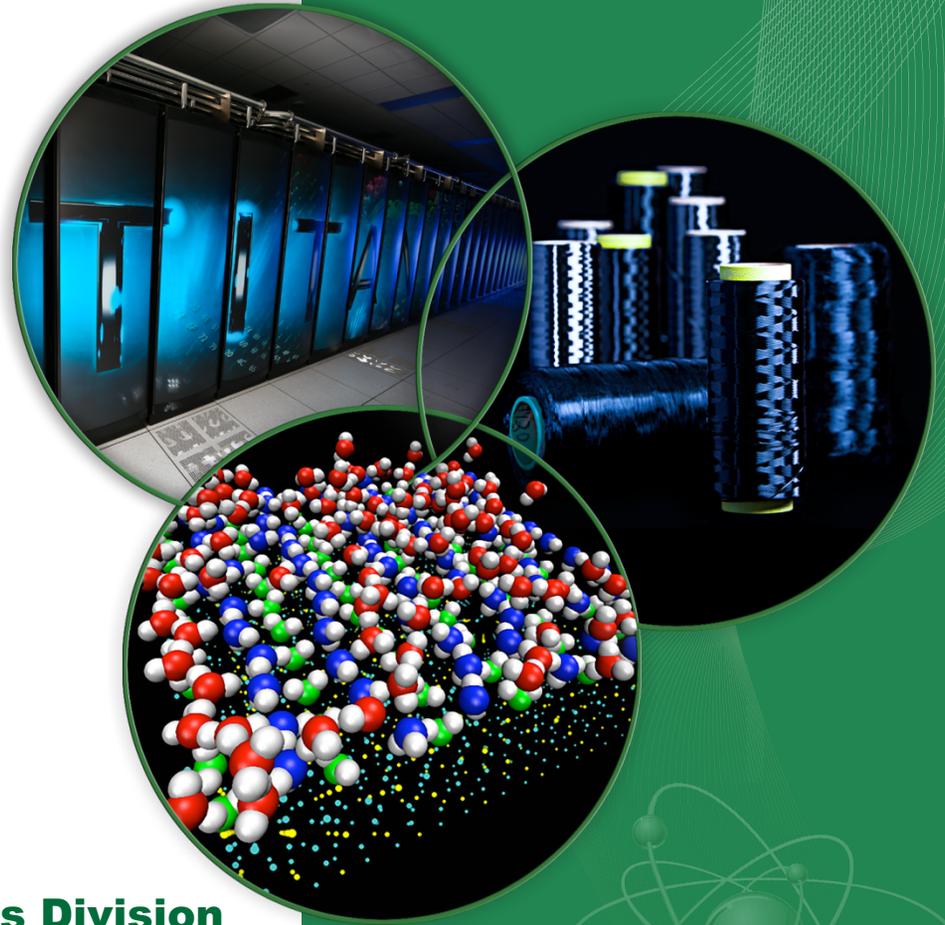


# Neutron Vibrational Spectroscopy

"Through the Looking Glass: Watching atomic dynamics with neutrons and numbers

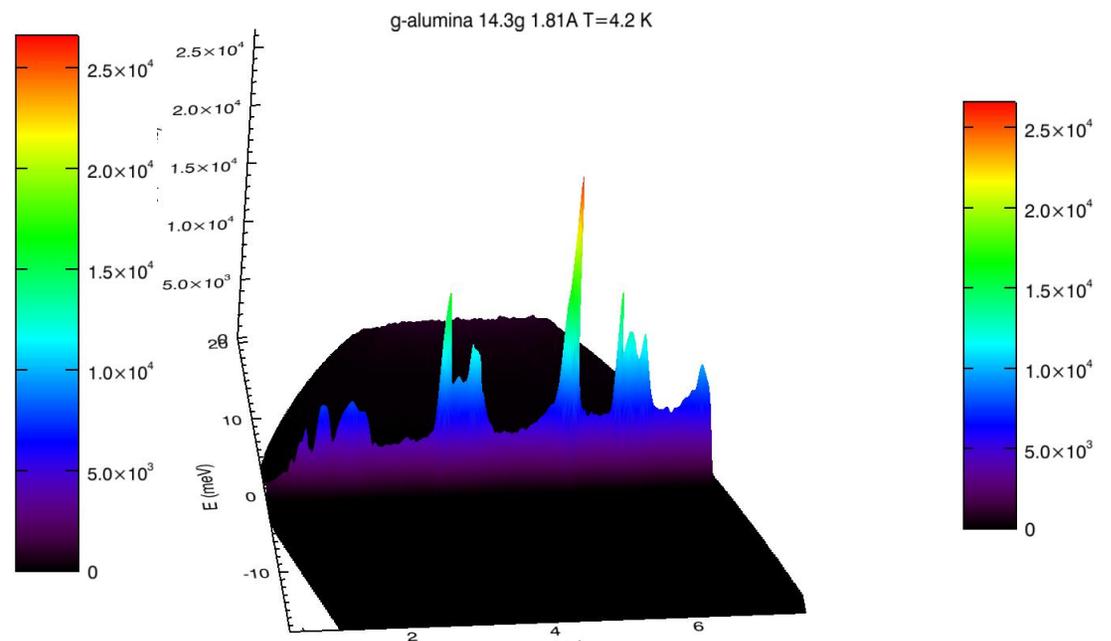
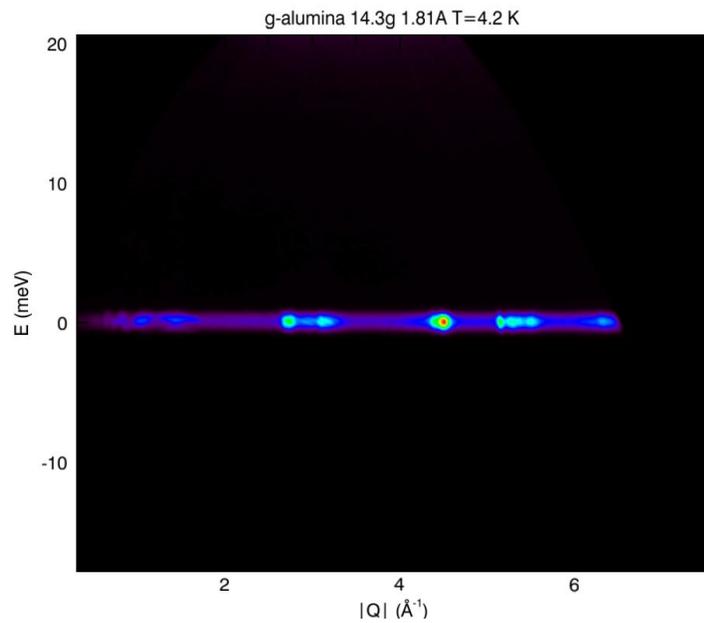
**AJ (Timmy) Ramirez-Cuesta**  
**Chemical and Engineering Materials Division**  
**Chemical Spectroscopy Group**  
**Oak Ridge National Laboratory**

ORNL is managed by UT-Battelle  
for the US Department of Energy





# The $S(Q, \omega)$ Map



$\omega=0$

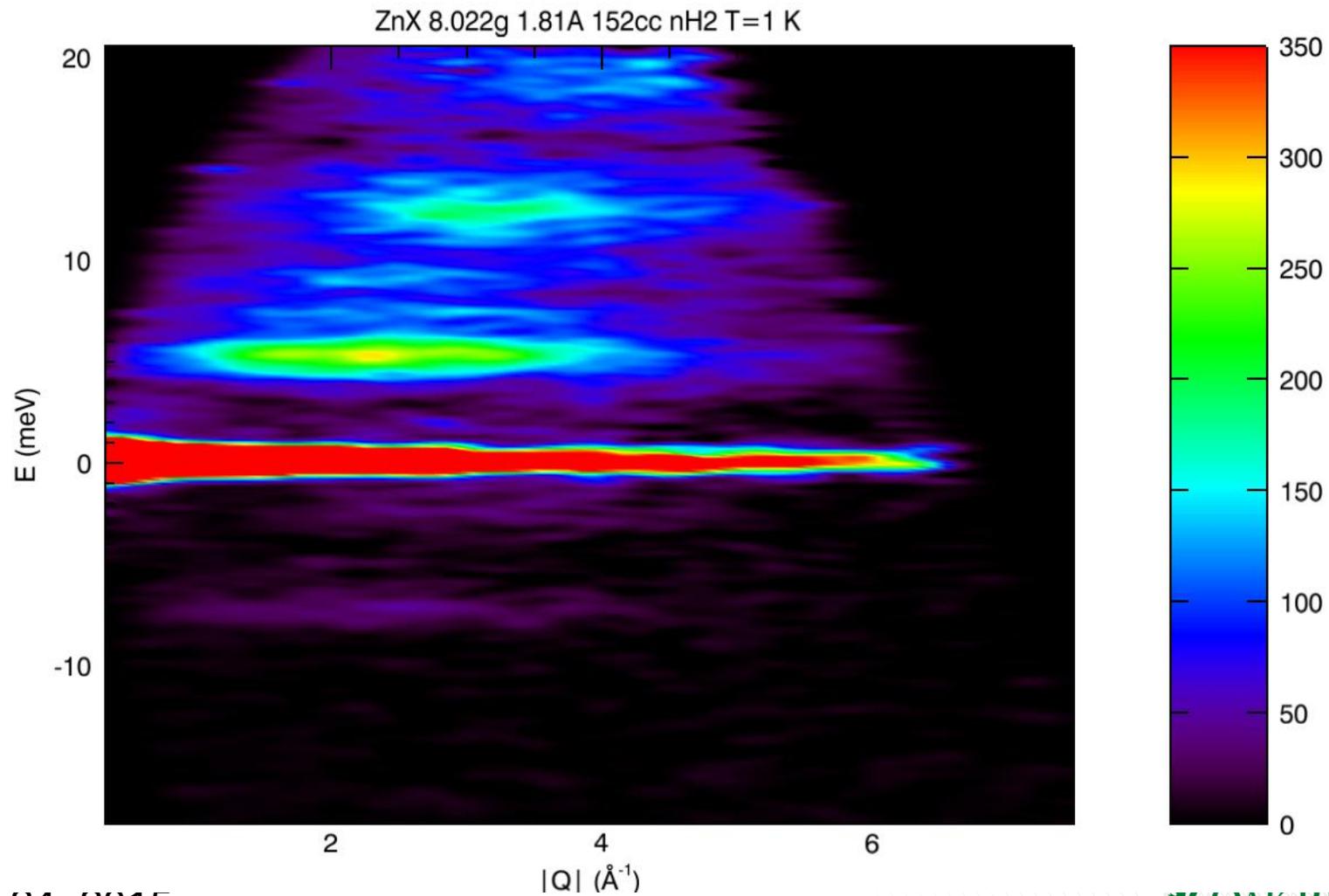
Elastic Scattering

Diffraction

Structural Information

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3 NXS2015

# The $S(Q, \omega)$ Map



June 24, 2015  
4 NXS2015

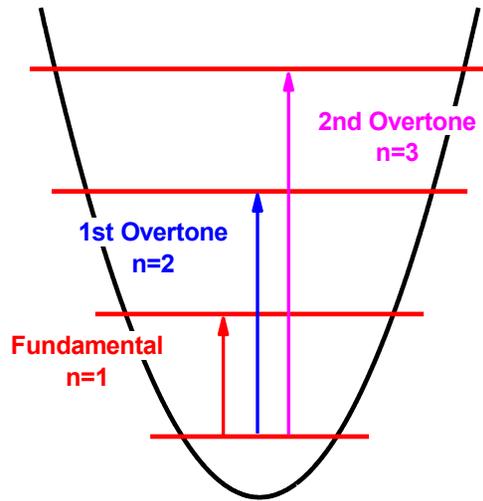
# Inelastic Neutron Scattering

- Transitions are proportional to the amplitude of motion and the cross section of the nuclei.
- Interaction between probe and nucleus
- Simultaneous transfer of energy and momentum.
- No selection rules.
- In this presentation I will be talking about incoherent INS.

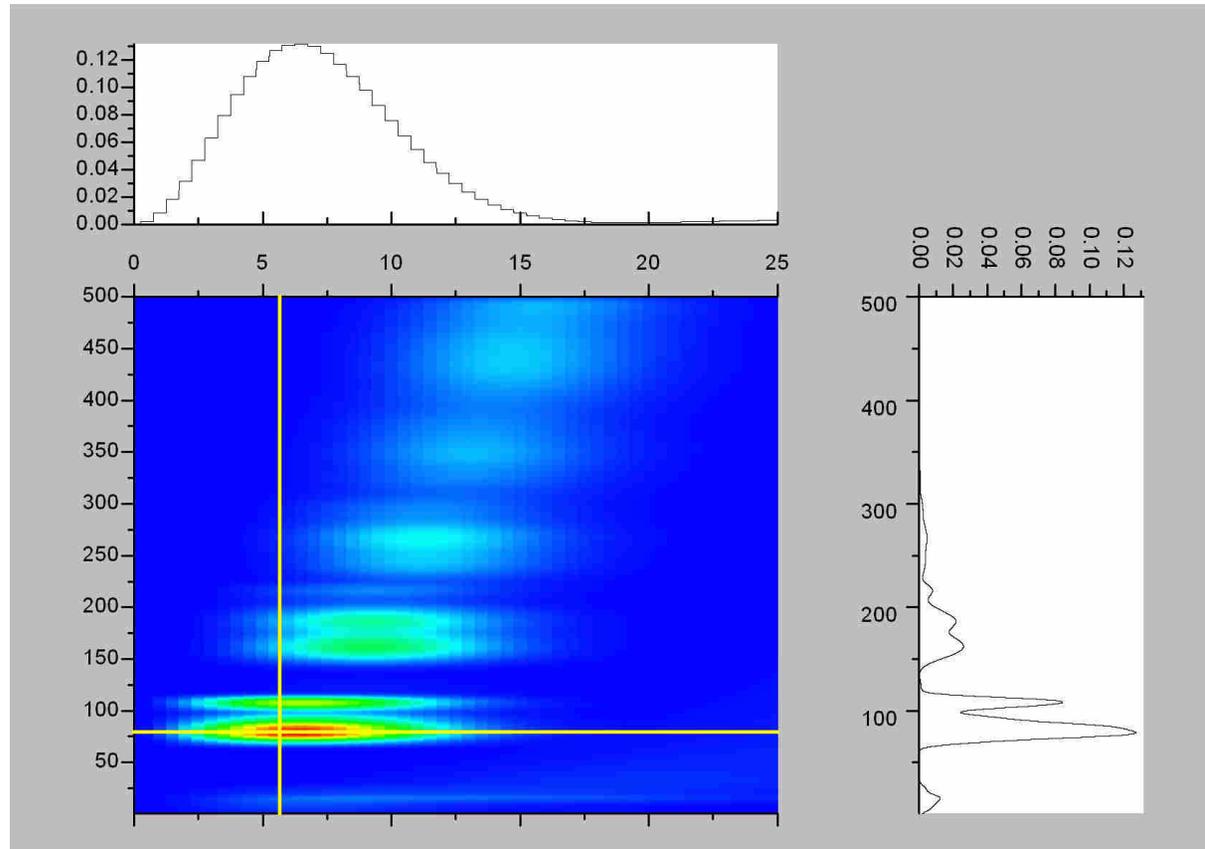
$$S^*(\mathbf{Q}, \omega_\nu)_l^n = y \sigma_l \frac{\left[ (\mathbf{Q} \cdot {}^\nu \mathbf{u}_l(\mathbf{Q}))^2 \right]^n}{n!} \exp\left( -\frac{1}{3} \left( \mathbf{Q} \cdot \sum_\nu {}^\nu \mathbf{u}_l(\mathbf{Q}) \right)^2 \right)$$

Mitchell, P. C. H.; Parker, S. F.; Ramirez-Cuesta, A. J.; Tomkinson, J. *Vibrational Spectroscopy with Neutrons: with applications in Chemistry, Materials Science and Catalysis*; World Scientific: **London**,

# The $S(Q, \omega)$ Map Fundamental

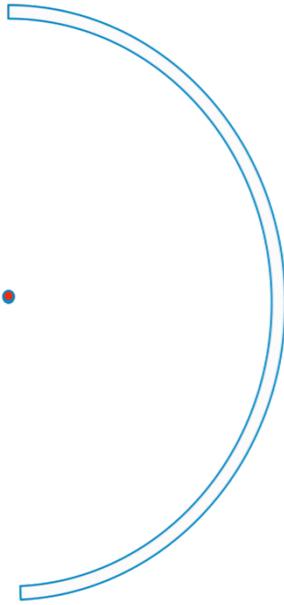


Overtones & combinations are very much apparent. Particularly if there is hydrogen in the system. This is a kinematic effect. The overtones fall within a parabola with a curvature associated with the mass of the scatterer atom.

