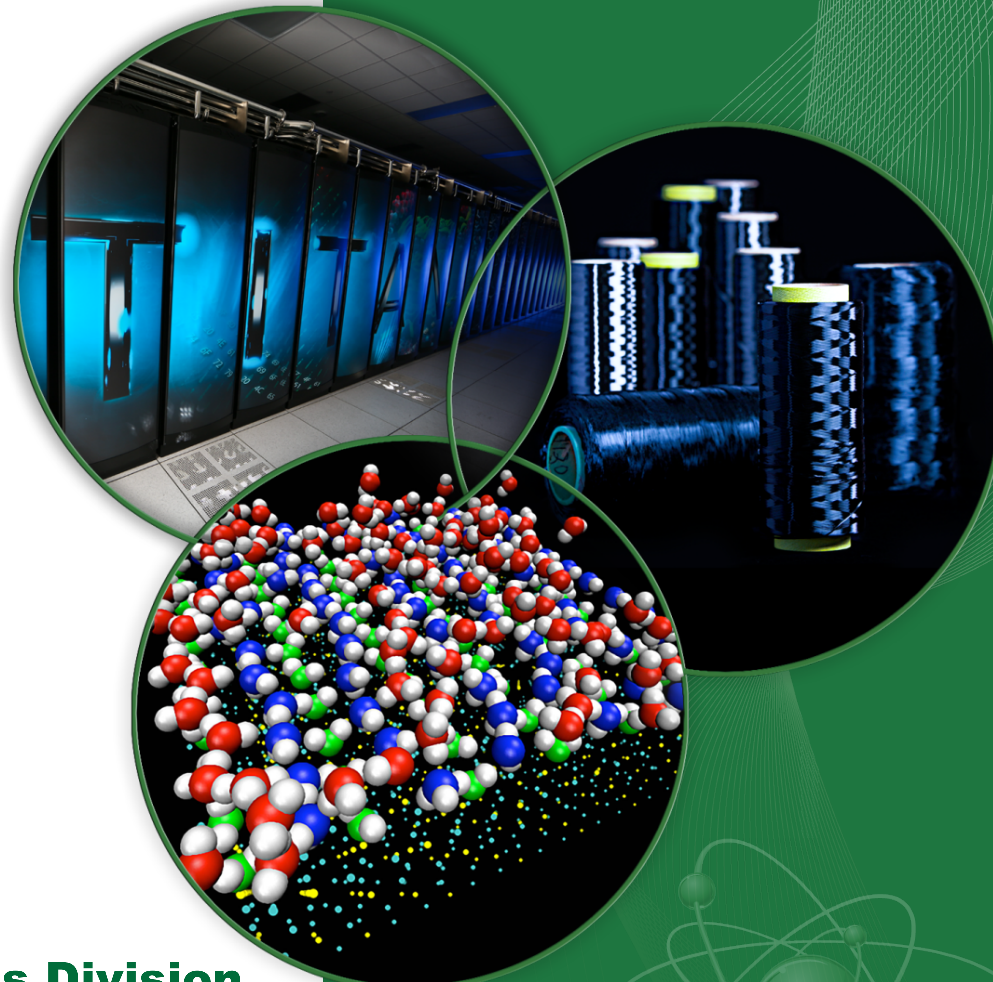
Neutron Vibrational Spectroscopy

"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

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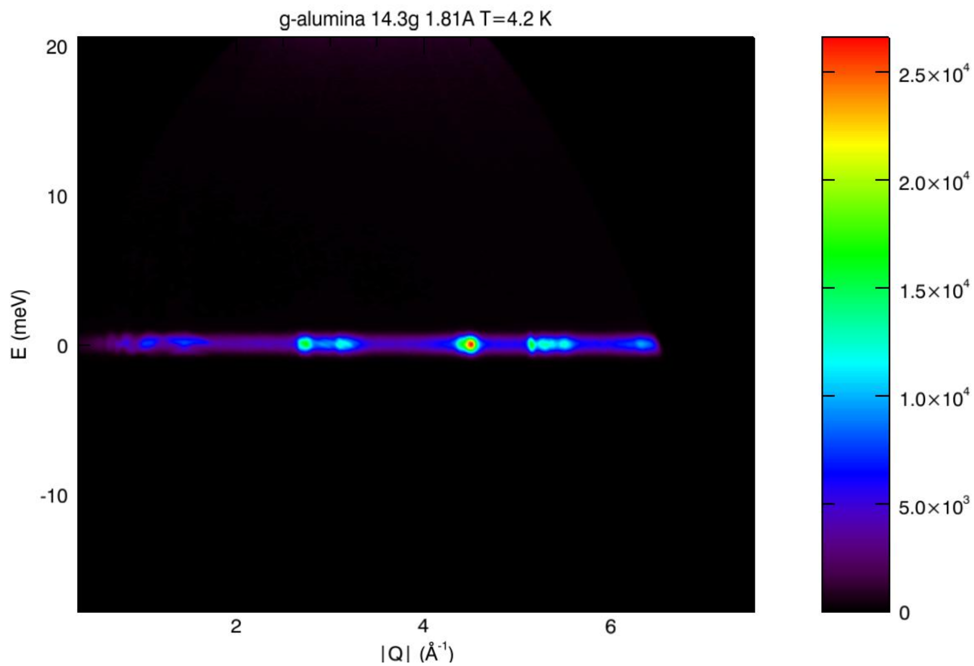
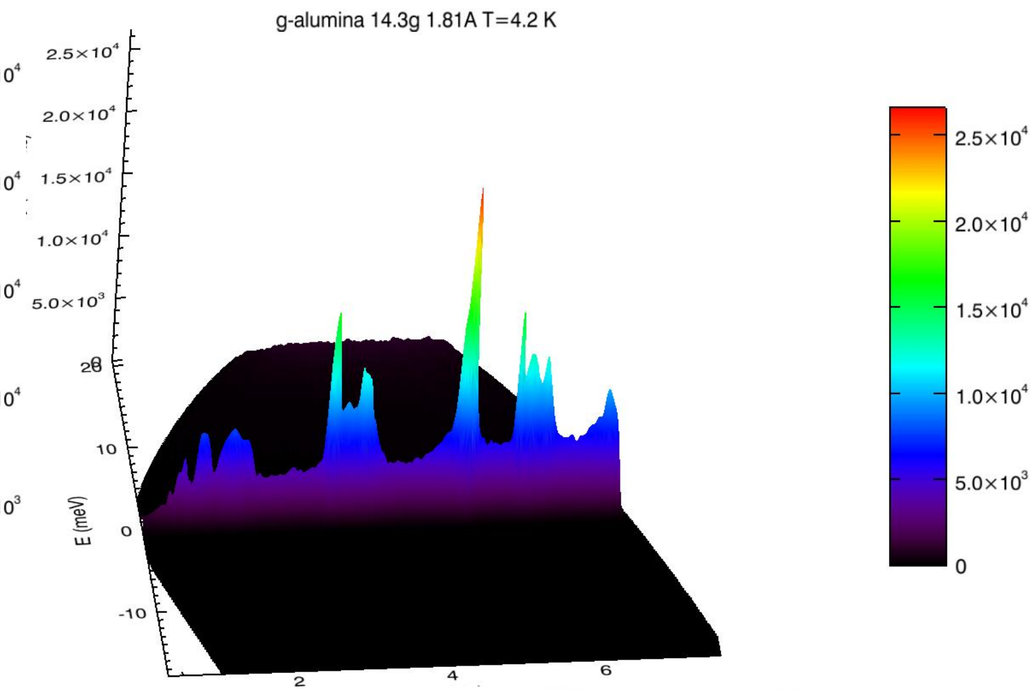
The S(Q,ω) Map



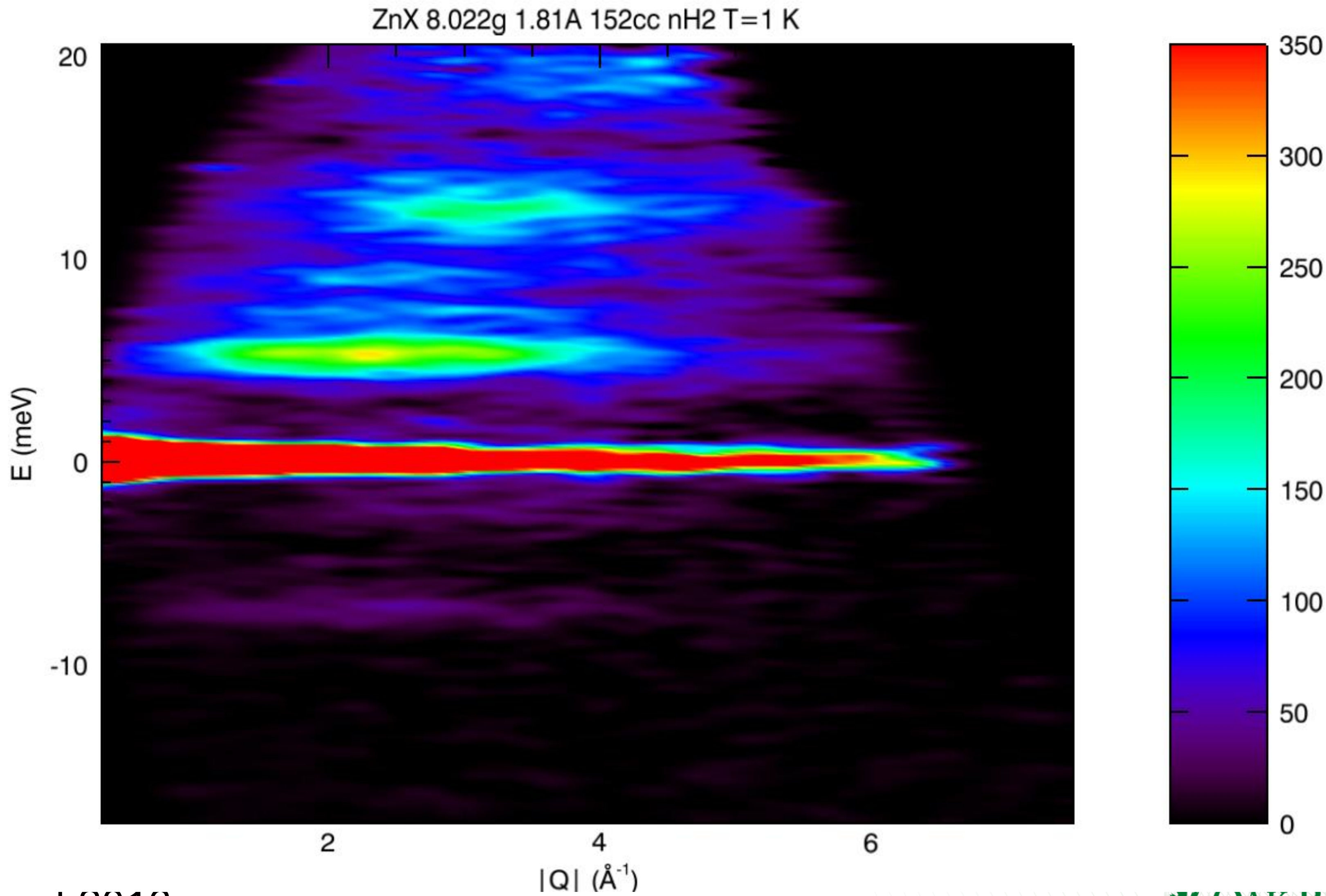


ω=0 Elastic Scattering Diffraction

Structural Information

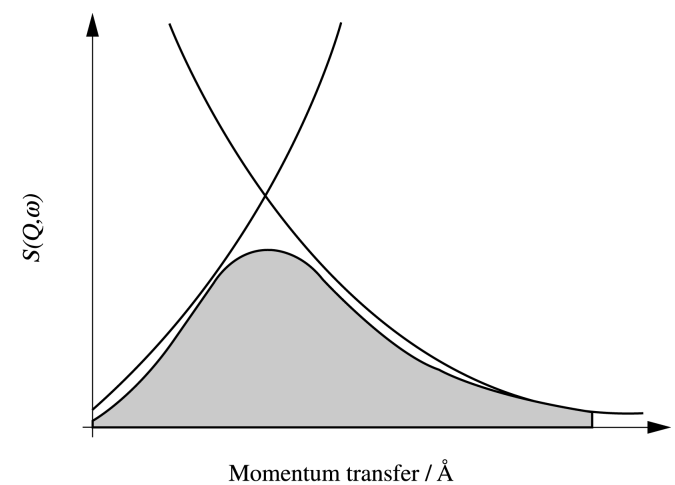
2 August 2016

The S(Q,ω) Map


ZnX 8.022g 1.81A 152cc nH2 T=1 K
20
10
0
-10
E (meV)
2
4
6
|Q| (Å-1)
350
300
250
200
150
100
50
0

Inelastic Neutron Scattering

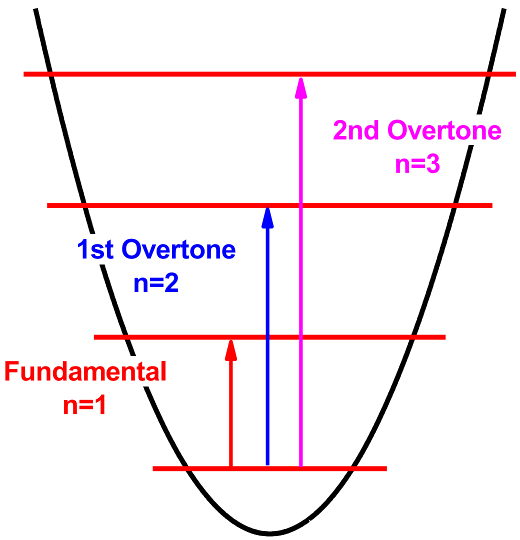
- Interaction between probe and nucleus
- Simultaneous transfer of energy and momentum by the same neutron
- Transitions are proportional to the amplitude of motion and the cross section of the nuclei.
- No selection rules.
- In this presentation I will be talking about incoherent INS and powders
- For incoherent inelastic neutron scattering, the spectral intensity is given by:

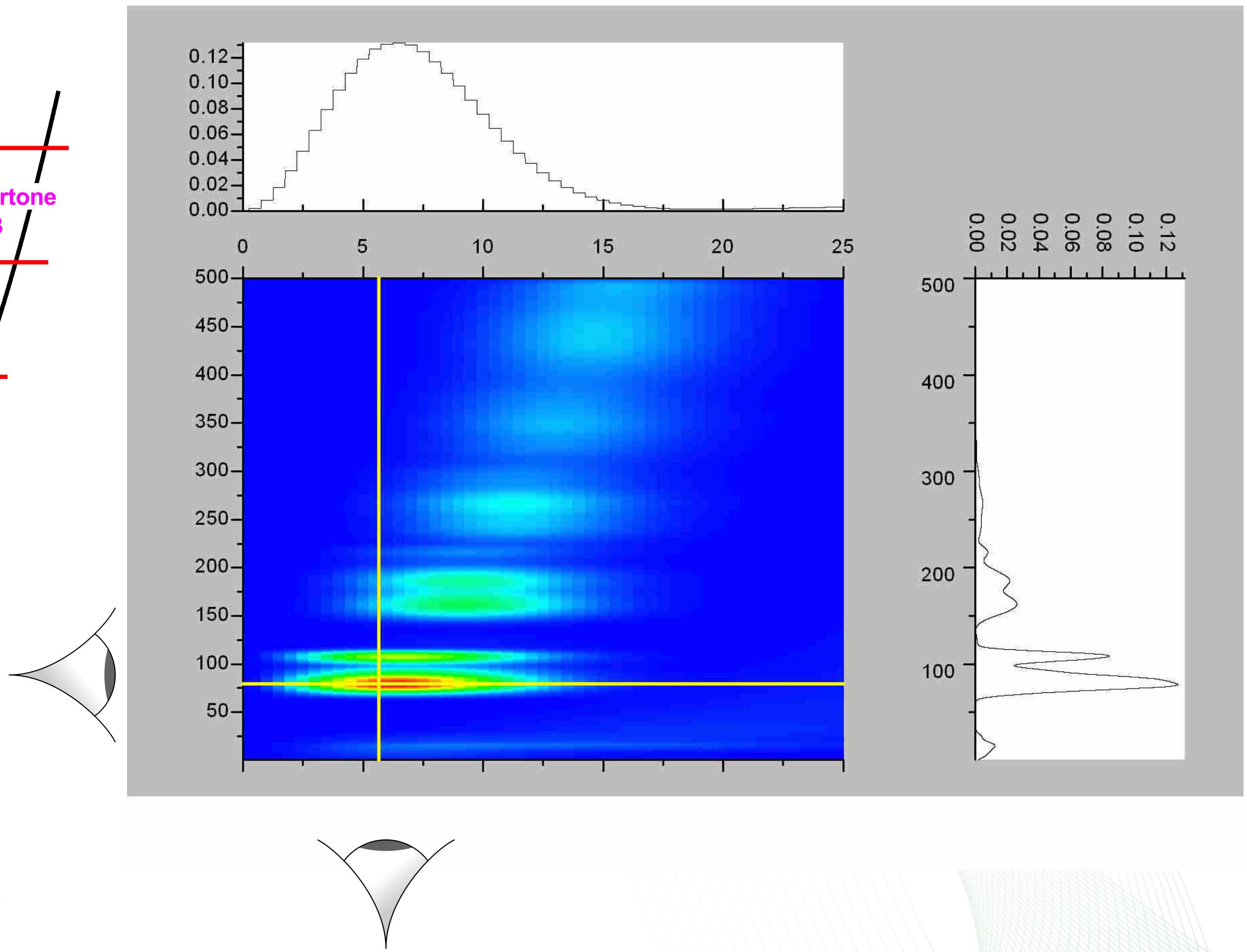


$$S(\mathbf{Q},\omega_v)_l^n = \sigma_l \frac{\left[\left(\mathbf{Q}\cdot \boldsymbol{u_{lv}}(\mathbf{Q})\right)^2\right]^n}{n!} \exp\left[\frac{1}{3}\left(\mathbf{Q}\sum_v \boldsymbol{u_{lv}}(\mathbf{Q})\right)^2\right]$$

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**, 2005

The S(Q,ω) Map Fundamental

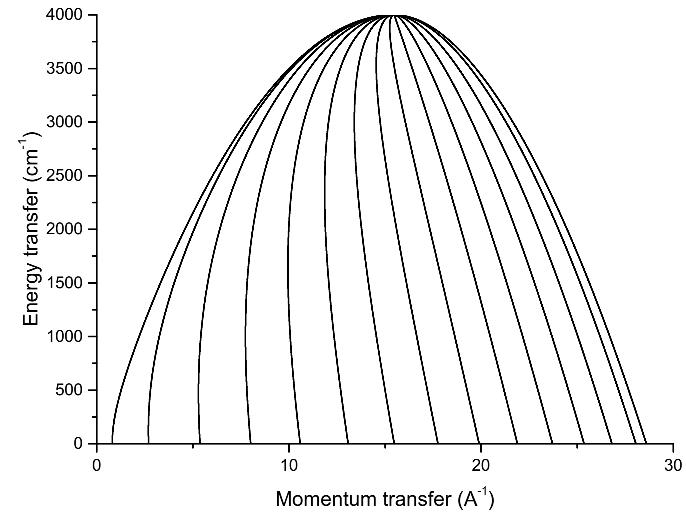




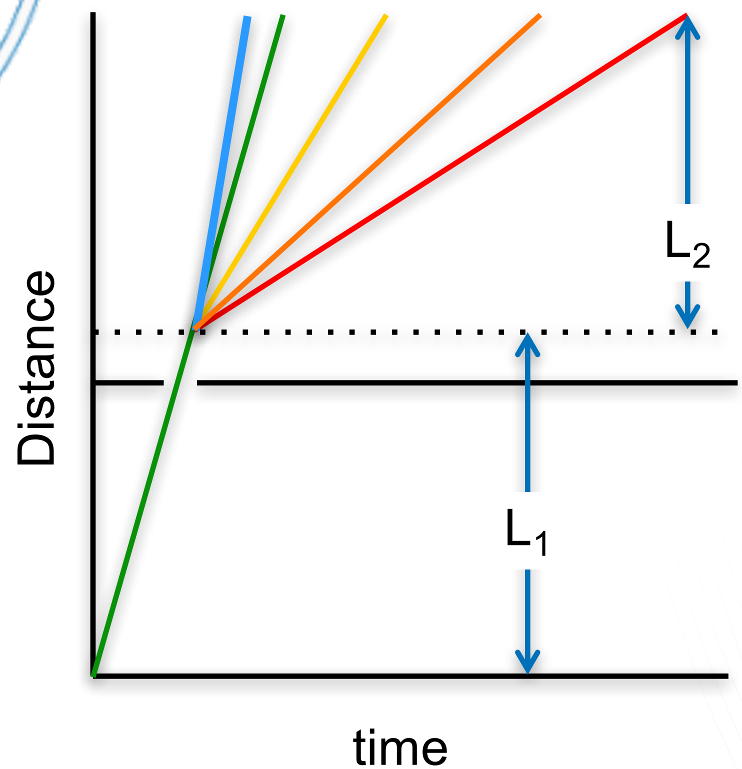
Overtones & combinations are very much apparent. Particularly if there is hydrogen in the system. This is a kinematic effect. The overtones fall within a parabola with a curvature associated with the mass of the scatterer atom.

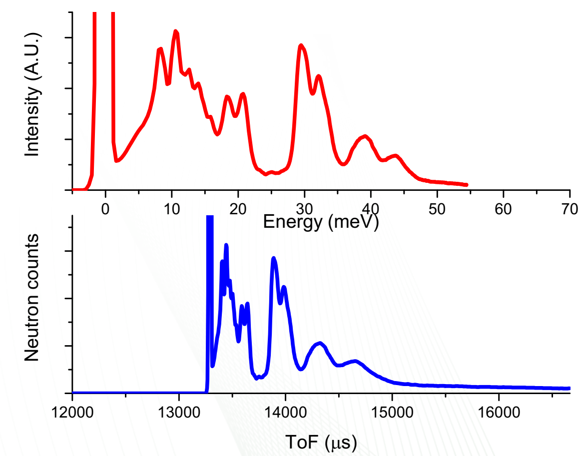
How to measure INS (1)
Direct Geometry Instrumentation

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

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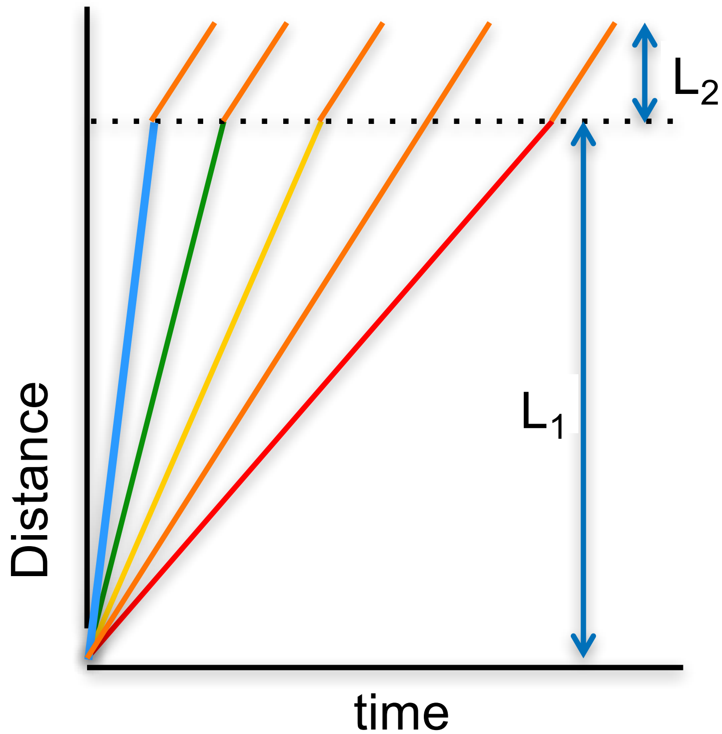
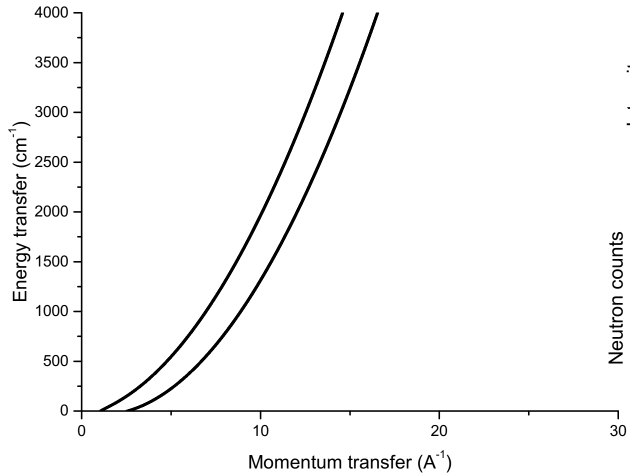
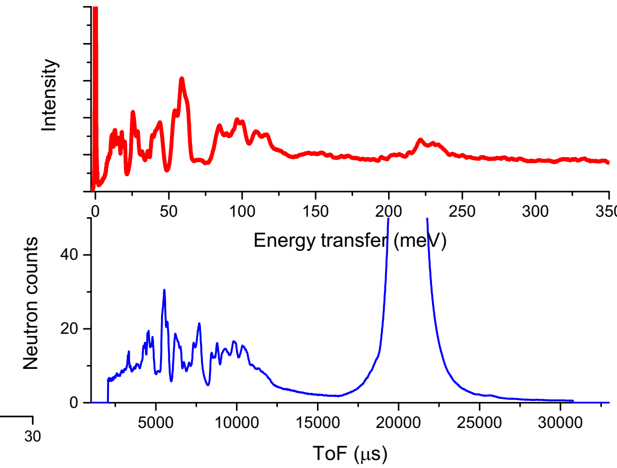
How to measure INS (2)
Indirect Geometry Instrumentation

