

Neutron Vibrational Spectroscopy

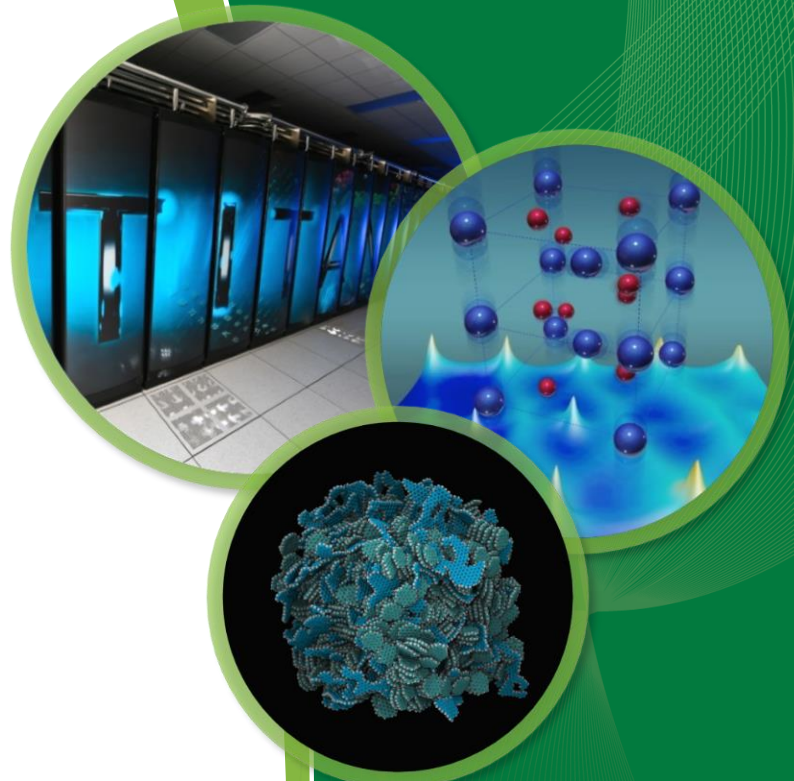
A.J. (Timmy) Ramirez-Cuesta

Luke L. Daemen

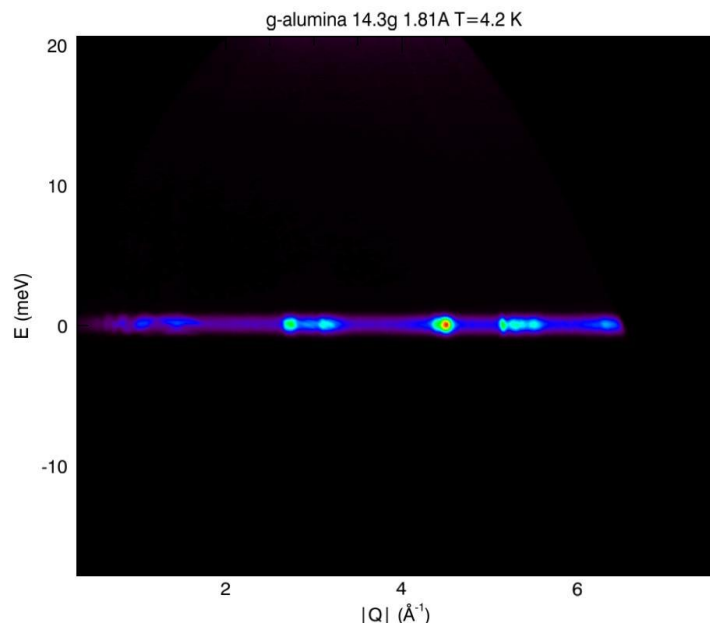
Yongqiang Cheng

Spallation Neutron Source

Oak Ridge National Laboratory

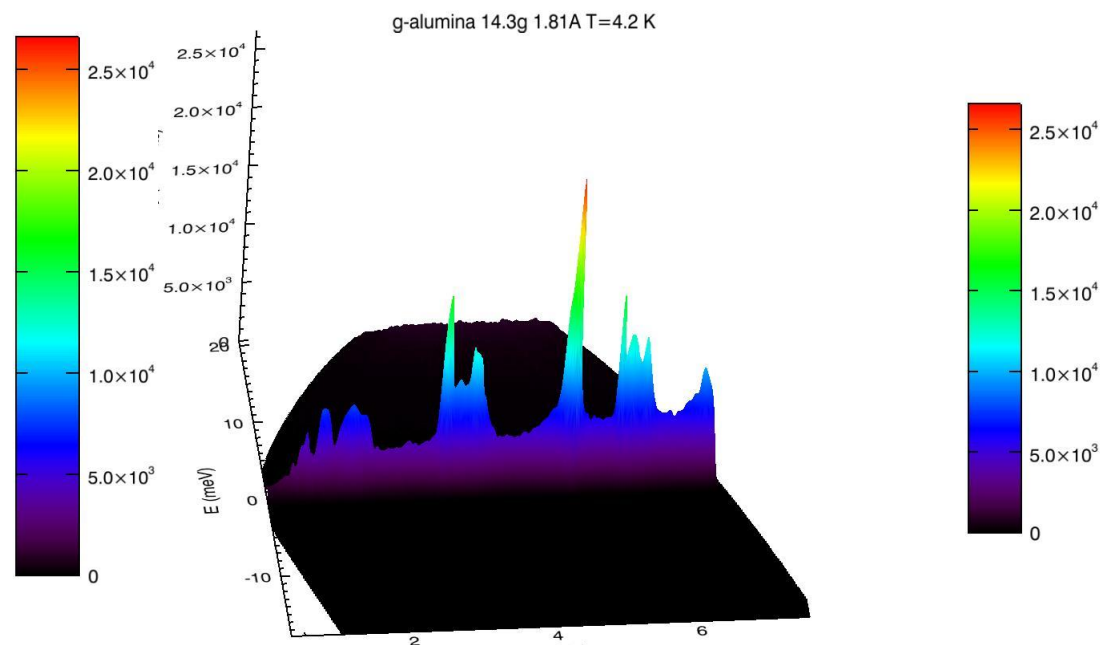


The $S(Q,\omega)$ Map



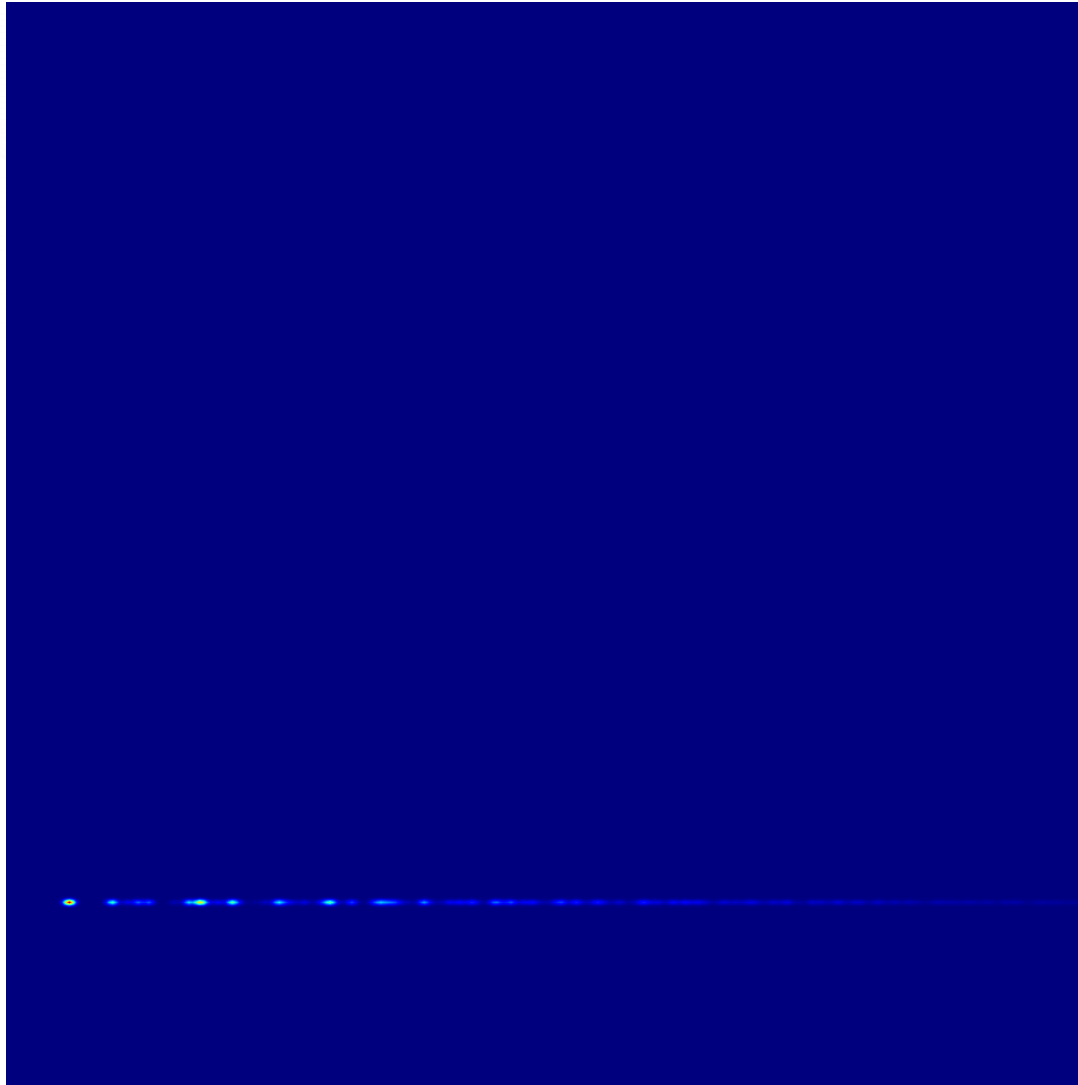