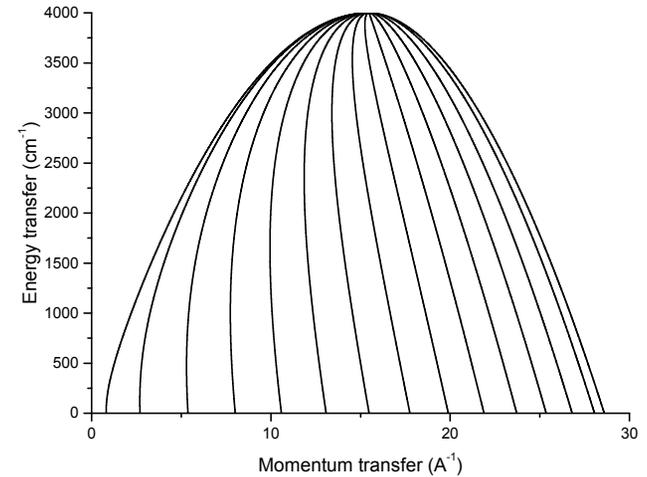


# How to measure INS (1)

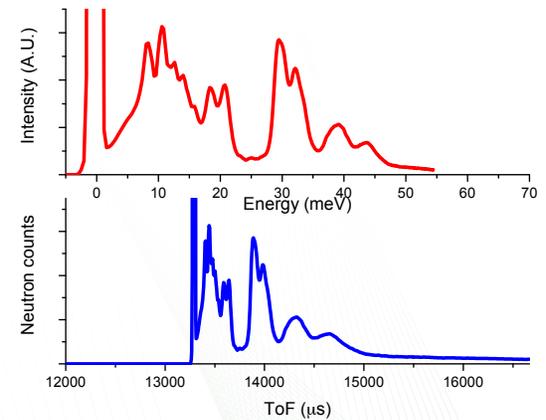
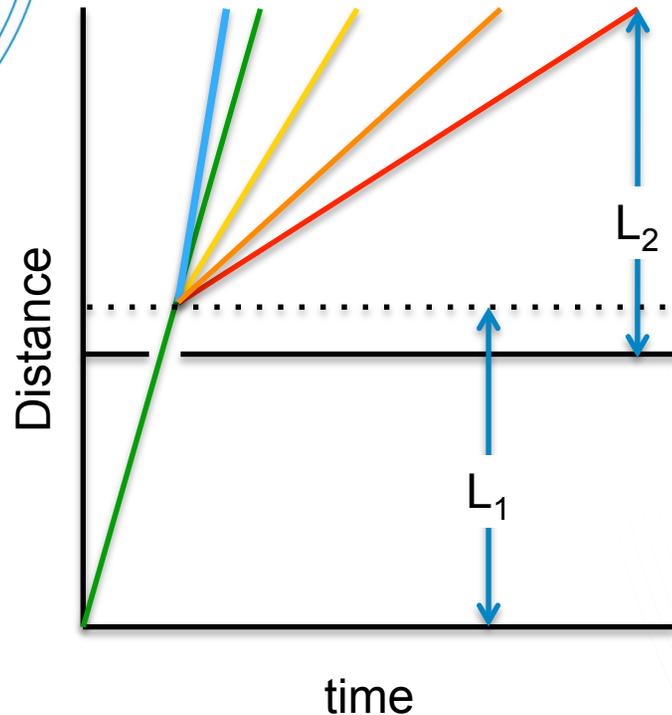
## Direct Geometry Instrumentation



Direct geometry instruments measure Q trajectory is determined by the angle and energy transfer.  
 Examples: ARCS, CNCS, HYSPEC, SEQUIOA



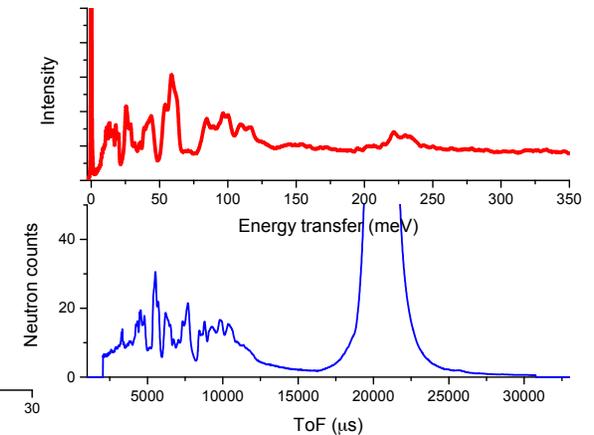
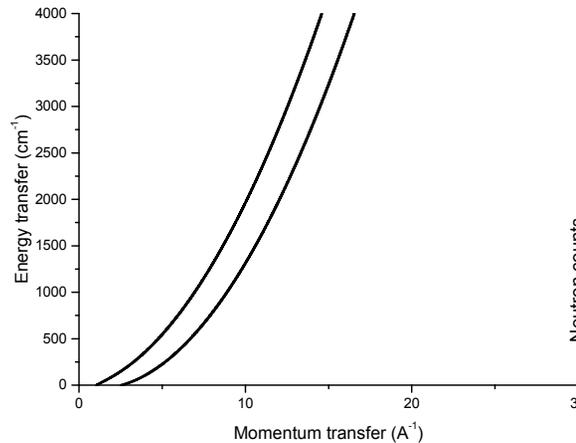
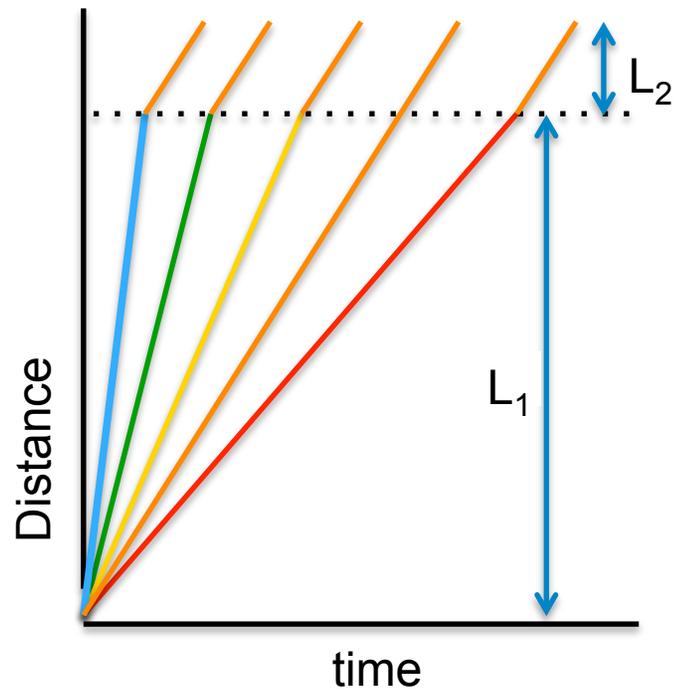
Incident neutron beam is monochromatic determining the incident energy  $E_1$ .  
 That determines  $T_1$ . We measure the ToF and we can work out  $T_2$ .



Resolution is almost constant in units of  $E_i$

# How to measure INS (2)

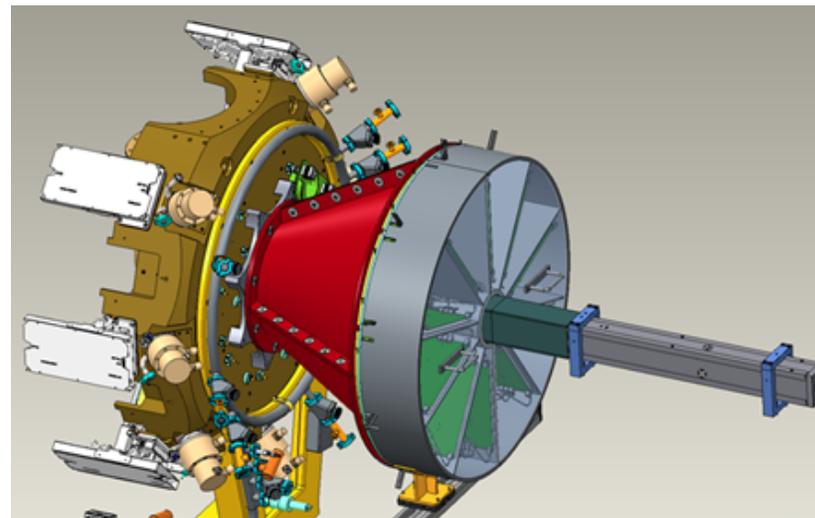
## Indirect Geometry Instrumentation



Resolution is almost constant in units of  $\Delta\omega/\omega \sim 1.5\%$

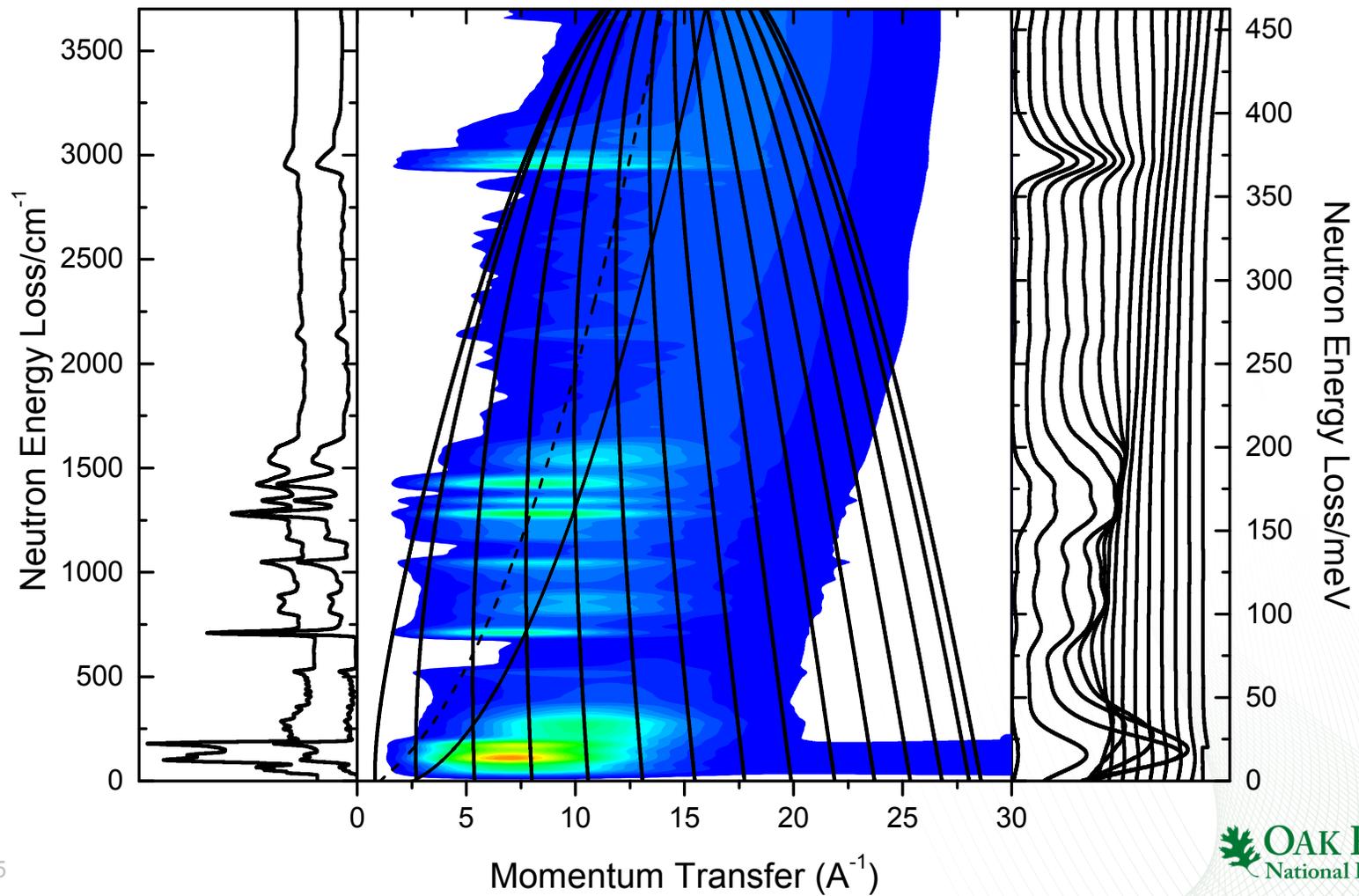
Incident neutron beam is white. We fix the energy of the scattered neutrons using an analyzer and filter device.

That determines  $T_2$ . We measure the ToF and we can work out  $T_1$ .

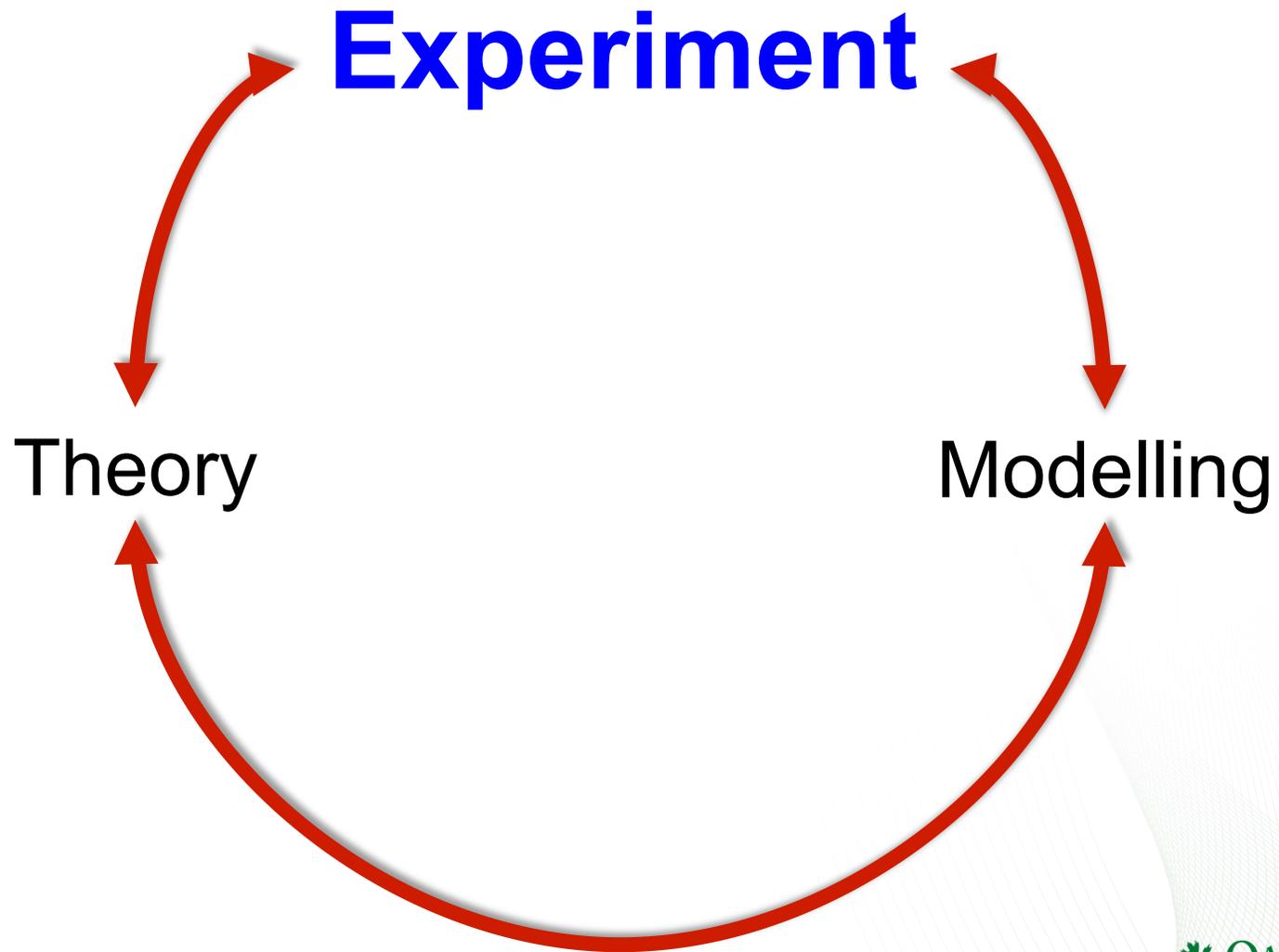


# The $S(Q, \omega)$ Map

Direct geometry advantages etc.