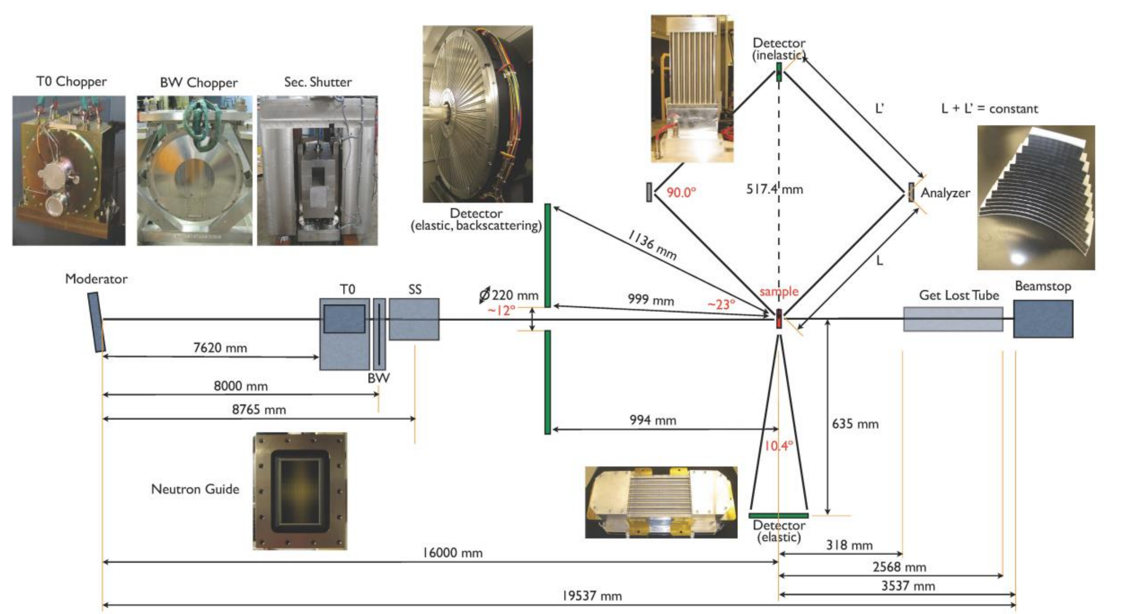






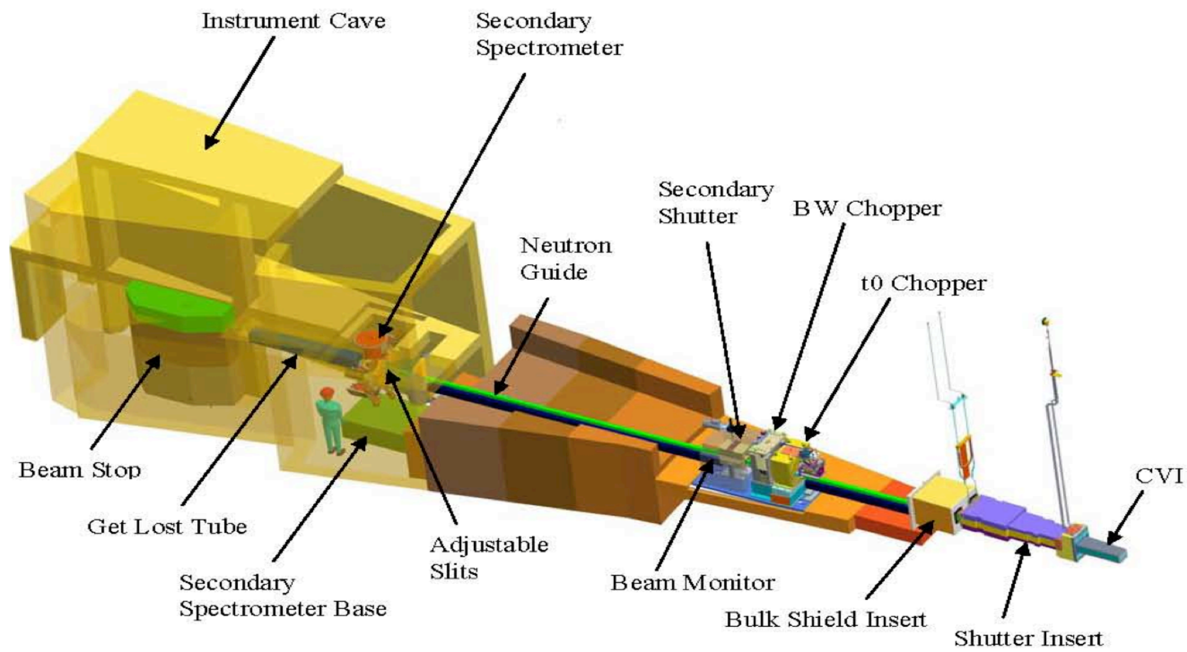
Resolution is almost constant in units of Δω/ω~1.5%

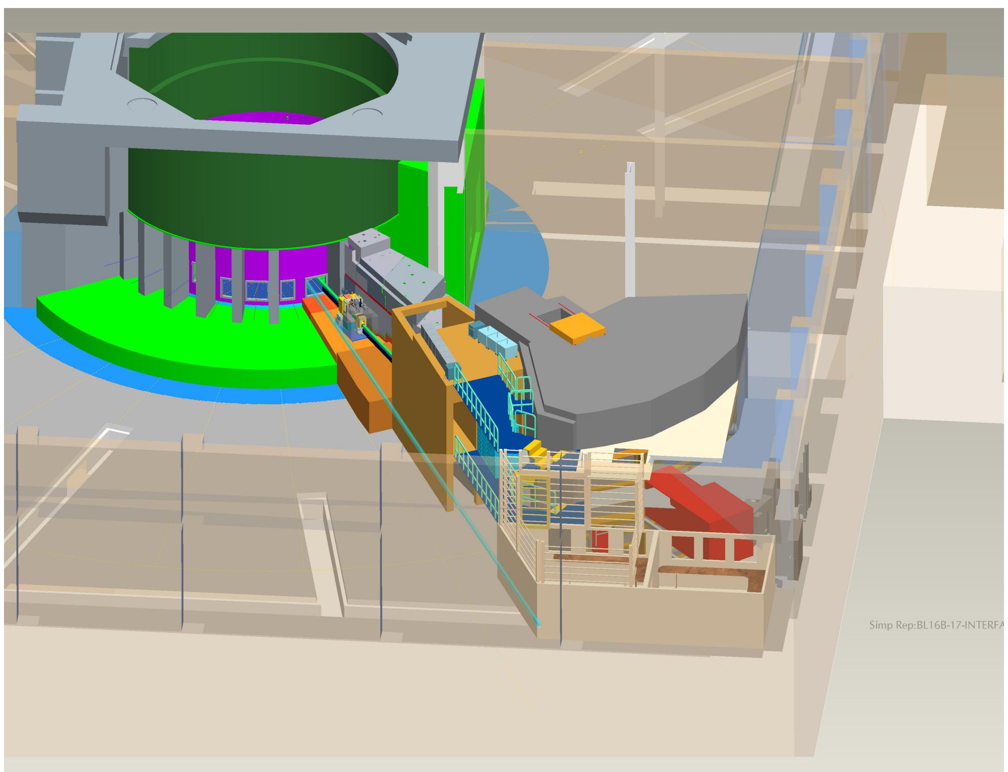
Incident neutron beam is white. We fix the energy of the scattered neutrons using a analyzer and filter device.
That fixes T_2. We measure the ToF and we can work out T_1.

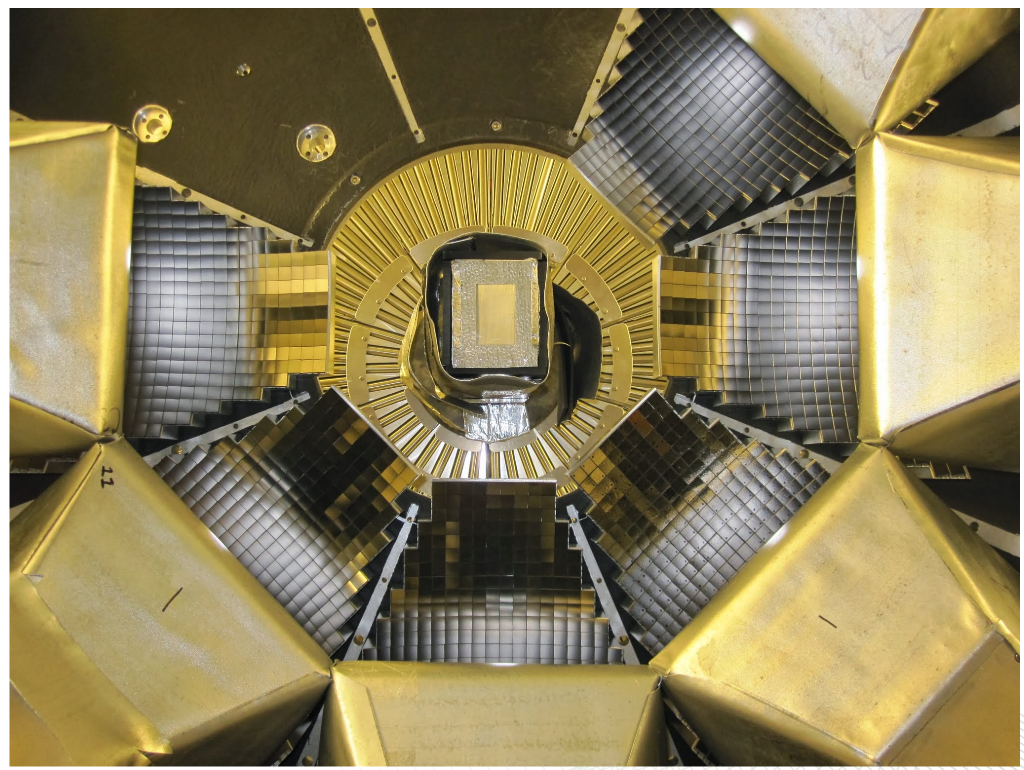


VISION @ SNS

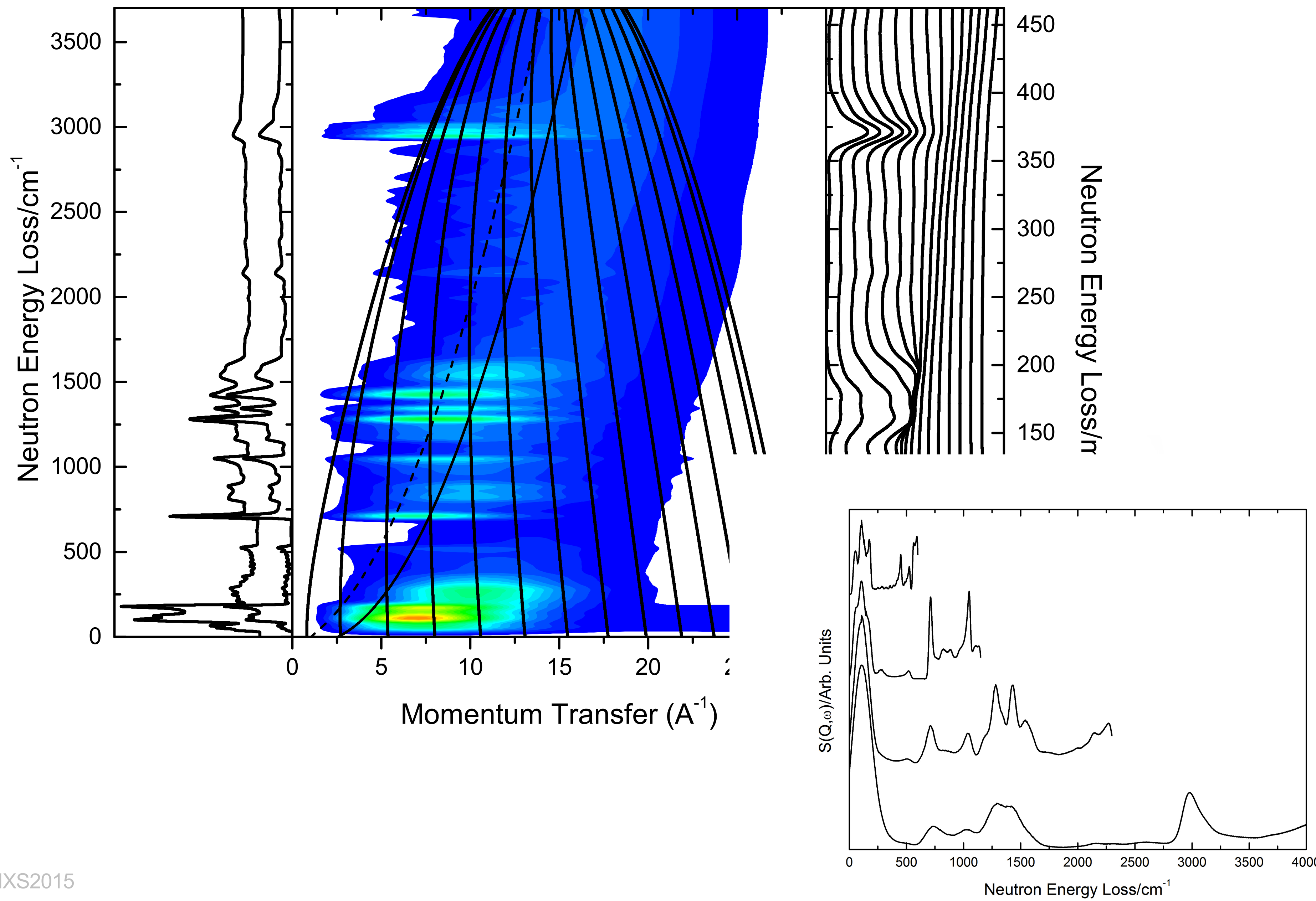
This instrument is up to 4000x its predecessor





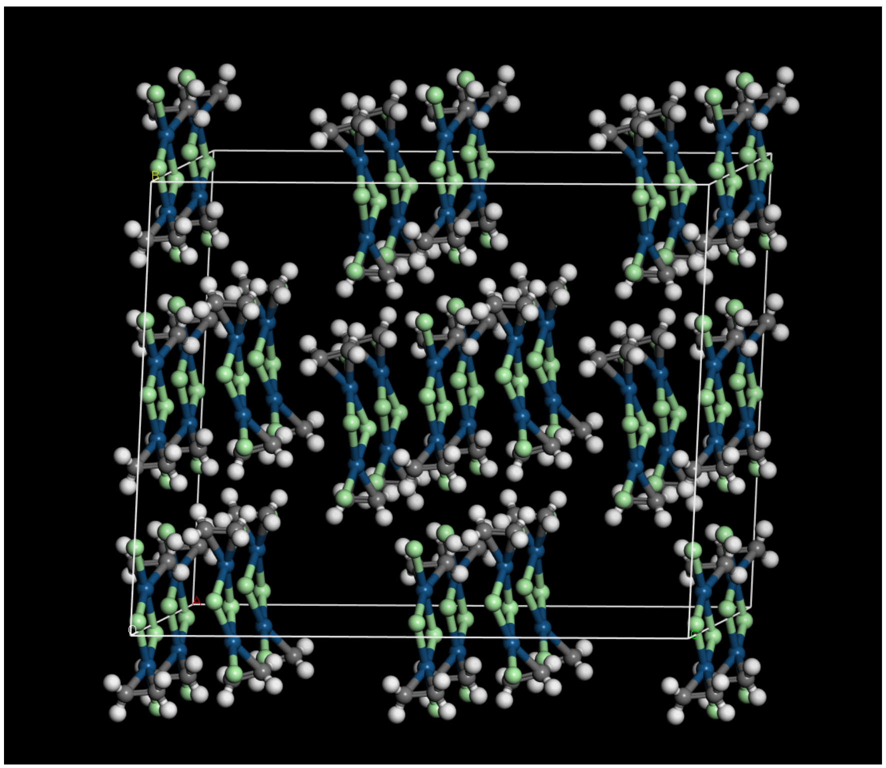


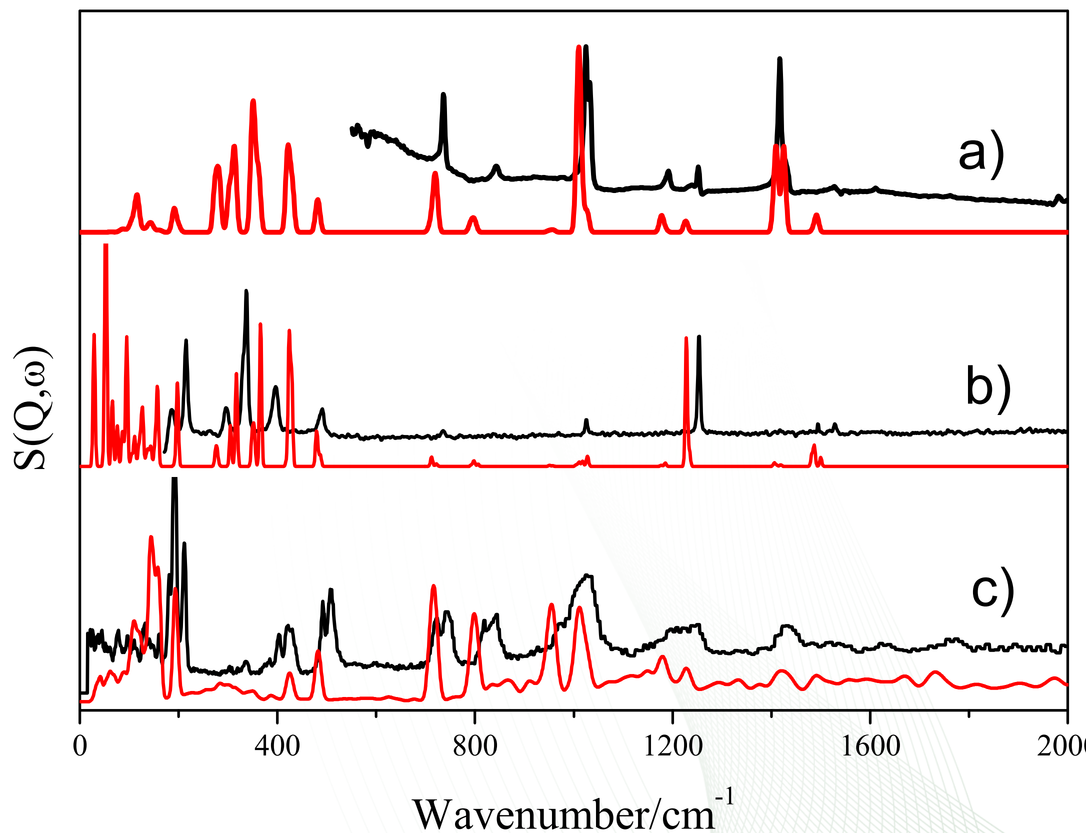
The S(Q,ω) Map


Neutron Energy Loss/cm^{-1}
3500
3000
2500
2000
1500
1000
500
0
0
5
10
15
20
Momentum Transfer (A^{-1})
450
400
350
300
250
200
150
Neutron Energy Loss/n
S(Q,ω)/Arb. Units
0
500
1000
1500
2000
2500
3000
3500
4000
Neutron Energy Loss/cm^{-1}

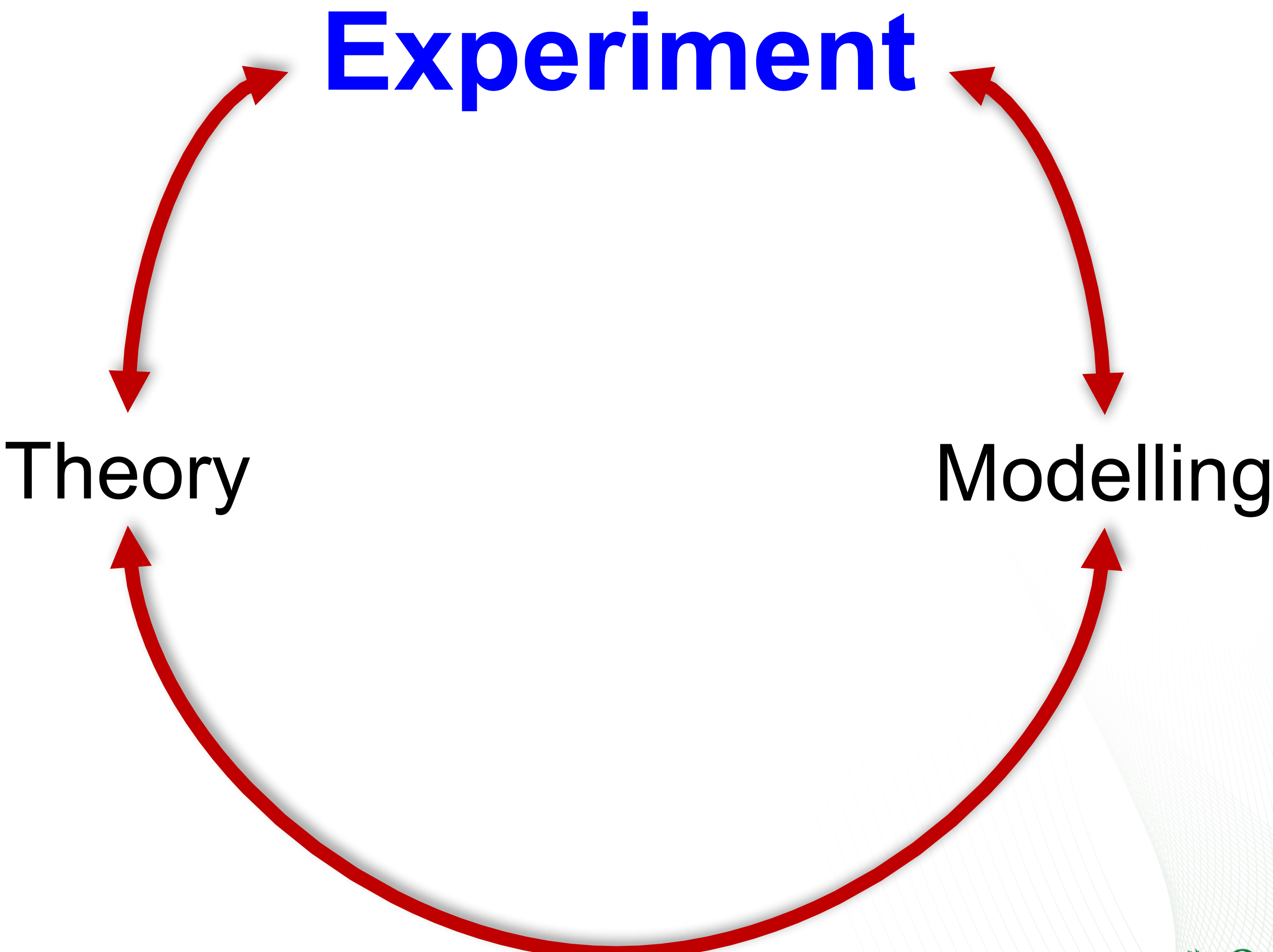
INS and other vibrational tools

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

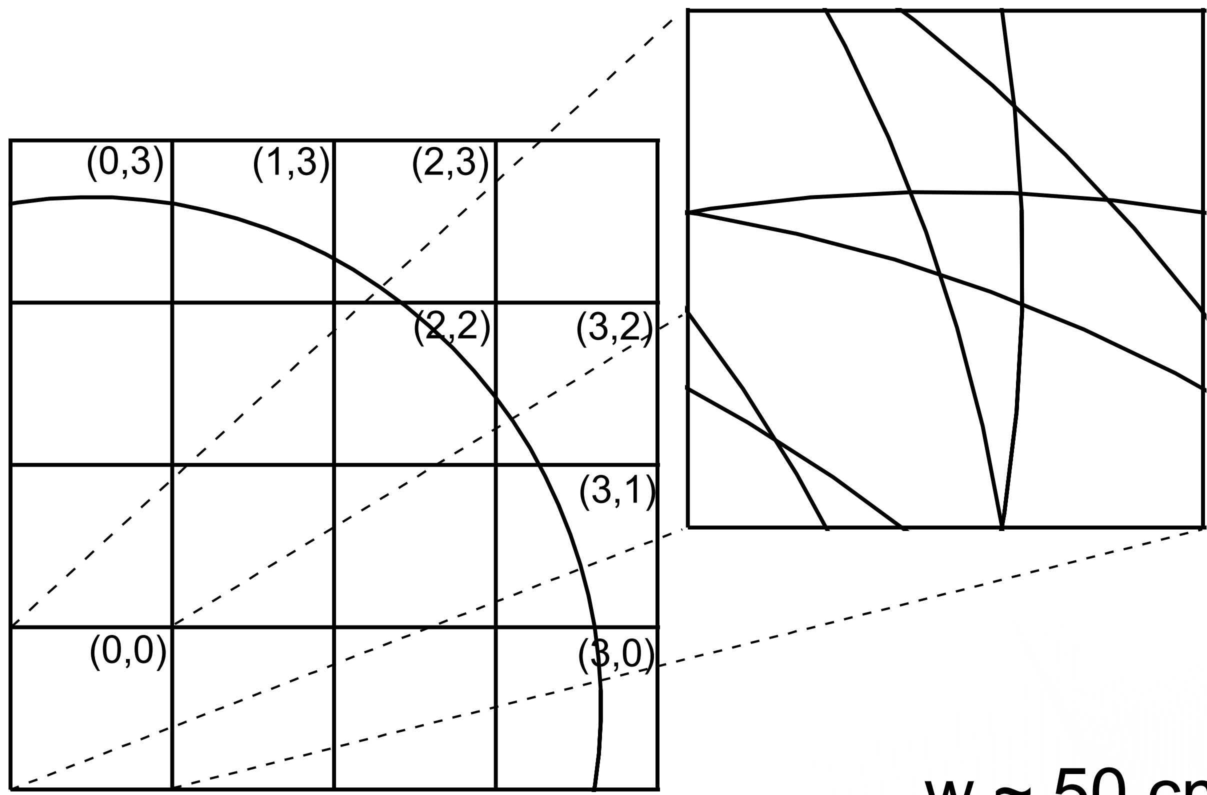




Playing the game



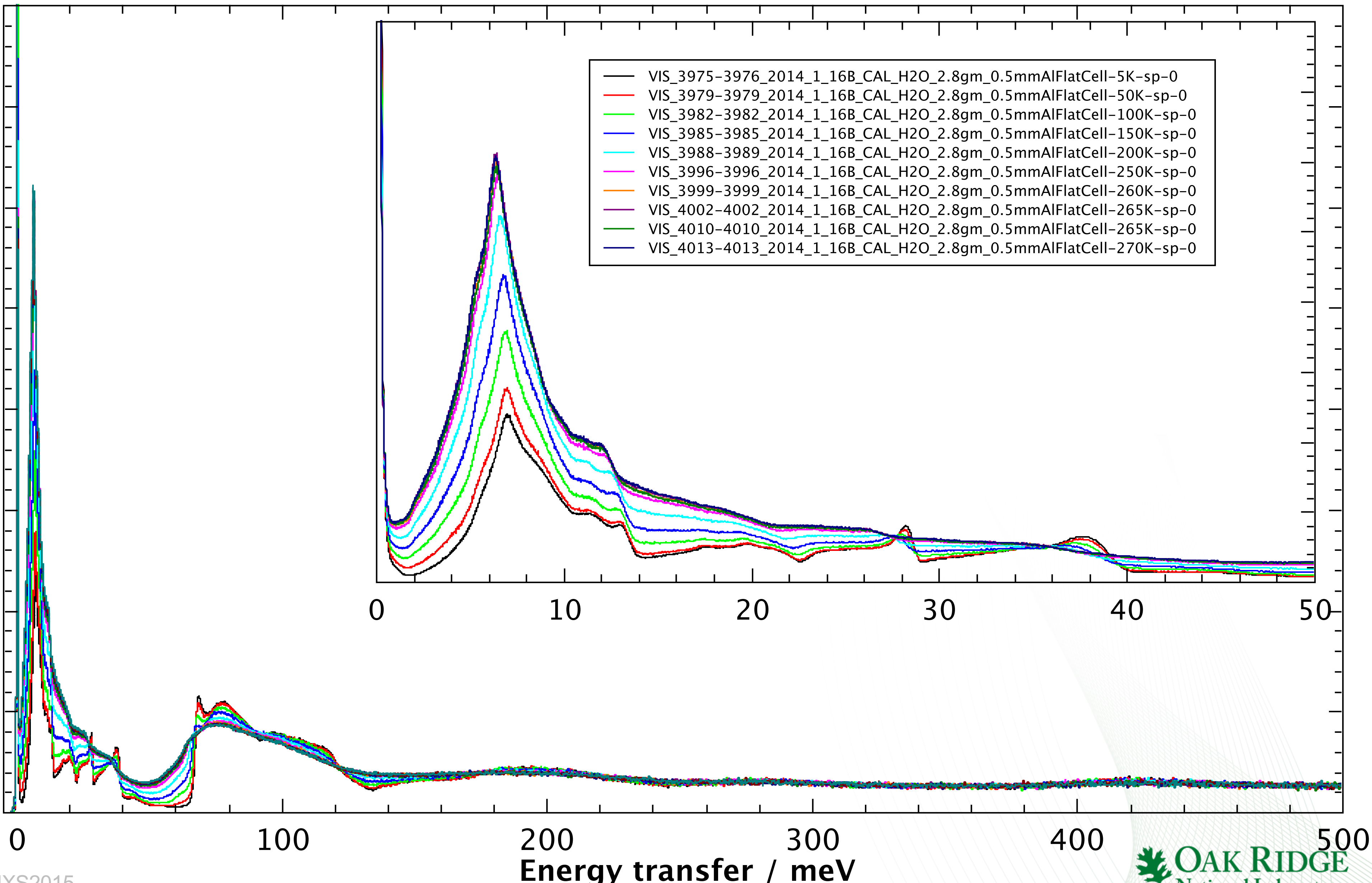
Powder Average



w ~ 50 cm^{-1}

Uniform sampling of the Brillouin zone

Water in VISION (as function of temperature)



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.

