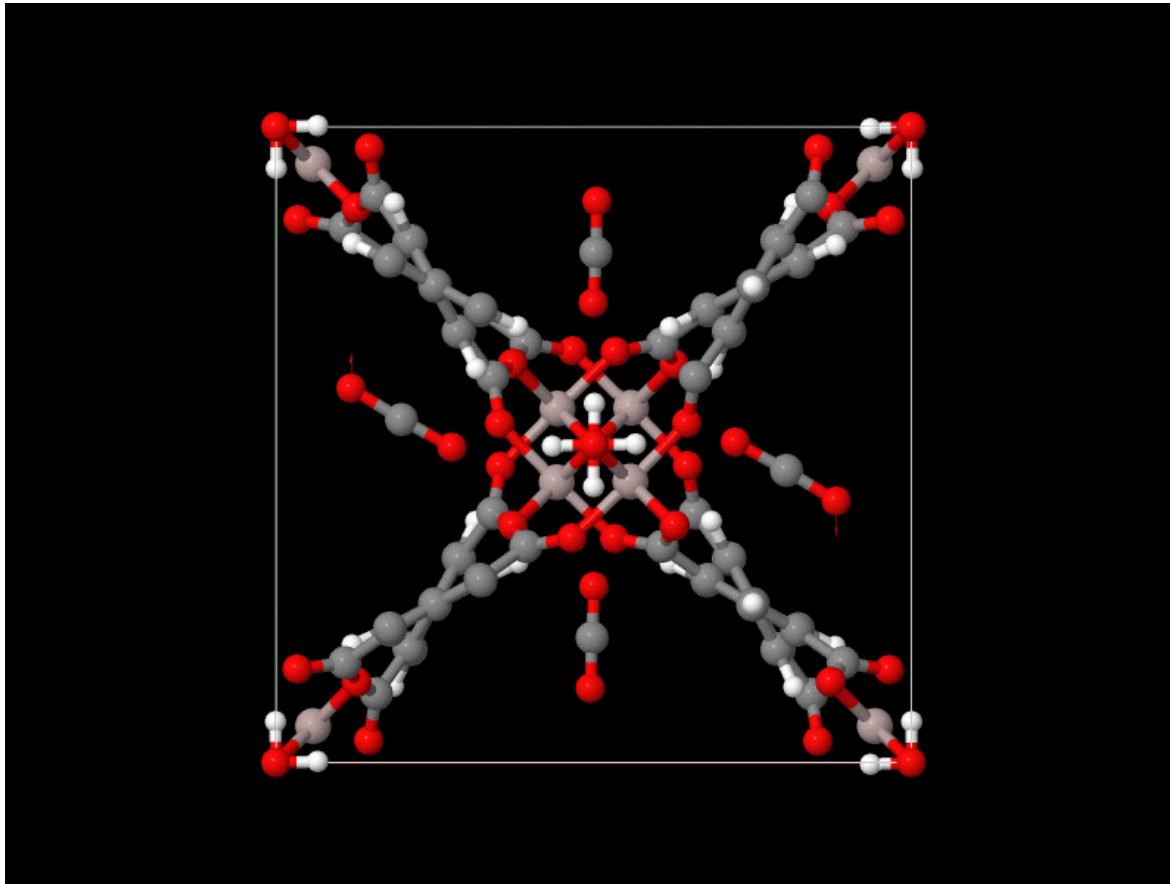
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CO₂ in NOTT-300 Modelling