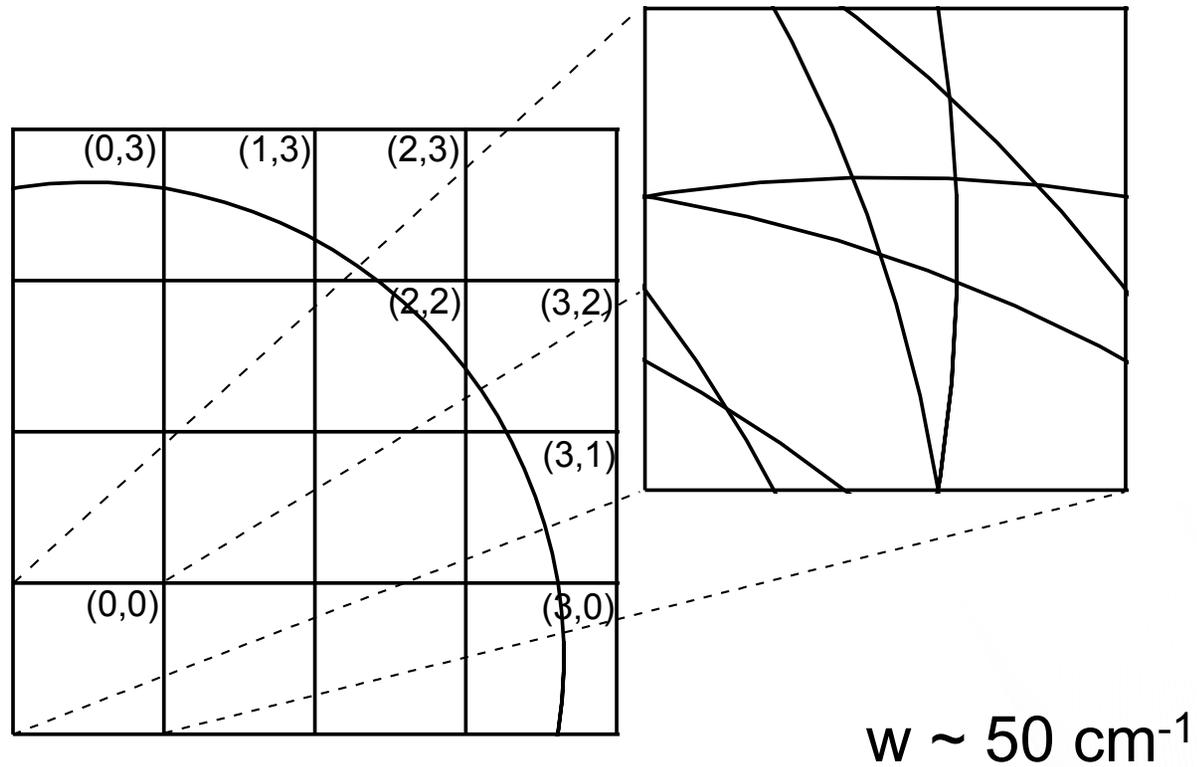


# Playing the game



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# Powder Average



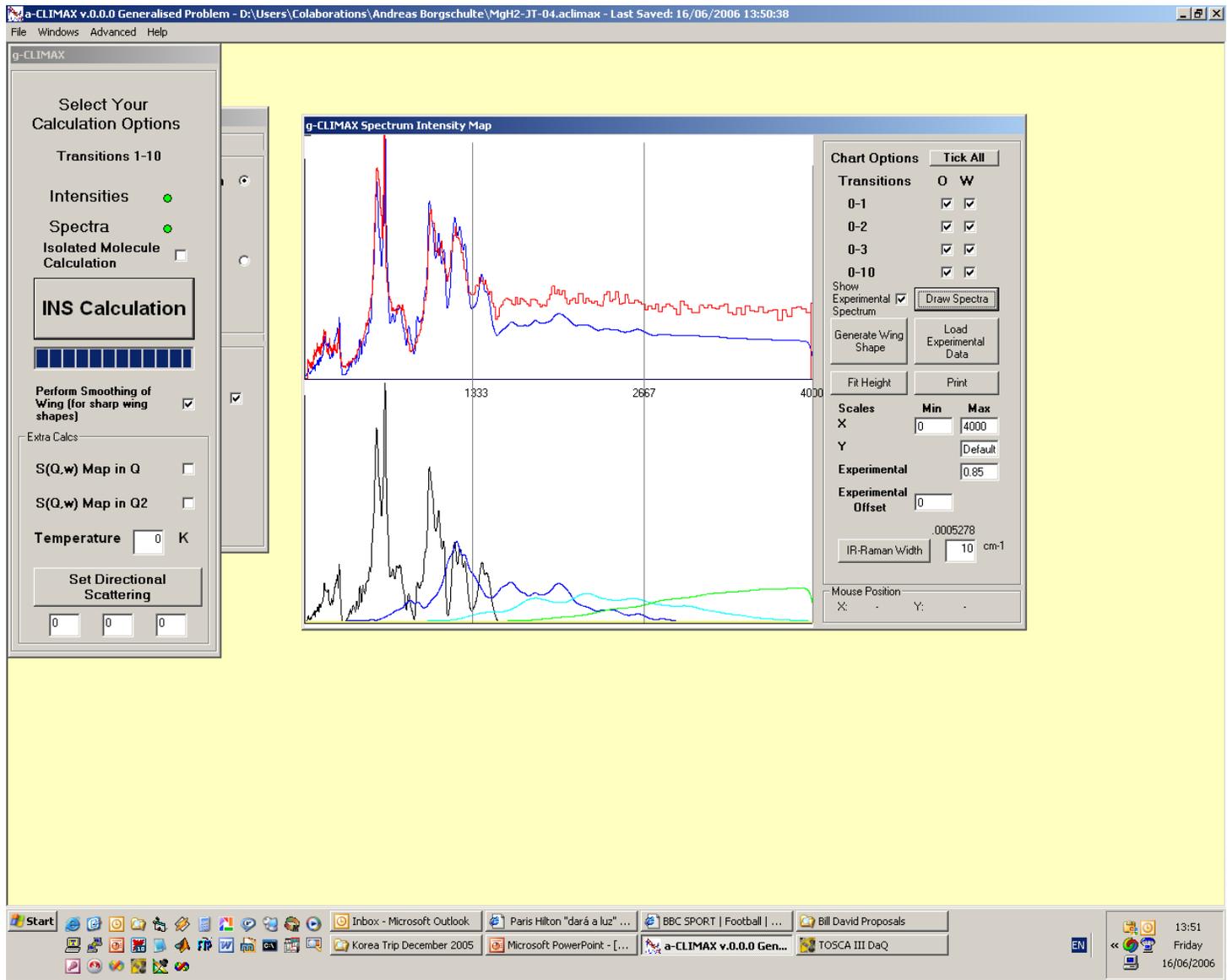
Uniform sampling of the Brillouin zone

# Calculation of INS spectra

## a-CLIMAX

- It uses the isolated molecule approximation for the study of molecular solids.
- For extended solid calculations, with a fine sampling of the Brillouin zone, it is rigorous; i.e. the isolated molecule approximation is not longer necessary since there is no distinction between external and internal modes. The only assumption is the harmonic approximation.

*Computer Physics Communications* **2004**, 157, 226-238

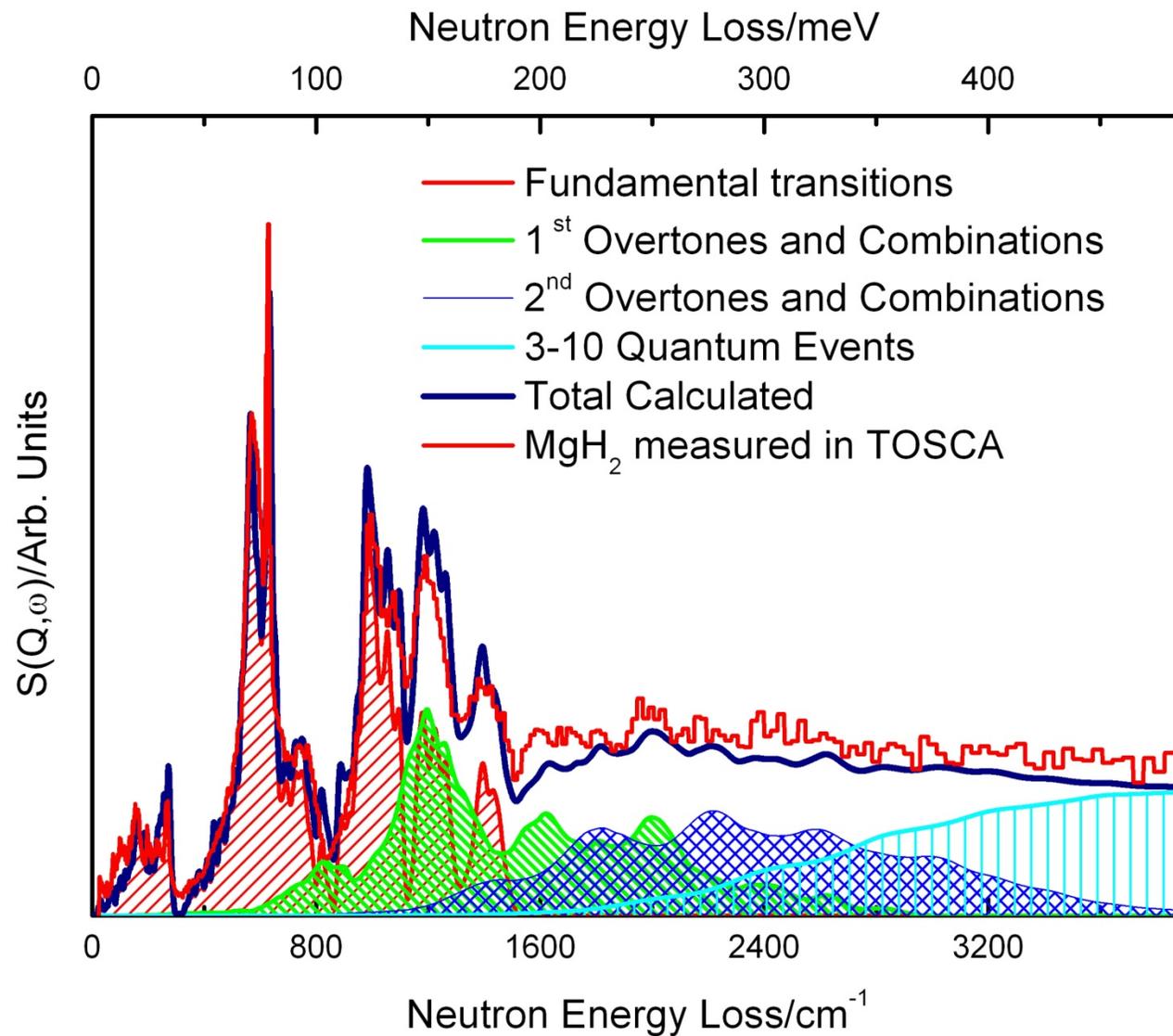


# DFT calculations

1. For the calculations shown in this talk I have used CASTEP from Accelrys
2. The convergence criteria used is “Fine”
3. Interpolation algorithms of the dynamical matrix allow the sampling of the Brillouin zone with different grid sizes

Vibrational Spectroscopy with Neutrons, World Scientific: London, **2005**  
Chemical Physics **2005**, 317, 119–129.  
Macromolecules **2006**, 2683–2690.

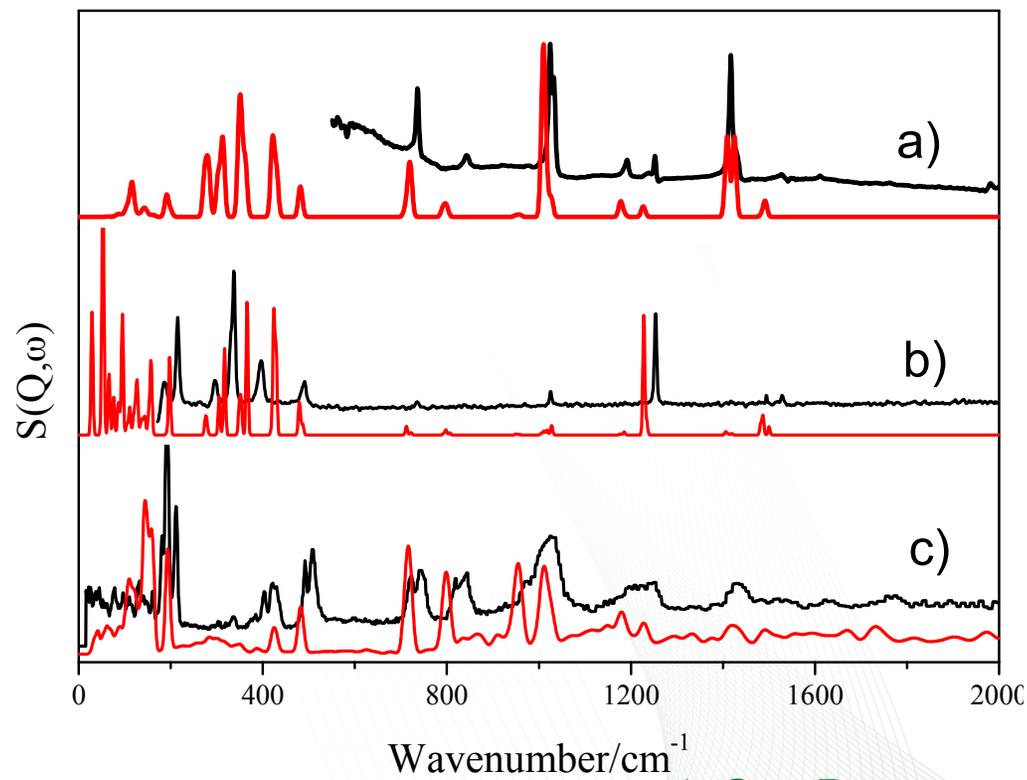
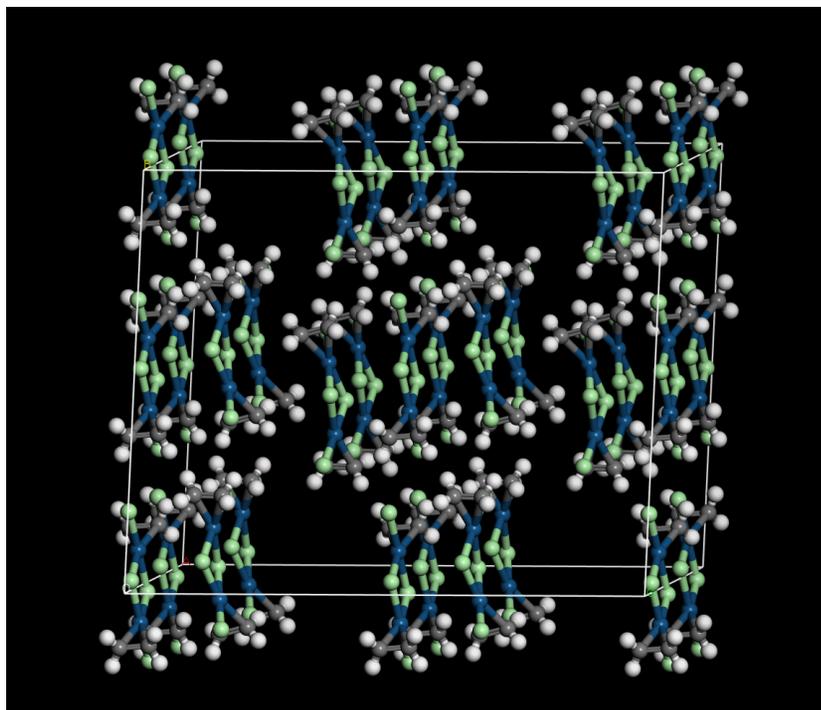
# Example MgH<sub>2</sub>