$\omega=0$

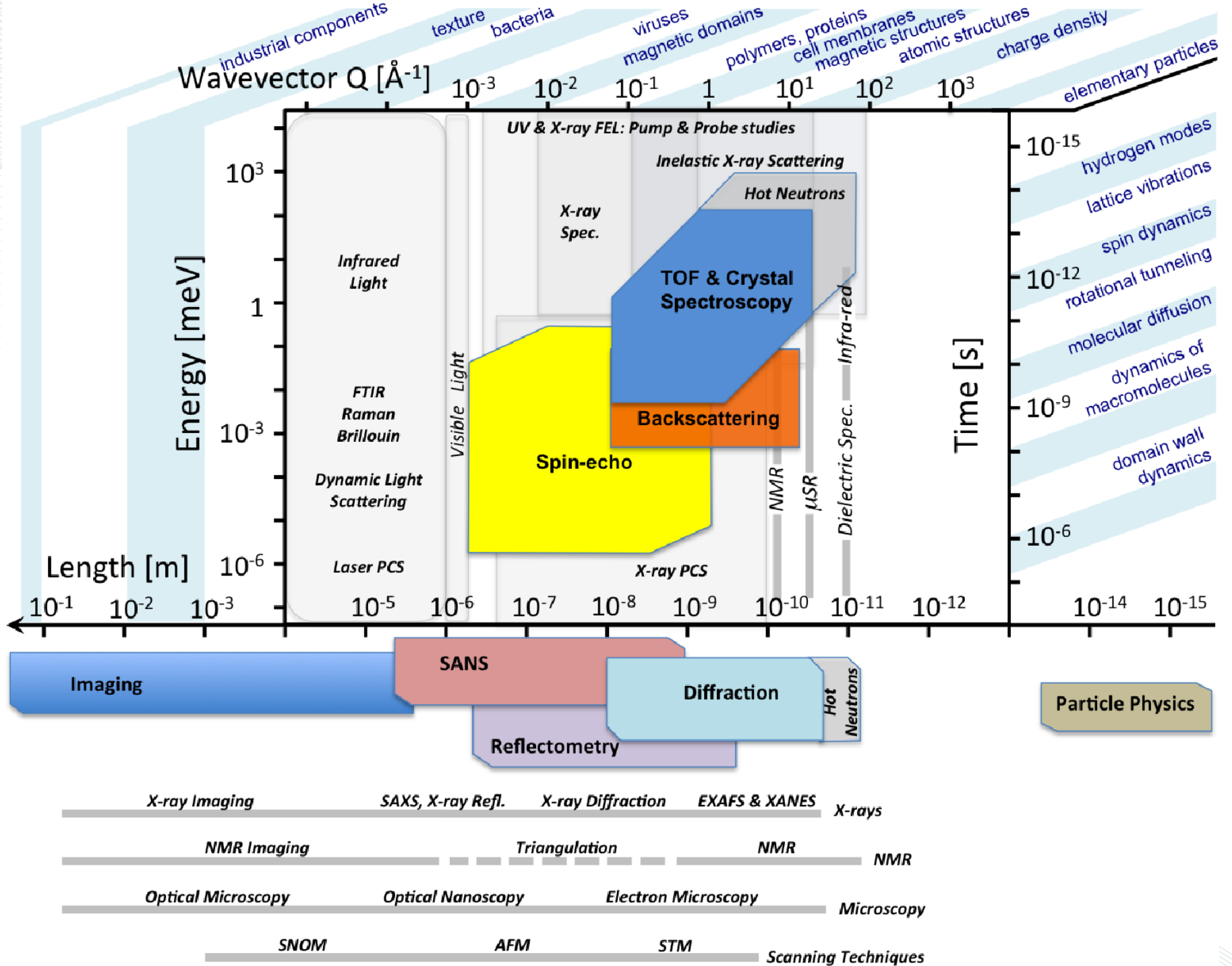
Elastic Scattering
Structural Information



Diffraction

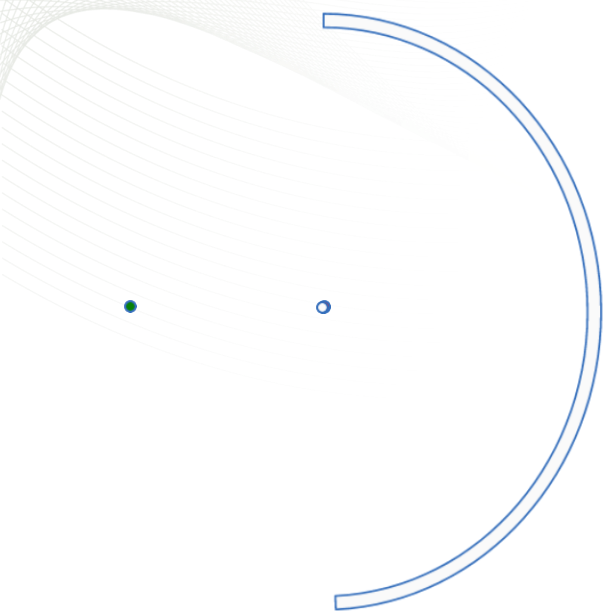
"Let there be light"





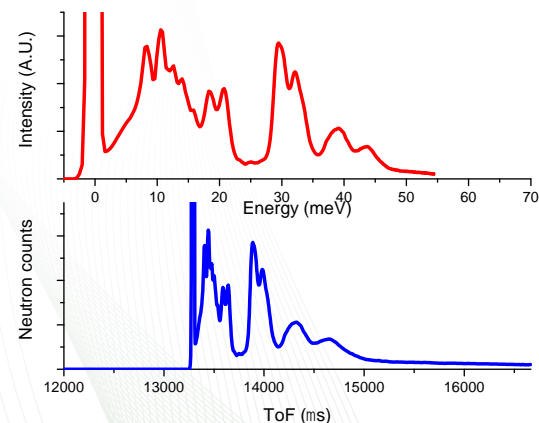
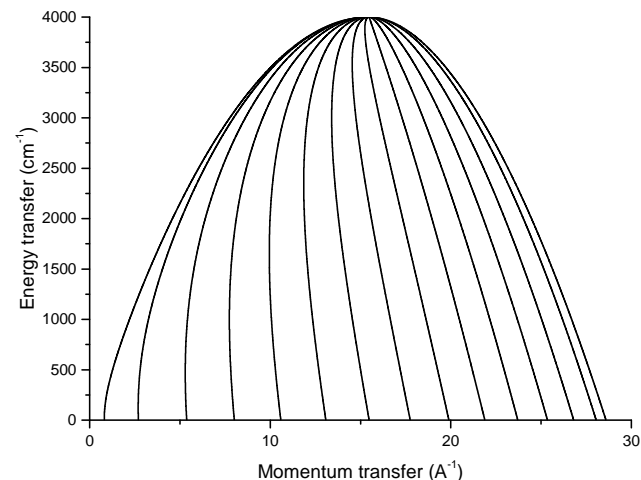
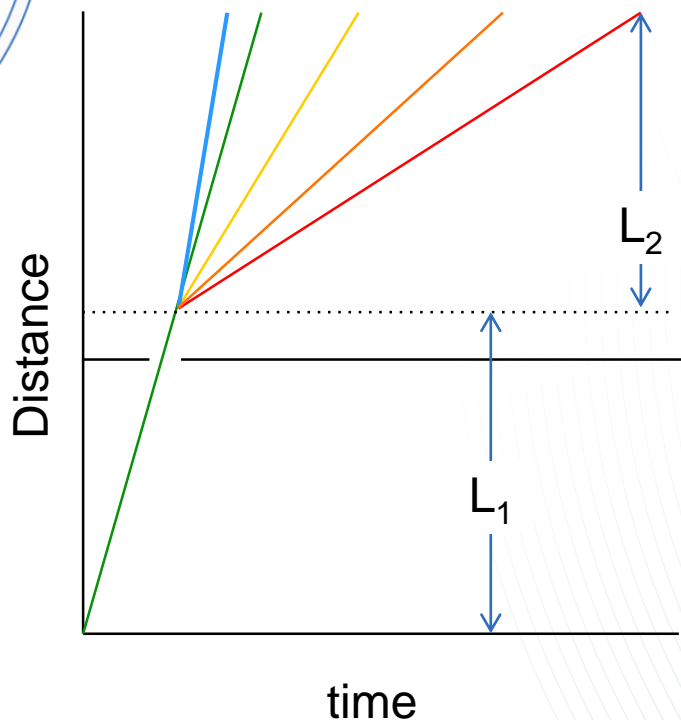
How to measure INS (1)