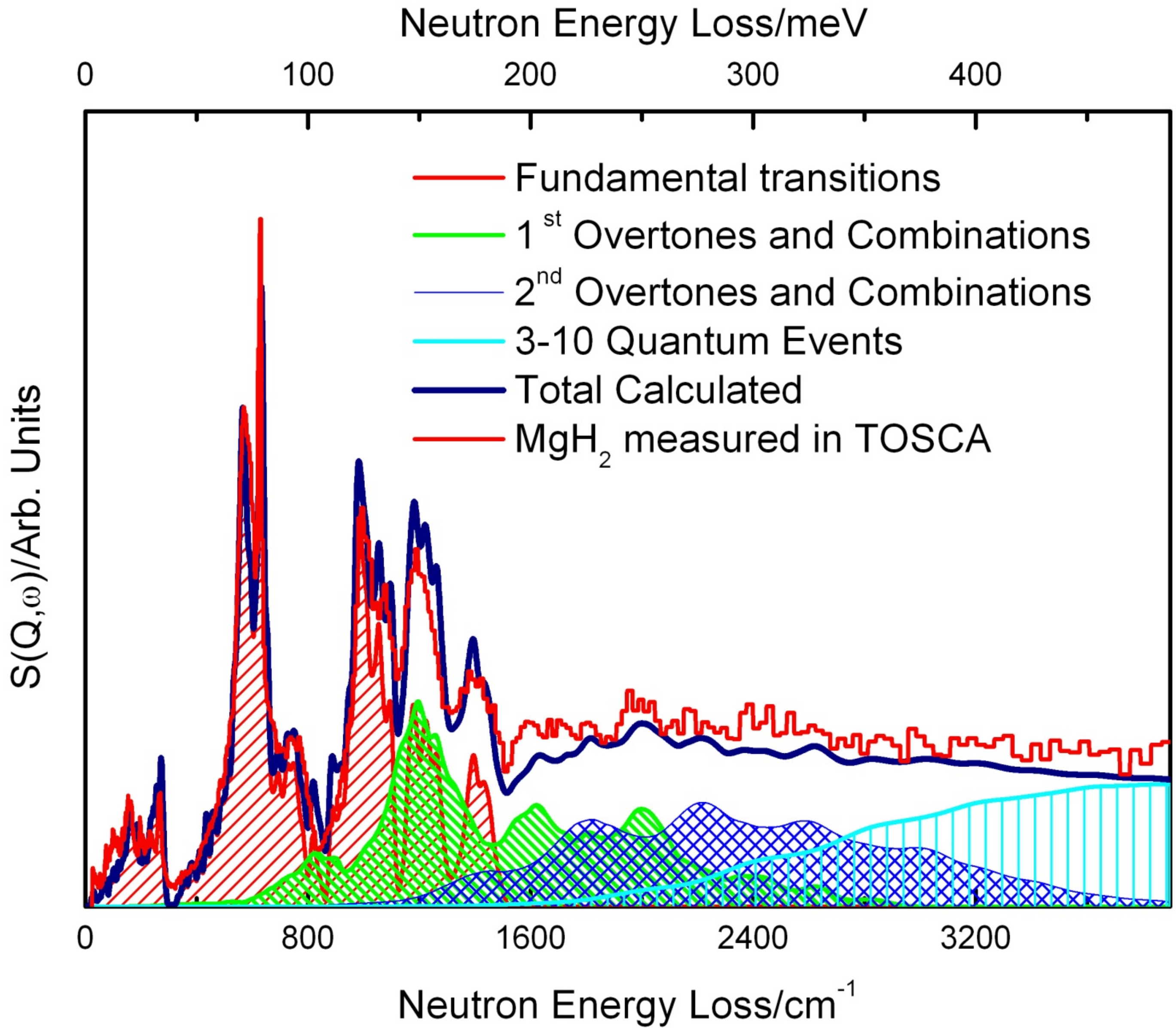
Computer Physics Communications **2004**, *157*, 226-238

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

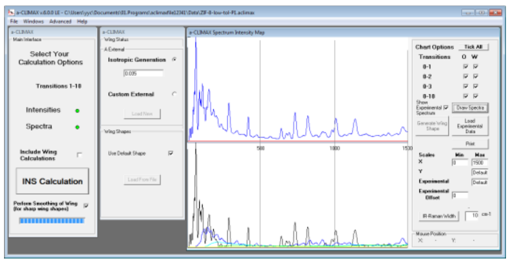
Vibrational Spectroscopy with Neutrons, World Scientific: London, **2005**
Chemical Physics **2005**, 317, 119–129.
Macromolecules **2006**, 2683–2690.

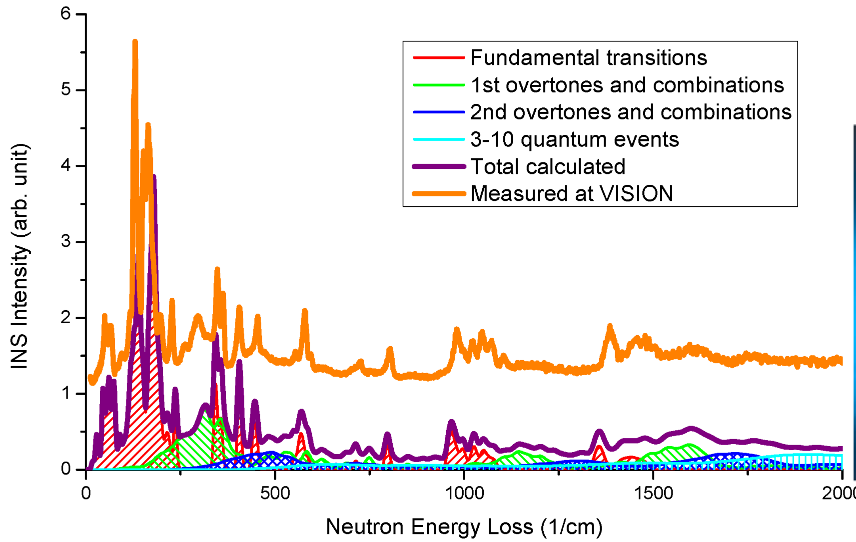
Example MgH_2



Integrated modeling for data interpretation

Today this is what we do at **VISION** using **VirtuES** (Virtual Experiments in Spectroscopy)
High throughout





CASTEP
VASP
Quantum Espresso
Gaussian
→ Vibrational modes and frequencies → INS simulation (aClimax) → Simulated INS spectra

Sample → VISION → Data reduction and analysis (Mantid) → Measured INS spectra; Measured diffraction

→ Peak assignment
- Structure-dynamics correlation → Understanding mechanisms and properties at atomic level
- (An)harmonicity → Mapping out the local potential energy profile using finite displacement, frozen phonon, molecular dynamics
- Phase transition → Revealing the kinetics and the transition pathway

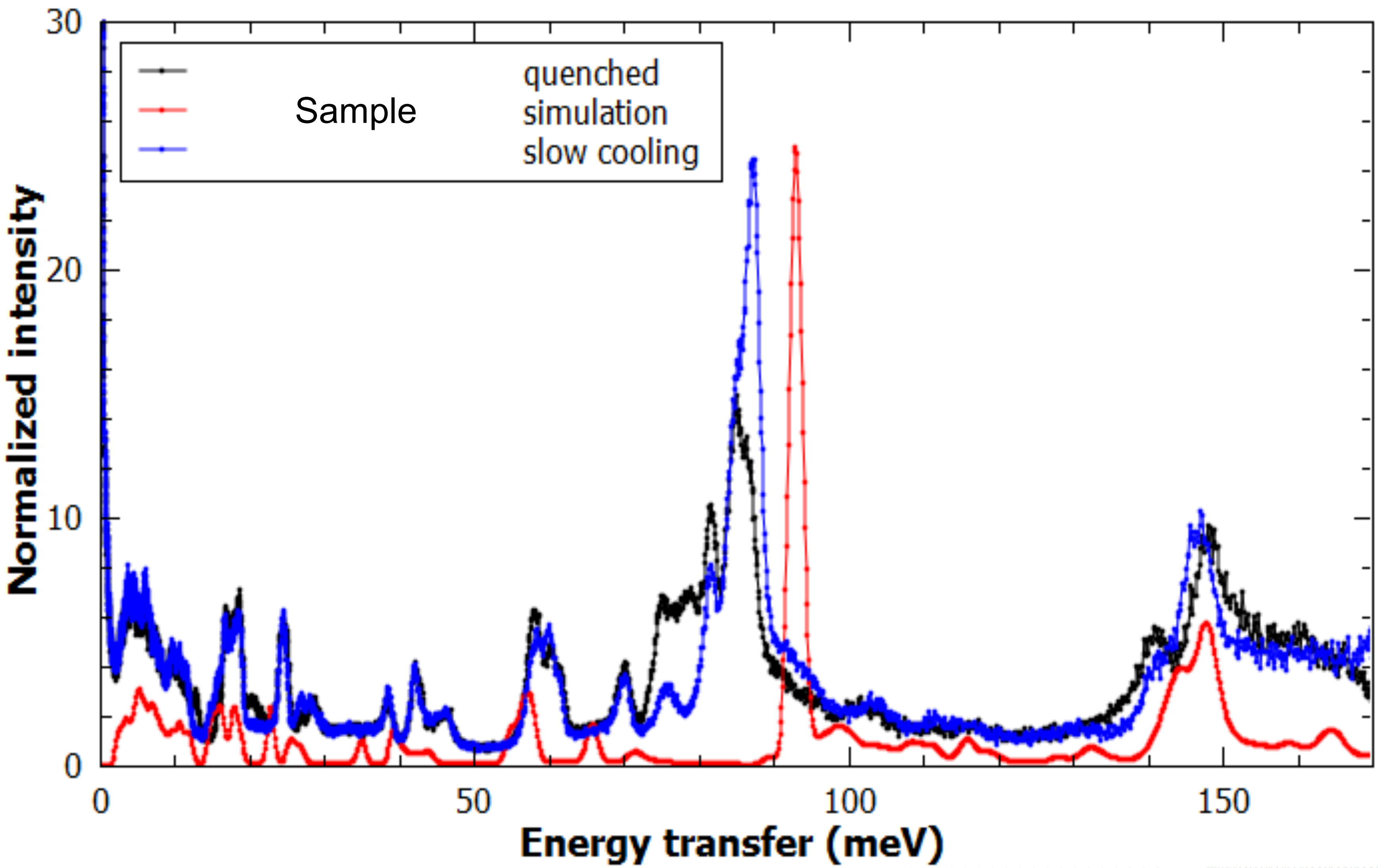
VirtuES helped users to make decisions on-the-fly

```
[yyc@or-condo-login02 CF3SO2OH]$ ls -lhtr
-rw-r--r-- 1 yyc users 3.6K Nov  4 15:50 cell
-rw-r--r-- 1 yyc users 1.1K Nov  4 15:50 param
-rw-r--r-- 1 yyc users 3.9K Nov  4 15:51 _PhonDOS.cell
-rw-r--r-- 1 yyc users  735 Nov  4 15:52 _PhonDOS.param
-rw-r----- 1 yyc users 1.1M Nov  4 16:46 castep
-rw-r----- 1 yyc users 7.3M Nov  5 06:15 _PhonDOS.phonon
-rw-r----- 1 yyc users 232K Nov  5 06:15 _PhonDOS.castep
-rw-r--r-- 1 yyc users 3.3M Nov  5 08:56 aclimax

[yyc@analysis-node02 manualreduce]$ ls -lhtr
-rw-rwx---+ 1 yyc users 2.2M Nov  5 12:34 VIS_20557_5K_for_0.9hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 13:28 VIS_20559_50K_for_0.9hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 14:23 VIS_20561_75K_for_0.9hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 15:56 VIS_20563_100K_for_0.9hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 17:21 VIS_20565_125K_for_0.9hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 18:44 VIS_20567_150K_for_0.9hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 20:23 VIS_20570_175K_for_1.2hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 21:58 VIS_20572_200K_for_1.2hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  5 23:29 VIS_20574_225K_for_1.2hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  6 01:00 VIS_20576_250K_for_1.2hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  6 02:28 VIS_20578_275K_for_1.2hr.nxs
-rw-rwx---+ 1 yyc users 2.2M Nov  6 03:57 VIS_20580_300K_for_1.2hr.nxs
```

Simulation was started at the beginning of the experiment. By the time when experimental data were collected, the calculation was already finished with theoretical predication available to be compared with experiment. This eventually led to a critical decision made by the user (see next slide).

VirtuES helped users to make decisions on-the-fly



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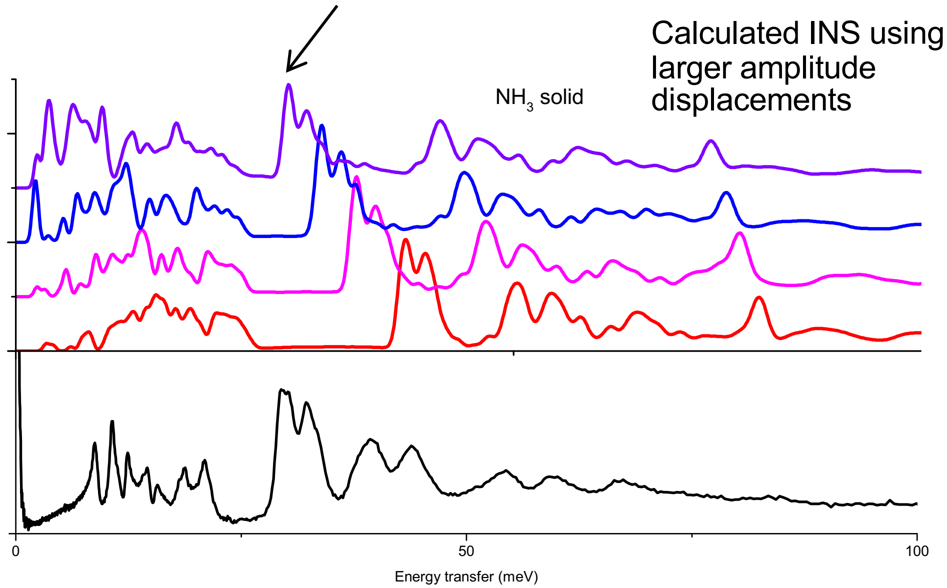
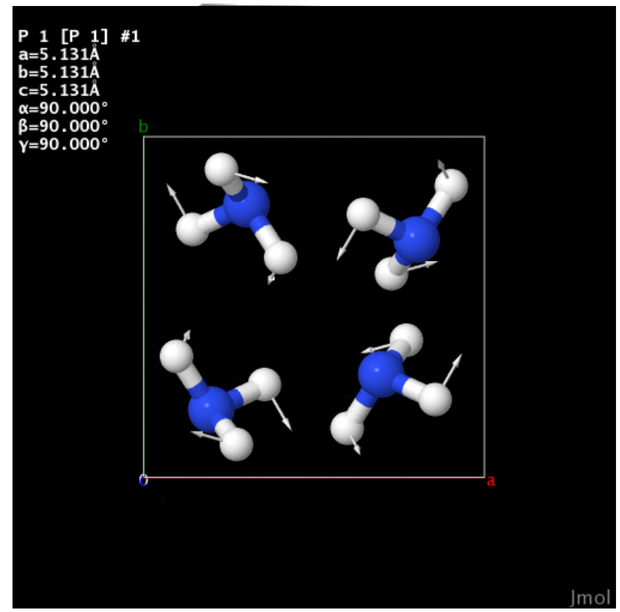
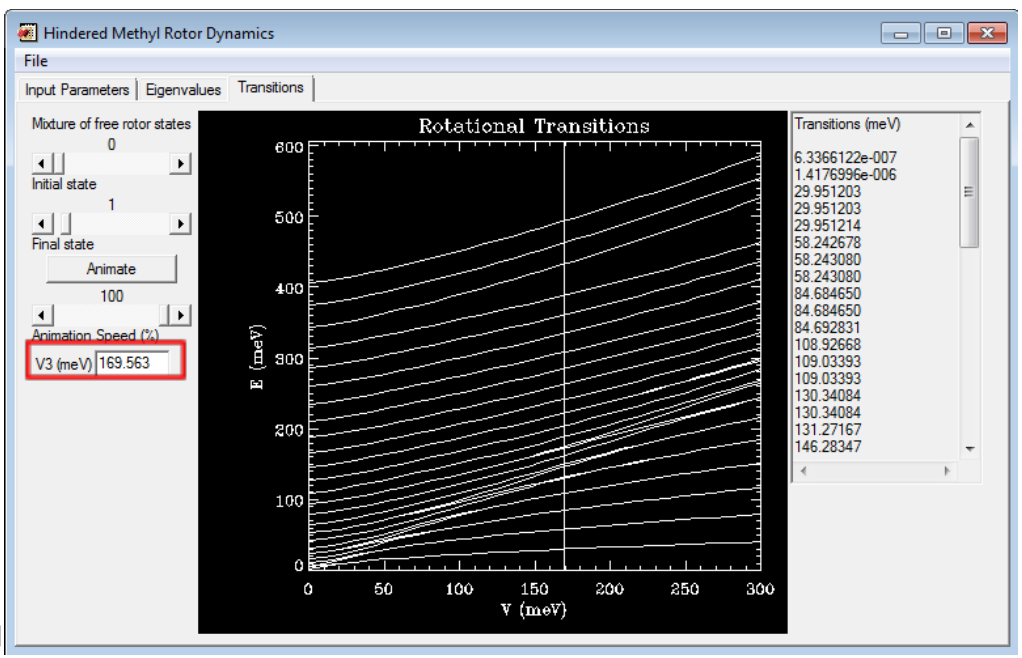
Hydrogen in a “simple” molecular solid: Beyond DFT and harmonic approximation

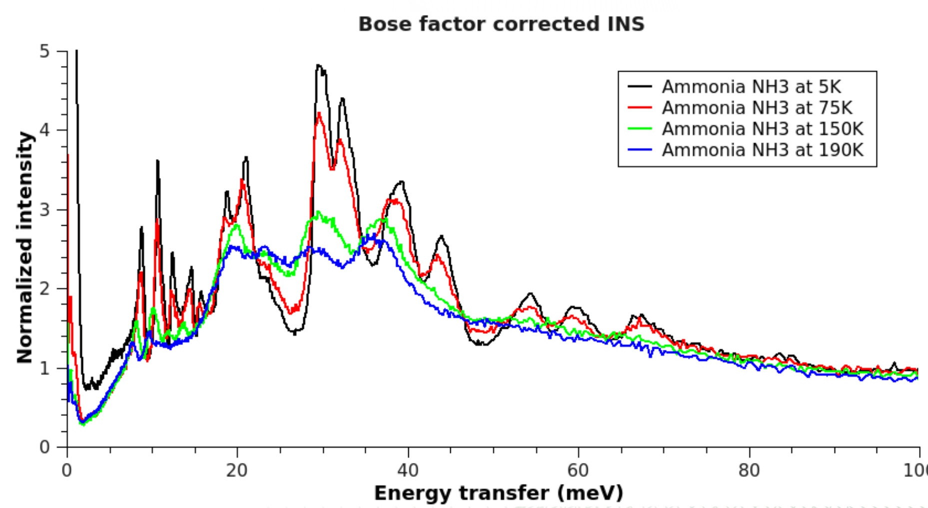
Libration/rotation of NH3 group



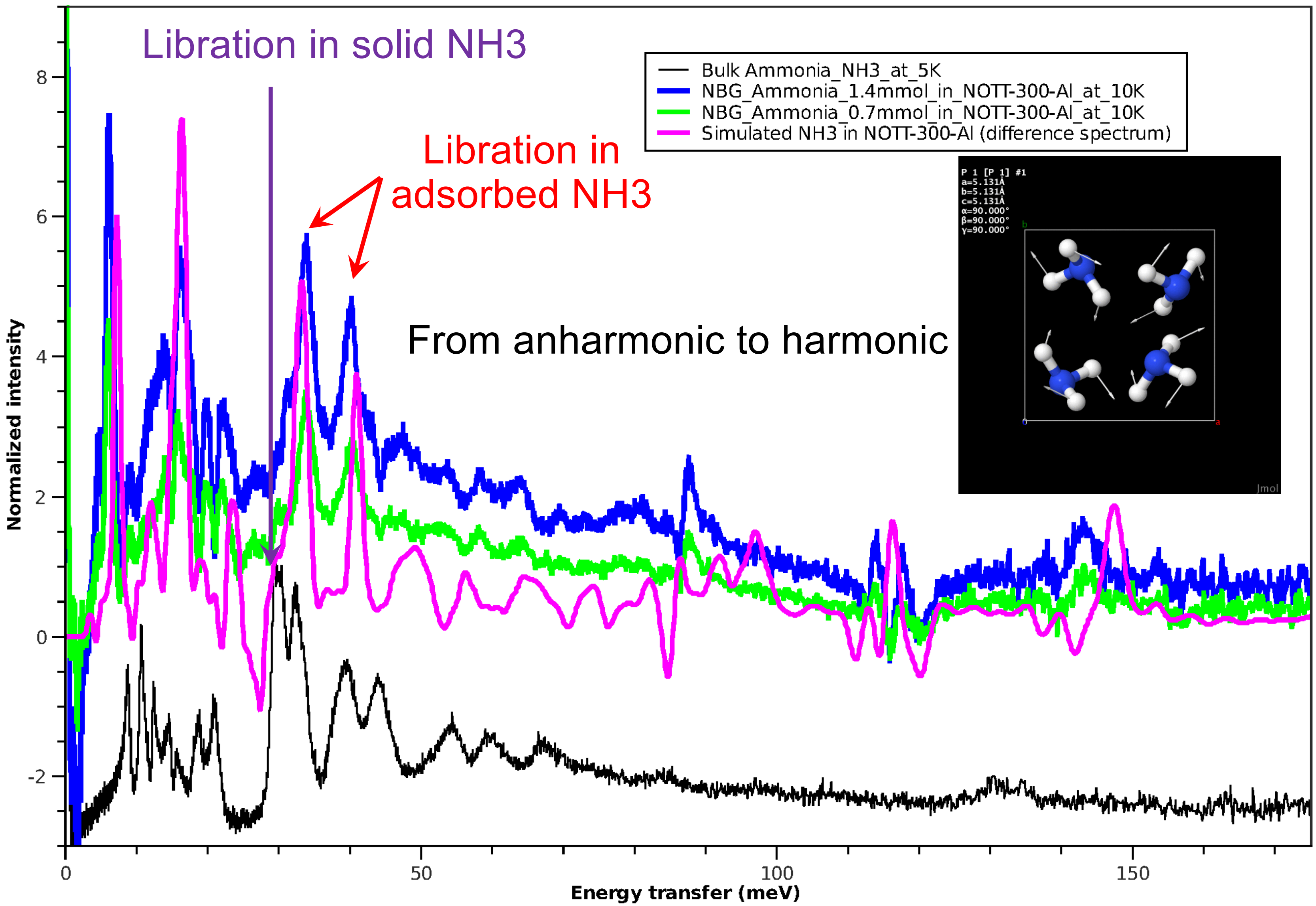




- DFT calculated energy barrier for rigid rotation of NH3: 180 meV
- Energy barrier solved from the rotor model : 170 meV