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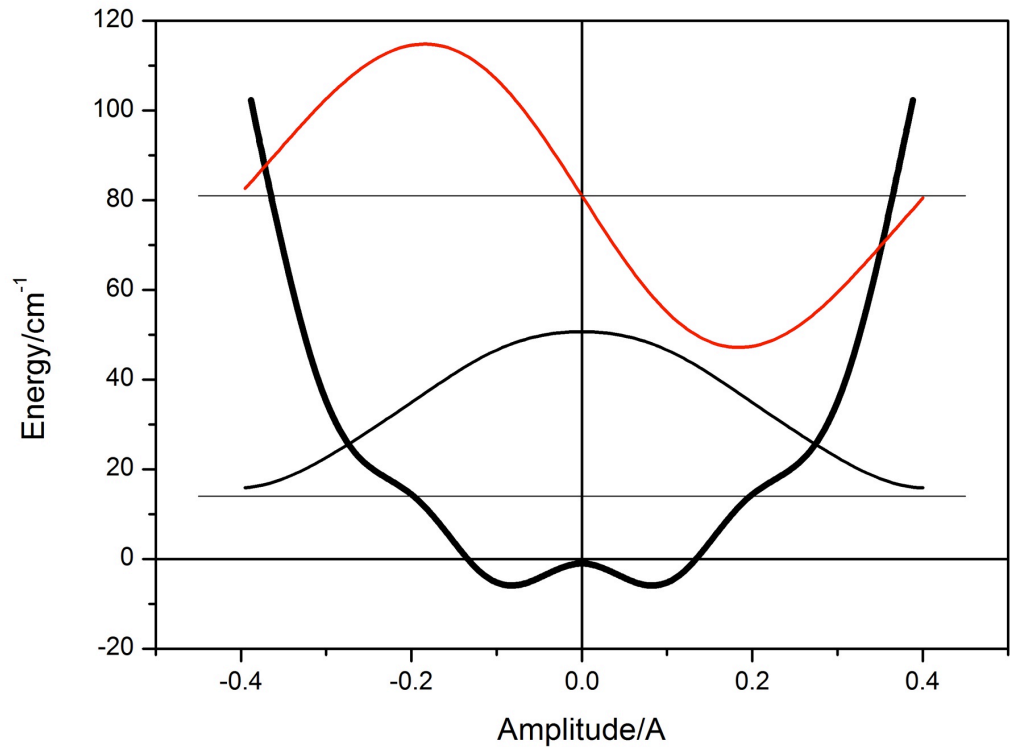
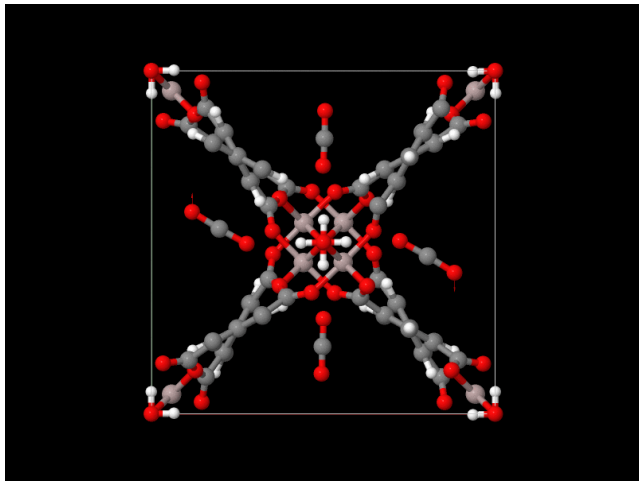
Unstable structures Negative Modes



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Unstable structures

Negative Modes



February 21, 2013



nature chemistry

NOVEMBER 2012 VOL 4 NO 11
www.nature.com/naturechemistry

A binding site to behold

ENZYME DESIGN
Reprogramming reactivity

RNA CATALYSIS
Consequences of compartmentalization

MATERIALS CHARACTERIZATION
Catalysts singled out

nature
chemistry

ARTICLES

PUBLISHED ONLINE: 23 SEPTEMBER 2012 | DOI: 10.1038/NCHEM.1457

Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host

Sihai Yang^{1*}, Junliang Sun², Anibal J. Ramirez-Cuesta³, Samantha K. Callear³, William I. F. David^{3,4}, Daniel P. Anderson¹, Ruth Newby¹, Alexander J. Blake¹, Julia E. Parker⁵, Chiu C. Tang⁵ and Martin Schröder^{1*}

Understanding the mechanism by which porous solids trap harmful gases such as CO₂ and SO₂ is essential for the design of new materials for their selective removal. Materials functionalized with amine groups dominate this field, largely because of their potential to form carbamates through H₂N(δ⁻)–C(δ⁺)O₂ interactions, thereby trapping CO₂ covalently. However, the use of these materials is energy-intensive, with significant environmental impact. Here, we report a non-amine-containing porous solid (NOTT-300) in which hydroxyl groups within pores bind CO₂ and SO₂ selectively. *In situ* powder X-ray diffraction and inelastic neutron scattering studies, combined with modelling, reveal that hydroxyl groups bind CO₂ and SO₂ through the formation of O=C(S)=O(δ⁻)–H(δ⁺)–O hydrogen bonds, which are reinforced by weak supramolecular interactions with C–H atoms on the aromatic rings of the framework. This offers the potential for the application of new ‘easy-on/easy-off’ capture systems for CO₂ and SO₂ that carry fewer economic and environmental penalties.