Direct Geometry Instrumentation



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

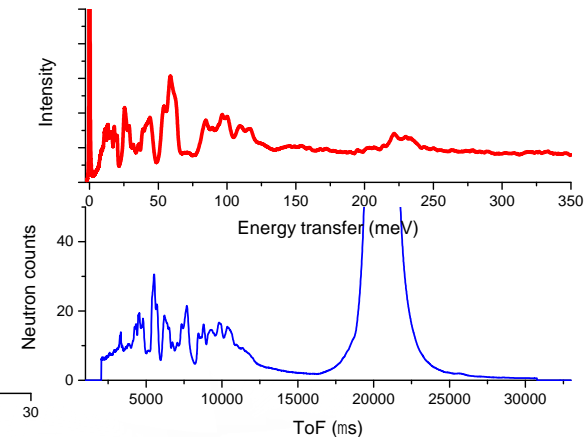
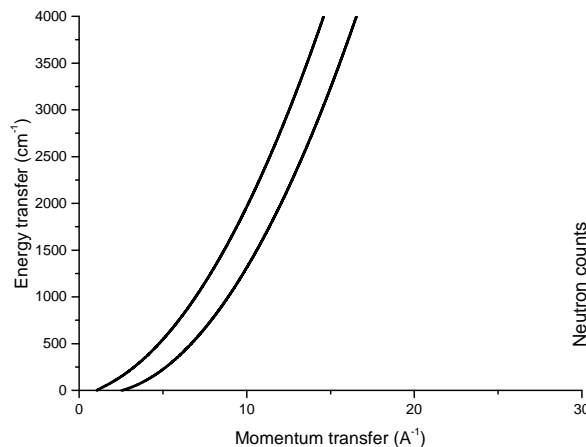
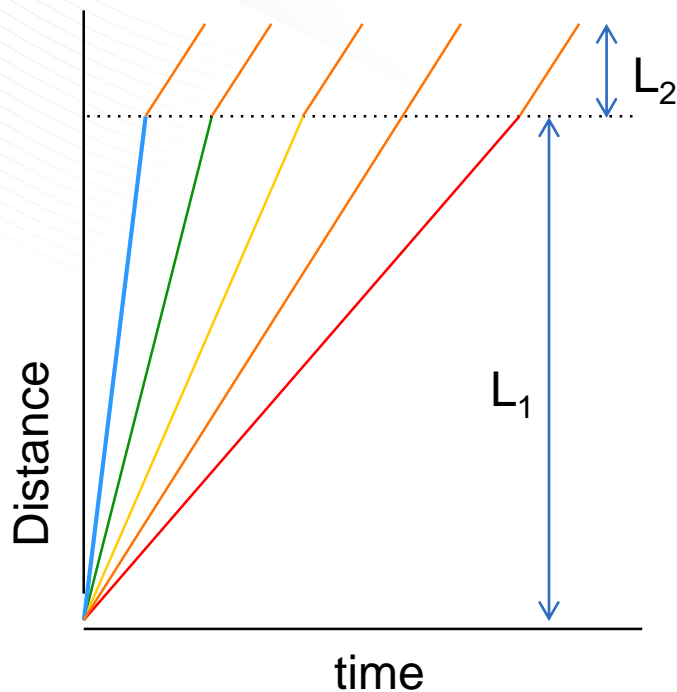
Incident neutron beam is monochromatic determining the incident energy E_1 .
 That determines T_1 . We measure the ToF and we can work out T_2 .



Resolution is almost constant in units of E_i

How to measure INS (2)

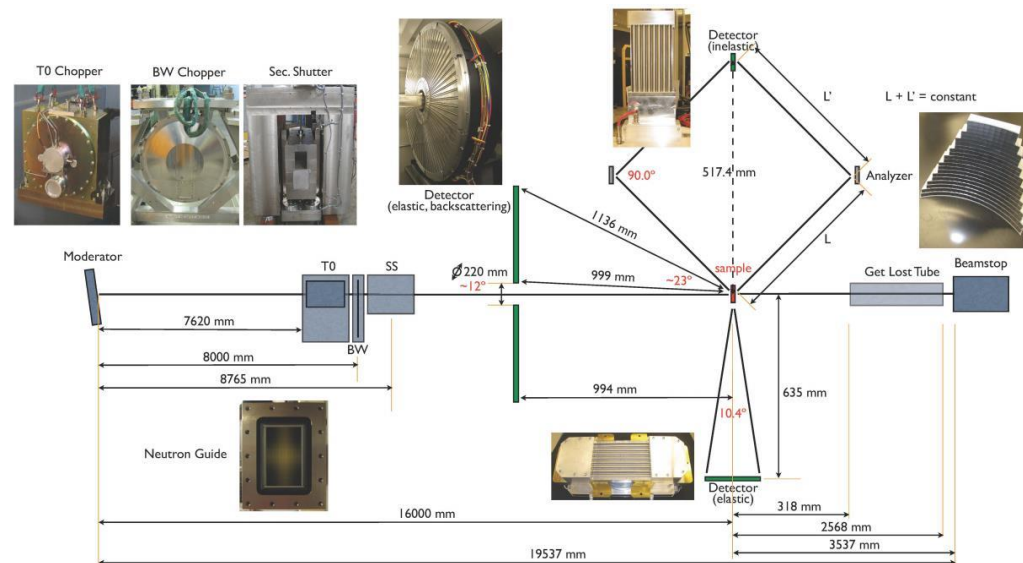
Indirect Geometry Instrumentation



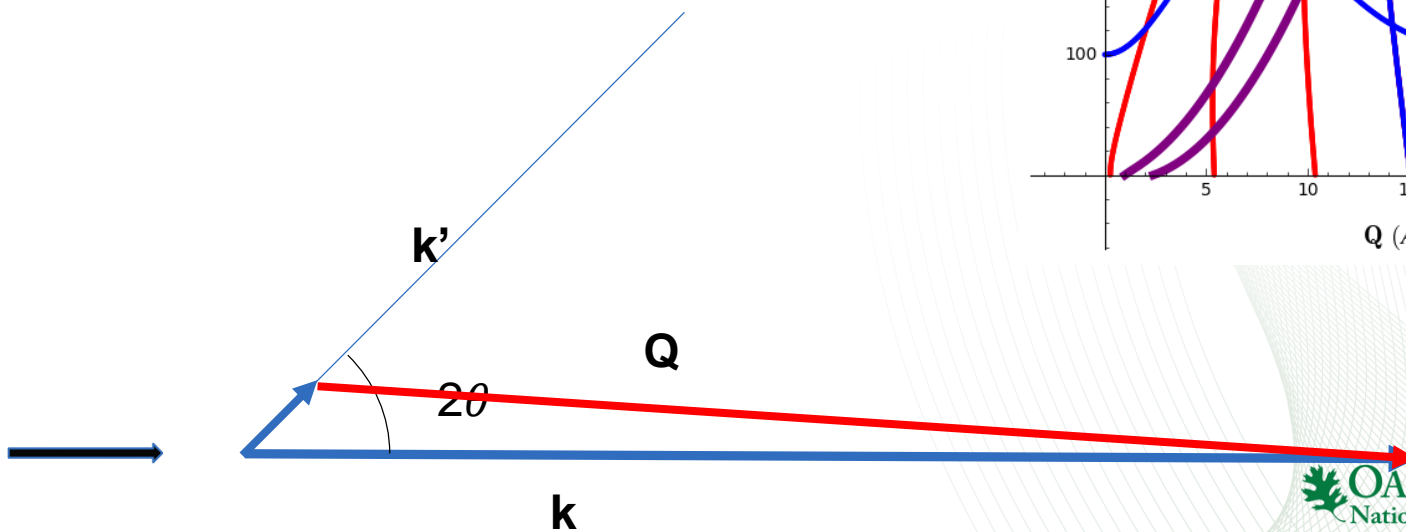
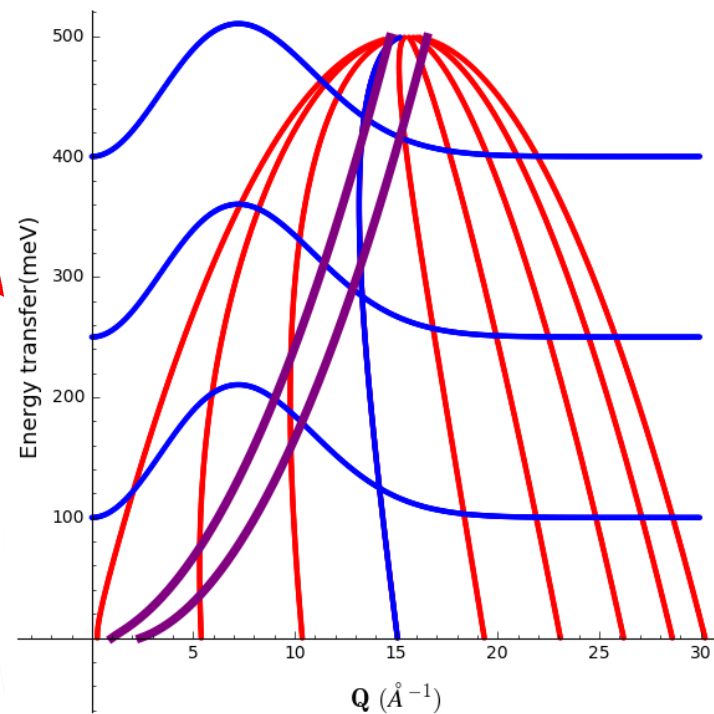
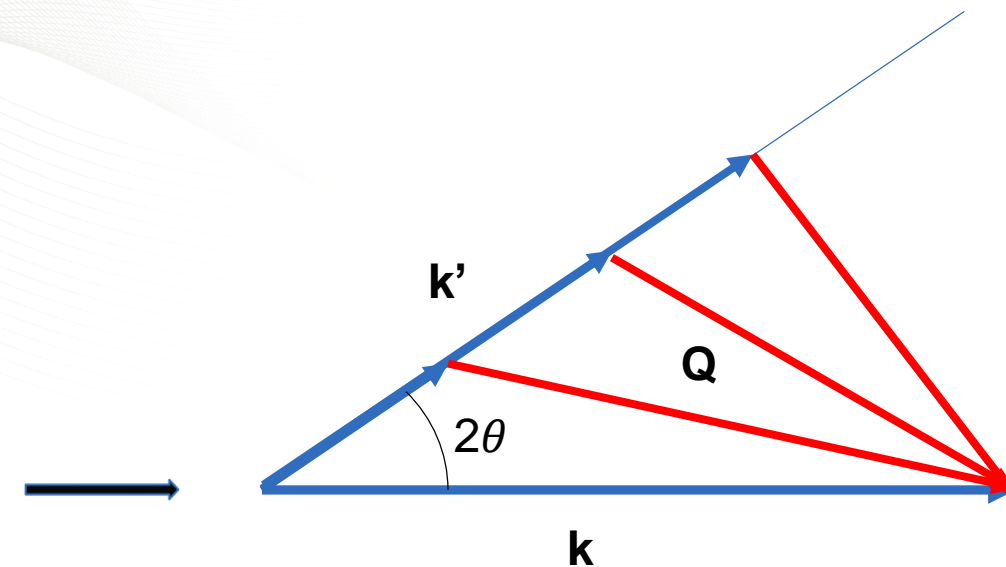
Resolution is almost constant in units of $\Delta\omega/\omega \sim 1.5\%$