Solid NH3 vs NH3 in MOF



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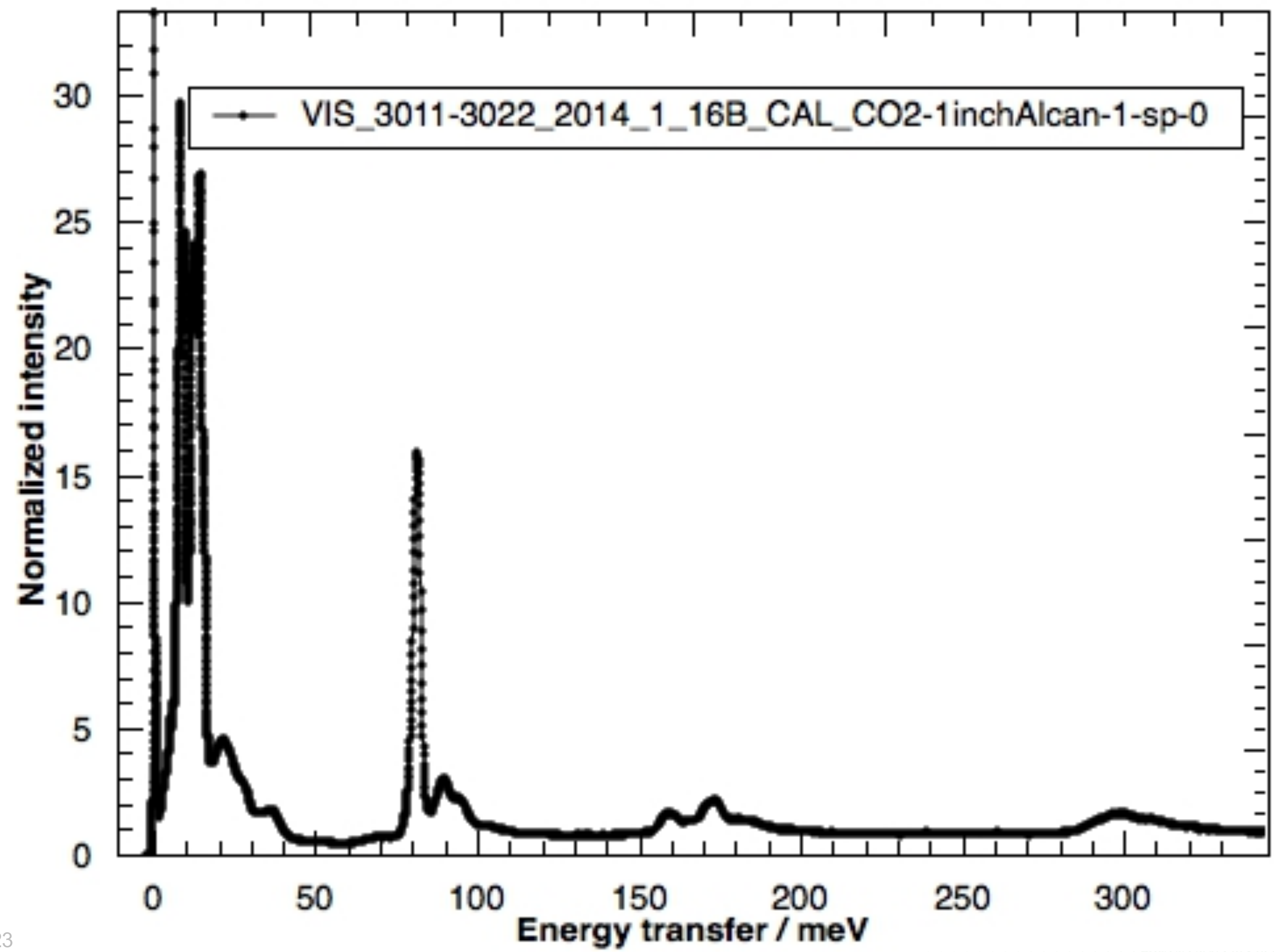
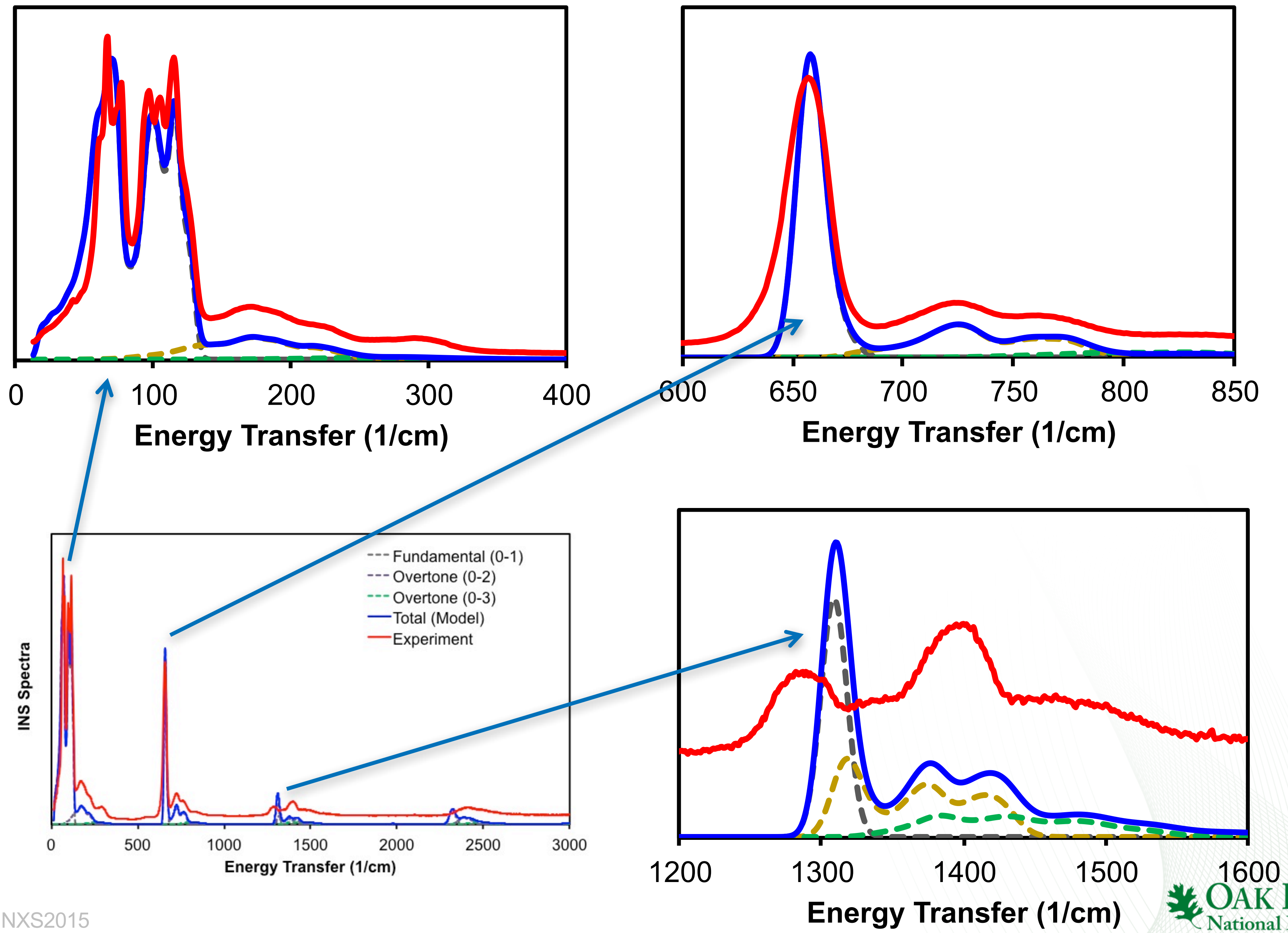
CO_2

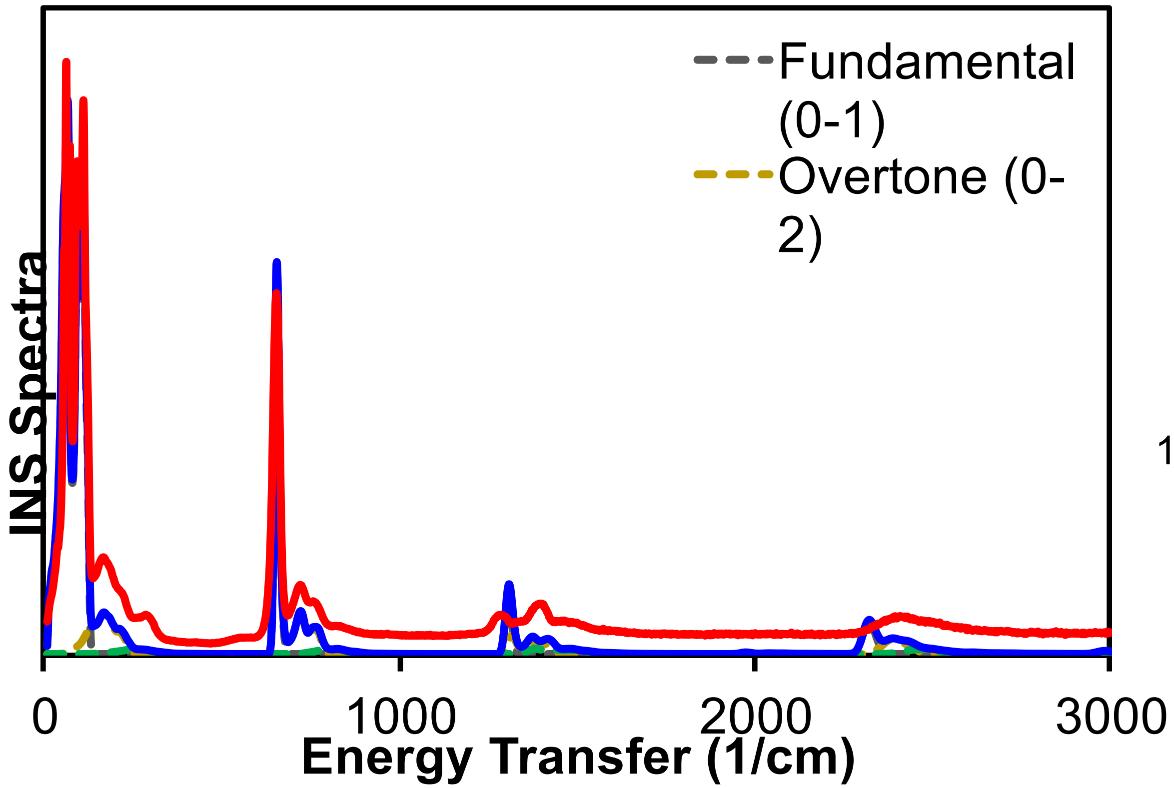


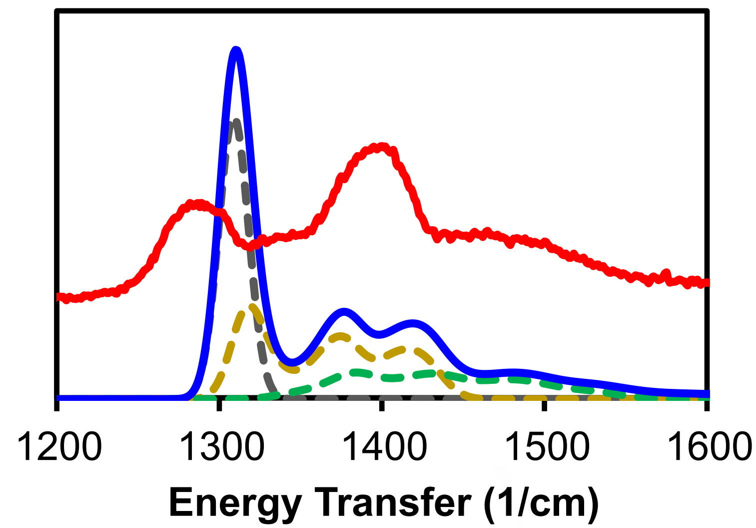
VIS_3011-3022_2014_1_16B_CAL_CO2-1inchAlcan-1-sp-0
Normalized intensity
0
5
10
15
20
25
30
0
50
100
150
200
250
300
Energy transfer / meV

CO_2 in the solid phase



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_2 Fermi resonance *using INS*

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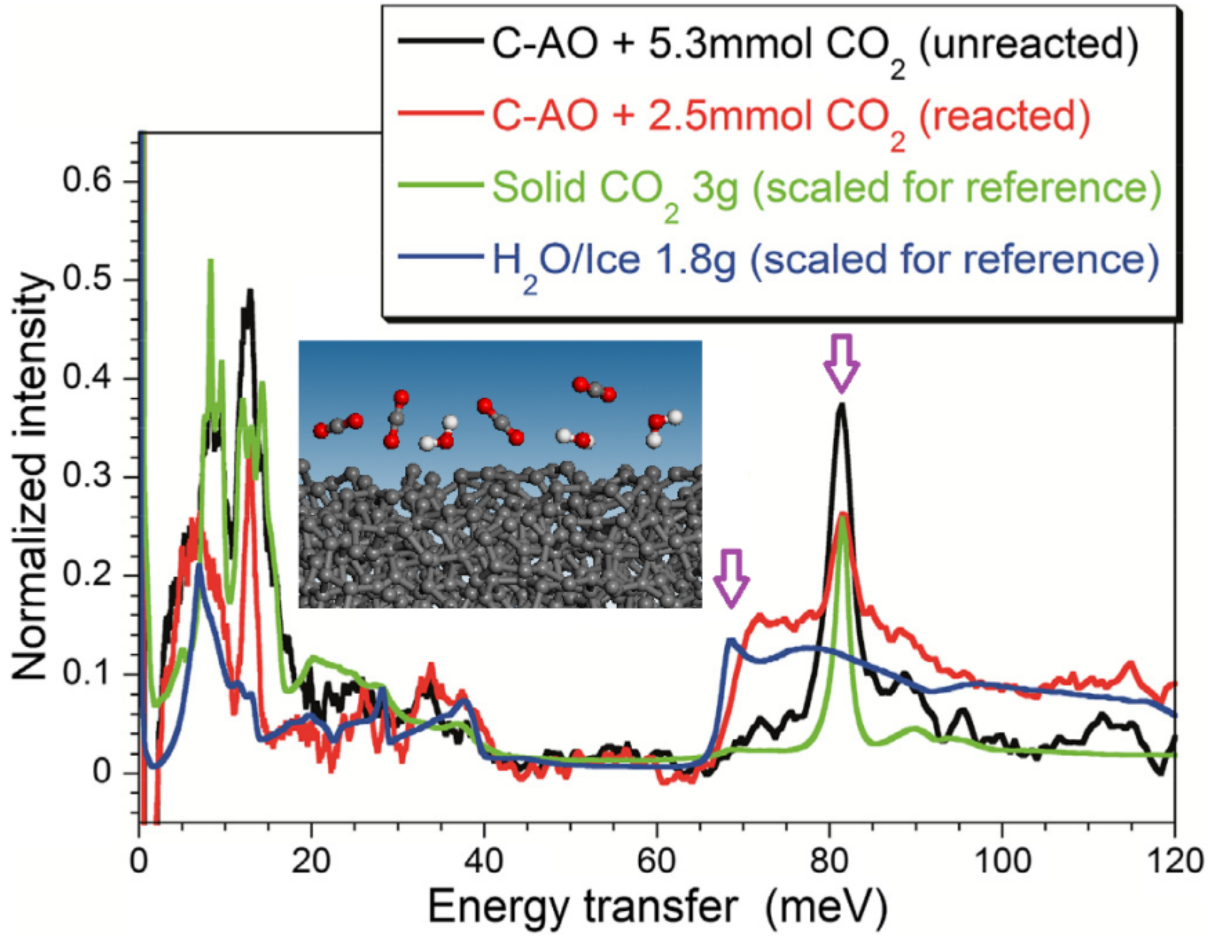
Small amount of non-hydrogenous samples

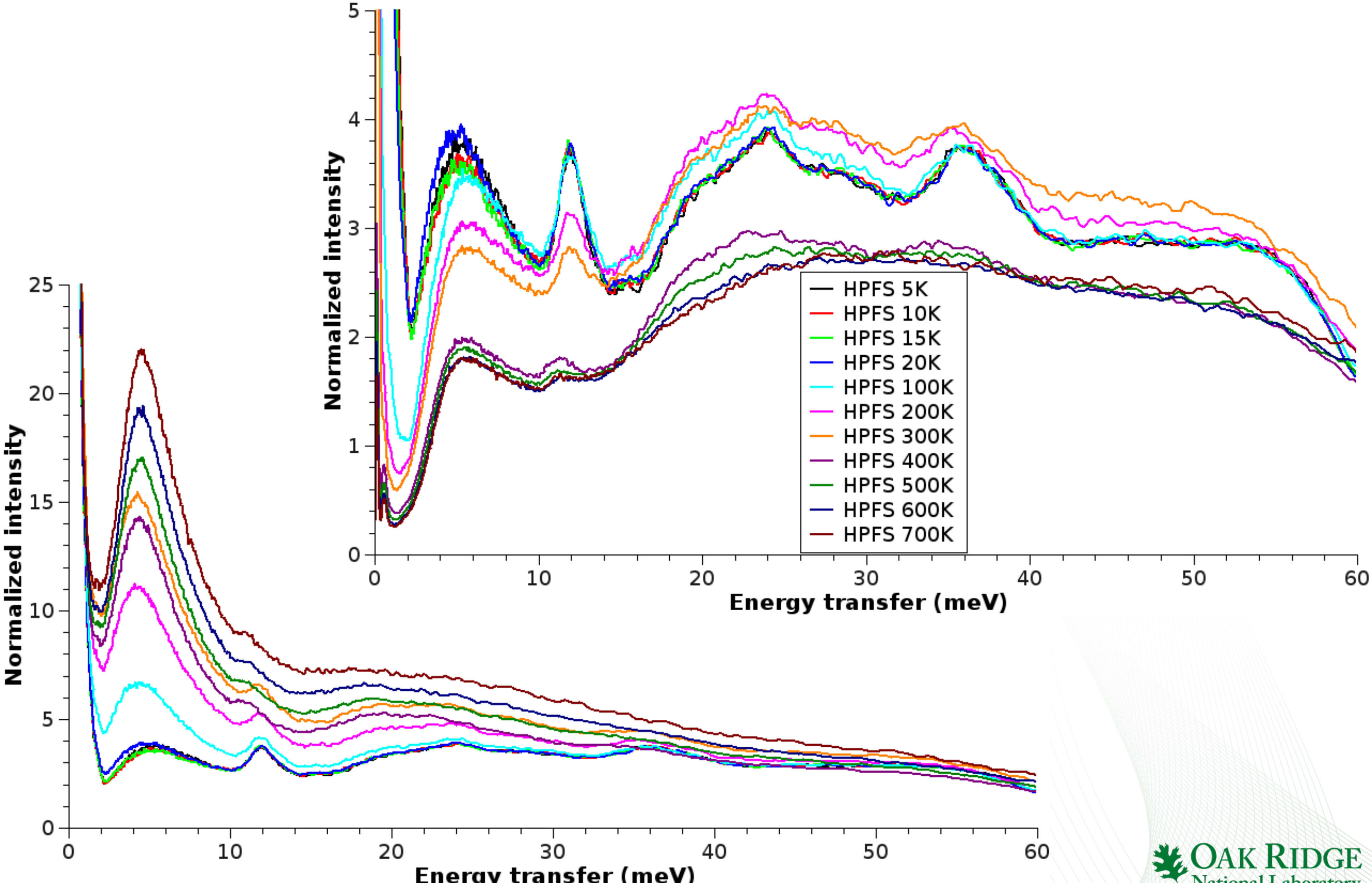


The difference INS spectra before and after CO_2 dosing in C-AO (a nanoporous carbon sample), in comparison with the reference spectra for bulk solid CO_2 and H_2O. Signal from the background and the blank C-AO has been subtracted.

Very small amount of non-hydrogenous gas. In situ observation of surface reactions. Surface science, catalysis, gas capture and storage.

T. J. Bandosz, M. Seredych, E. Rodríguez-Castellón, Y. Q. Cheng, L. L. Daemen, and A. J. Ramírez-Cuesta. *Carbon*. 96 (2016): 856–863.

High temperature measurement up to 700K



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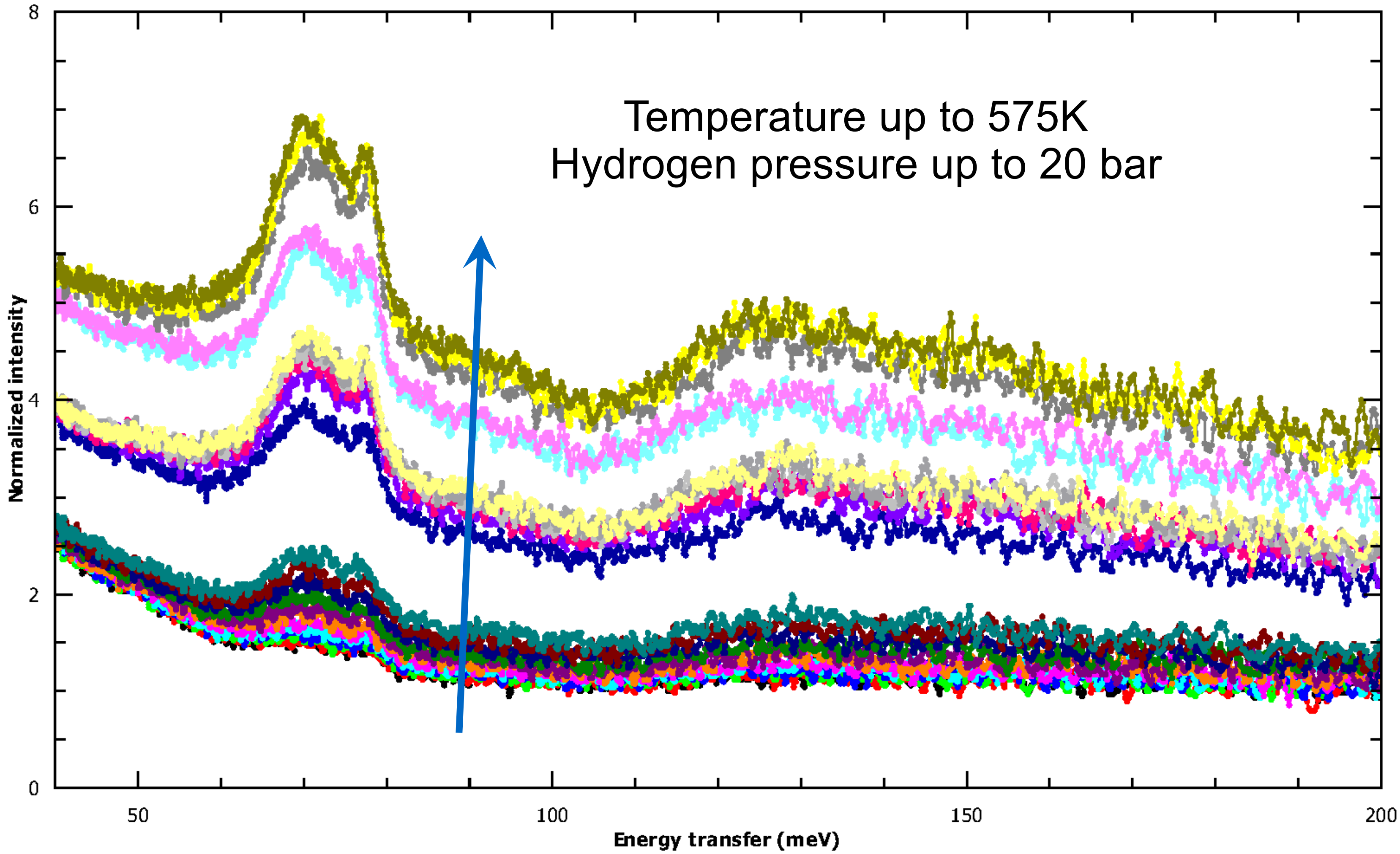
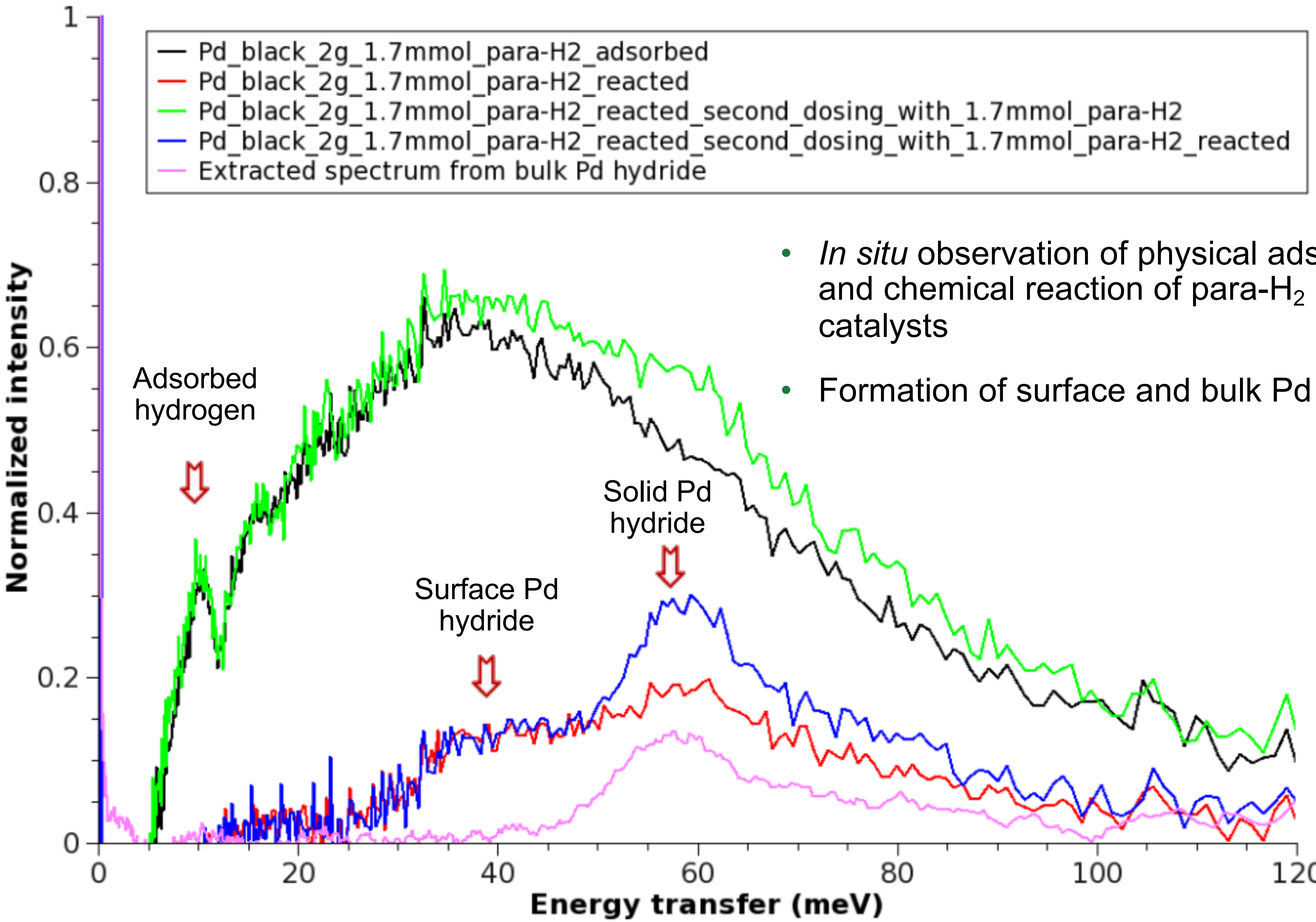
In situ observation of metal hydride formation



Collaboration with Jacques Huot at UQTR Canada.