The efficient removal of CO₂ and SO₂ represents a major challenge in the development of the ‘low-carbon economy’¹. At present, solutions of organic amine are widely used to capture the CO₂ generated by power plants, but the considerable costs associated with the substantial energy input required for the regeneration of the amine solutions, as well as their highly corrosive nature, significantly limit their long-term application². Powerful drivers therefore exist to develop efficient strategies to remove CO₂ using alternative materials that simultaneously demonstrate high adsorption capacity, high selectivity and high rates of regeneration at an economically viable cost.

Porous metal–organic framework (MOF) complexes³ are a subclass of coordination polymers that show great promise for gas storage and separation because of their high surface area and tunable functional pore environment^{4–6}. Within the field of gas capture, there is particular emphasis on optimizing the interactions between the MOF hosts and the adsorbed gas molecules, leading to the discovery of new functional materials with better capture properties^{7,8}. Accordingly, the identification of preferred adsorption sites within a pore structure and the direct visualization of binding interactions represent important methodologies for understanding the mechanisms for the selective capture of CO₂ and SO₂.

In situ single-crystal diffraction has been used previously to determine the locations of CO₂ within an amine-functionalized MOF, providing an invaluable structural rationale for its high binding energy^{9–12}. However, it is critical to the success of this technique that the MOF complex retains a high degree of crystallinity upon inclusion and removal of guest molecules. This is usually difficult to achieve, particularly for those MOFs that feature extra-large pore cavities¹³. Furthermore, static crystallographic studies cannot

provide insights into the dynamics of the crystal lattice and gas molecules upon gas loading. Here, we report the novel application of *in situ* inelastic neutron scattering (INS) combined with density functional theory (DFT) calculations to permit direct visualization of the dynamics of the binding interaction between adsorbed X₂ (X=C, S) molecules and a metal-hydroxyl-functionalized porous solid (NOTT-300) exhibiting high chemical and thermal stability, as well as high selectivity and uptake capacity for CO₂ and SO₂. In addition, *in situ* high-resolution powder X-ray diffraction (PXRD) has been used to probe the preferred binding sites for both CO₂ and SO₂ molecules within NOTT-300.

These complementary experiments using dynamic and static techniques lead to the same conclusion: the active hydroxyl groups within the pore channels interact directly with CO₂ and SO₂ through the formation of Al–OH–O=C(S)=O hydrogen bonds, supplemented by weaker phenyl C–H–O=C(S)=O supramolecular contacts surrounding the pore (Fig. 1).

Results and discussion

Synthesis and transmission electron microscopy (TEM) characterization. The solvated framework complex [Al₂(OH)₂(C₁₀H₈)₂](H₂O)₂ (NOTT-300-solvate) was prepared by hydrothermal reaction of H₂L¹ (biphenyl-3,3',5,5'-tetracarboxylic acid) and Al(NO₃)₃·9H₂O in water containing HNO₃, and was isolated as a microcrystalline material. TEM images confirmed that the crystals have a uniform morphology (~1 μm plates; Supplementary Fig. S7). Compared to traditional methods for the production of MOF materials, the synthetic conditions developed here for NOTT-300-solvate can be viewed as constituting a green synthesis¹⁷, not only because no organic

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Conclusions

- INS is a technique ideally suited to study hydrogen containing materials.
- The rotational line of hydrogen can be use to determine the interaction of the hydrogen molecule with porous materials and the nature of the adsorption site.
- Zeolites and MOF' s show a very strong interaction with molecular hydrogen. For some applications they may be tailored as hydrogen storage materials.
- INS can look at the adsorption of non-hydrogenous materials when the substrate contains hydrogen by the changes induced by the adsorbed species
- Computer modelling is crucial in understanding the experimental results.
- When the experiments match the experiment, the conclusions from theory can be trusted.
- The stability of structures depends on the quantum nature of the motion, this can be important at low frequency modes

References

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February 21, 2013

Acknowledgements

ISIS/STFC

Keith Refson

Bill David

Martin Owen Jones

Sam Callear

Laurent Chapon

Jon Taylor

Silvia Imberti

Reading University

Philip Mitchell

Warwick University

Richard Walton

University of Versailles

Frank Millage

CNR (Italy)

Danielle Colognesi

Marco Zoppi

Alessandra Gianassi

NIST

Craig Brown

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