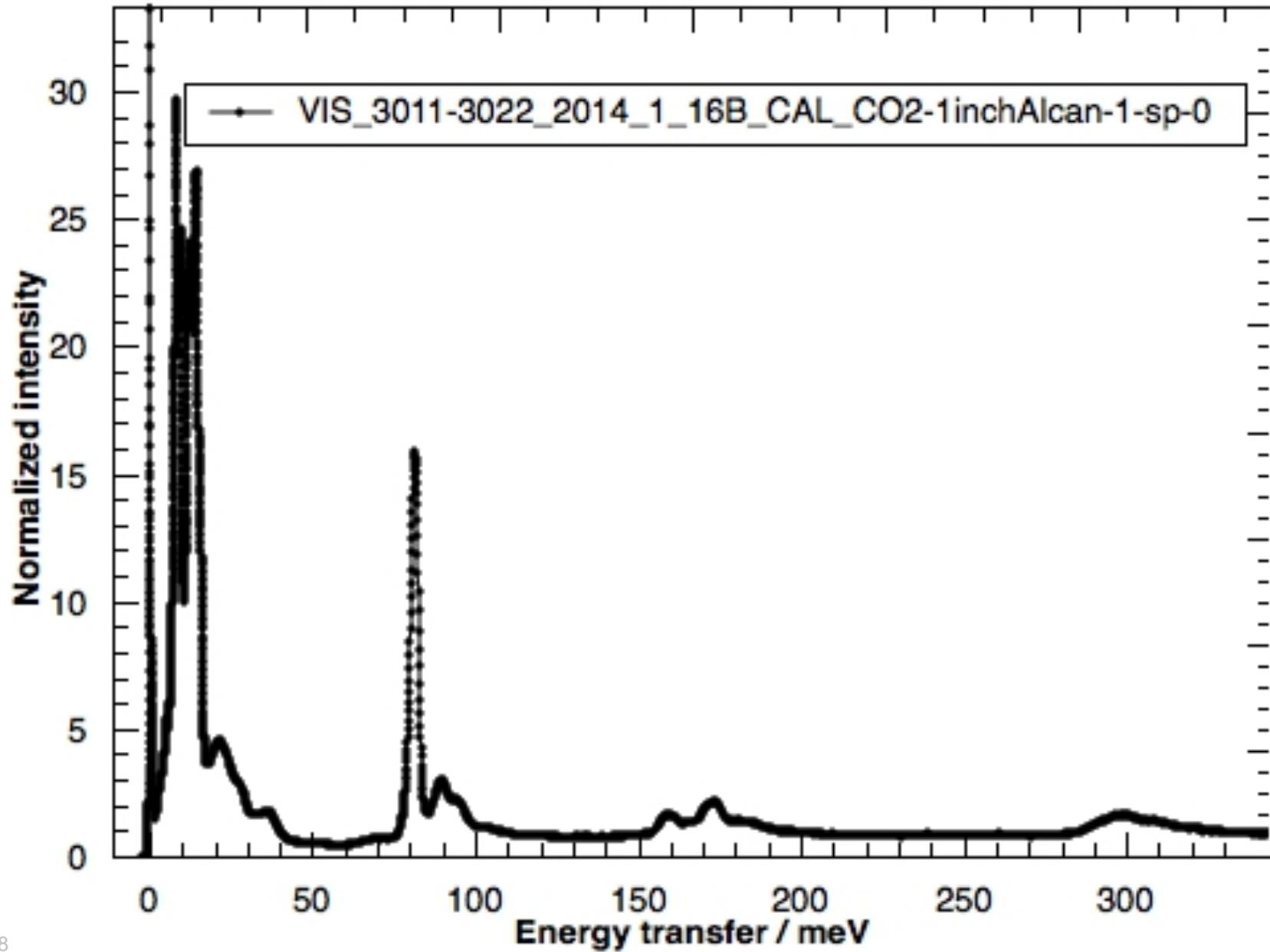
# INS and other vibrational tools

Zeise's salt. The anion features a platinum atom with a square planar geometry. The salt is of historical importance in the area of organometallic chemistry as one of the first examples of an transition metal alkene complex.

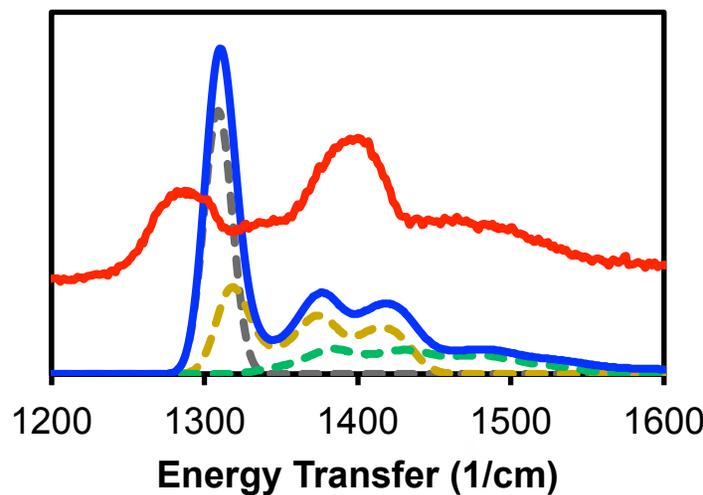
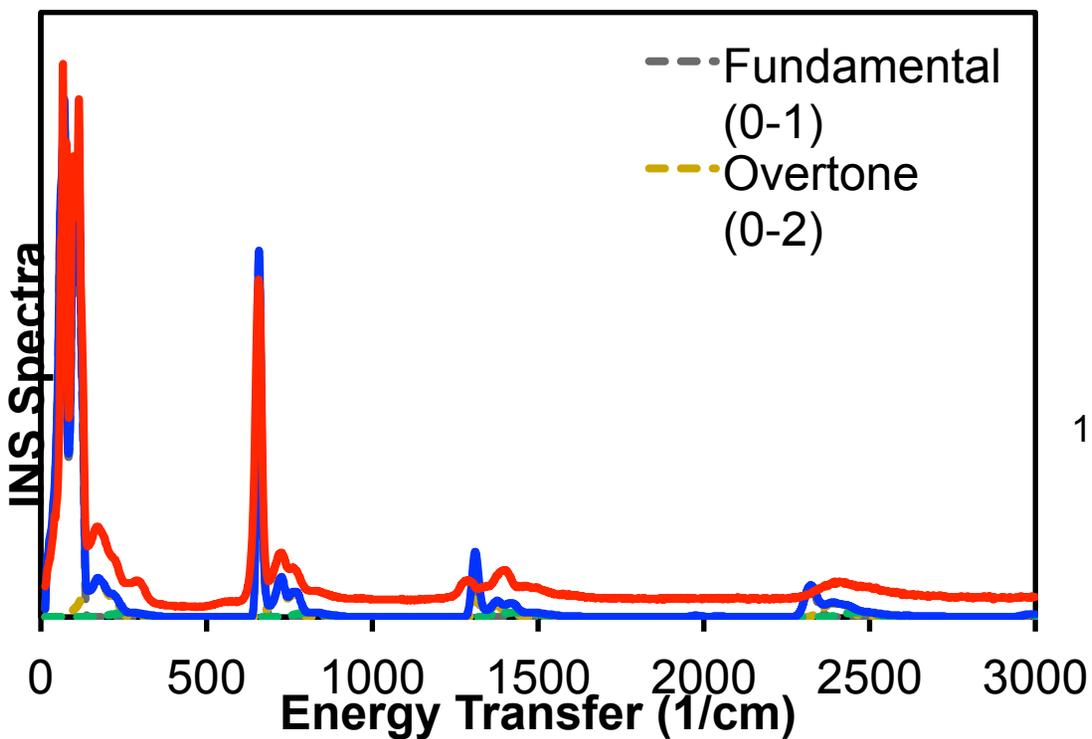
INS gives quantitative information, IR and Raman, not necessarily so



CO<sub>2</sub>



# Examples from VISION



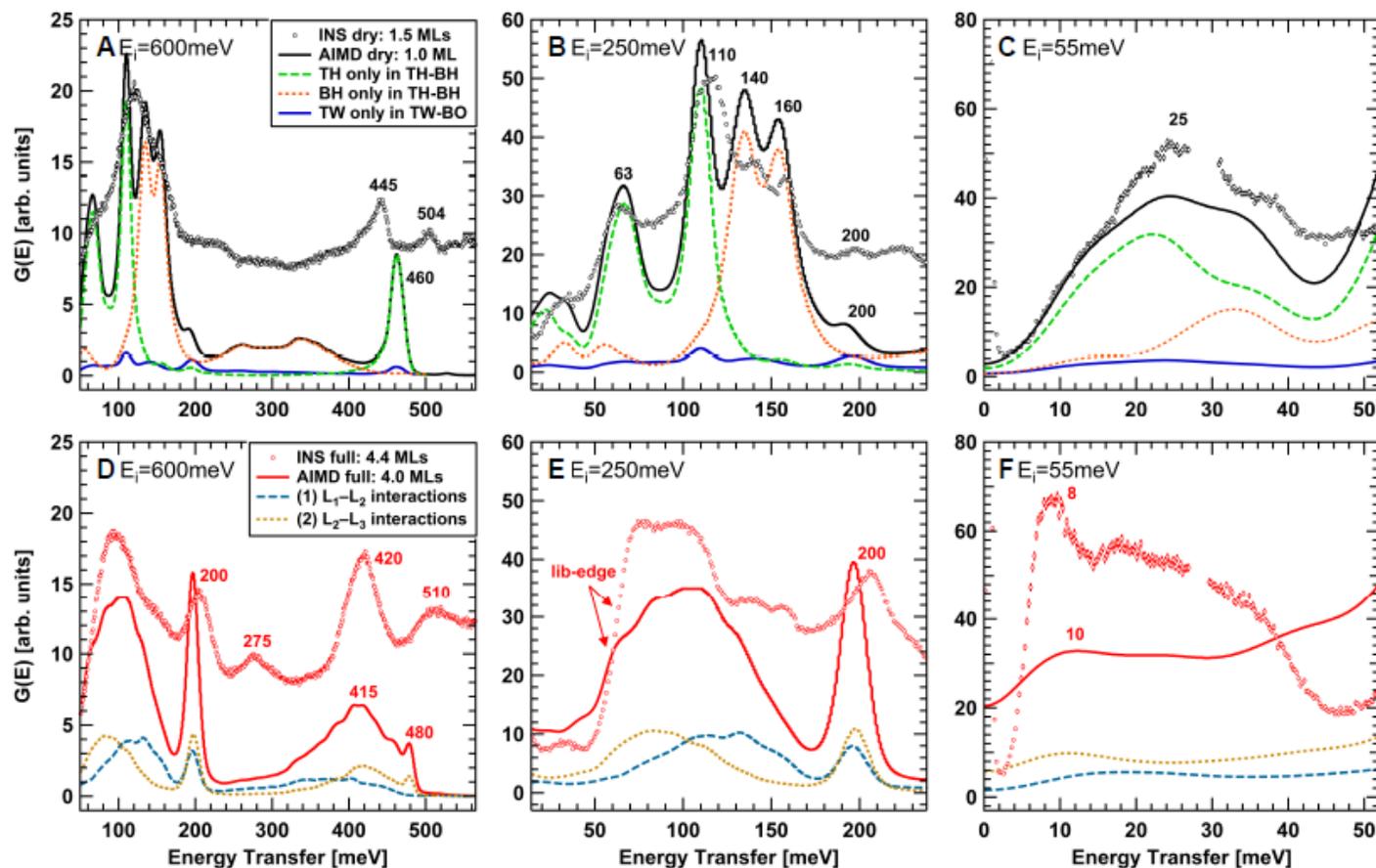
- Overlap of the an overtone (of the translational modes) with a fundamental (the C-O symmetric stretching): the *Fermi resonance*
- First observation of CO<sub>2</sub> Fermi resonance *using INS*

## **Vibrational Density of States of Strongly H-Bonded Interfacial Water: Insights from Inelastic Neutron Scattering and Theory**

H.-W. Wang<sup>1</sup>, M.J. DelloStritto<sup>2</sup>, N. Kumar<sup>2</sup>, A.I. Kolesnikov<sup>1</sup>, P.R.C. Kent<sup>1</sup>, J.D. Kubicki<sup>2</sup>, D.J. Wesolowski<sup>1</sup>, and J.O. Sofo<sup>2</sup>

<sup>1</sup>ORNL, <sup>2</sup>The Pennsylvania State University

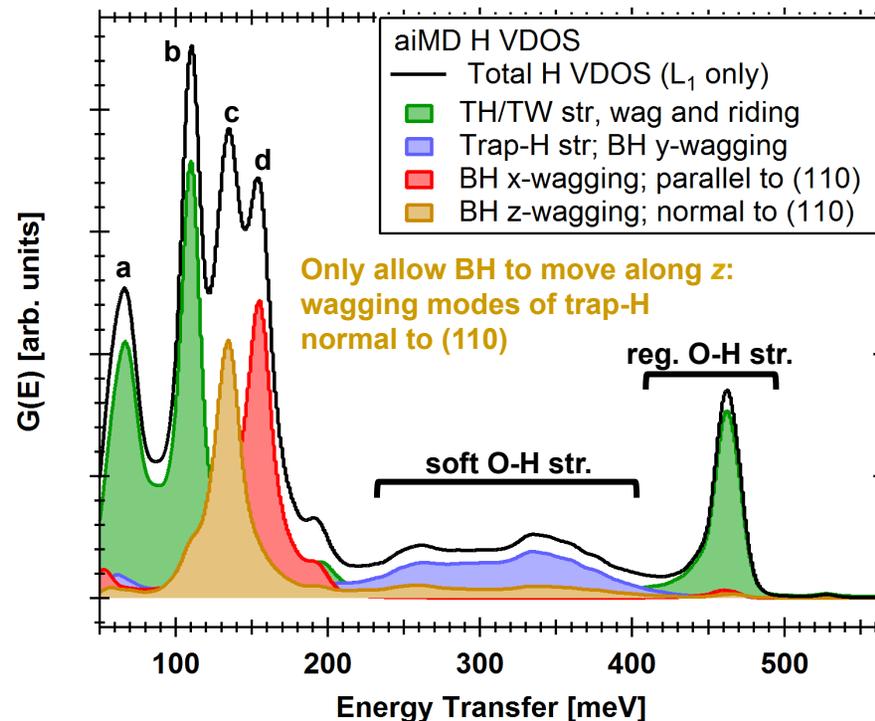
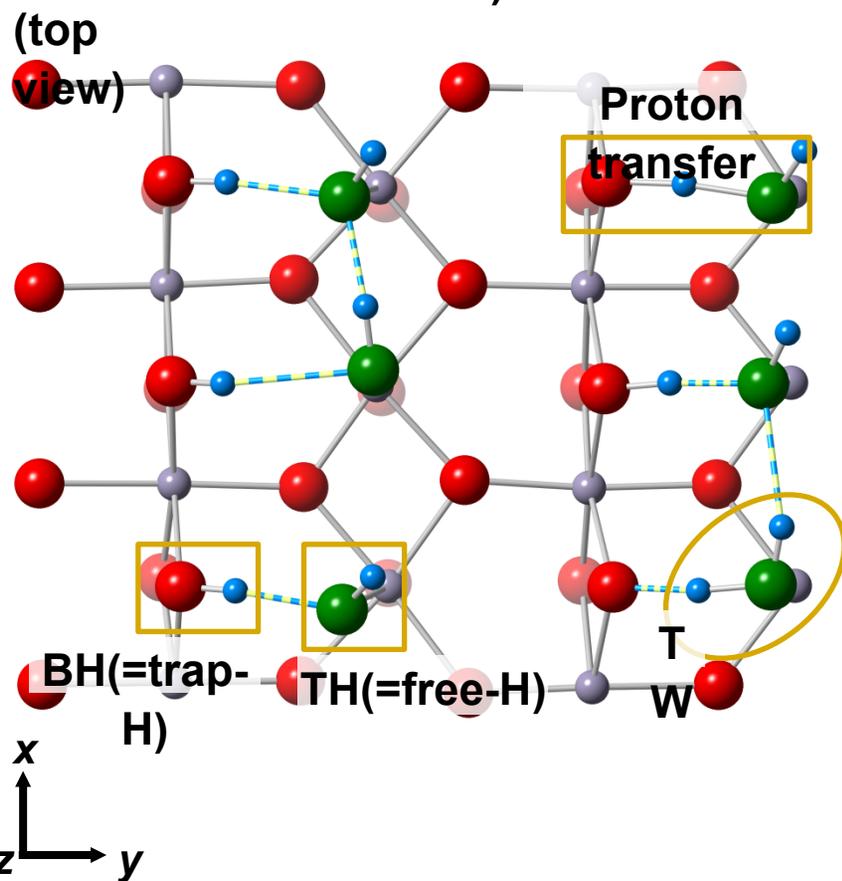
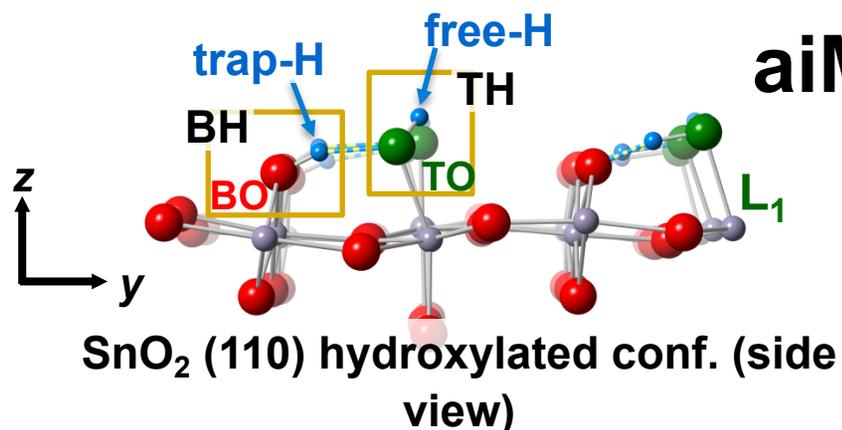
In this study we show that the vibrational dynamics of H<sub>2</sub>O and OH sorbed on SnO<sub>2</sub> nanoparticles, probed with inelastic neutron scattering and analyzed with ab-initio molecular dynamics, reveals very strong surface H-bonds, with a formation enthalpy twice that of liquid water. This unusually strong interaction results in (i) decoupling of the hydrated surface from additional water layers due to an epitaxial screening layer of H<sub>2</sub>O and OH species, (ii) high energy of OH wagging modes that provides an experimental indicator of surface H-bond strengths, and (iii) high proton exchange rates at the interface.