Hydrogen in catalysts



- *In situ* observation of physical adsorption and chemical reaction of para-H_2 on Pd catalysts
- Formation of surface and bulk Pd hydride

Collaboration with Dario Stacchiola, Brookhaven National Laboratory

Studying H_2 adsorption in Porous Materials & Surfaces with INS

Probing the interactions of molecules with the host material

Characterization of the interaction strength

The Theory

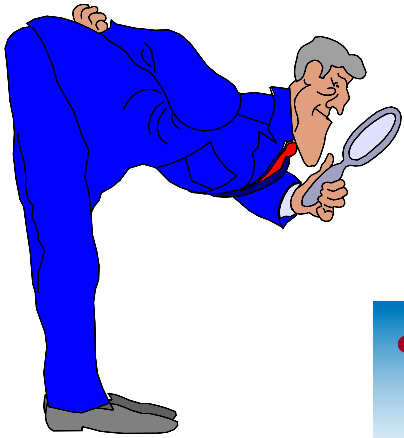
- H_2 ground state (J=0) parahydrogen (p-H_2) antisymmetric nuclear spin wavefunction (↑↓) and symmetric rotational wavefunction.
- The first rotational state, (J=1) orthohydrogen (o-H_2) symmetric nuclear spin wavefunction (↑↑) and antisymmetric rotational wavefunction.
- Transitions p-H_2 ↔ o-H_2 are 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 cm^{-1}). Its energy levels are:

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

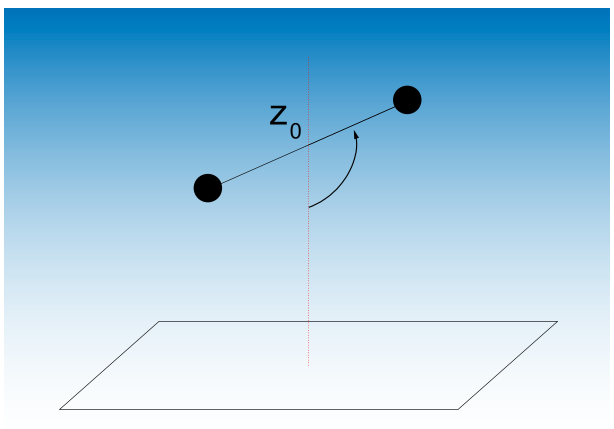
The minimum separation between energy levels is

$$E = 2B$$



The Interactions

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



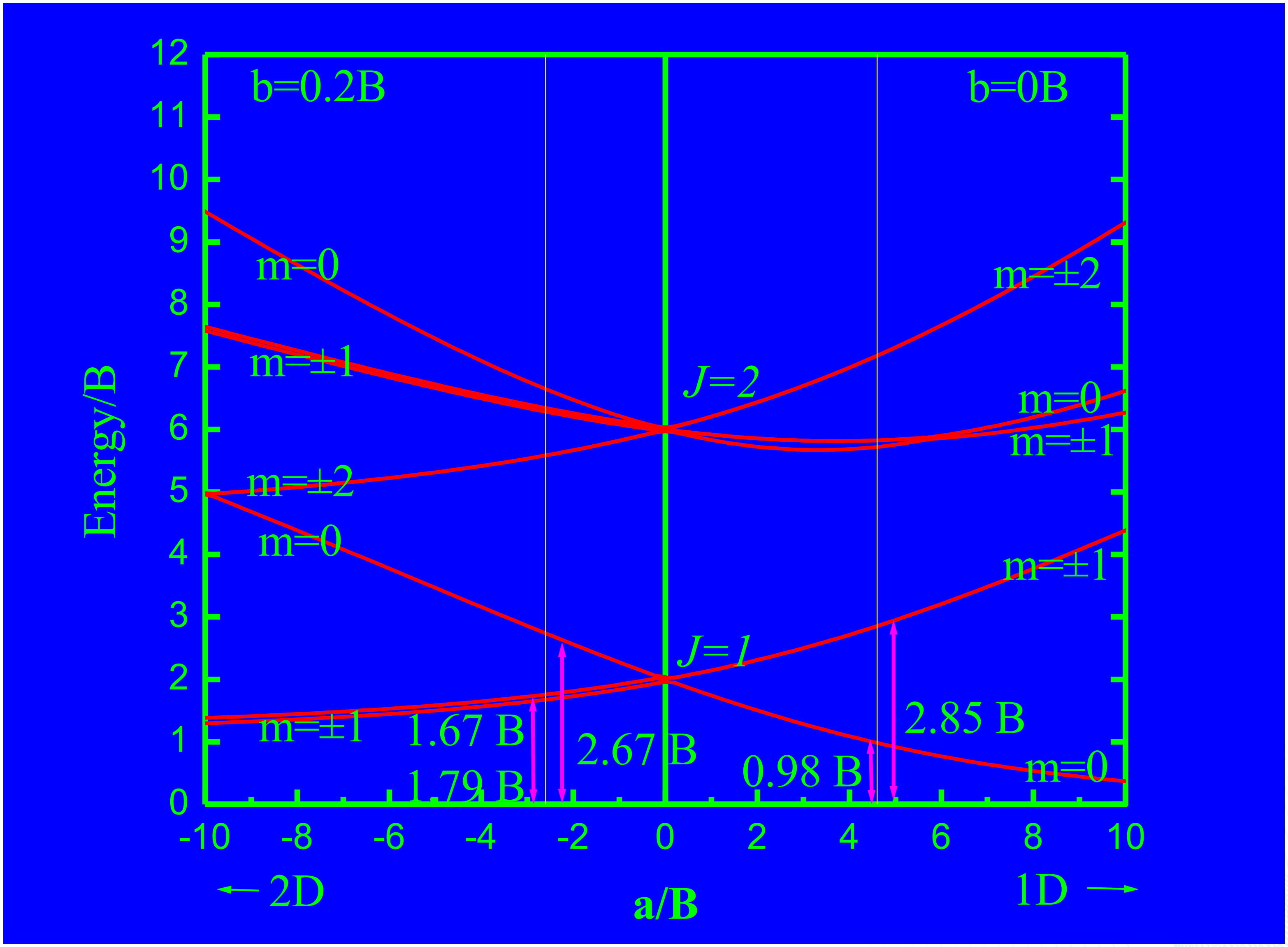
The potential that governs the motion of a H_2 molecule on a surface may be expressed as

$$V(\ ,\ ,z) = K(z \quad z_0)^2 + \sin^2 \quad (a + b\ \cos\ )$$

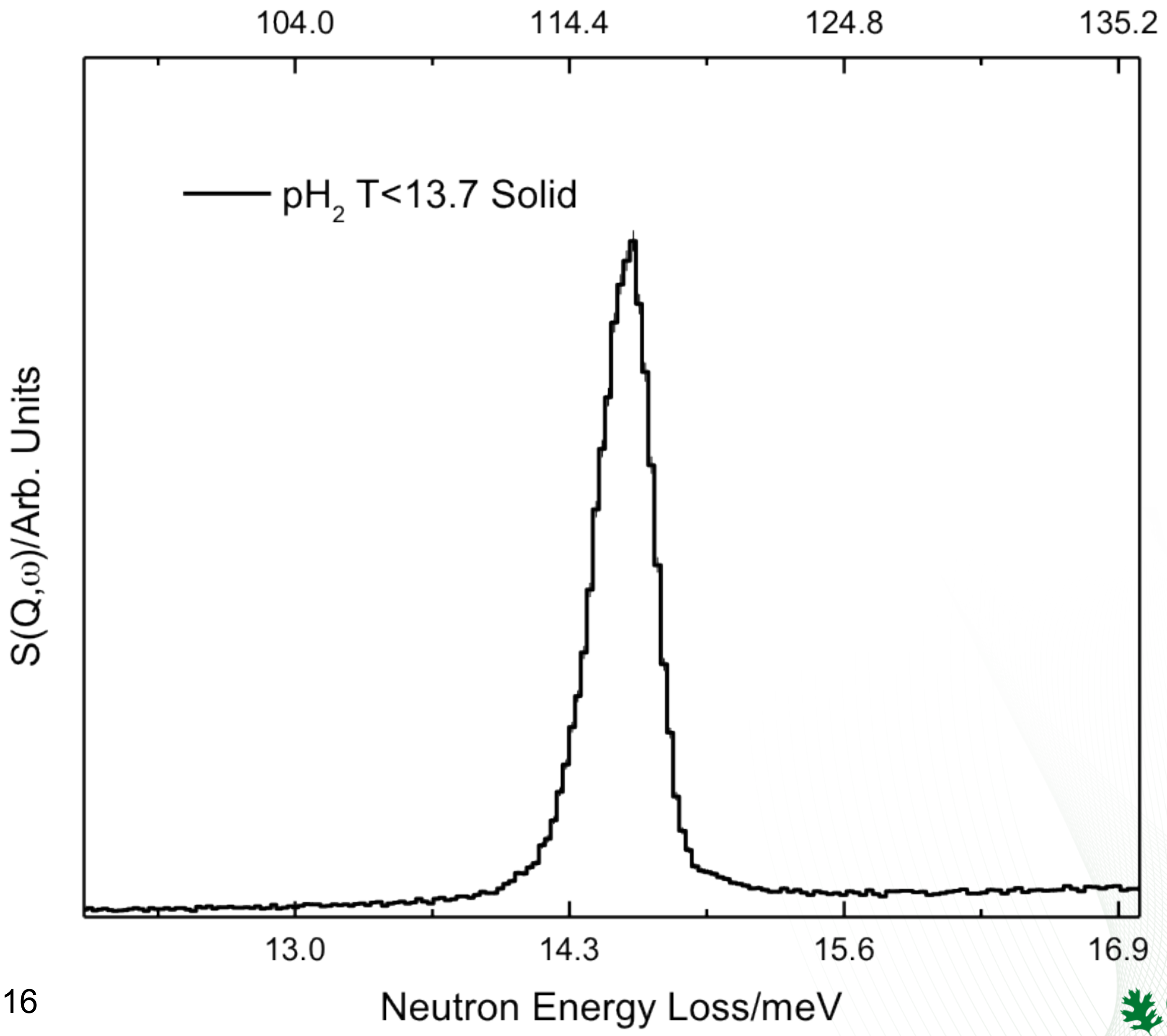
- a>0 the molecule is aligned to an axis (1D case).
- a<0 the molecule is constrained in a plane (2D case)
- The splitting between levels is 1***B*** if a is large and negative, because the energy levels are:

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

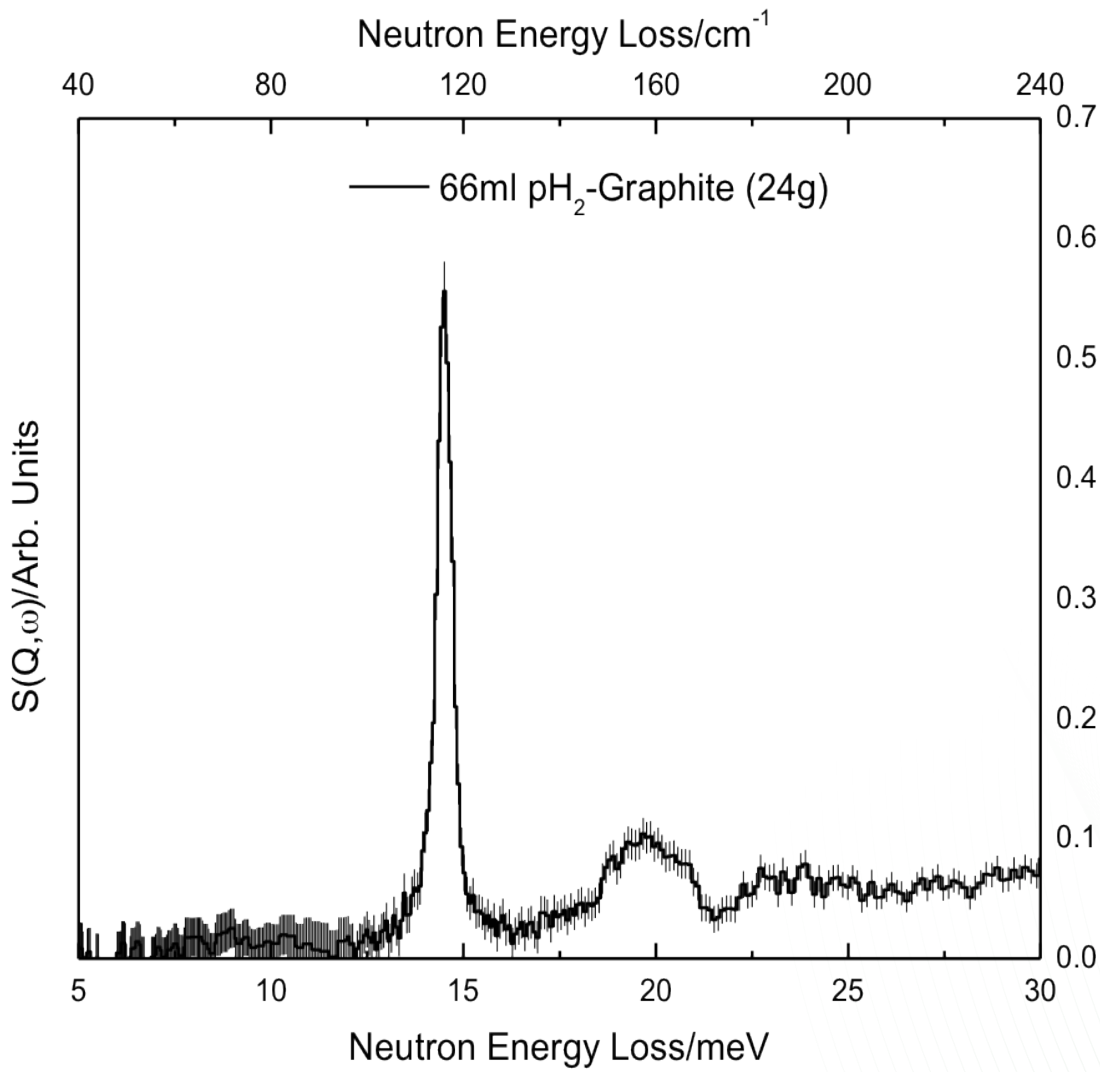
The Energy Levels



What are we expecting?



Interaction of graphite with Hydrogen



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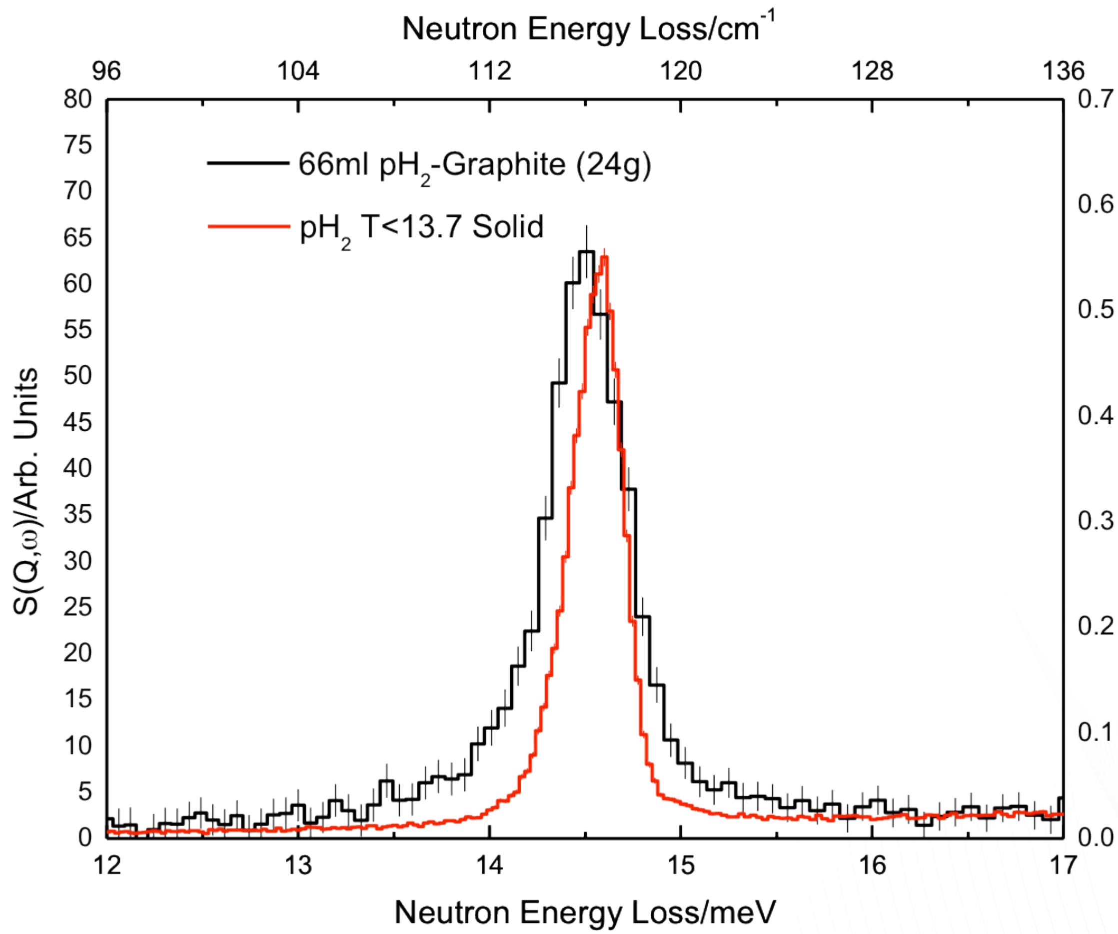
Interaction of graphite with Hydrogen



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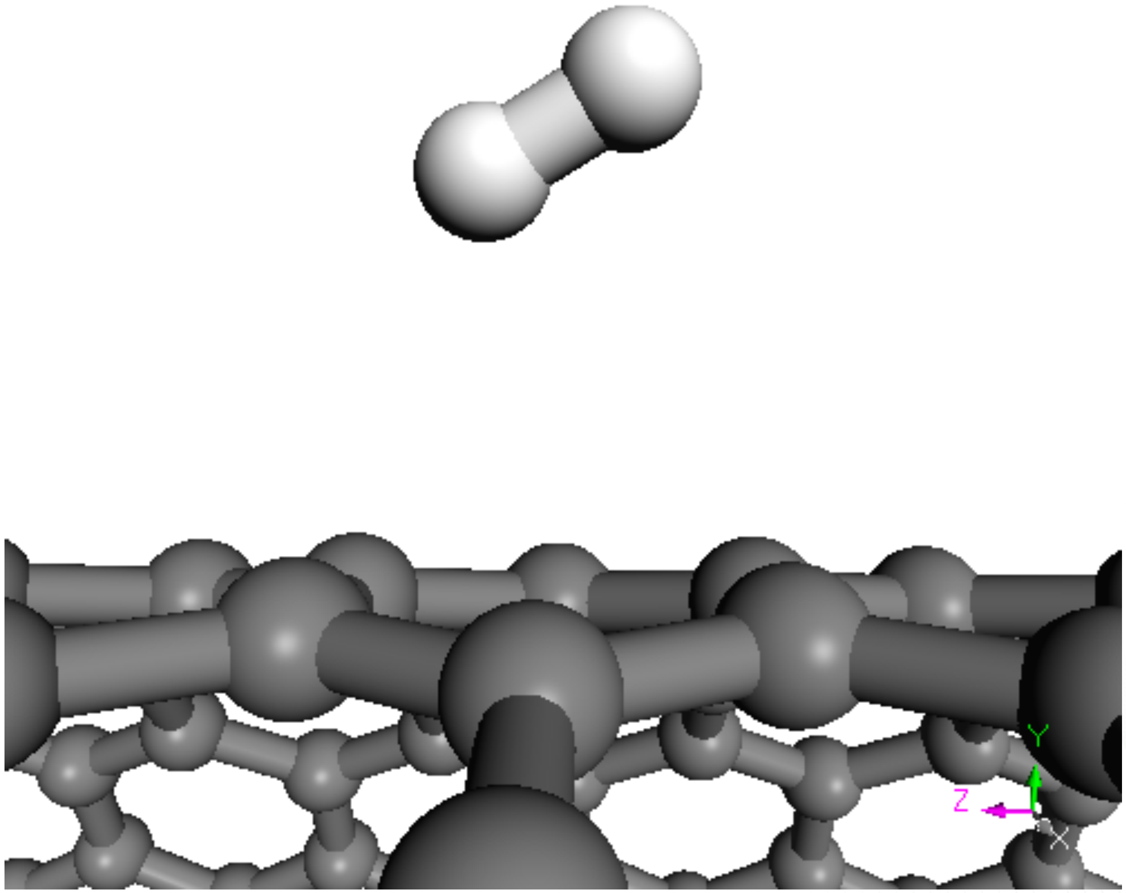
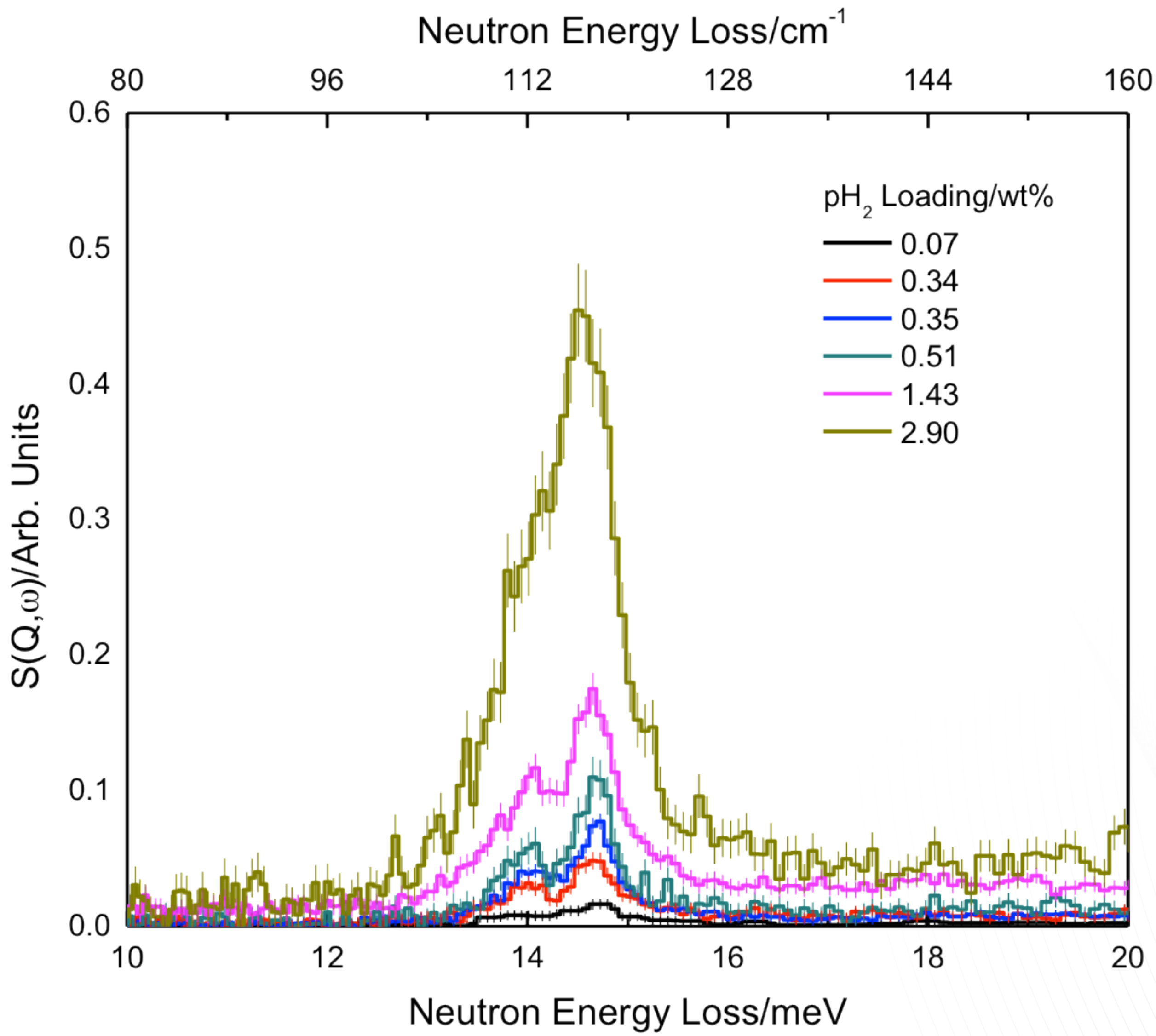
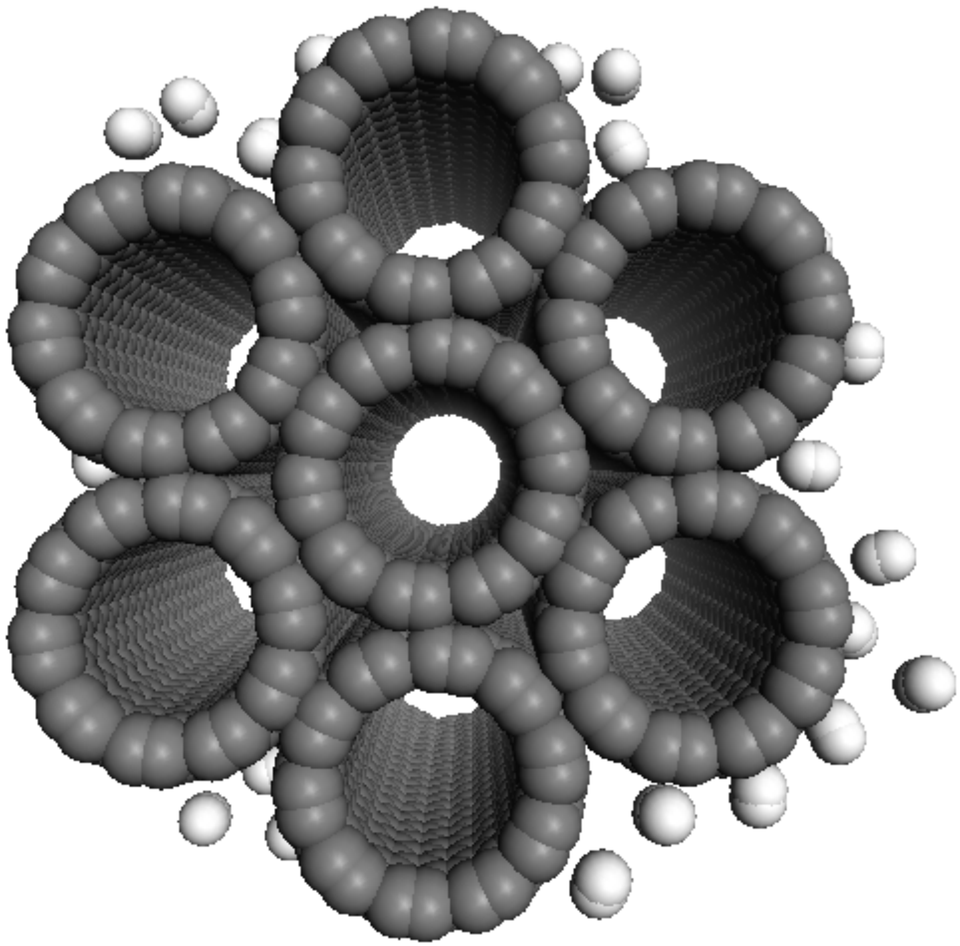
Interaction of SWNT with Hydrogen