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

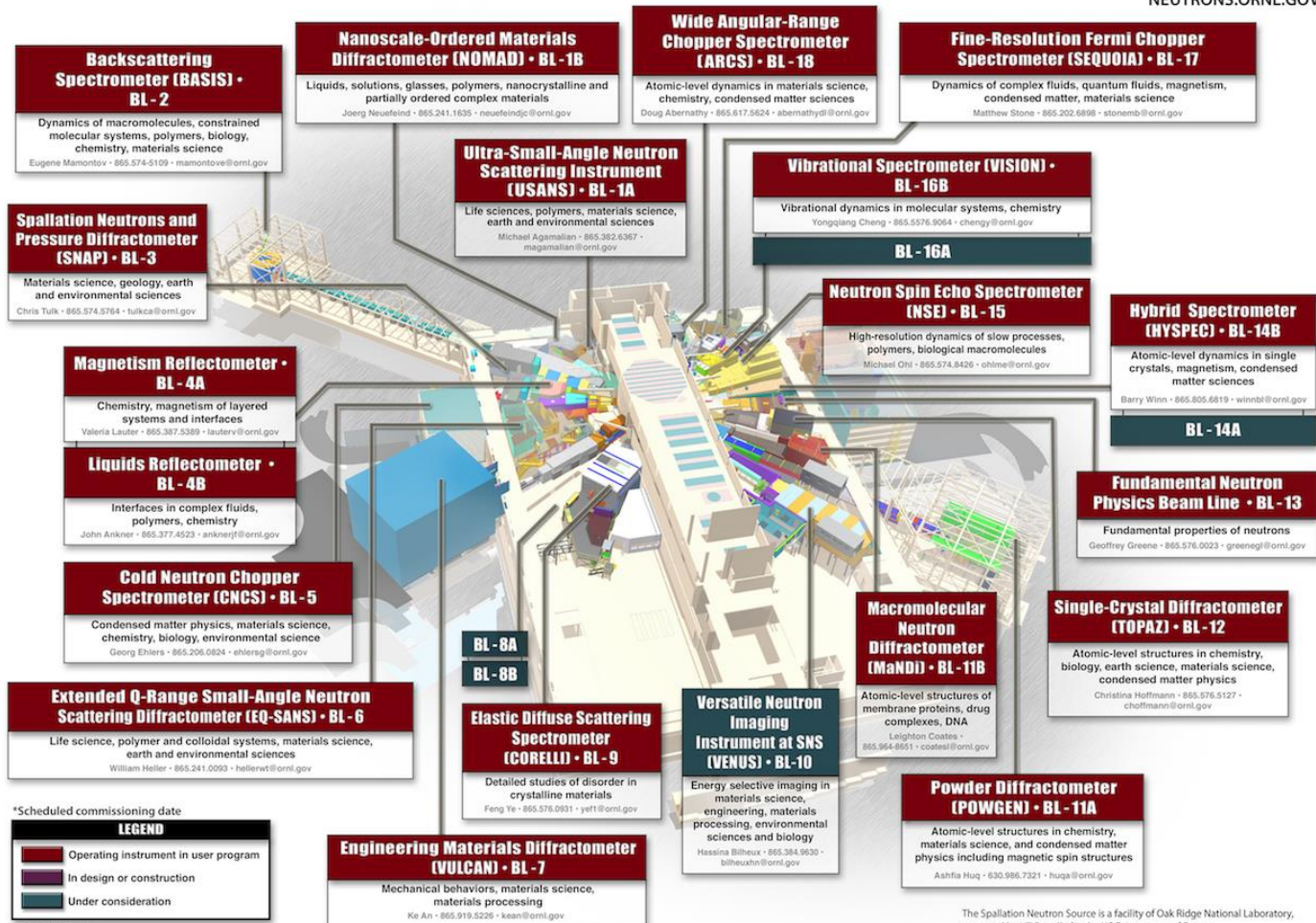
That fixes T_2 . We measure the ToF and we can work out T_1 .