### INS spectra measured at SEQUOIA of water on nano-SnO<sub>2</sub> compared with aiMD simulations.

Measured INS (circles) and calculated aiMD-VDOS (lines) spectra for the *dry* (A-C) and the *fully* hydrated nanoparticles (D-F). The data were collected at three different neutron incident energies,  $E_i$ , indicated in the figure. The labels indicate the energy transfers of the most relevant features in meV. In panels (A)-(C), the three decomposed spectra (green, orange and blue lines) show distinct contributions from each subset of hydroxyl (TH and BH) and water (TW) configurations. In panels (D)-(F), contributions from only interlayer H-bonding interactions are marked by blue and brown lines.

# aiMD mode assignments



## During entire timesteps (40ps):

- free-H's spent 90% of time as a part of TH, and 30% of time H-bond to nearby TO .
- trap-H's spent 90% of time as a part of BH and spent equal amounts of time H-bonded to TO.
- TW forms only 10% of time.

# **Studying H<sub>2</sub> adsorption in Porous Materials & Surfaces with INS**

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

**Characterization of the interaction  
strength**

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23 NXS2015



# The Theory



- H<sub>2</sub> ground state ( $J=0$ ) parahydrogen (p-H<sub>2</sub>) antisymmetric nuclear spin wavefunction ( $\uparrow\downarrow$ ) and symmetric rotational wavefunction.
- The first rotational state, ( $J=1$ ) orthohydrogen (o-H<sub>2</sub>) symmetric nuclear spin wavefunction ( $\uparrow\uparrow$ ) and antisymmetric rotational wavefunction.
- Transitions p-H<sub>2</sub>  $\leftrightarrow$  o-H<sub>2</sub> are detected with neutrons because neutrons exchange spin states with the H<sub>2</sub> molecule.

In solid dihydrogen, H<sub>2</sub> 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

$$\Delta E = 2B$$

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24 NXS2015

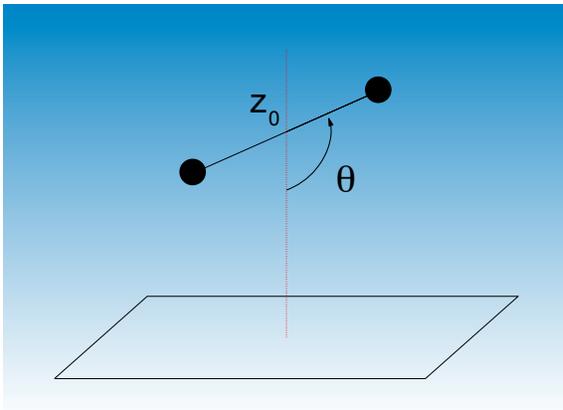


# The Interactions

- A hydrogen compound that has a value of  $B=29.3 \text{ cm}^{-1}$ ,  $\text{H}_3$  would do the trick,  $\text{D}_2$  also works.
- A hindered  $\text{H}_2$  rotor constrained to move in two dimensions.

The potential that governs the motion of a  $\text{H}_2$  molecule on a surface may be expressed as

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



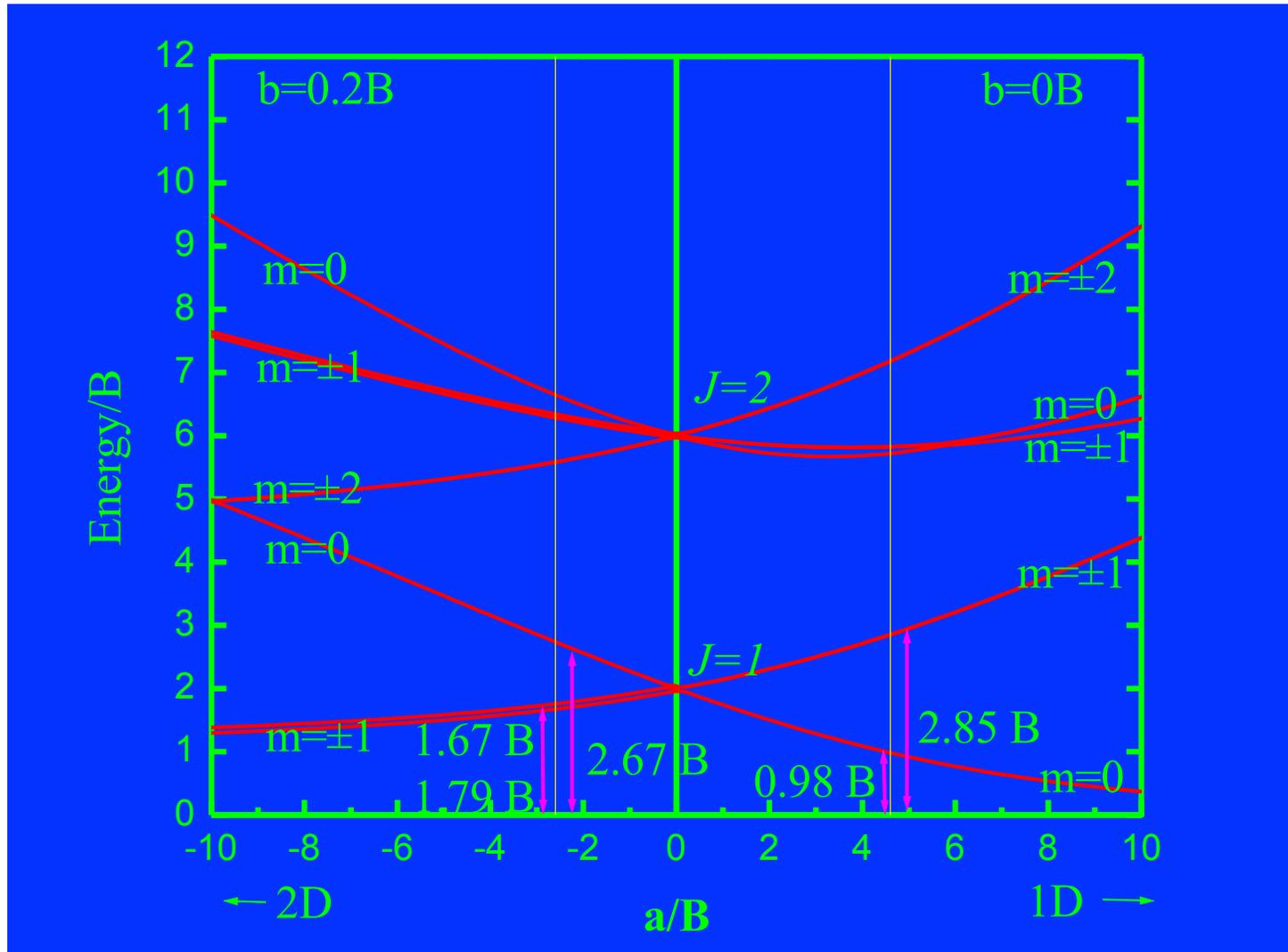
- $a > 0$  the molecule is aligned to an axis (1D case).
- $a < 0$  the molecule is constrained in a plane (2D case)
- The splitting between levels is  $1B$  if  $a$  is large and negative, because the energy levels are:

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

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25 NXS2015

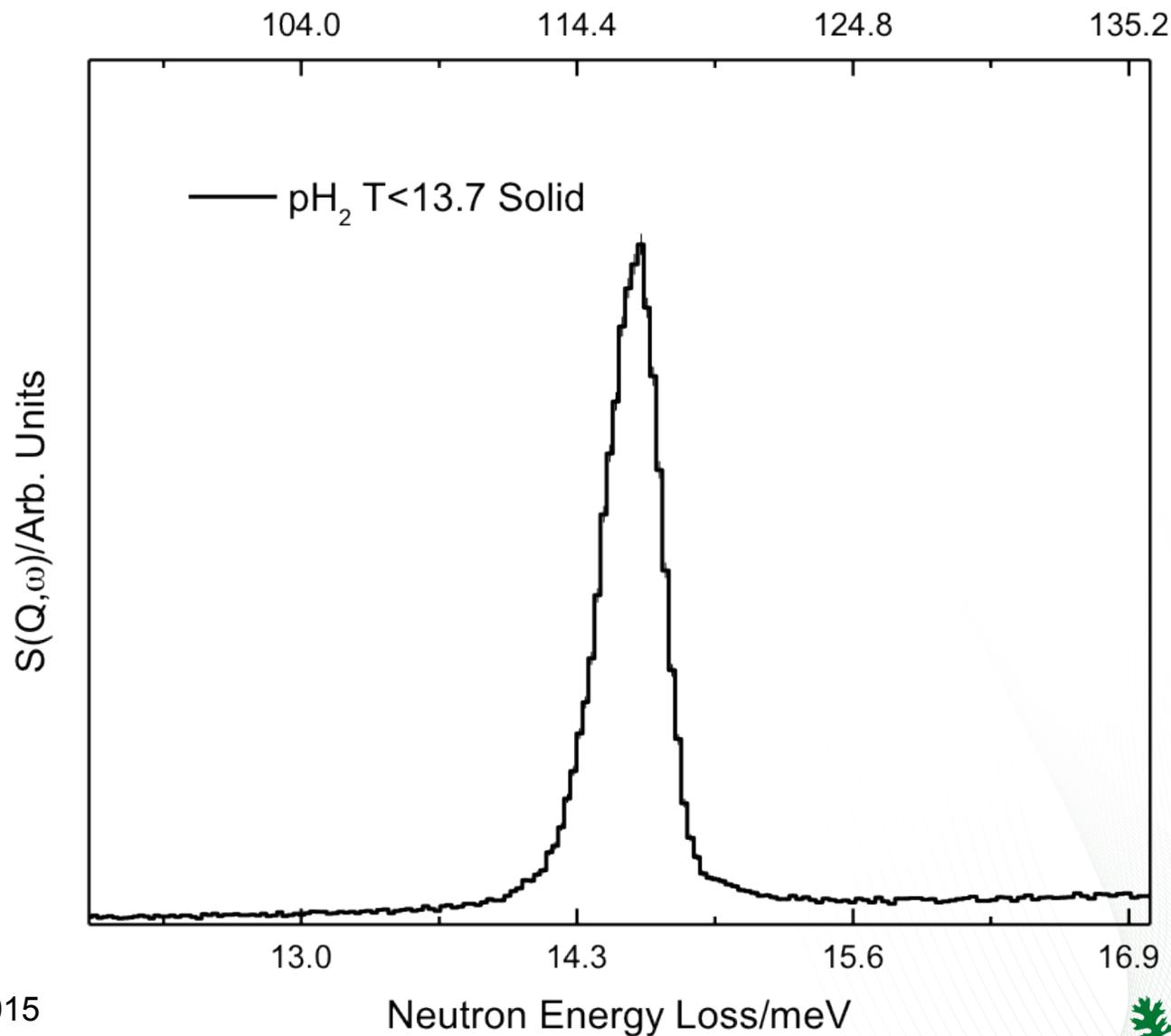
# The Energy Levels



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26 NXS2015

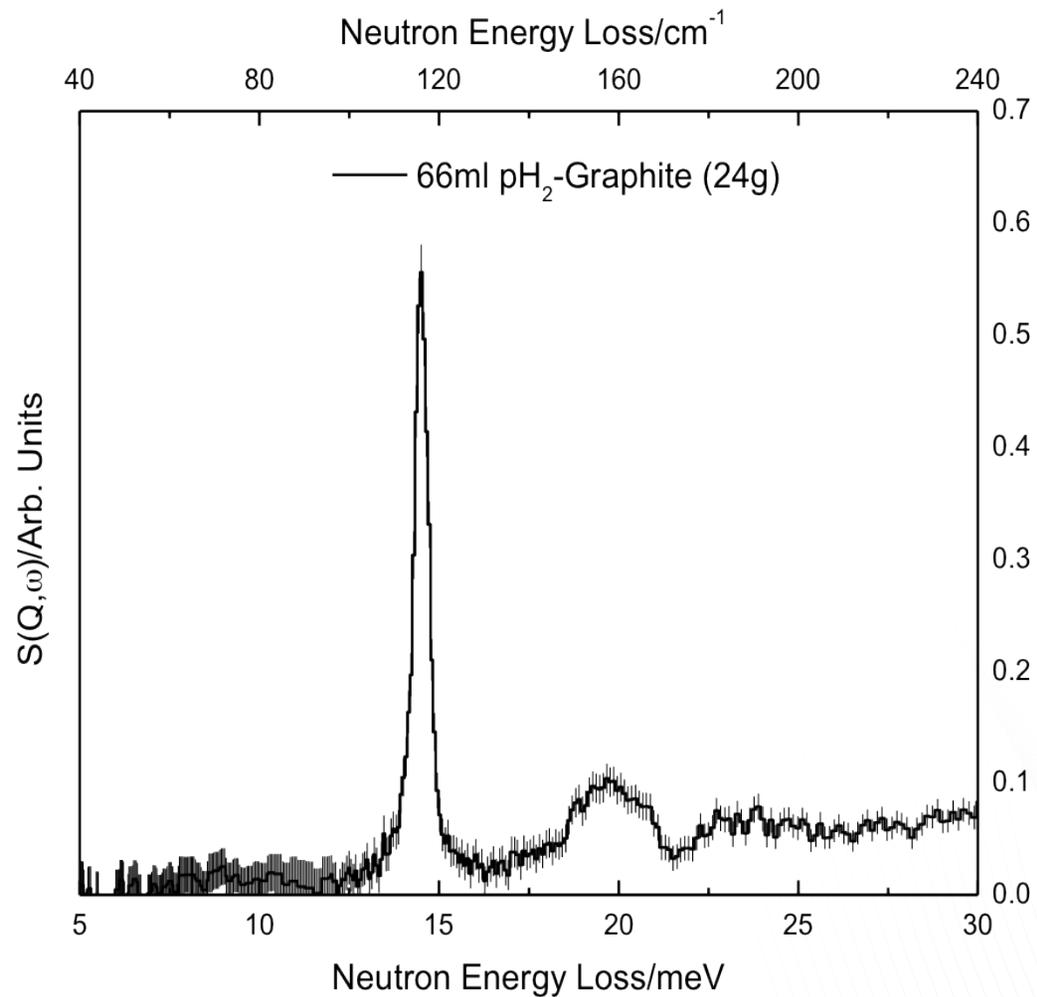
# What are we expecting?