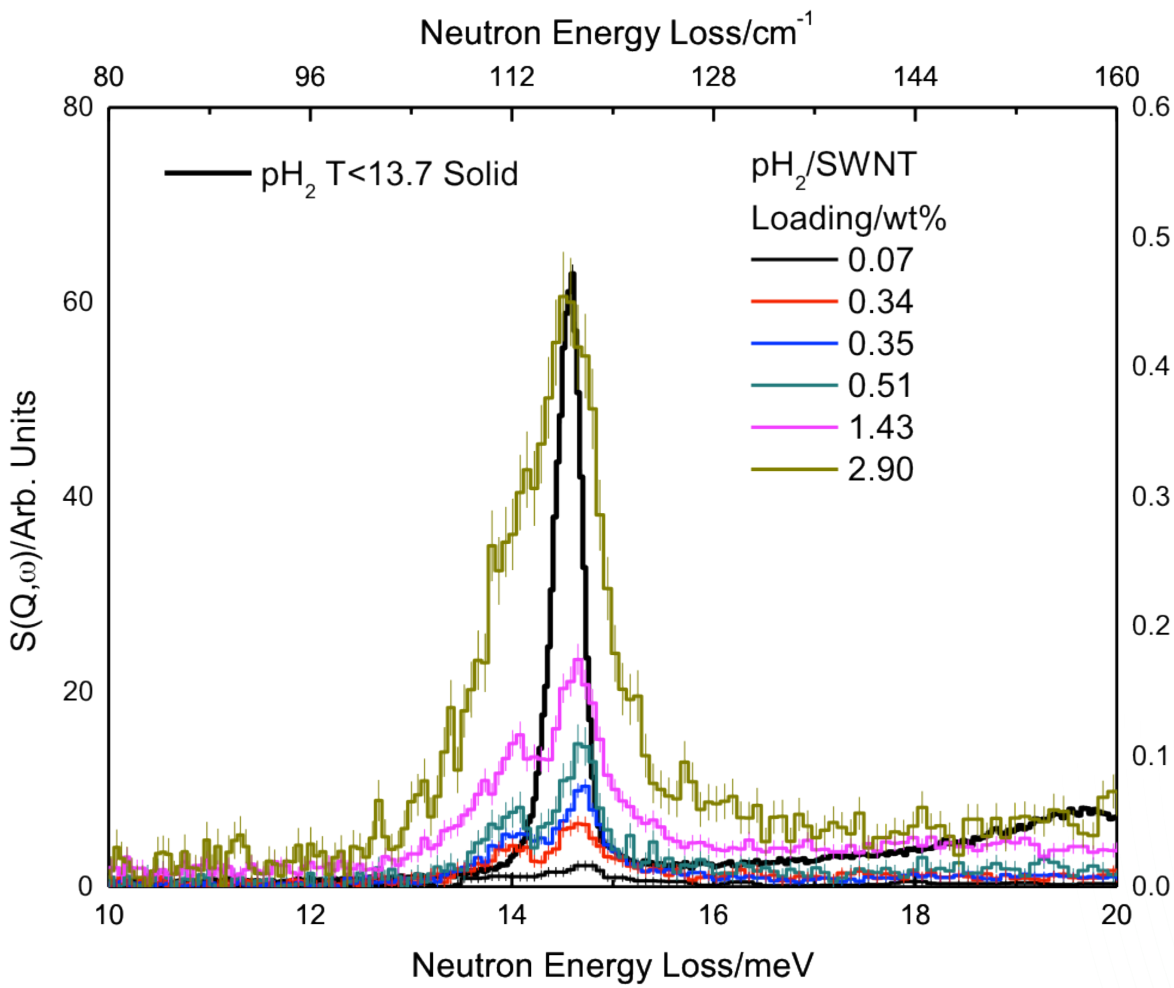
Interaction of SWNT with Hydrogen



Interaction of SWNT with Hydrogen

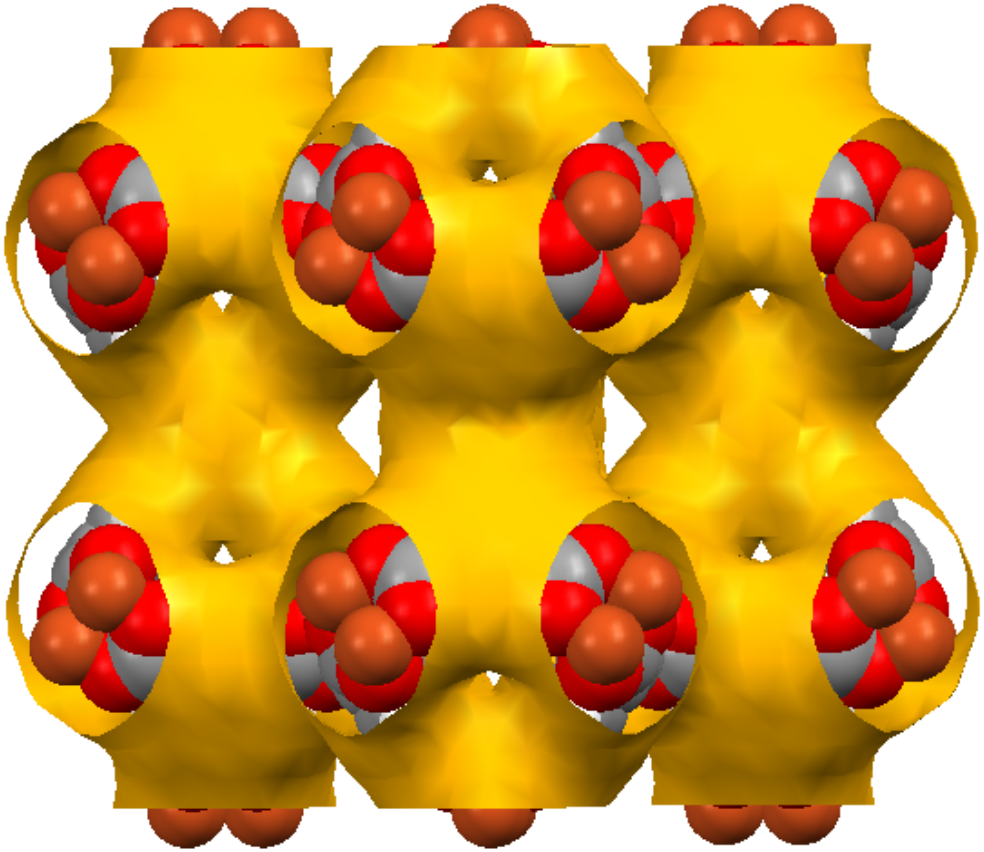


Interaction of SWNT with Hydrogen



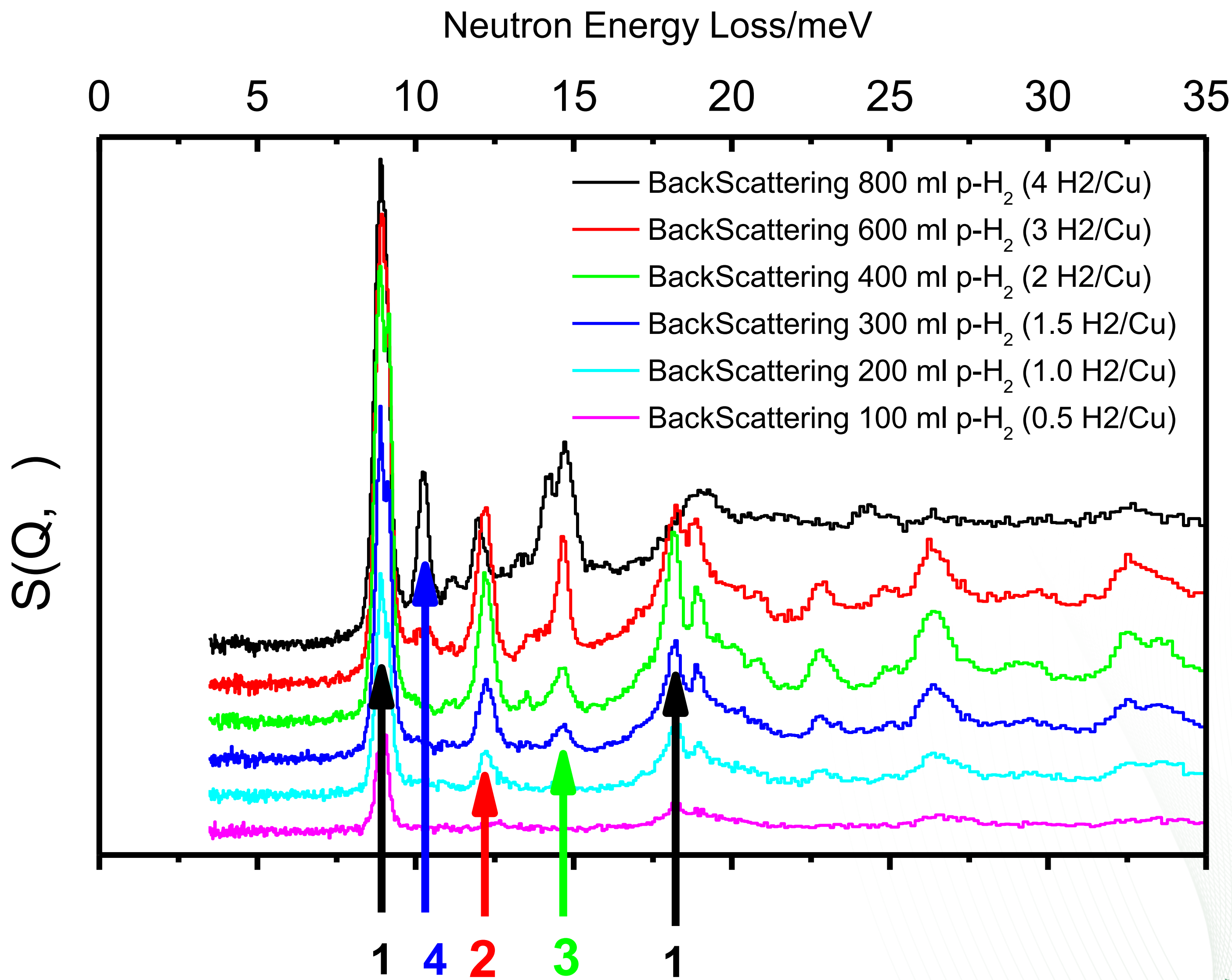
Rotational line splits
Molecule aligns in one directi
Probably along the grooves
between the SWNT

Example #1 H_2 in Cu-MOF



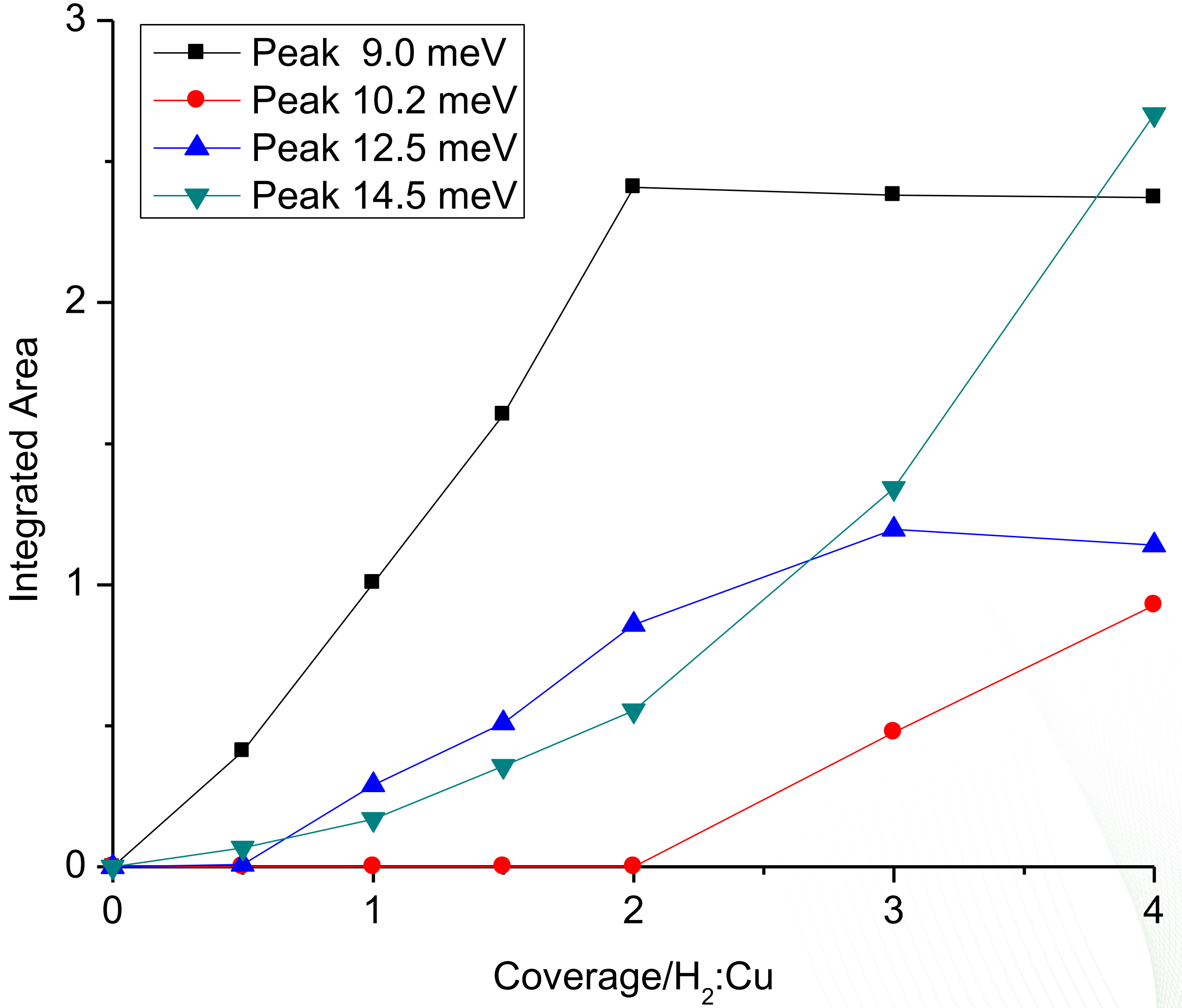
Franck Millange, Sam Callear, Richard Walton, Timmy Ramirez-Cuesta
Chemical Physics 427 (2013) 9
doi:http://dx.doi.org/10.1016/j.chemphys.2013.07.020.

H_2 in Cu-MOF #1



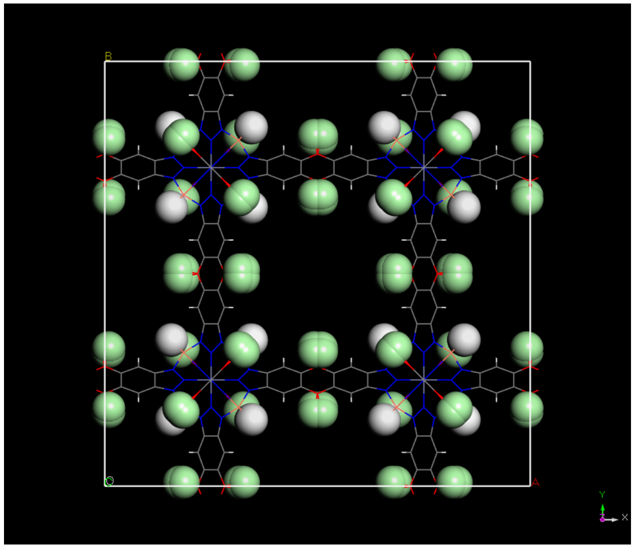
Neutron Energy Loss/meV
0
5
10
15
20
25
30
35
S(Q,)
BackScattering 800 ml p-H2 (4 H2/Cu)
BackScattering 600 ml p-H2 (3 H2/Cu)
BackScattering 400 ml p-H2 (2 H2/Cu)
BackScattering 300 ml p-H2 (1.5 H2/Cu)
BackScattering 200 ml p-H2 (1.0 H2/Cu)
BackScattering 100 ml p-H2 (0.5 H2/Cu)
1
4
2
3
1

H_2 in Cu-MOF #1

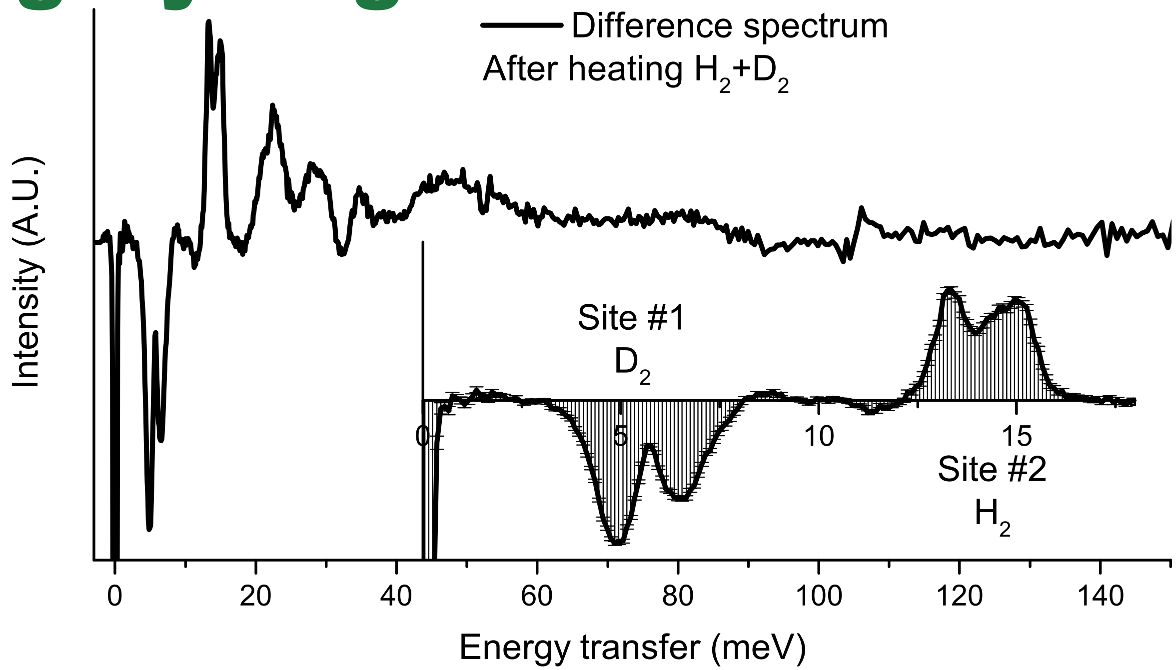


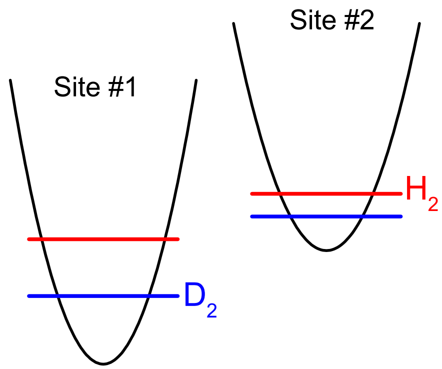
OAK RIDGE National Laboratory

Quantum Sieving Hydrogen in a MOF

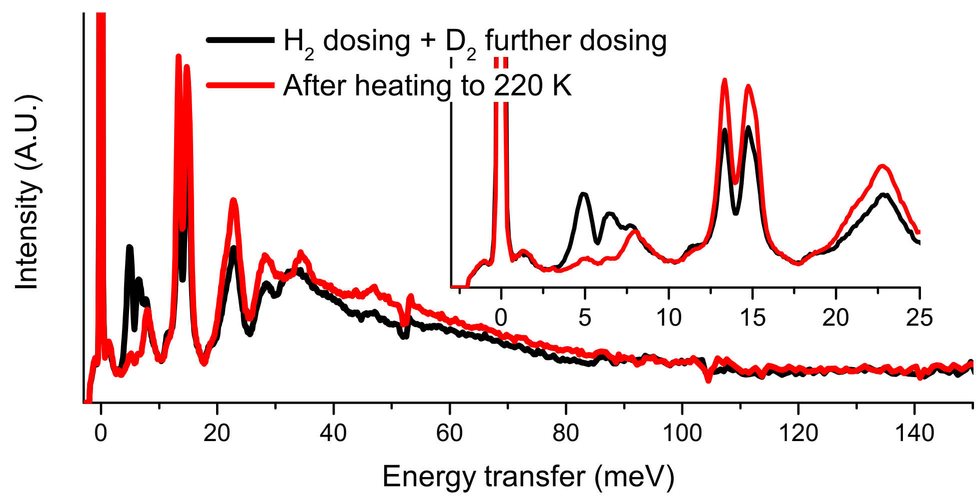


Quantum sieving is a technique for isotope separations; heavier isotopes induce favorable adsorption in nanoscale pores due to the difference in zero point energy of isotopes.





Hydrogen is dosed first, so it mostly takes the lower energy site (Site #1), afterwards deuterium gas is added and has to go to the available site (Site #2)

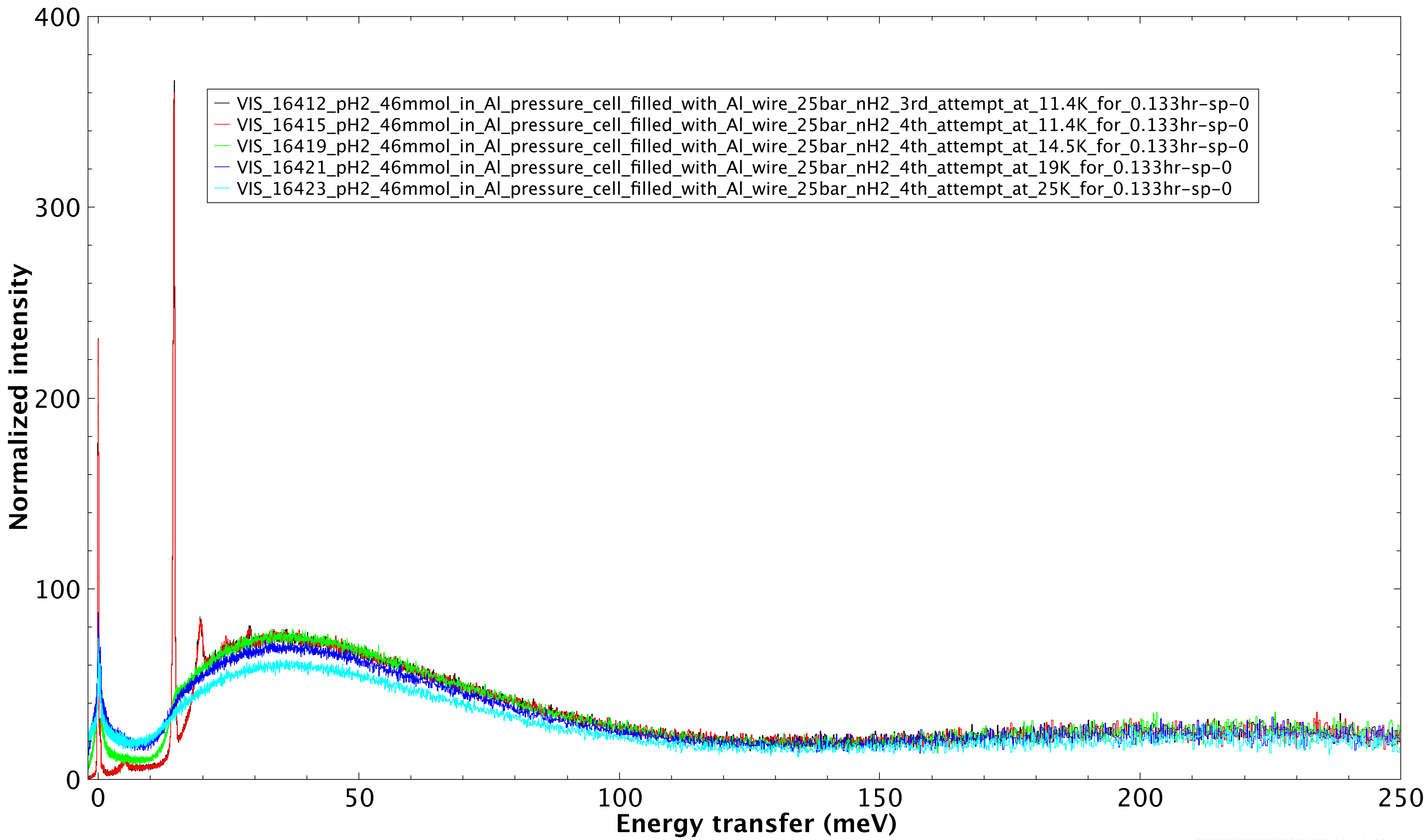


Black trace is hydrogen dosed at 77K and cooled down, further deuterium is added at 77K. Red trace is spectrum after warming sample to 220K and cool down. The hydrogen in site #1 has been displaced to site #2