Effect of the Instrument Geometry



SNS Instrument Suite



VISION

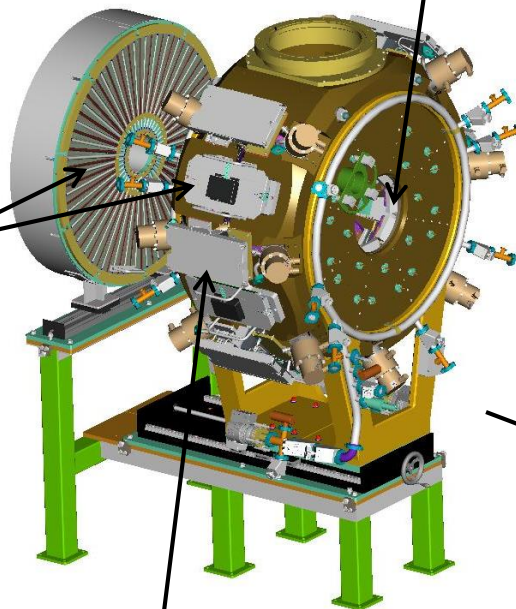
neutron beam



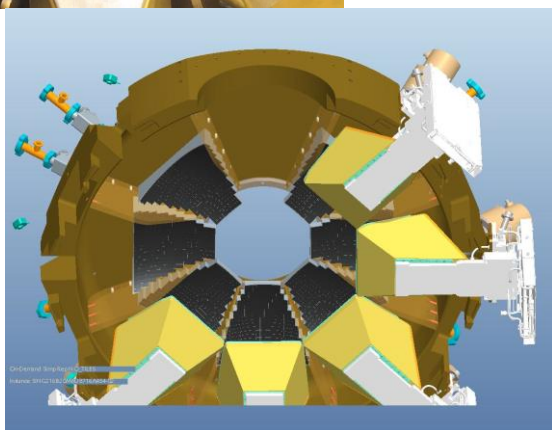
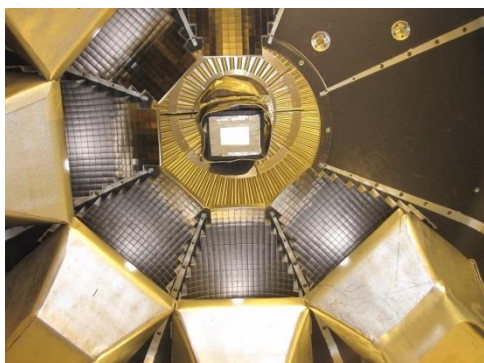
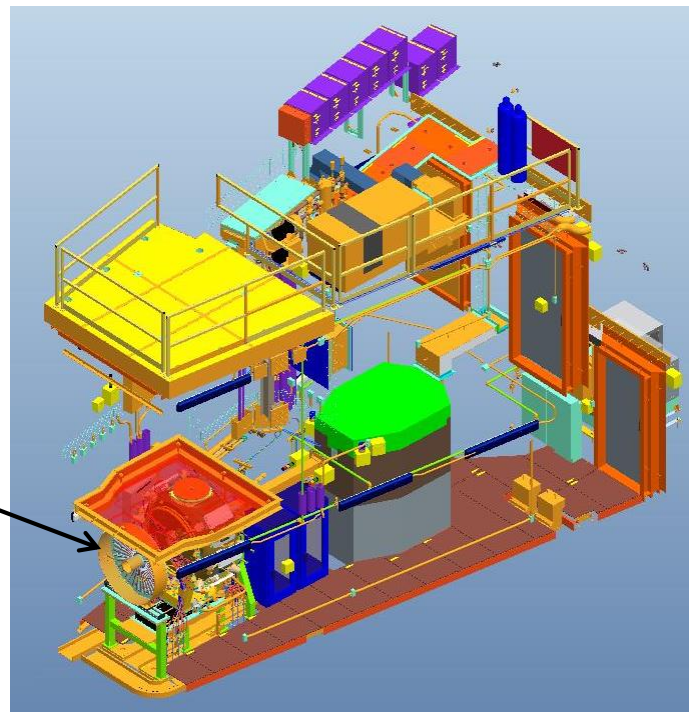
diffraction detectors



analyzers



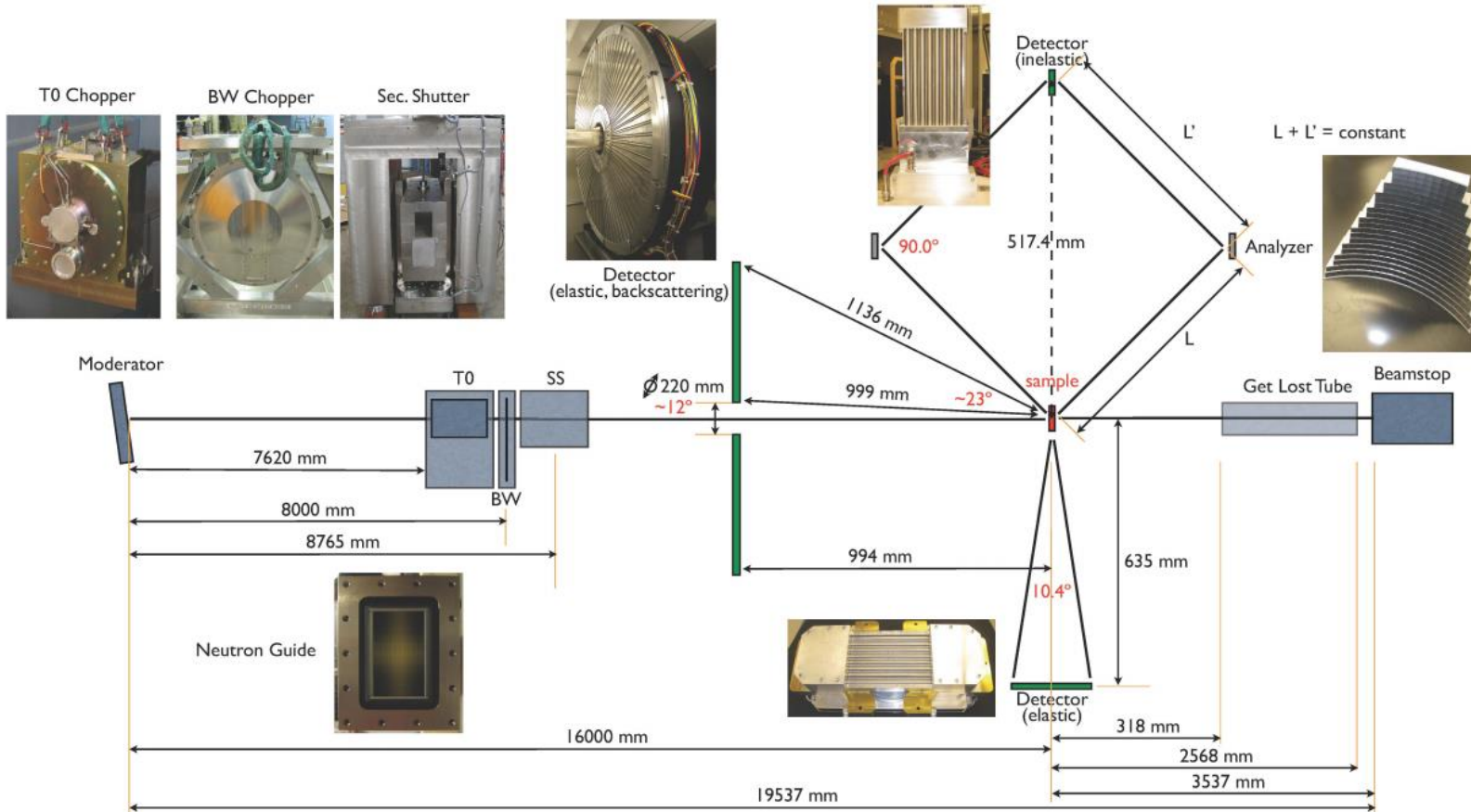
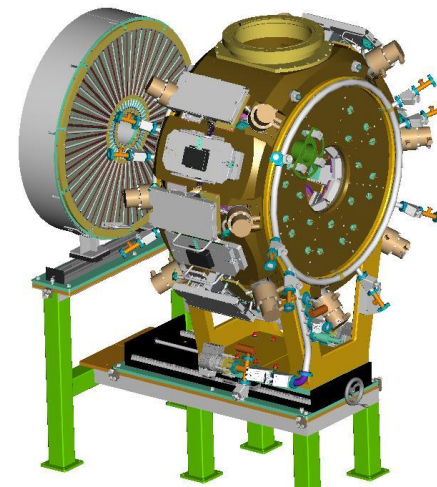
inelastic detectors



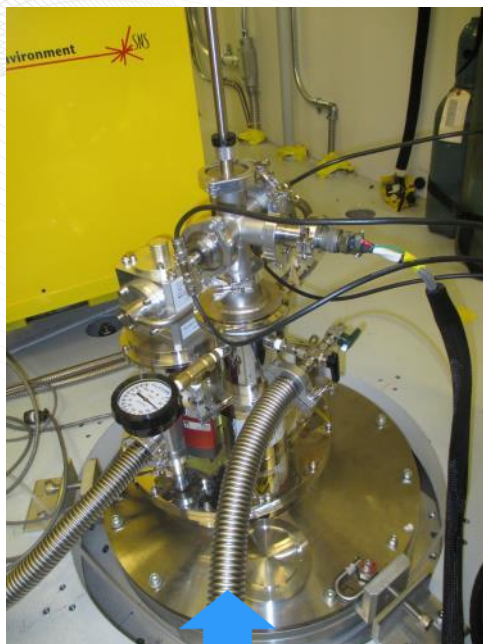
- Vibrational spectroscopy with neutrons
- Beam line started commissioning 2 years ago
- **Multifunctional beam line: simultaneous spectroscopy and diffraction**
- Dynamic range: 0-1000 meV; resolution: $< 1.5\%$
- Diffraction: $1.5 - 30 \text{ \AA}^{-1}$
- Temperature range: 5-700K
- Sample environment: high pressure, electric field, gas loading, ...
- Great sensitivity to hydrogen, no selection rules, penetration through matter, ...

The VISION instrument

- White incident beam, fixed final energy (indirect geometry)
- High flux ($\sim 5 \times 10^7$ neutrons/cm²/s) and double-focusing
- Broadband (-2 to 1000 meV at 30Hz, 5 to 500 meV at 60 Hz)
- Constant dE/E throughout the spectrum ($\sim 1.5\%$)
- Elastic line HMFWD $\sim 150 \mu\text{s}$
- Backward and 90° diffraction banks



Sample environment



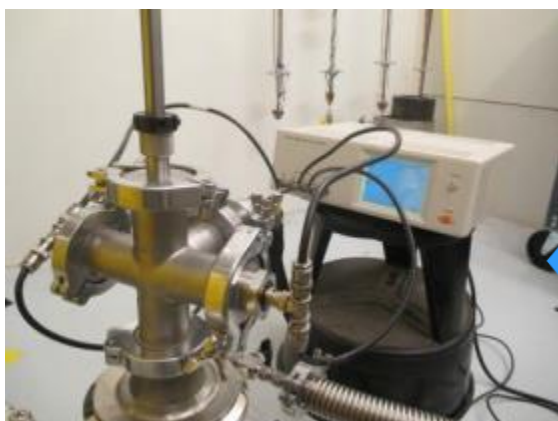
JANIS closed-cycle refrigerator (5-700K)



Pressure cells (piston, gas, diamond anvil).