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27 NXS2015

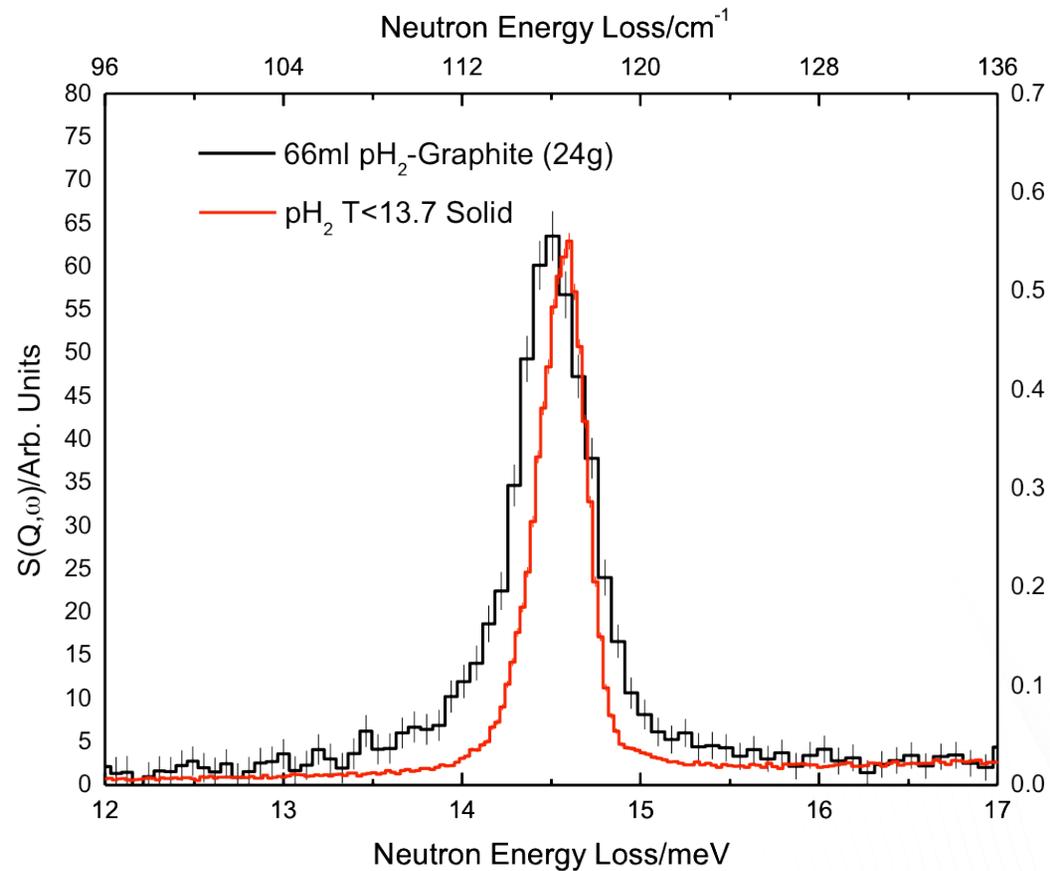
# Interaction of graphite with Hydrogen



June 24, 2015

28 NXS2015

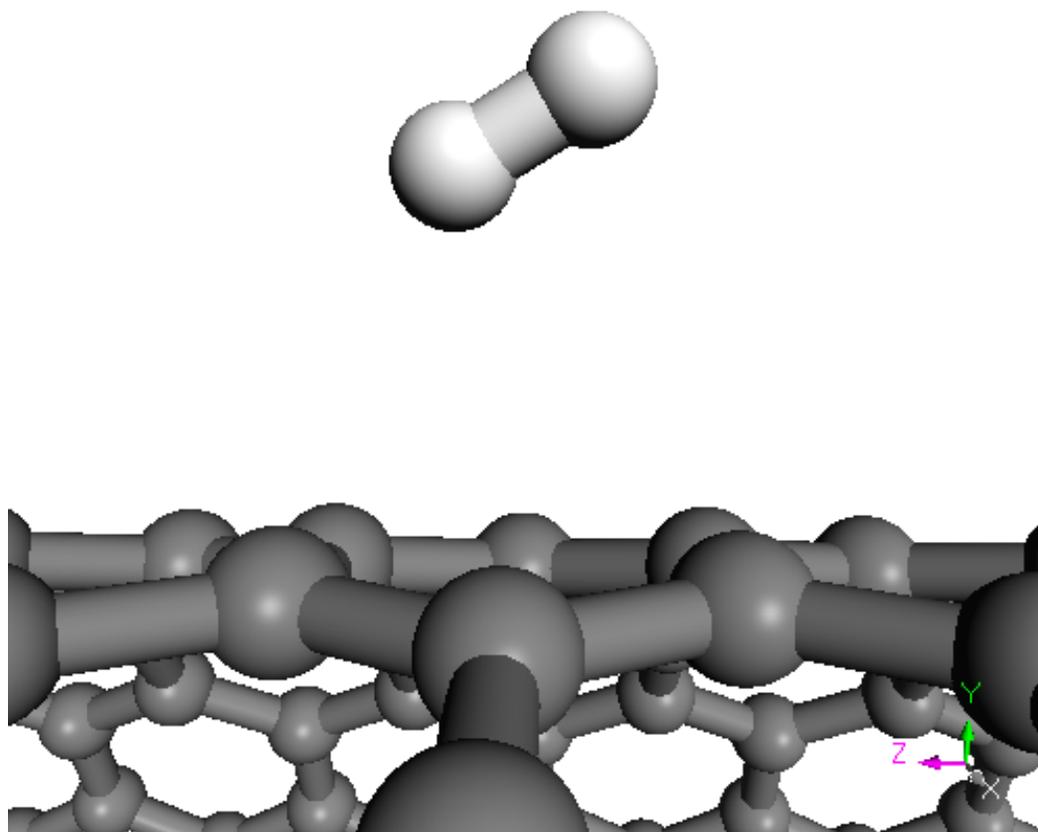
# Interaction of graphite with Hydrogen



June 24, 2015

29 NXS2015

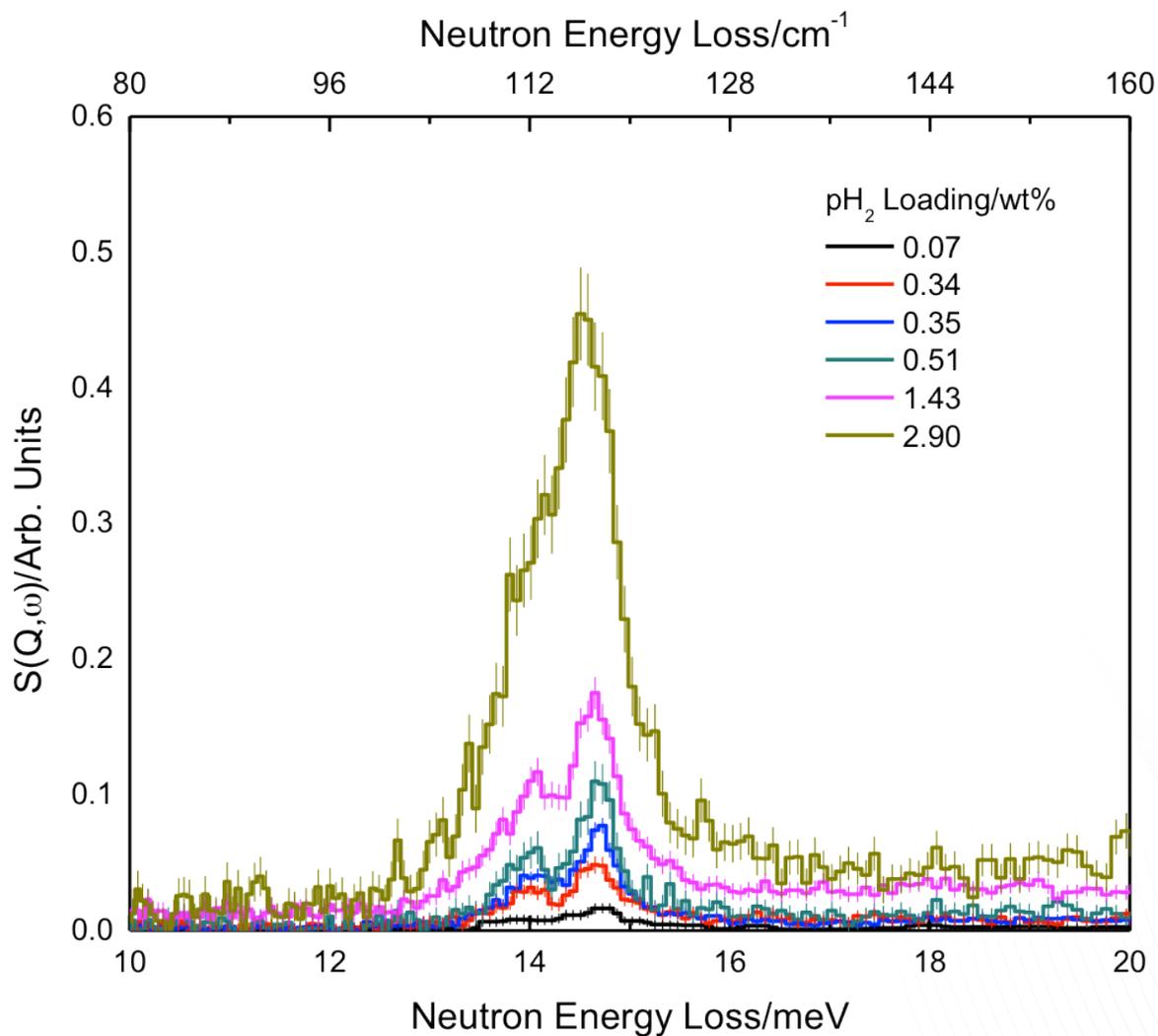
# Interaction of SWNT with Hydrogen



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30 NXS2015

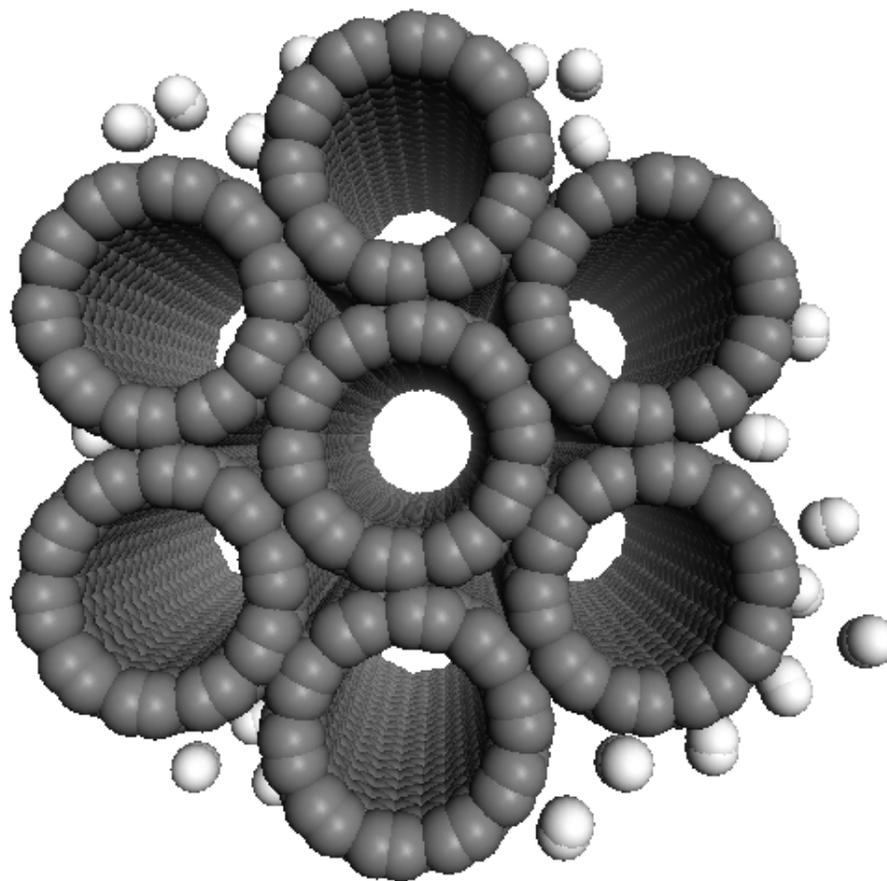
# Interaction of SWNT with Hydrogen



June 24, 2015

31 NXS2015

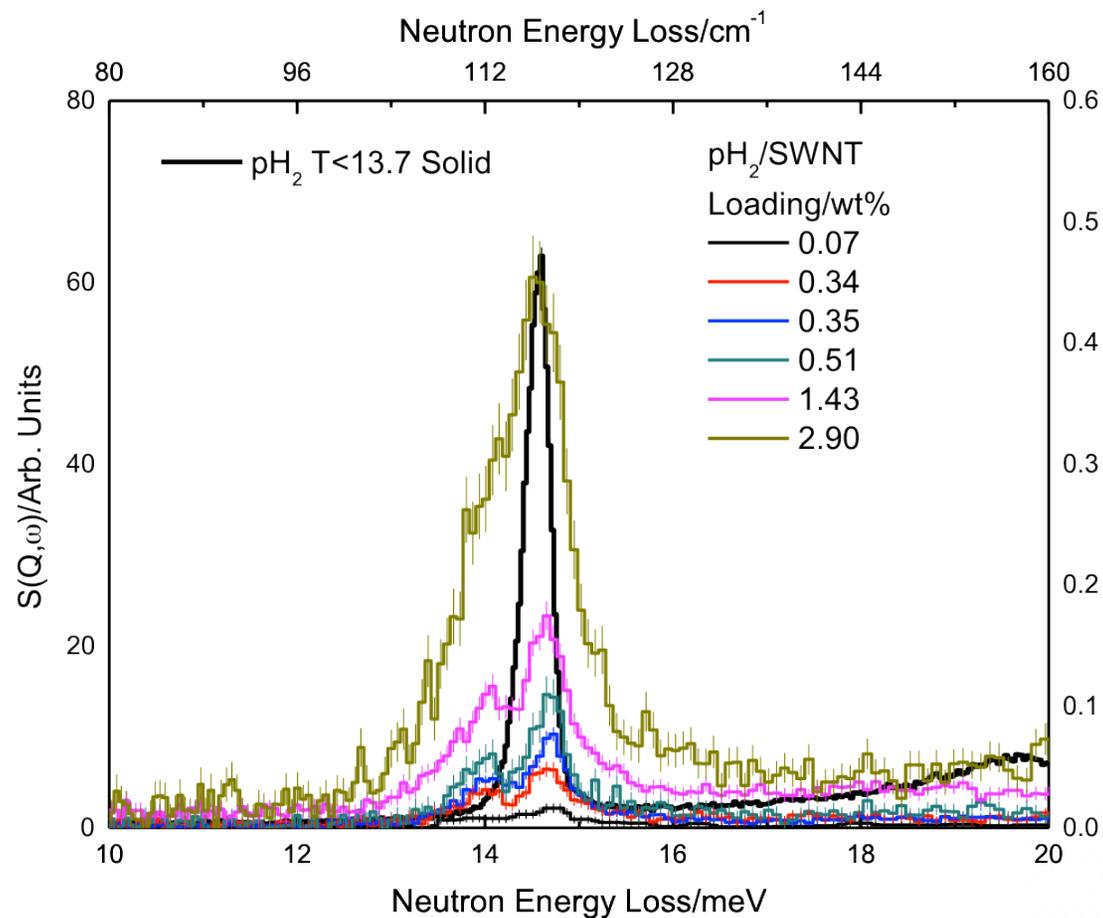