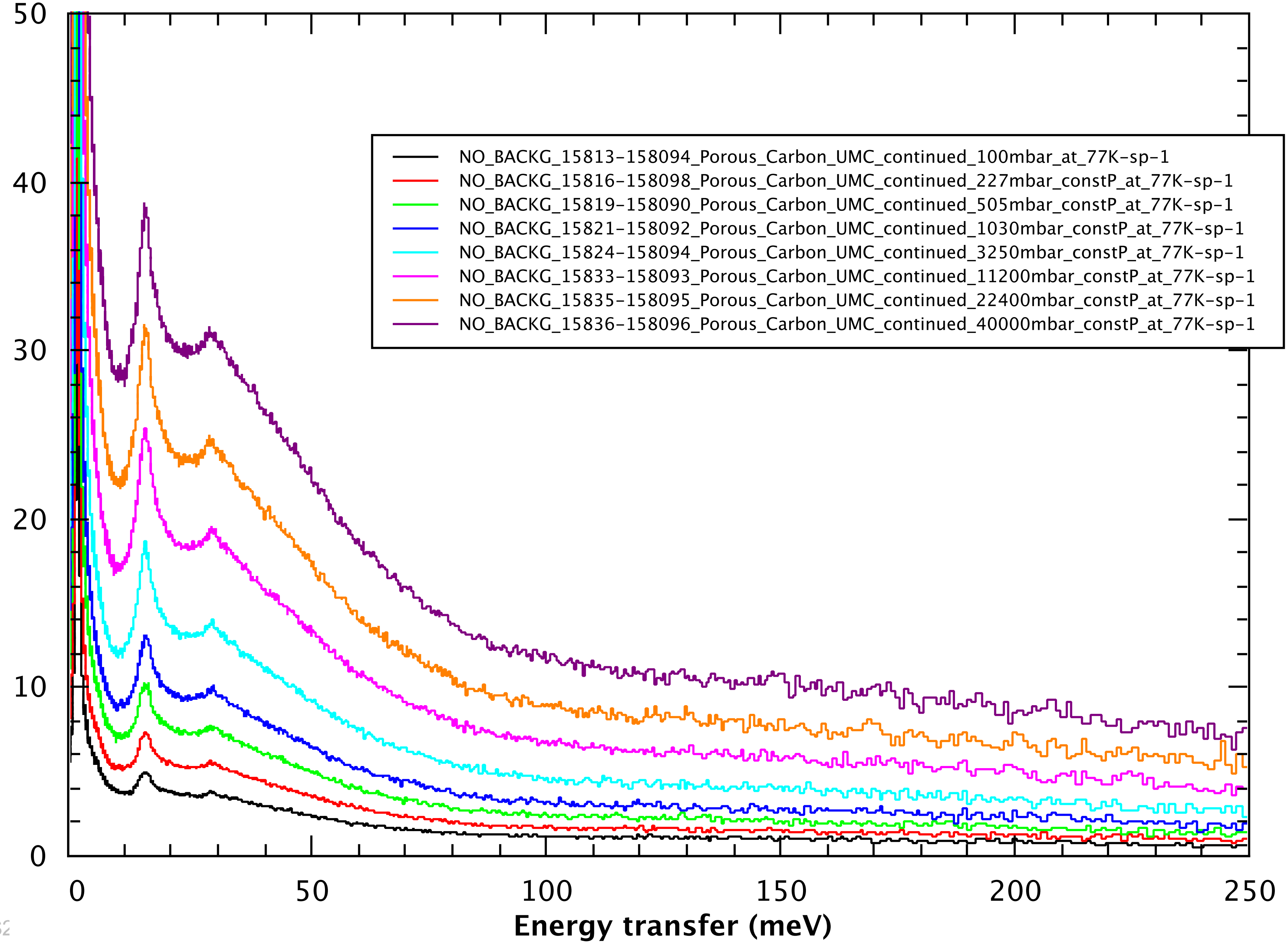
Collaboration with Ingrid Weinrauch and Michael Hirscher, Max Planck Institute for Intelligent Systems, Germany

OAK RIDGE National Laboratory

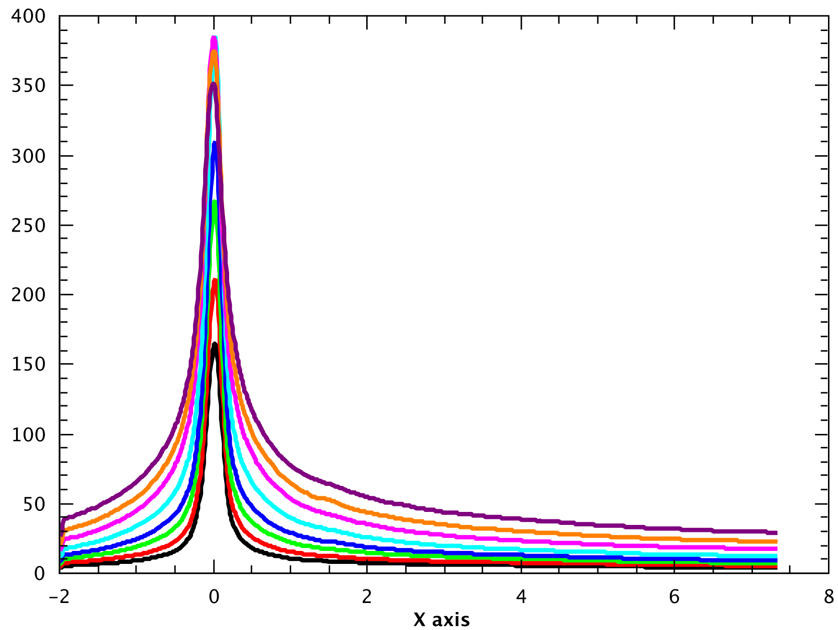
Molecular hydrogen solid



Molecular hydrogen in porous carbon

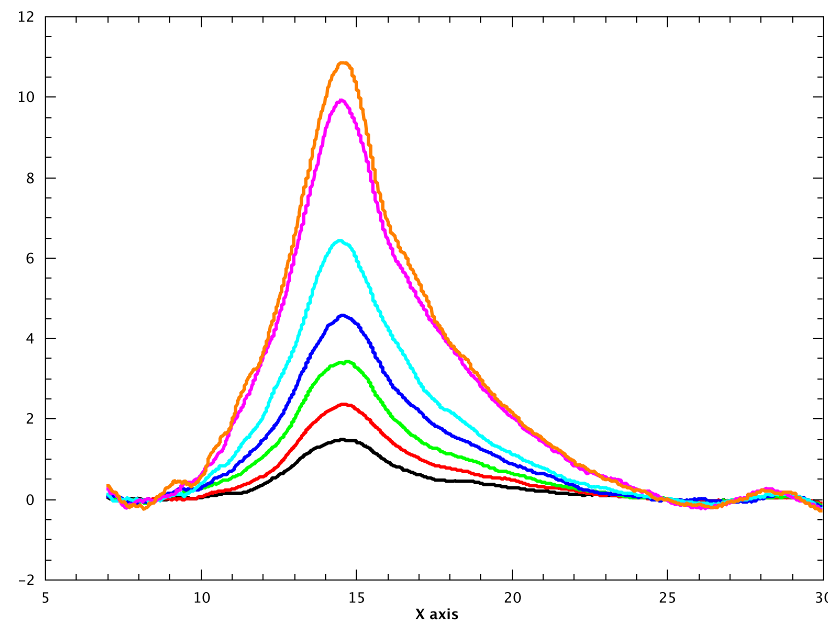


Molecular hydrogen in porous carbon



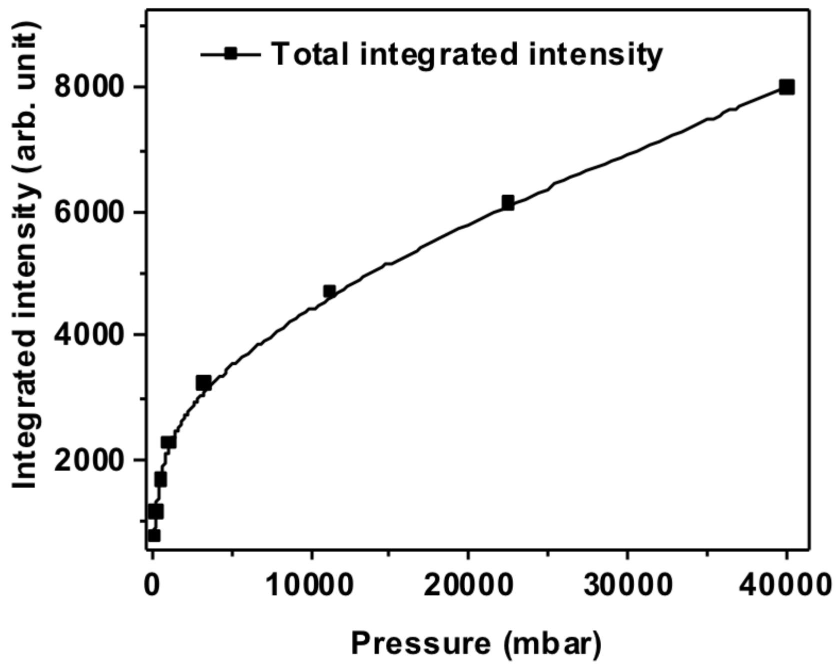
Presence of elastic line at 77K is indication of highly dense molecular hydrogen in the pores.
The broadening of the elastic line is a consequence of the enhanced mobility of the molecules as the amount of hydrogen increases in the system. Larger pores, where hydrogen is less constrained have more mobility. In the gas the signal is extremely broad.

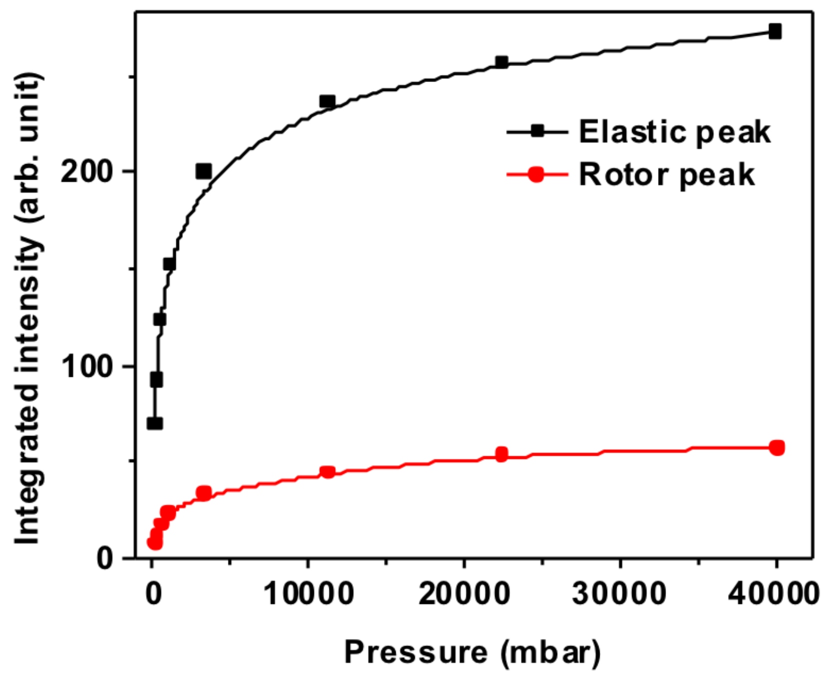
Presence of the rotor line at 77K is indication of completely immobile molecular hydrogen in the pores. In the case of pure para-hydrogen (previous figure) the line disappears when the hydrogen melts.
There is very little broadening of the rotor line, since the momentum transfer is larger that the corresponding one at the elastic line (dynamical trajectory of indirect geometry).
The load keeps increasing even at 40 bar.



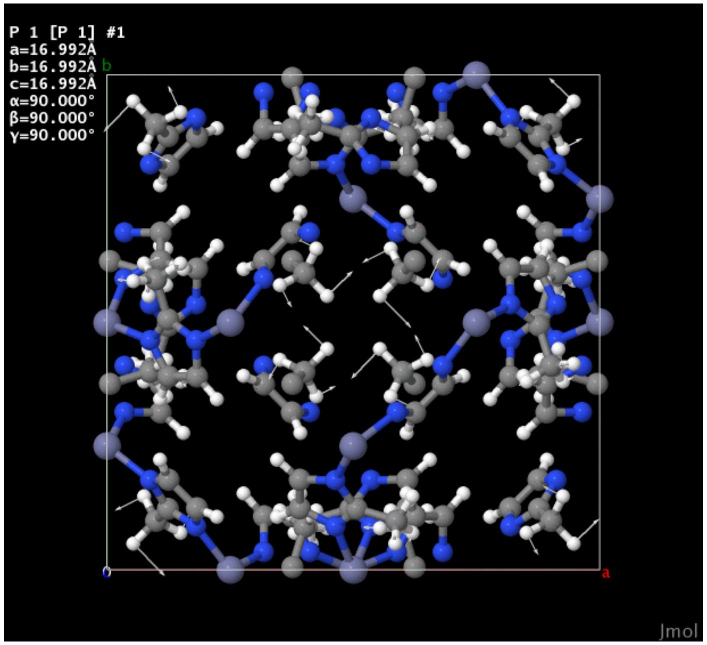
Molecular hydrogen in porous carbon

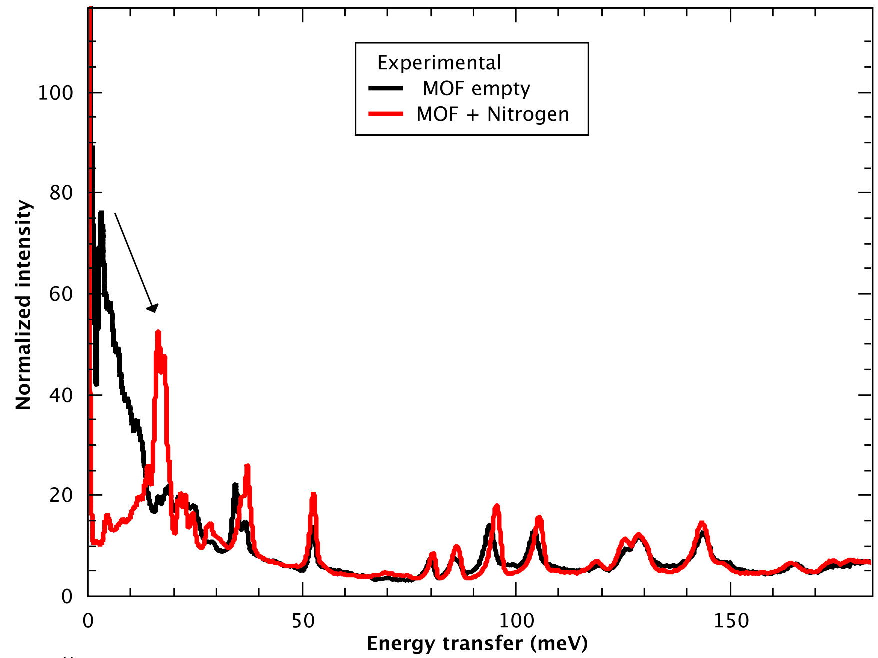
1. The total integral of the spectral intensity is proportional to the amount of hydrogen in the system (left plot)
2. The integrated area under the elastic peak is proportional to the amount of hydrogen that is in a liquid like and solid like phase (right panel)
3. The integrated area under the rotor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