Gas handling panel for gas dosing, mixing, flow, adsorption (vacuum to 200 bar)

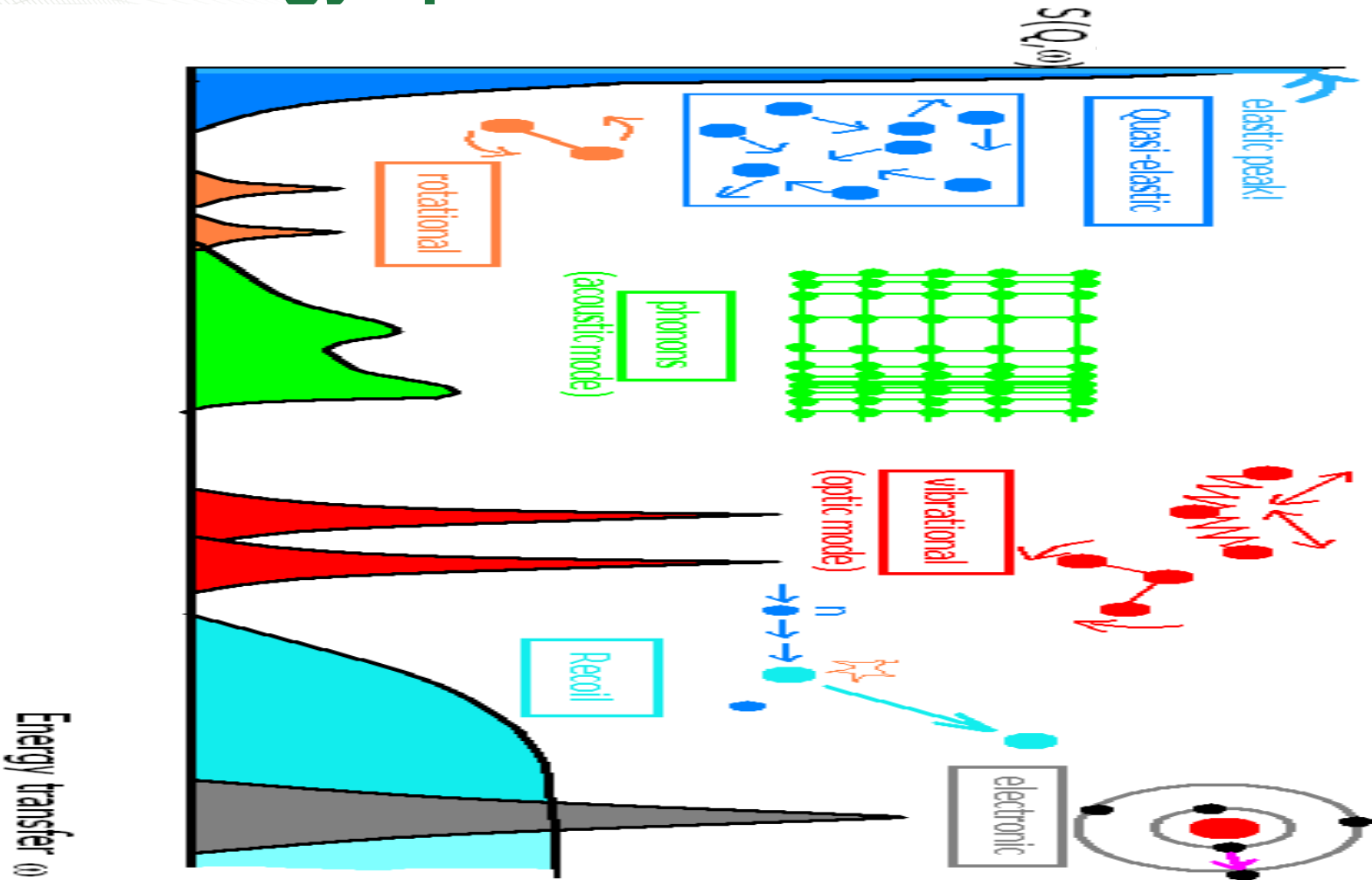


in situ electrochemical impedance spectroscopy (EIS)