# Interaction of SWNT with Hydrogen



June 24, 2015

32 NXS2015

# Interaction of SWNT with Hydrogen

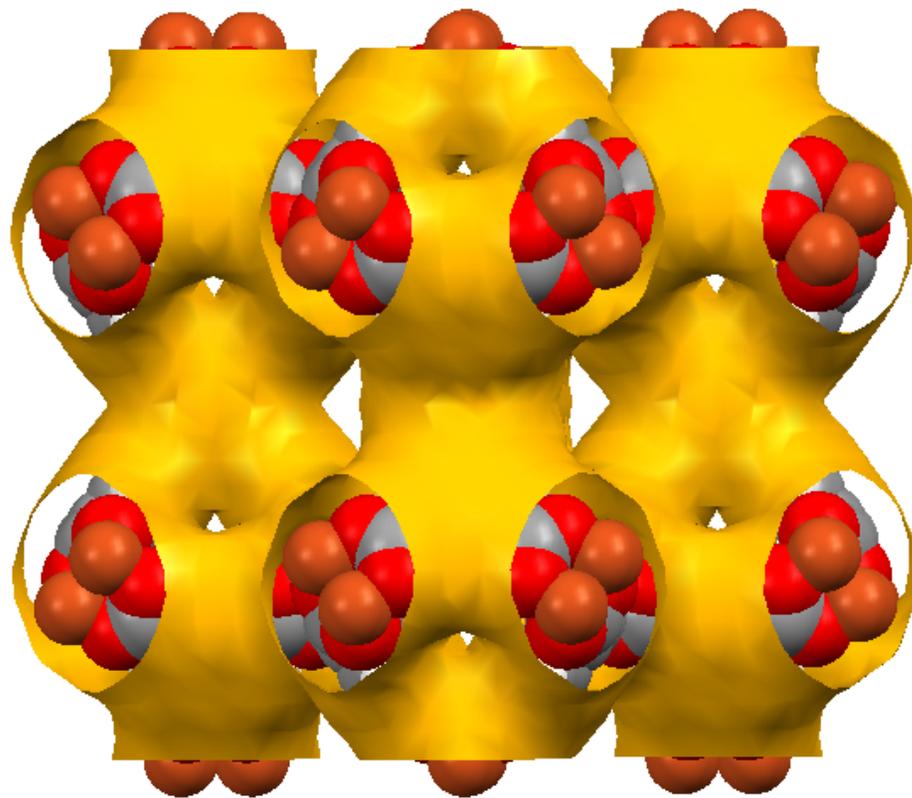


Rotational line splits  
Molecule aligns in one direction  
Probably along the grooves  
between the SWNT

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33 NXS2015

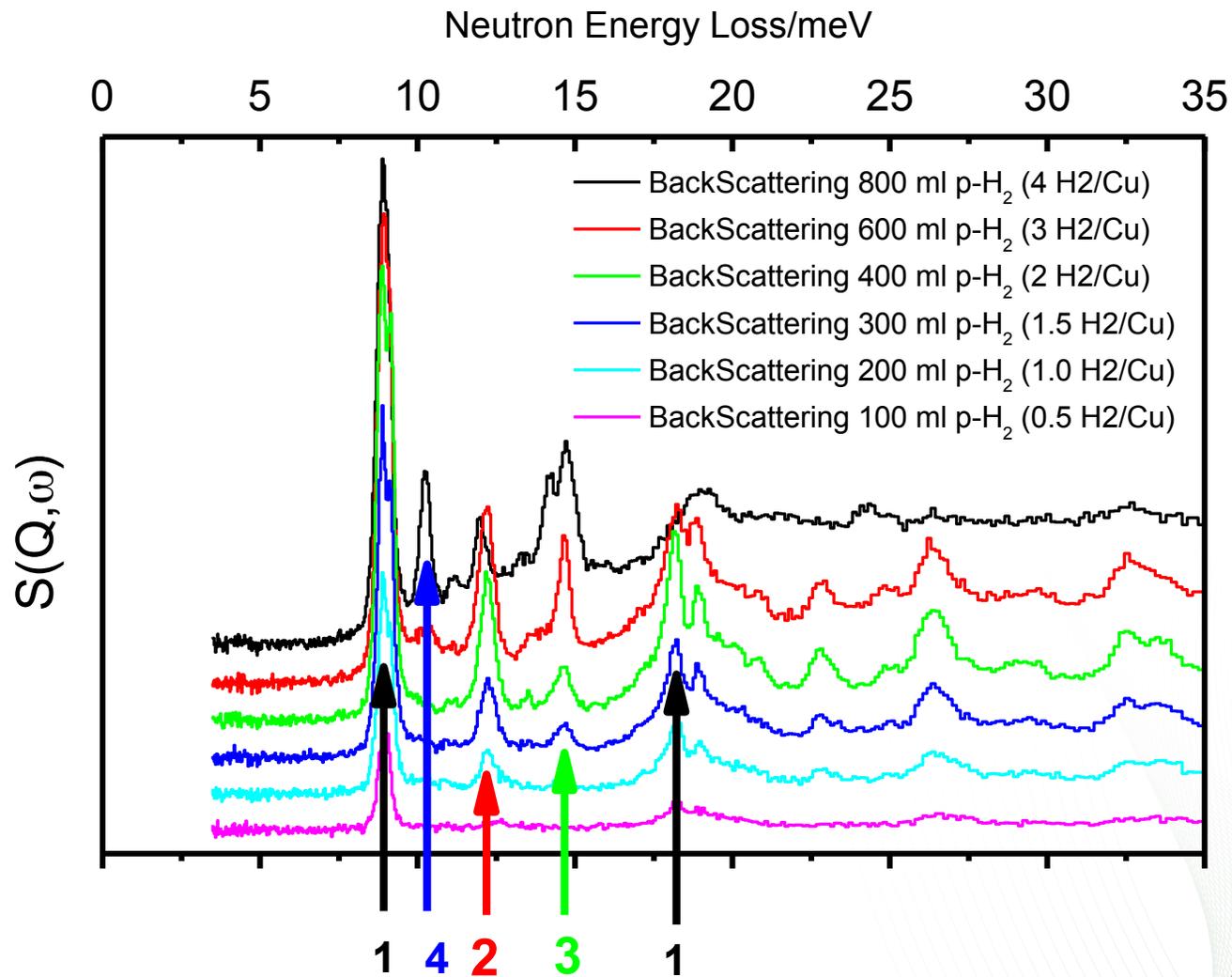
# Example #1 H<sub>2</sub> in Cu-MOF



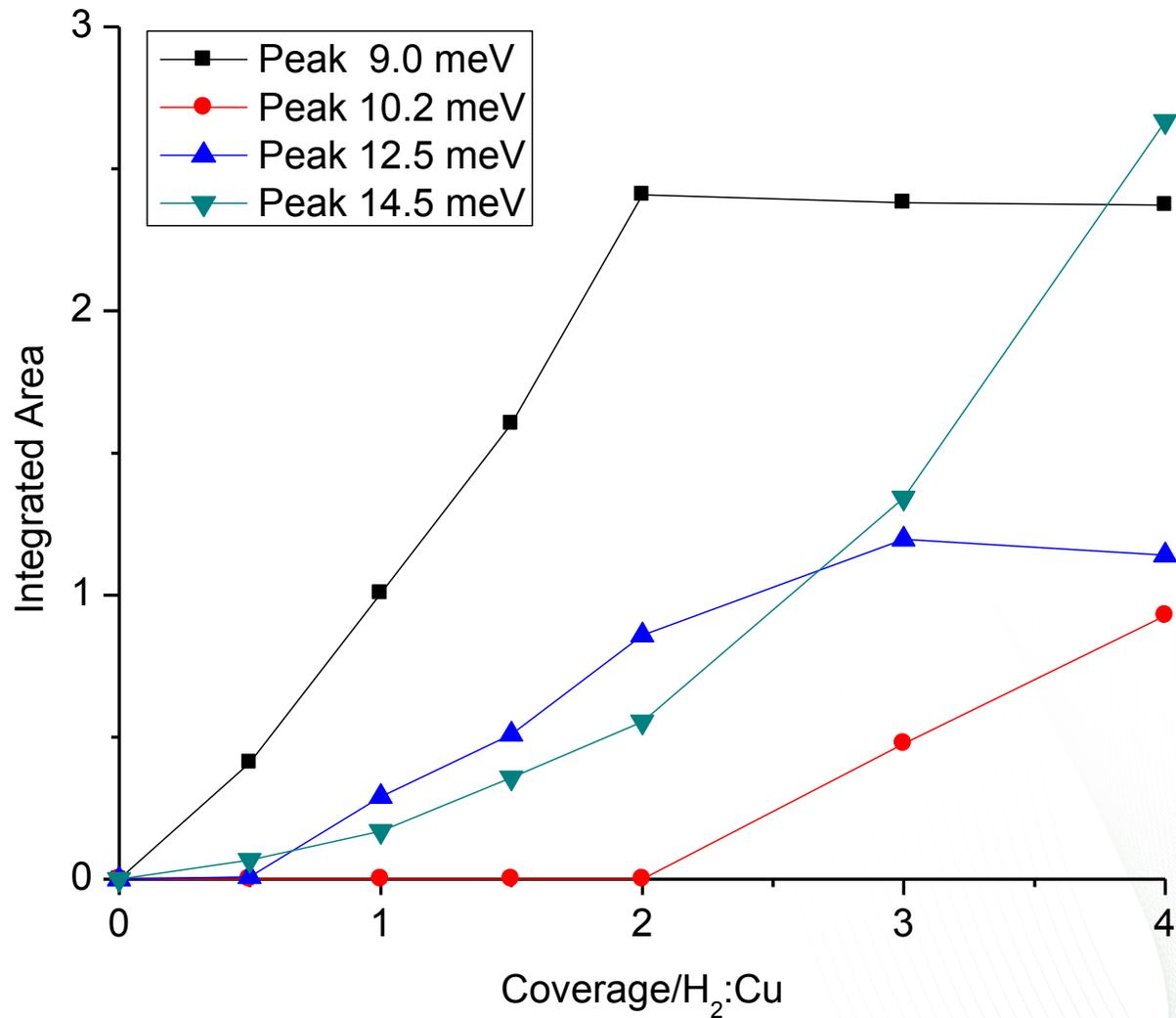
Franck Millange, Sam Callear, Richard Walton, Timmy Ramirez-Cuesta  
Chemical Physics 427 (2013) 9  
doi:<http://dx.doi.org/10.1016/j.chemphys.2013.07.020>.