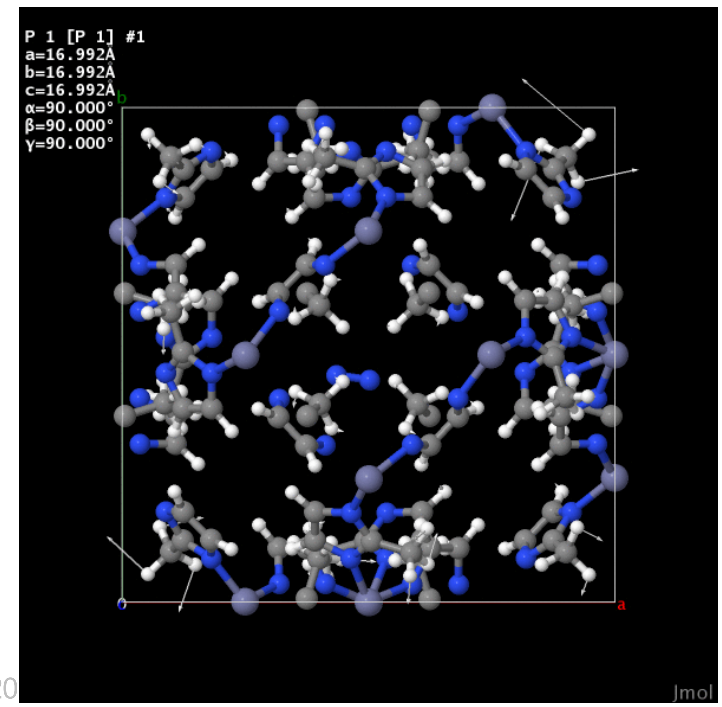


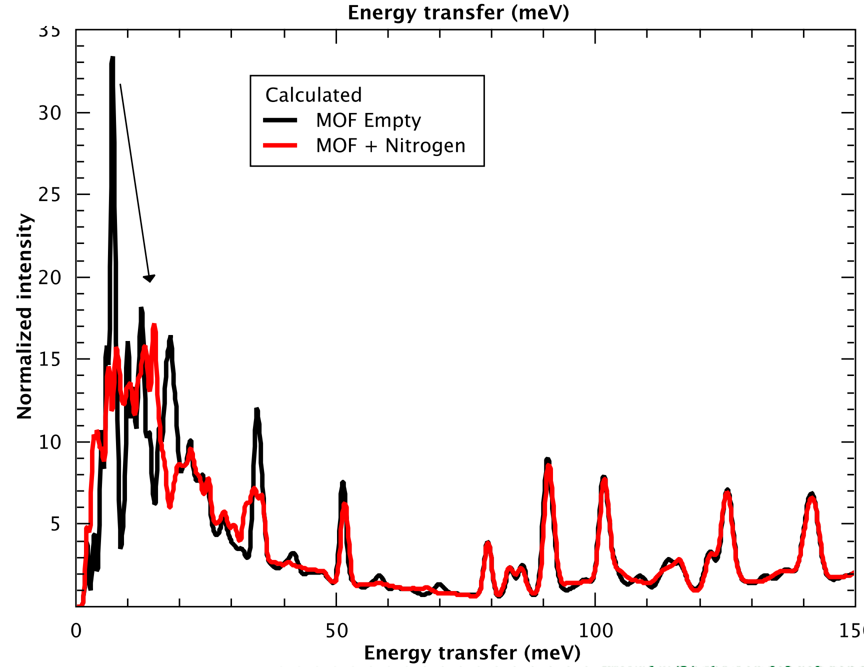


Nitrogen in a MOF

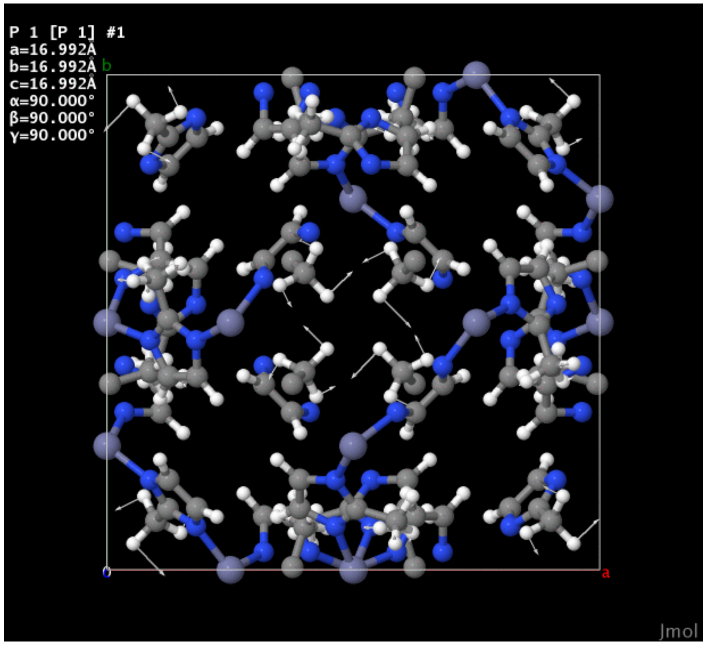


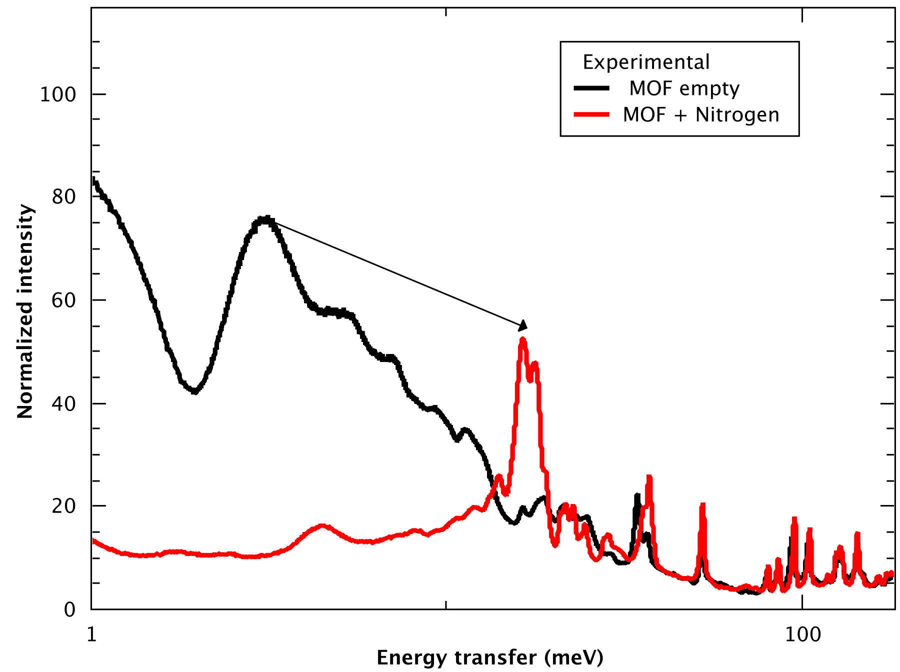


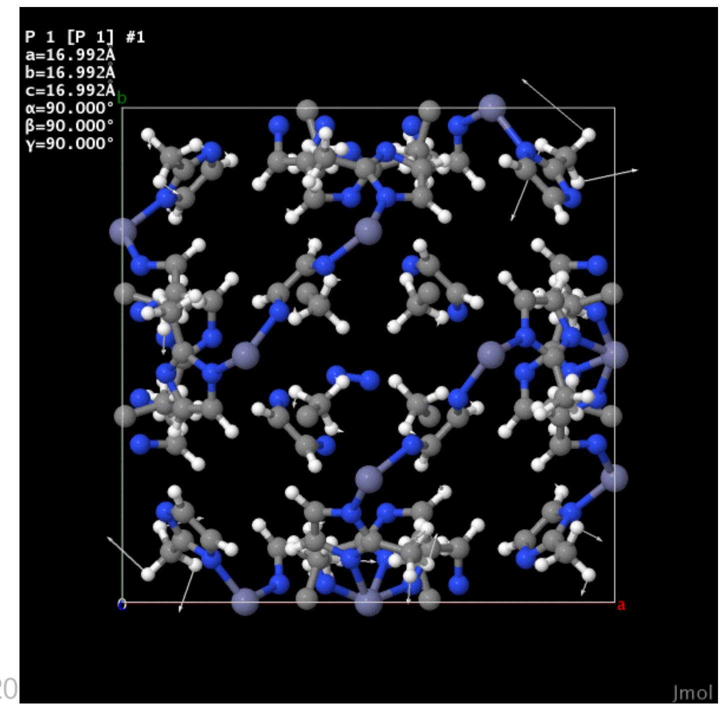


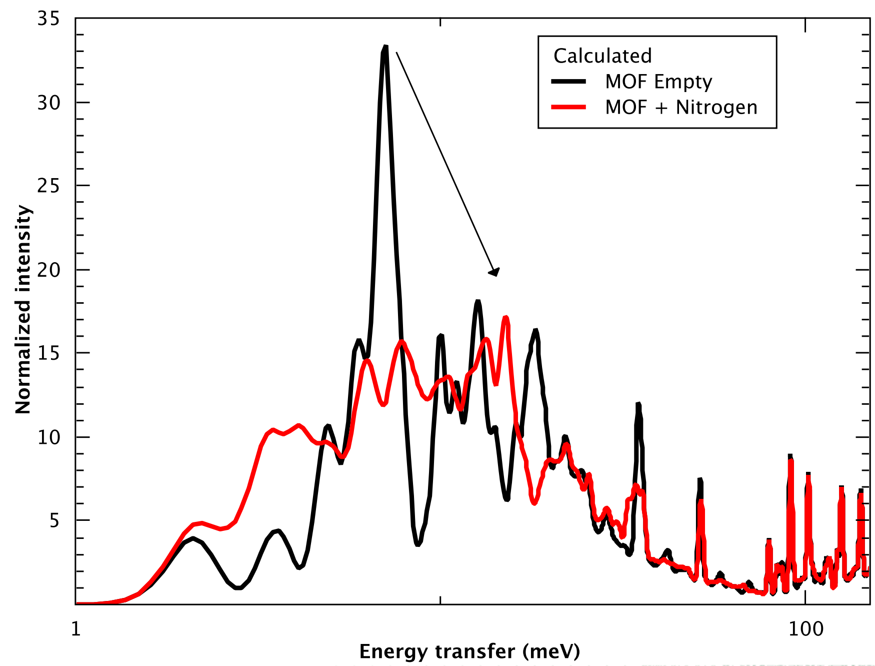


Nitrogen in a MOF

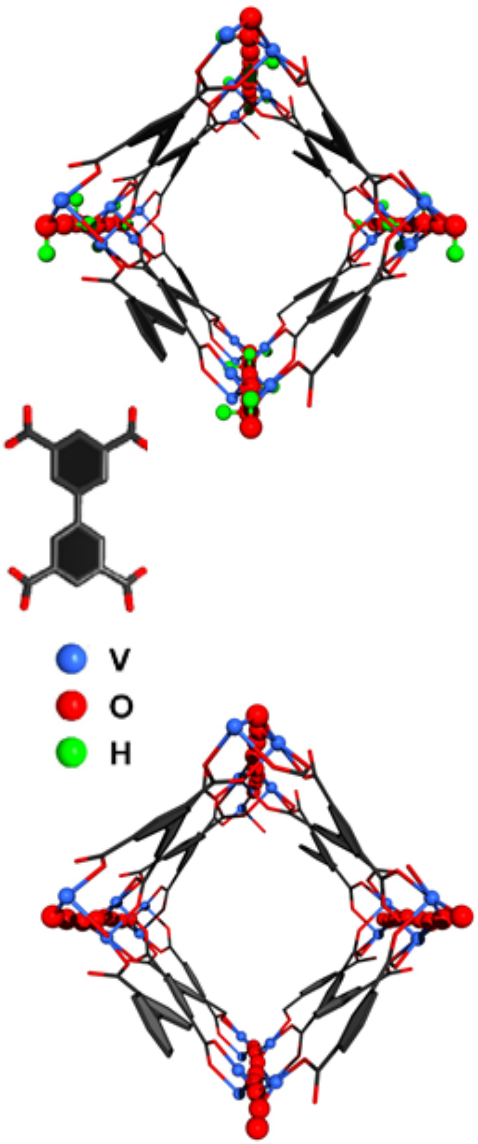


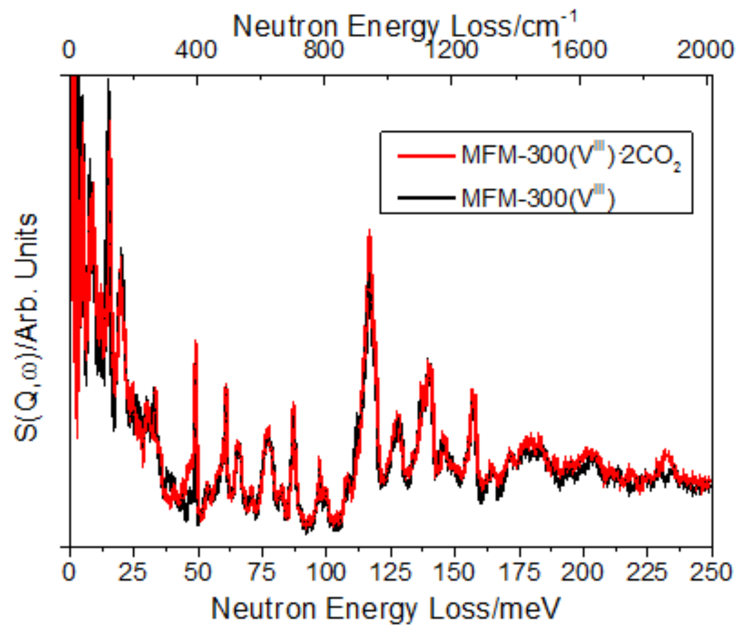


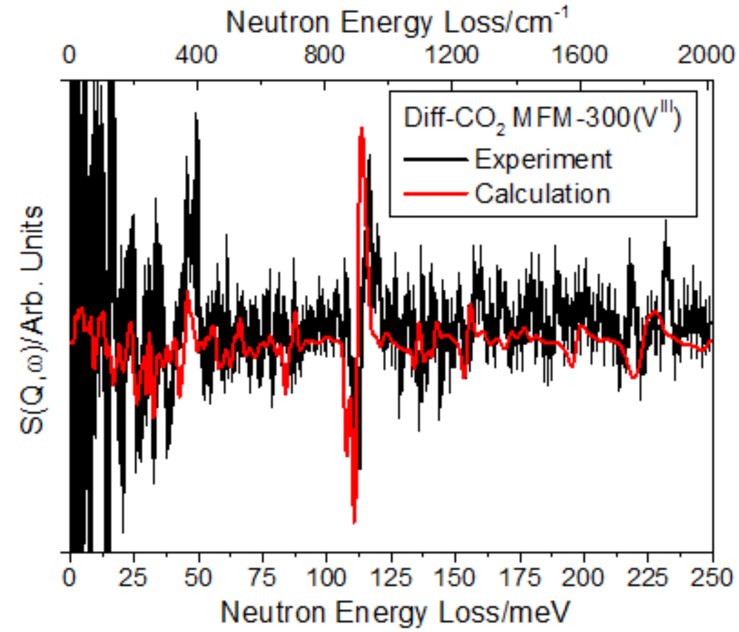


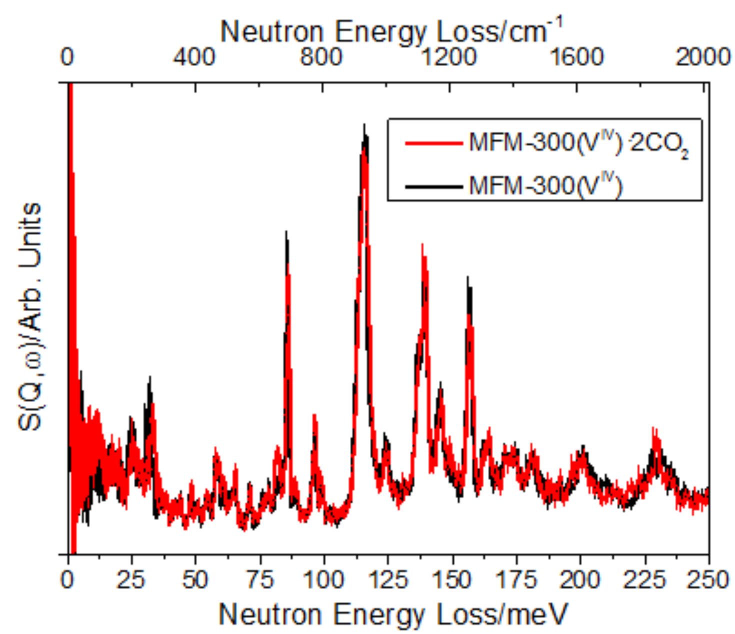


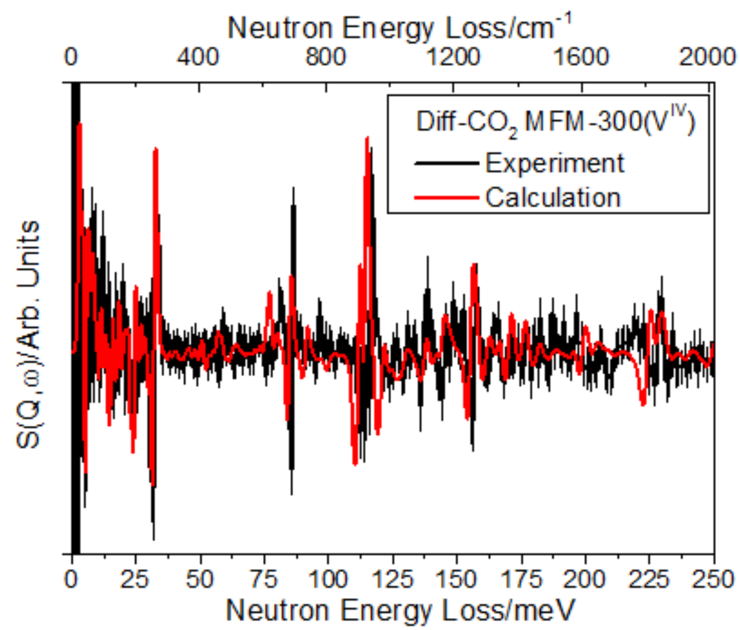
NOTT-V MOF and CO2 adsorption









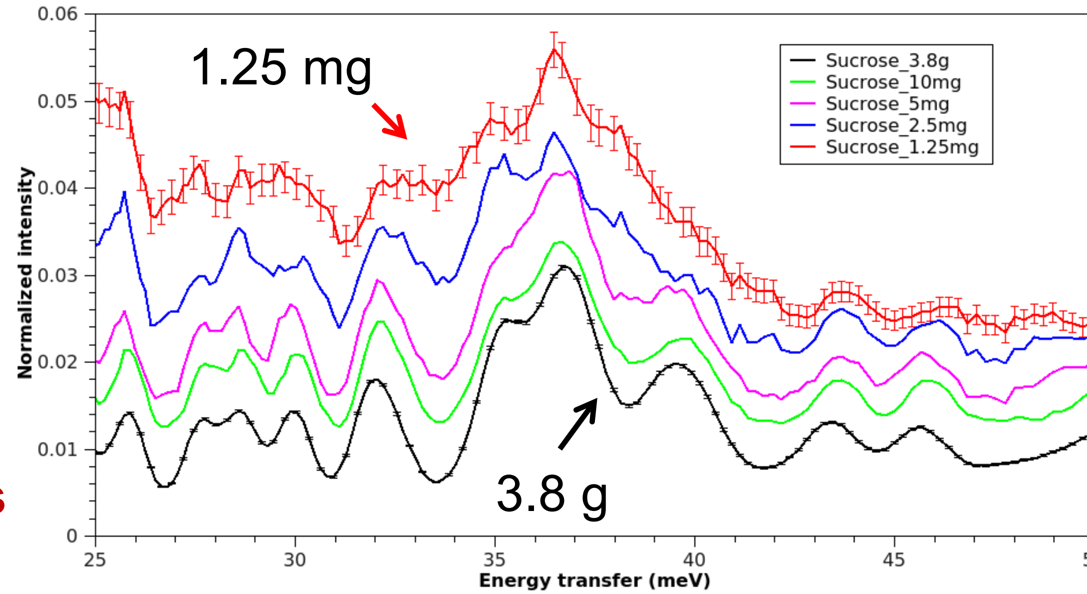


Collaboration with Sihai Yang and Martin Schroder at University of Manchester.

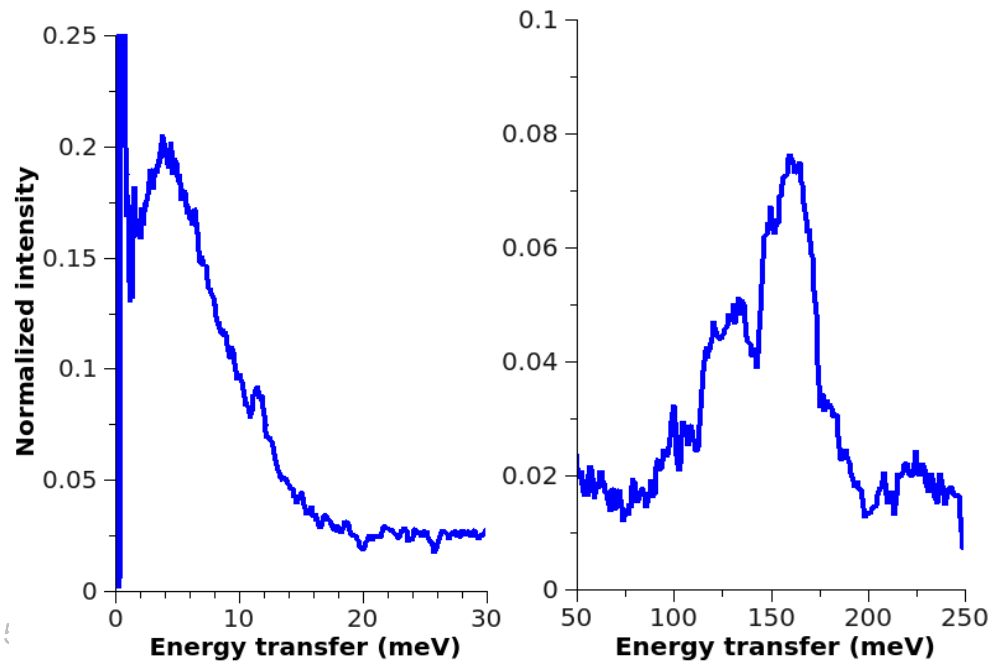
The ultra-high sensitivity of VISION: INS measured on milligrams of samples

- 1.25 mg of sucrose (table sugar)

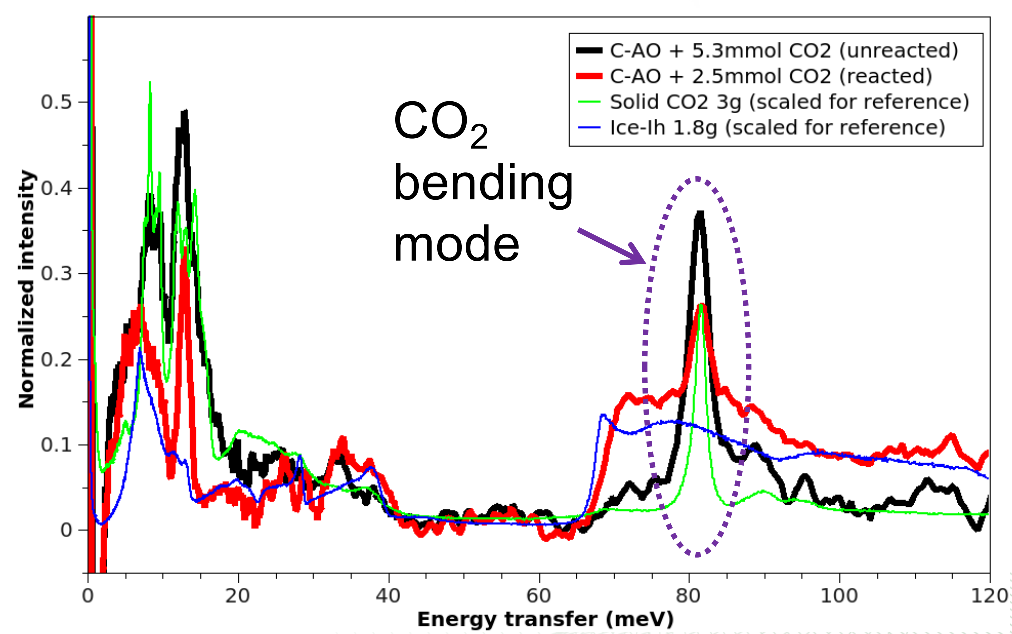
Sugar grains on Al foil (magnified, the total volume of the grains is about 0.8 mm^3)



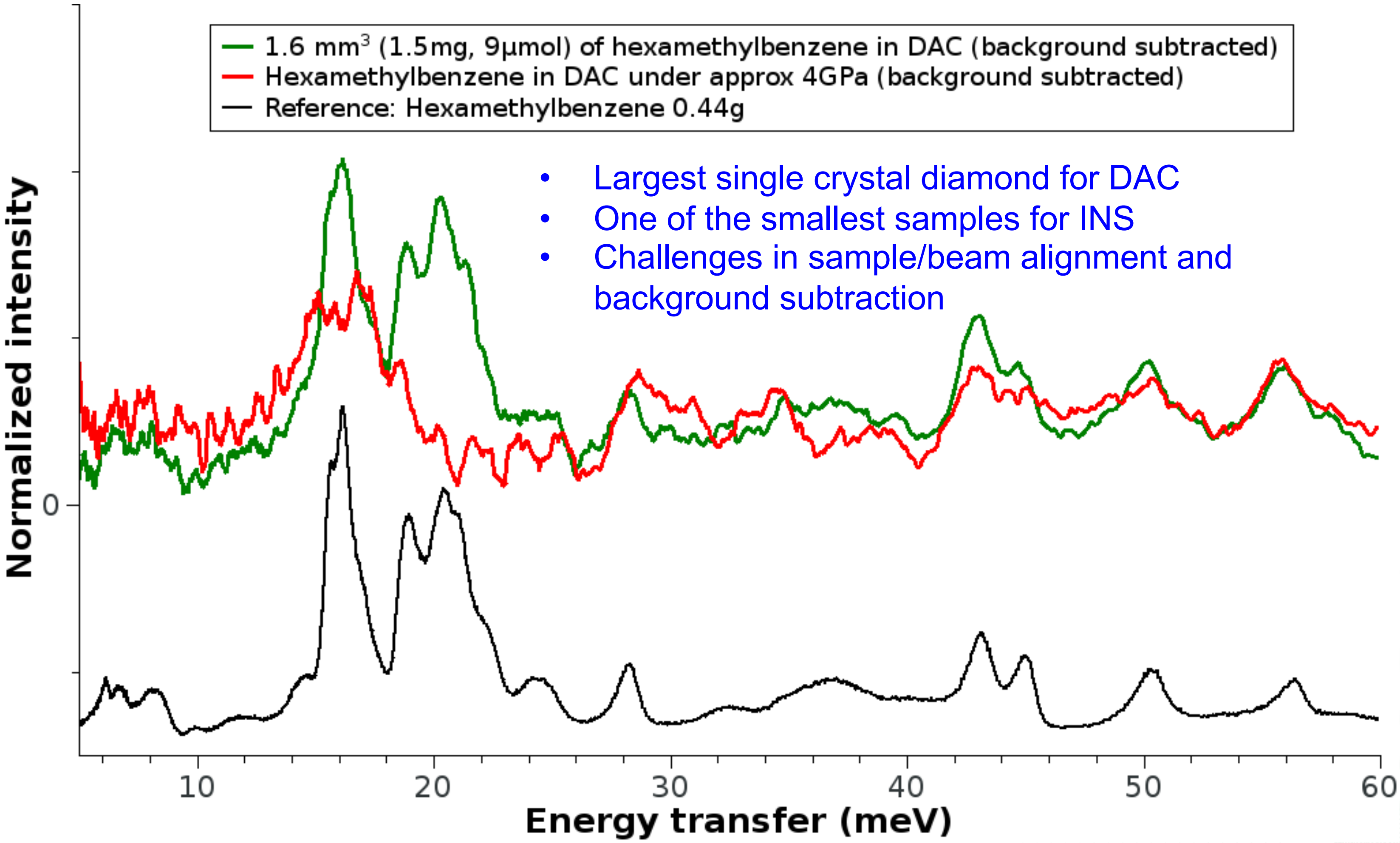
- 3 mg of polybenzene nanothreads



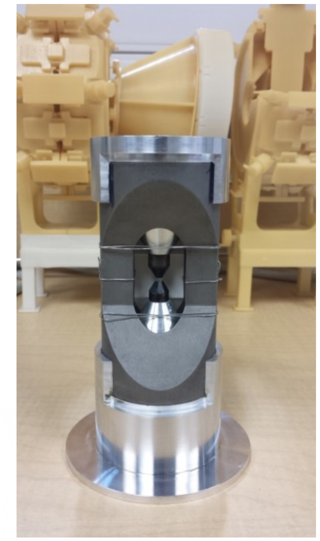
- 2.5 mmol of CO_2



A successful proof-of-principle test at VISION: using diamond anvil cell (DAC) for high pressure INS experiments

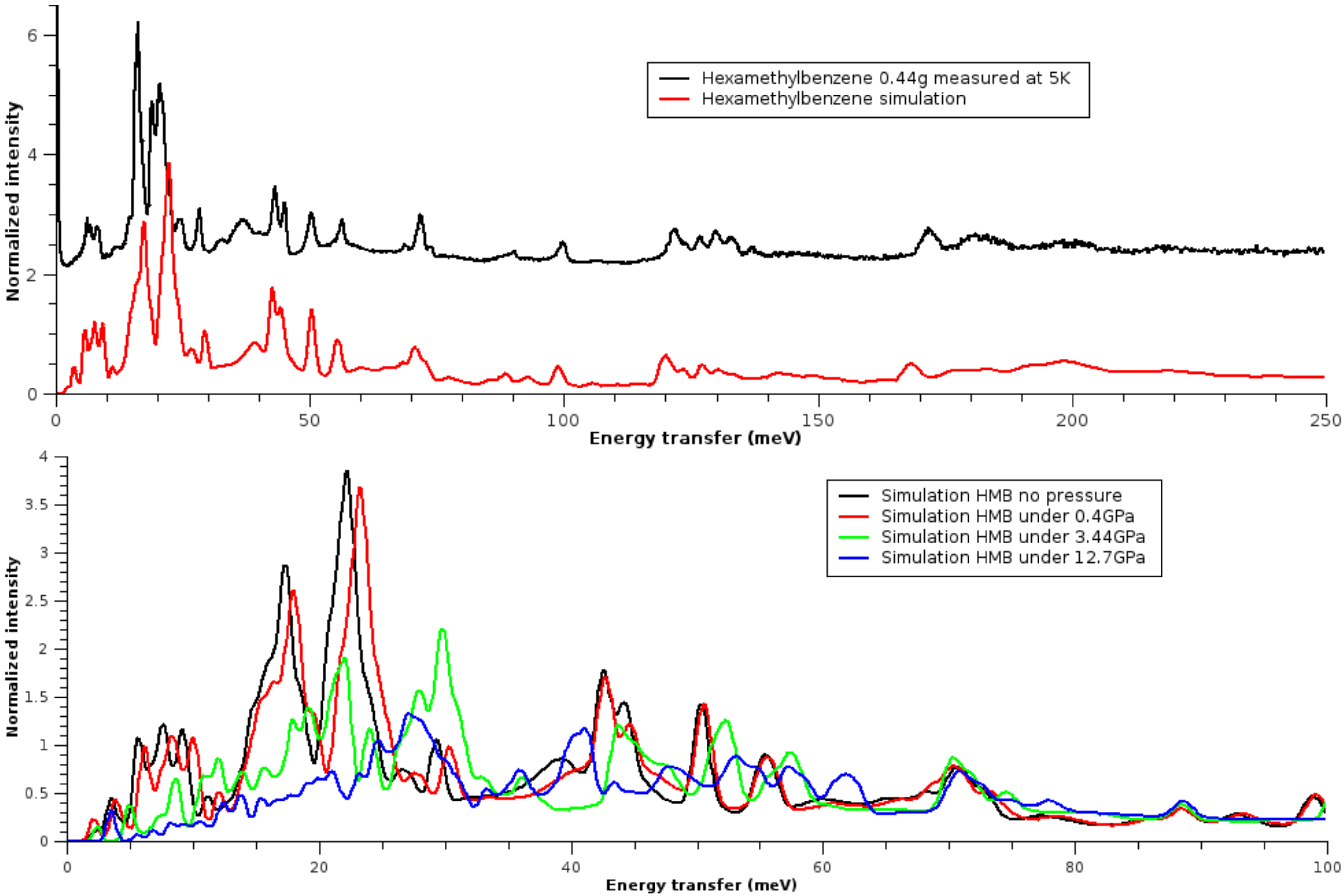


- Largest single crystal diamond for DAC
- One of the smallest samples for INS
- Challenges in sample/beam alignment and background subtraction

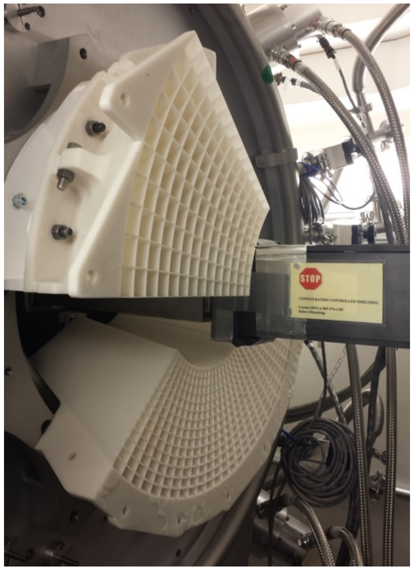


- INS spectrum from 1.6mm^3 (1.5mg, 9µmol) sample loaded in the DAC was successfully extracted, with significant details retained.
- Approx. 4GPa pressure was applied, leading to major changes in the spectrum.
- The unprecedented capability will open the door to many new areas using INS to study materials dynamical behavior under high pressure.

VirtuES for high pressure experiments

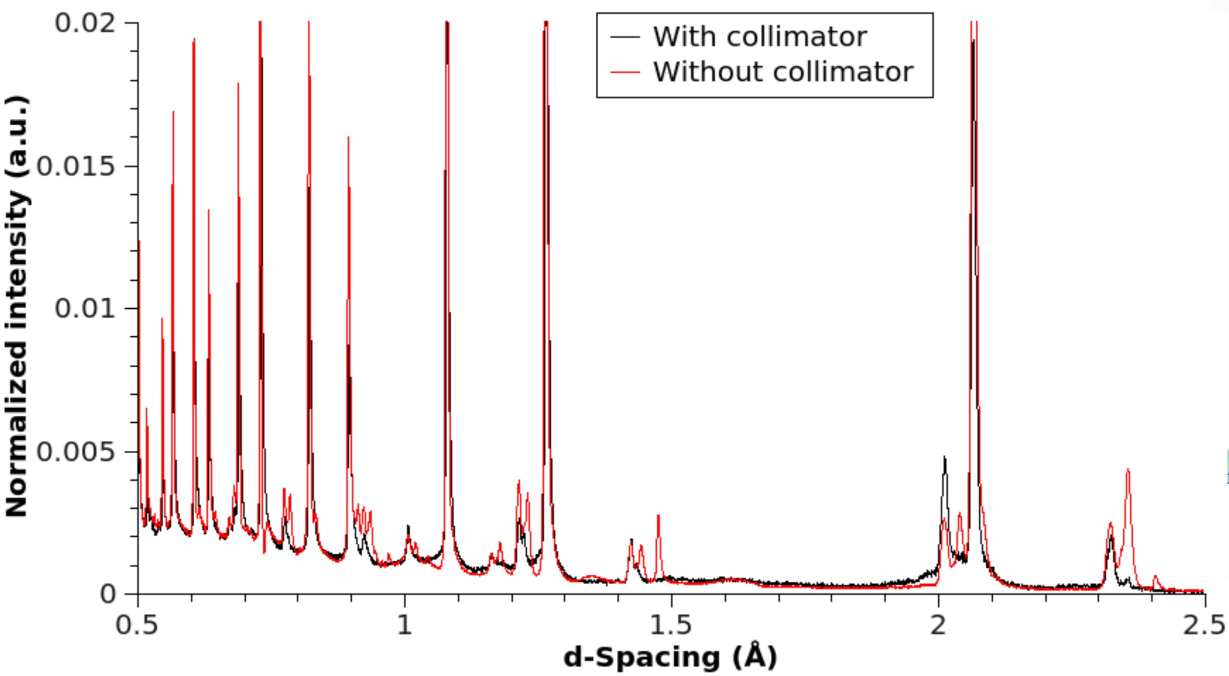


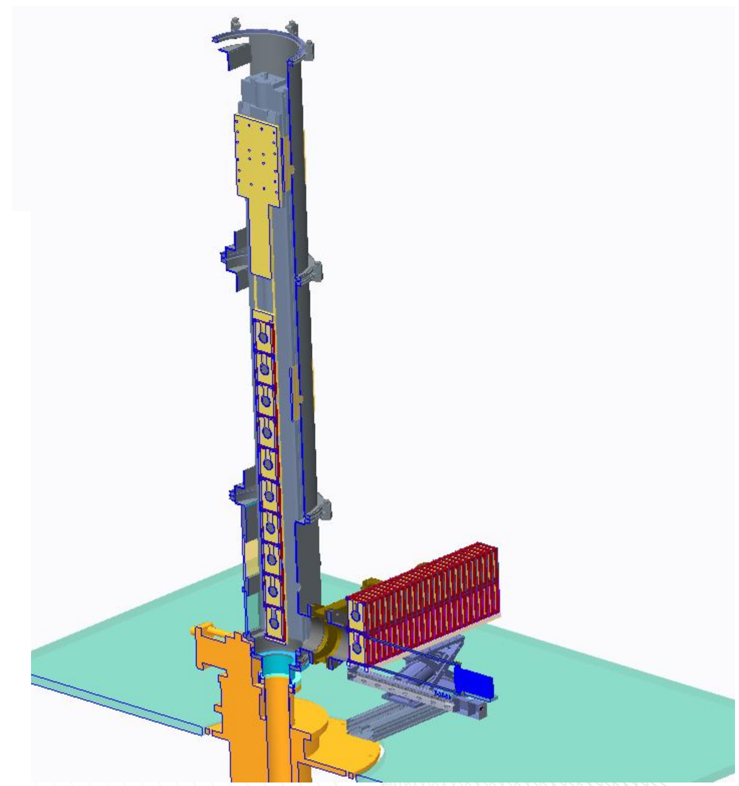
VISION Sample changer and 3D printed collimator



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





Conclusions

- INS is a very powerful technique to study the dynamics of materials
- Hydrogen scatters very well
- No selection rules
- Provides the phonon density of states averaged over the first Brilloiun zone weighted by the cross sections
- Neutrons slice through most metals, so sample environment is relatively easy
- Hydrogen in a molecular form behaves very differently from atomic hydrogen
- Rotational INS of hydrogen is an indication of the state of hydrogen in the system
- INS can be used on hydrogen bonded systems
- Direct and indirect geometry spectrometers complement each other when looking at vibrations at different energy ranges
  - In general Direct geometry is better at looking higher frequencies at low Q
  - Indirect has better resolution and fluxes at low frequencies

Questions?