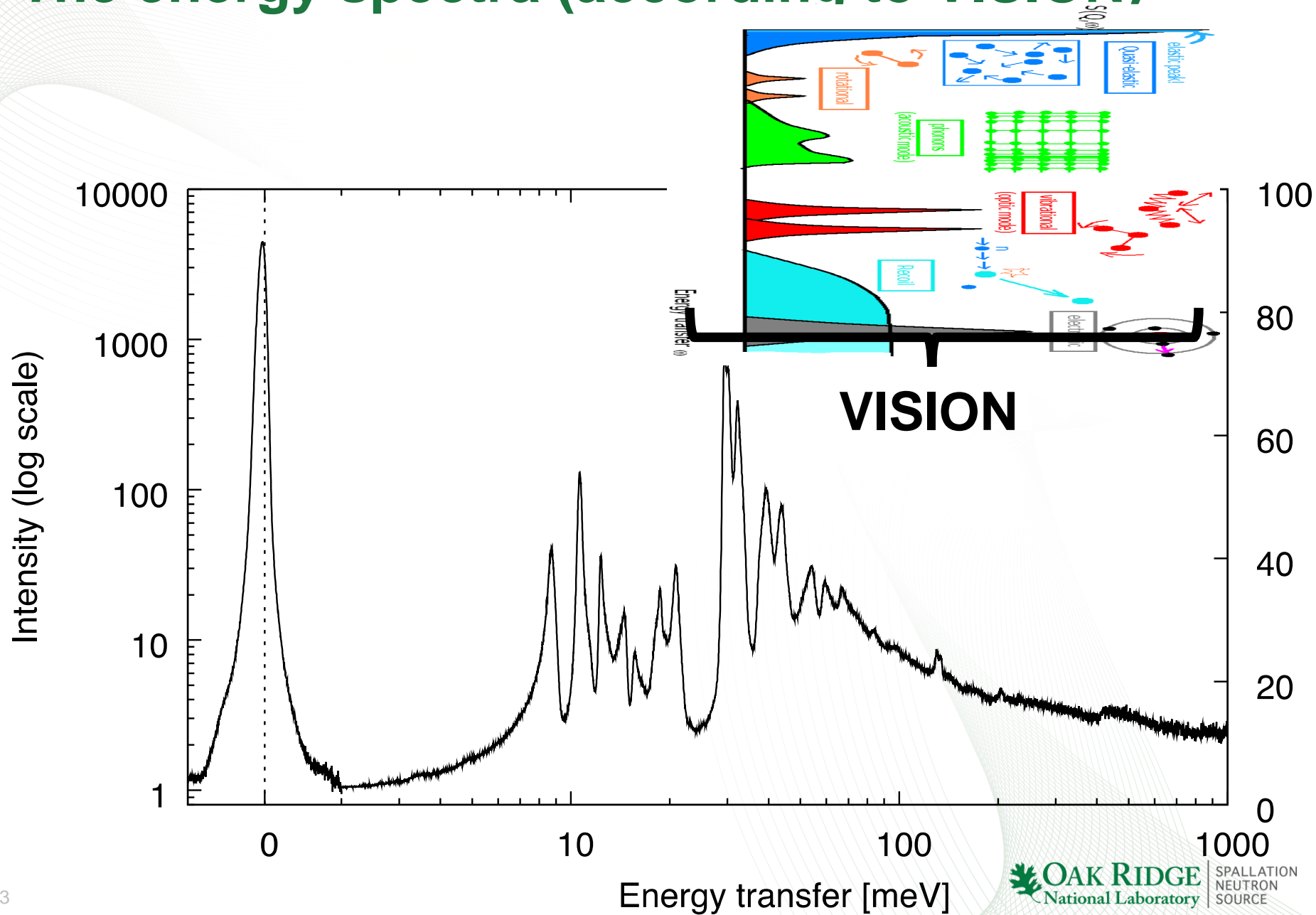


ortho/para H₂ converter

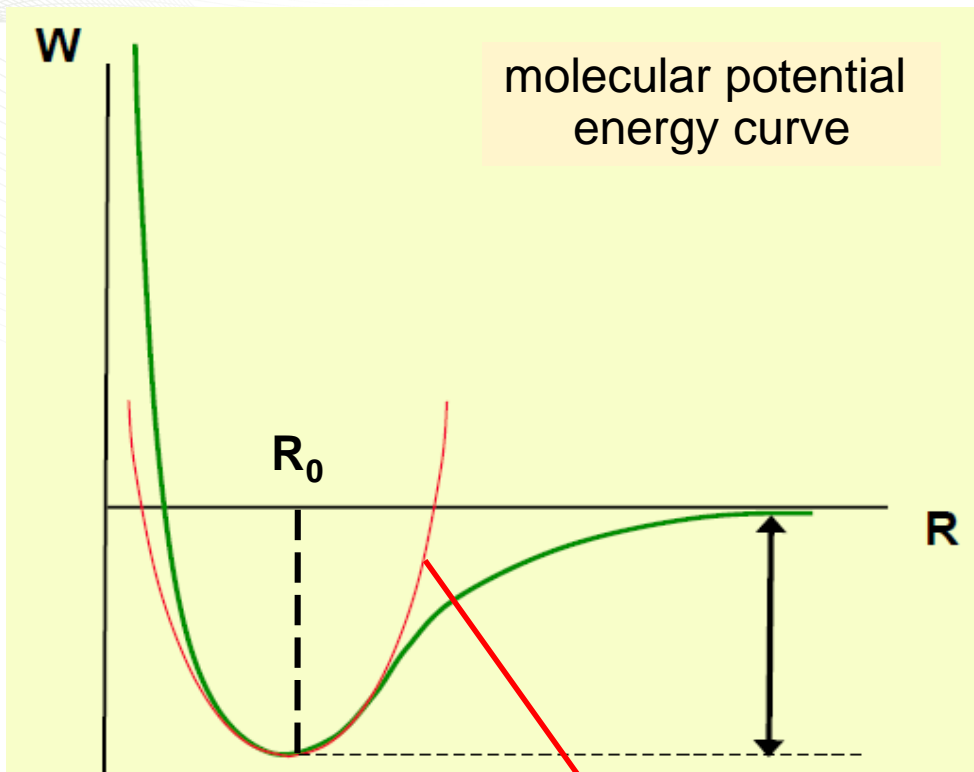
The energy spectra



The energy spectra (according to VISION)



Vibrational spectroscopy



harmonic approximation

As a first approximation, a chemical bond between two atoms can be thought of as a spring connecting two masses:



Classical mechanics shows that this system vibrates with a characteristic frequency:

$$\nu = \left(\frac{1}{2\pi}\right) \sqrt{k/\mu}$$

where μ is the reduced mass:

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

Vibrational spectroscopy

Dynamics at the atomic level is determined by quantum mechanics rather than by classical mechanics. The relevant problem here is the quantum harmonic oscillator.

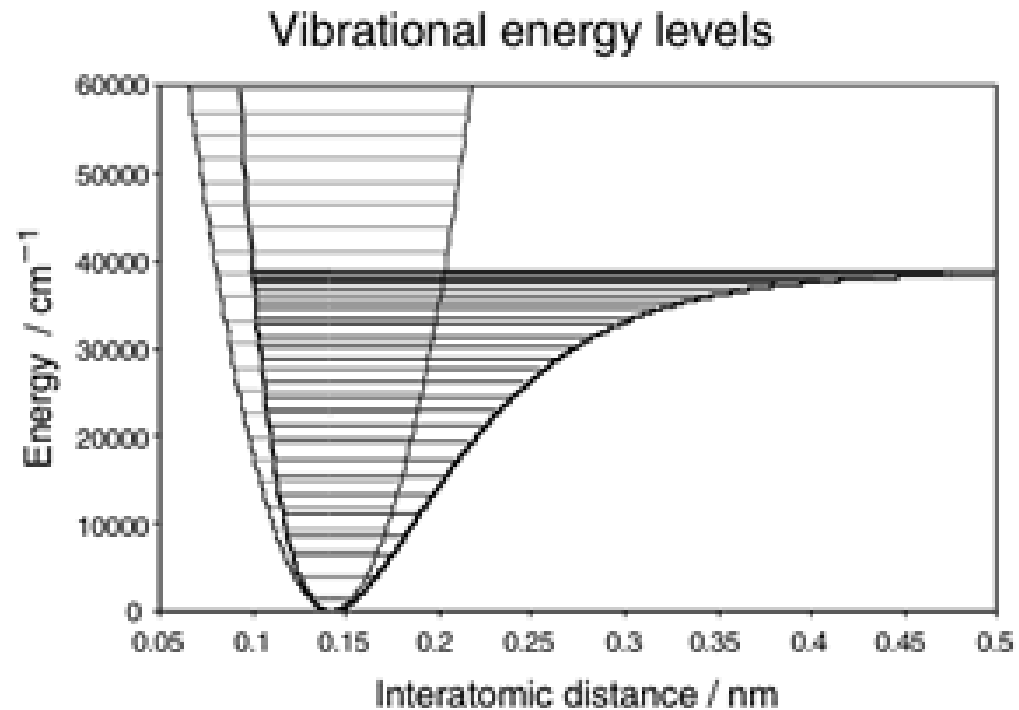
This is still an elementary problem of quantum mechanics. The energy levels of the oscillator are quantized and given by:

$$E_n = h\nu \left(n + \frac{1}{2} \right)$$

$$(n = 0, 1, 2, 3, \dots)$$

but the characteristic frequency, ν , is still given by the classical value:

$$\nu = \left(\frac{1}{2\pi} \right) \sqrt{k/\mu}$$



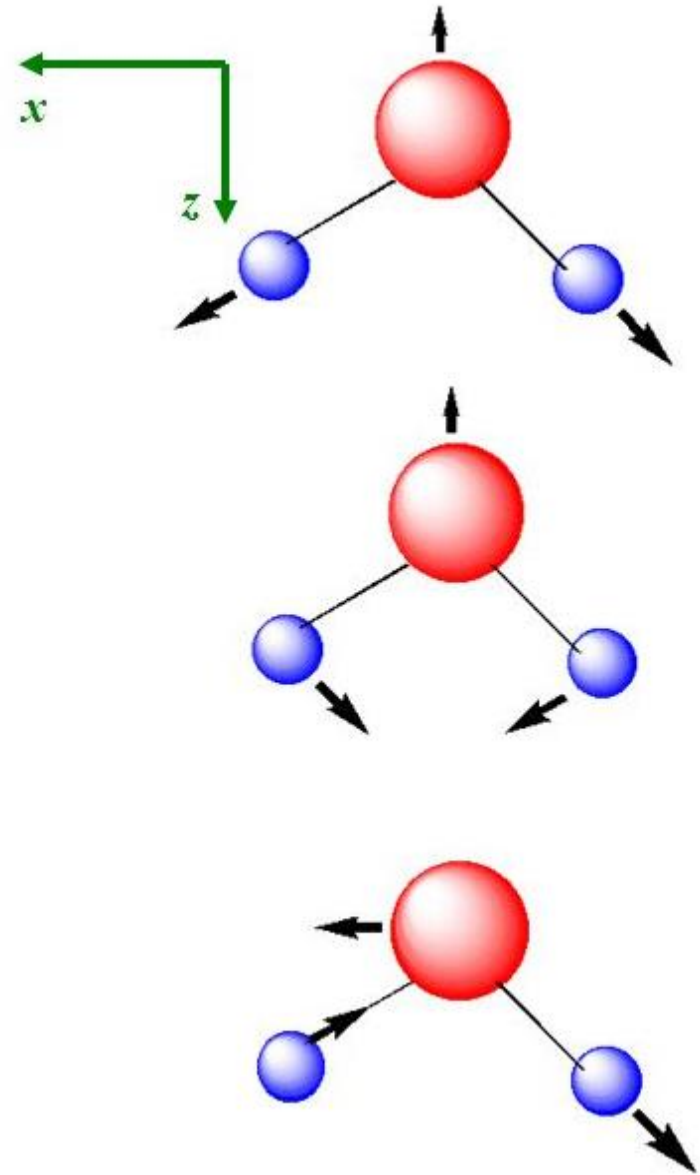
Vibrational spectroscopy

- A molecule with N atoms is a collection of N masses connected with harmonic springs.
- Classical mechanics tells us that such a system has $3N$ degrees of freedom.
- Three of these degrees of freedom correspond to translation of the molecule (position of its center of gravity in space), and three correspond to the orientation of the molecule in space (rotation about the center of gravity). This leaves

$$3.N - 3 - 3 = 3.N - 6$$

vibrational modes.

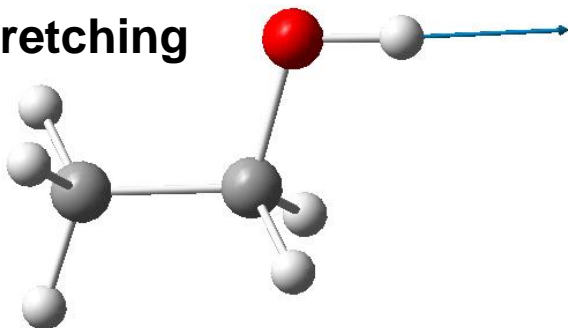
- For example H_2O ($N=3$) has $3 \cdot 3 - 6 = 3$ modes of vibration.