June 24, 2015

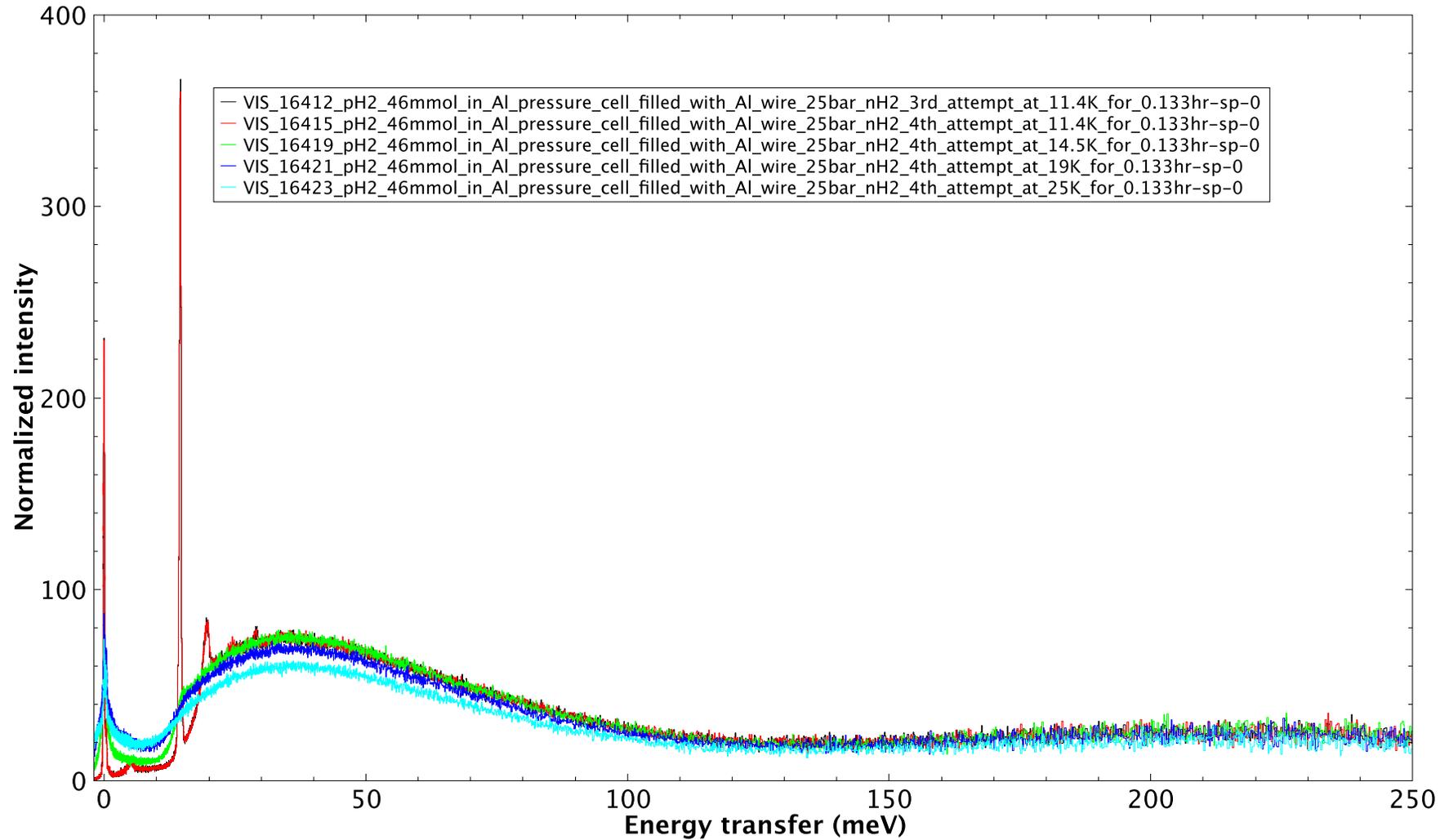
# H<sub>2</sub> in Cu-MOF #1



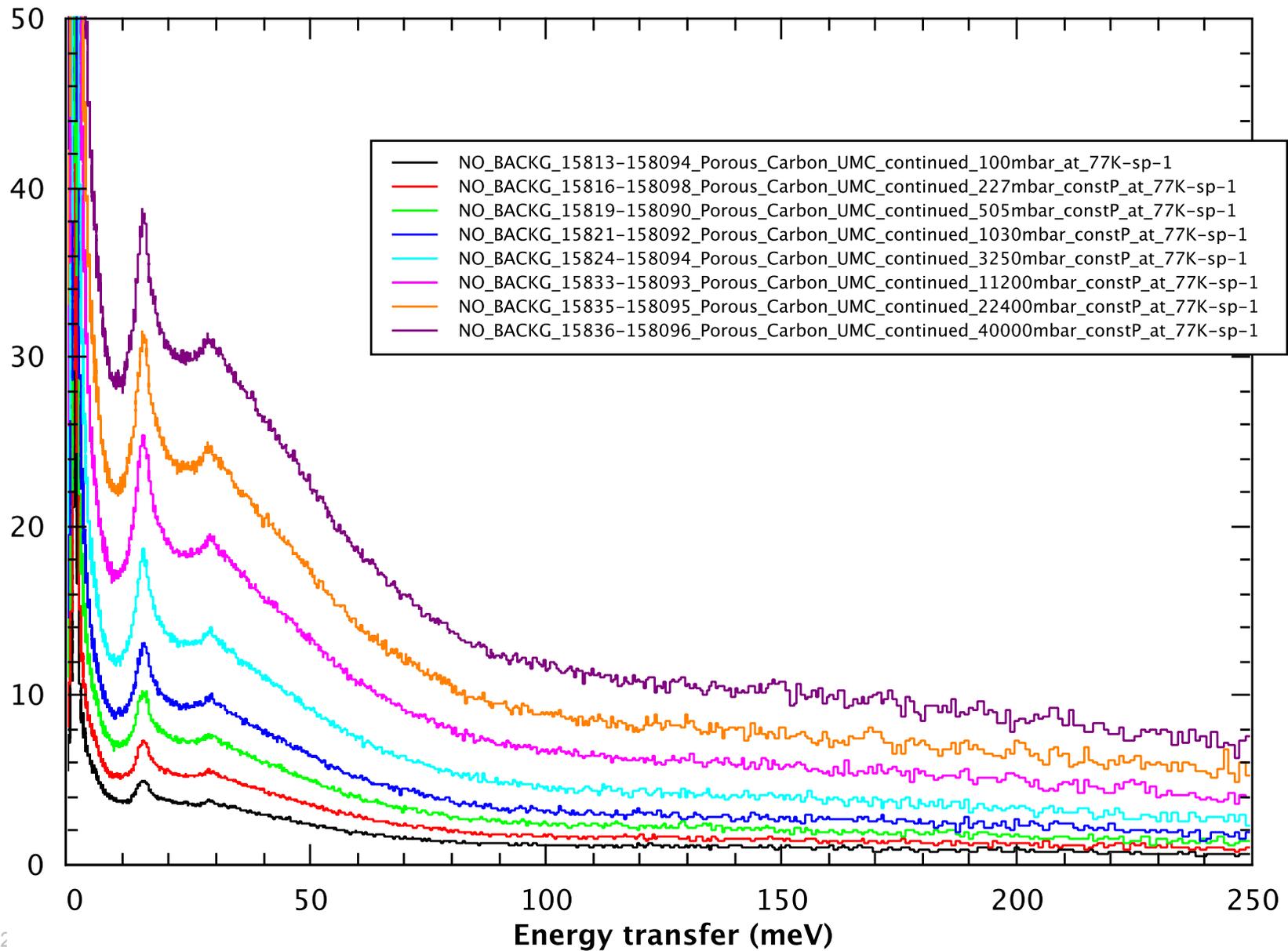
# H<sub>2</sub> in Cu-MOF #1



# Molecular hydrogen solid

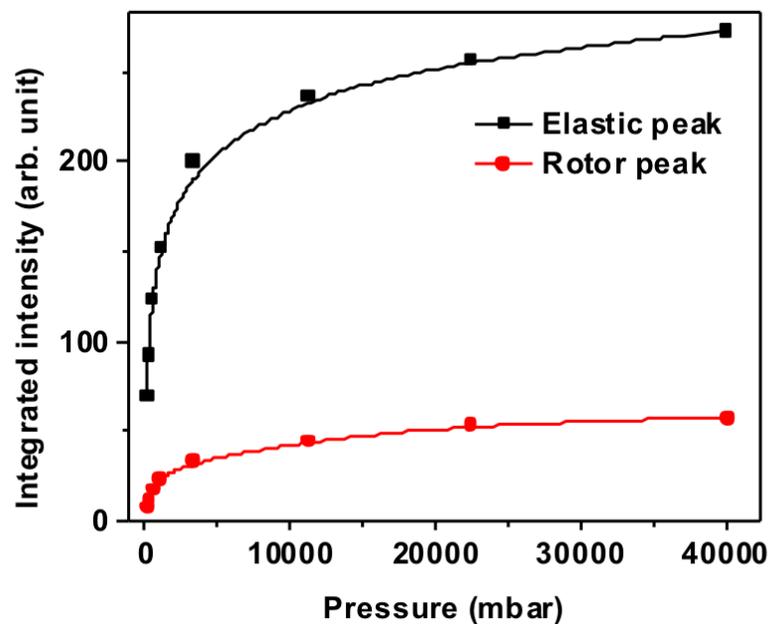
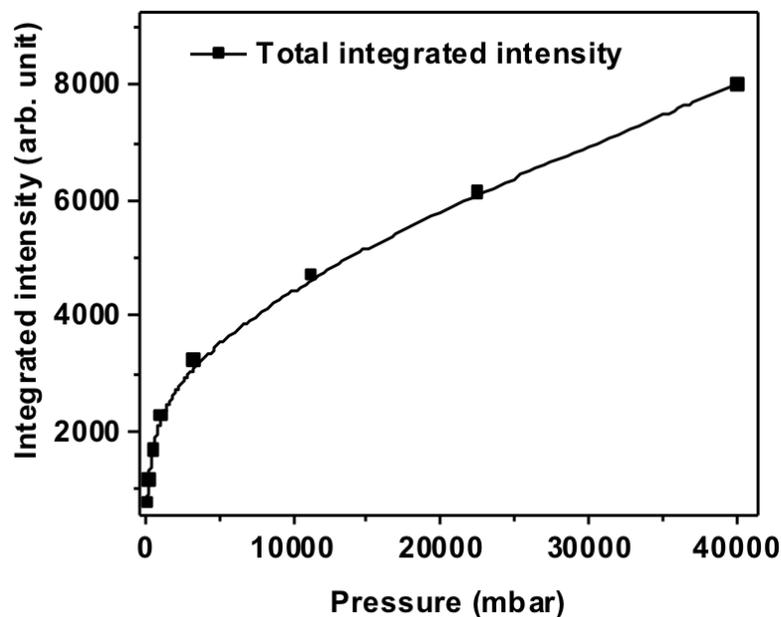


# Molecular hydrogen in porous carbon



# Molecular hydrogen in porous carbon

1. The total integral of the spectral intensity is proportional to the amount of hydrogen in the system (left plot)
2. The integrated area under the elastic peak is proportional to the amount of hydrogen that is in a liquid like and solid like phase (right panel)
3. The integrated area under the rotor line is proportional to the amount of hydrogen in solid like phase (right panel)

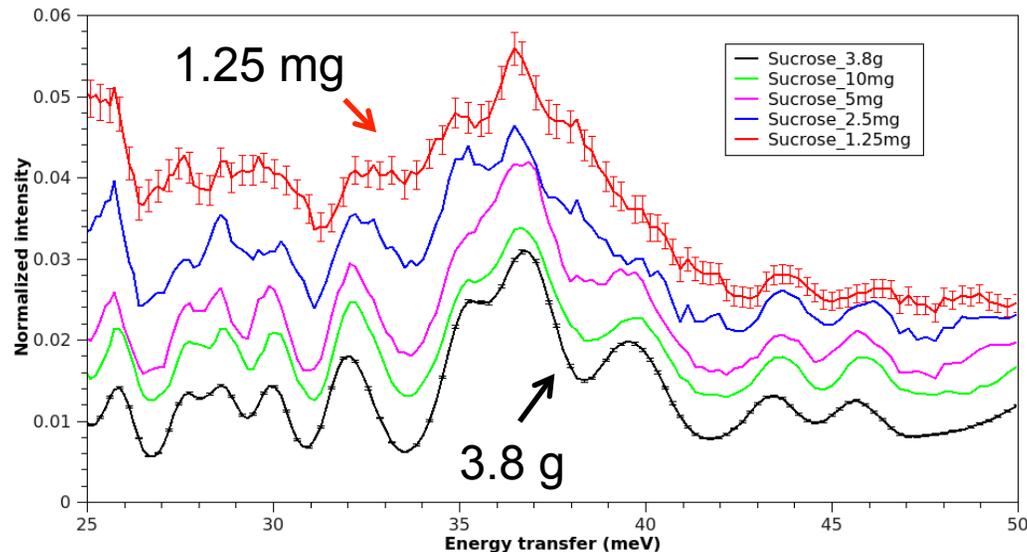


# The ultra-high sensitivity of VISION: INS measured on milligrams of samples

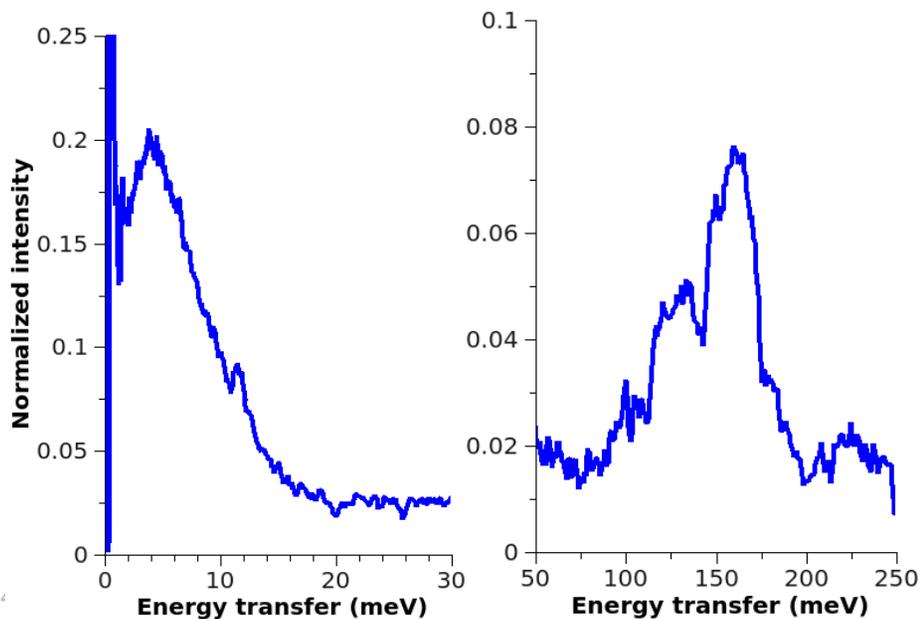
## 1.25 mg of sucrose (table sugar)



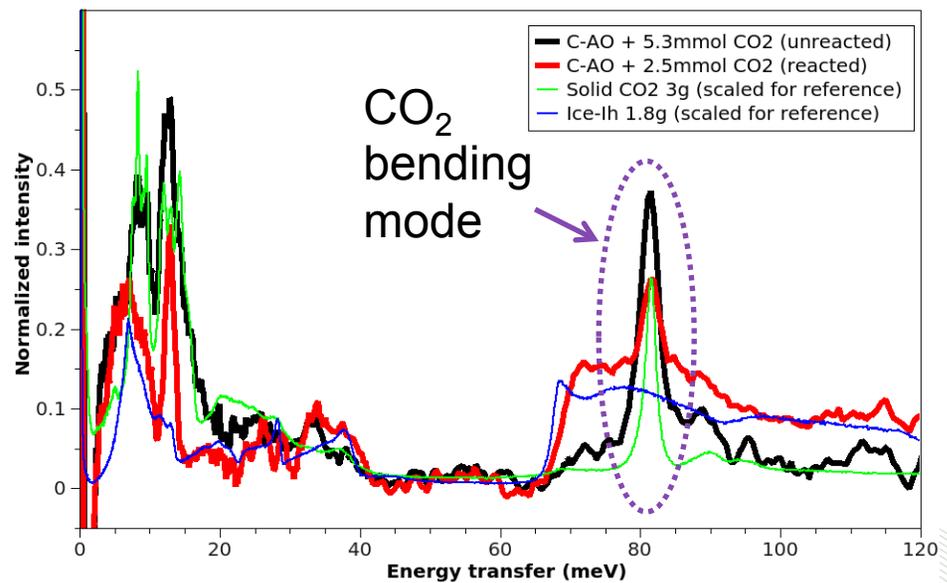
Sugar grains on Al foil (magnified, the total volume of the grains is about  $0.8 \text{ mm}^3$ )



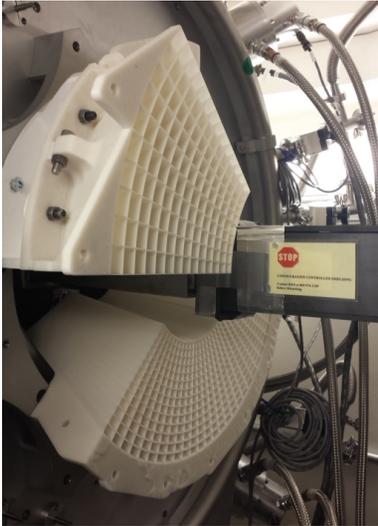
## 3 mg of polybenzene nanothreads



## 2.5 mmol of CO<sub>2</sub>

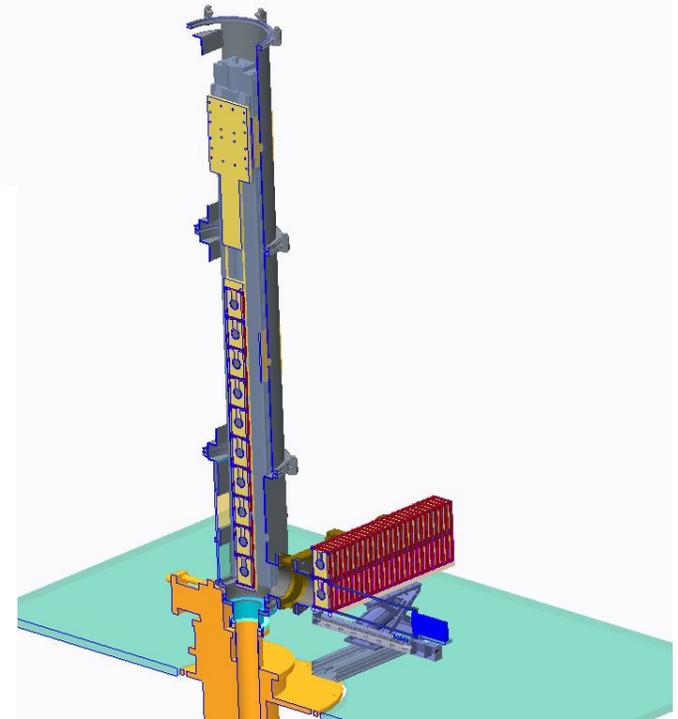
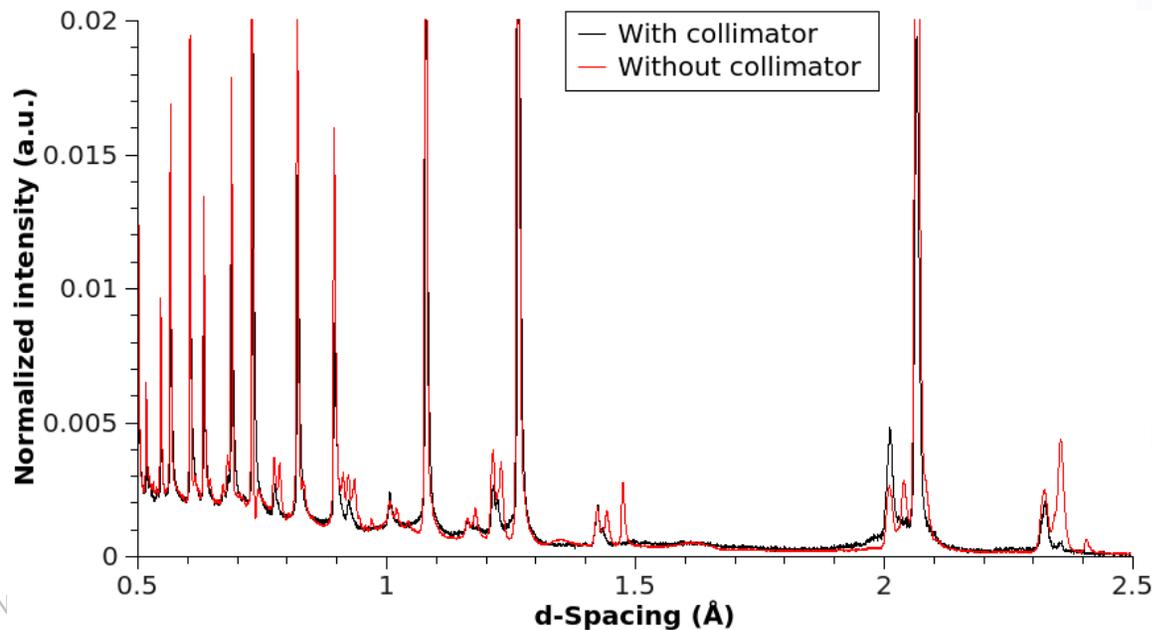


# VISION Sample changer and 3D printed collimator



3D printed collimators have been tested for VISION to be used in the backscattering diffraction bank. The reduction of the spurious peaks from the sample is very much noticeable.

The high throughput rate of VISION requires very rapid sample changes to make the best use of neutron beamtime and run mail-in program. A sample changer design is being finalized and will be tested December 2015



# Questions?