Vibrational spectroscopy

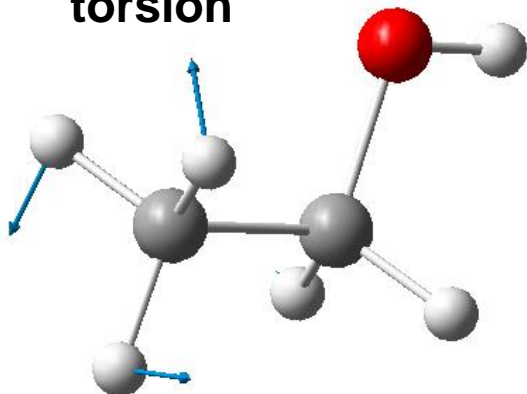
Several types of vibrational modes in molecules

stretching



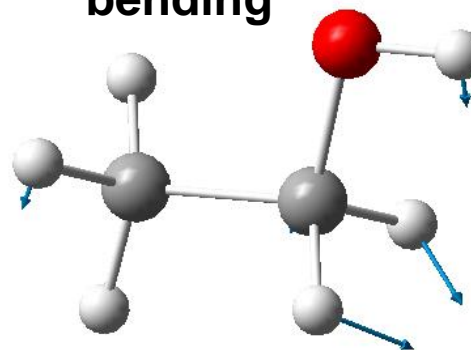
(bond distance changes)

torsion



(rotation about bond axis;
dihedral angle changes)

bending



(bond angle changes)

Two quantities define a vibrational mode:

- frequency
- set of atomic displacements

Notice that in a normal mode of vibration all atoms move in phase.

Vibrational spectroscopy

Molecular vibrations are useful to chemists because:

- they depend on molecular structure and interatomic or intermolecular forces (chemical bonding)
- specific bonds and functional groups are easily identified (analytical tool)

Table 1 Absorption frequencies of some common bonds (shown in bold type)

<i>bond</i>		<i>type of compound</i>	<i>frequency</i>
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	(stretch)	alkanes	2800–3000
$\begin{array}{c} \\ =\text{C}-\text{H} \\ \end{array}$	(stretch)	alkenes, aromatics	3000–3100
$\equiv\text{C}-\text{H}$	(stretch)	alkynes	3300
$-\text{O}-\text{H}$	(stretch)	alcohols, phenols	3600–3650 (free) 3200–3500 (H-bonded) (broad)
$-\text{O}-\text{H}$	(stretch)	carboxylic acids	2500–3300
$-\text{N}-\text{H}$	(stretch)	amines	3300–3500 (doublet for NH_2)
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \\ \end{array}$	(stretch)	aldehydes	2720 and 2820
$\begin{array}{c} \\ -\text{C}=\text{C}- \\ \end{array}$	(stretch)	alkenes	1600–1680
$\begin{array}{c} \\ -\text{C}=\text{C}- \\ \end{array}$	(stretch)	aromatics	1500–1600
$-\text{C}\equiv\text{C}-\text{H}$	(stretch)	alkynes	2100–2270
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	(stretch)	aldehyde, ketones, carboxylic acids	1680–1740
$-\text{C}\equiv\text{N}$	(stretch)	nitriles	2220–2260
$\text{C}-\text{N}$	(stretch)	amines	1180–1360
$-\text{C}-\text{H}$	(bending)	alkanes	1375 (methyl)
$-\text{C}-\text{H}$	(bending)	alkanes	1460 (methyl and methylene)
$-\text{C}-\text{H}$	(bending)	alkanes	1370 and 1385 (isopropyl split)

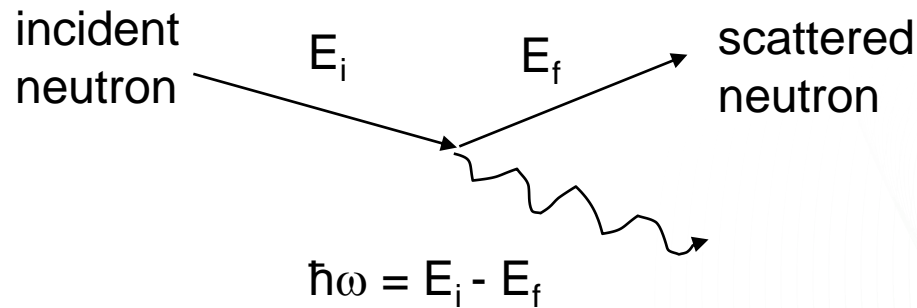


Vibrational spectroscopy

How do we observe vibrational modes experimentally ?

Crystallographers use diffraction of some form of radiation (light, electron, x-ray, neutron,...) to obtain information on the periodic arrangement of atoms in space. The wavelength of the radiation is comparable to interatomic distances.

Spectroscopists use (inelastic) scattering of radiation (light, x-ray, neutron,...) to excite vibrational modes. The energy of the radiation is comparable to the energy associated with the vibrational excitations.



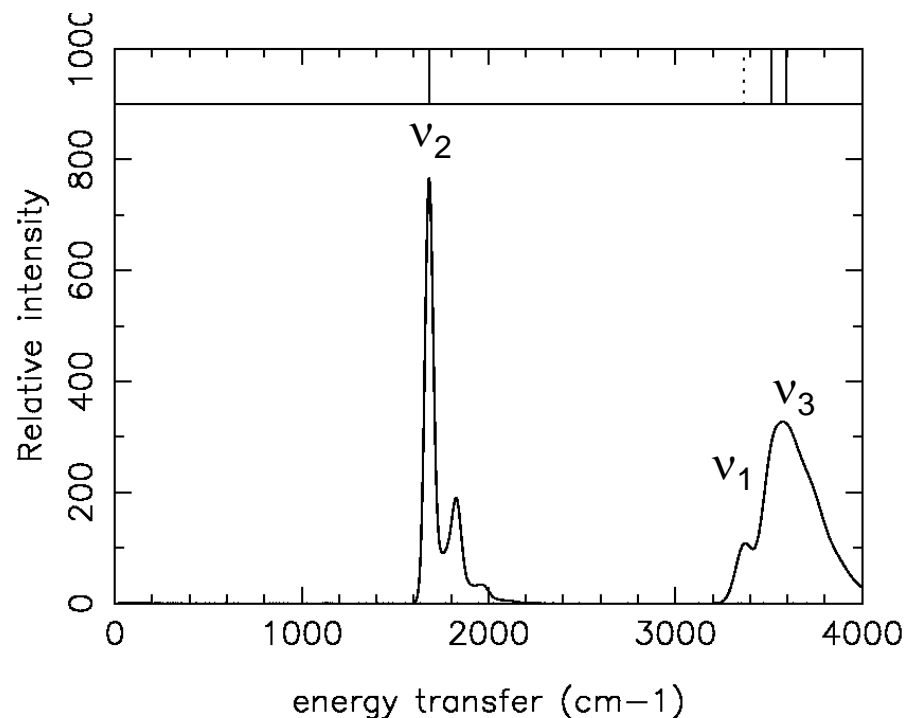
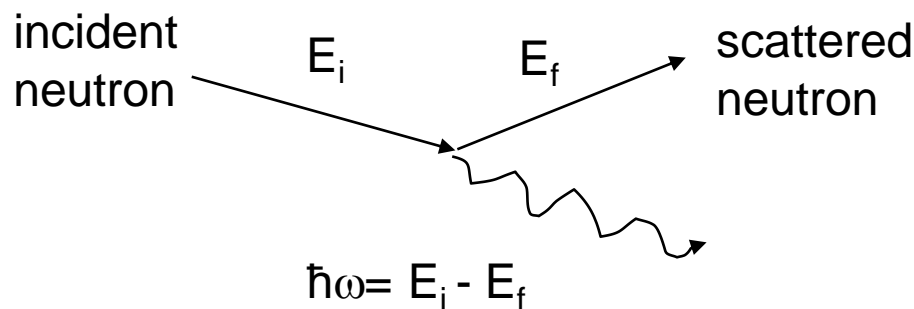
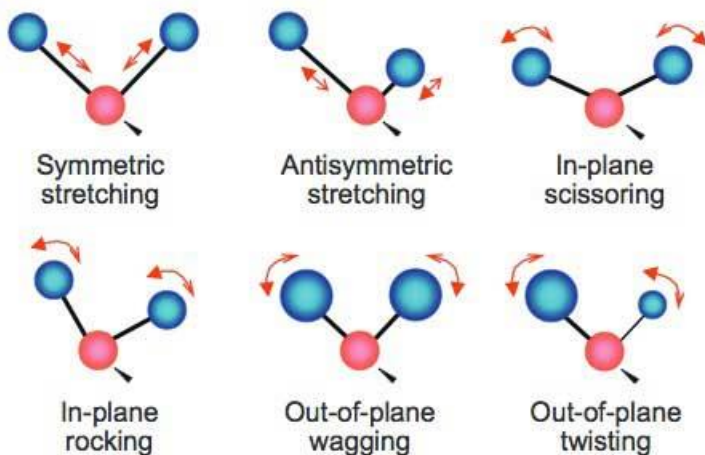
(conservation of energy)

Upon interacting with a vibrational mode, the incident neutron loses energy (from E_i to E_f). The difference in kinetic energy is used to create a vibrational quantum.

Momentum is also exchanged !

Vibrational spectroscopy

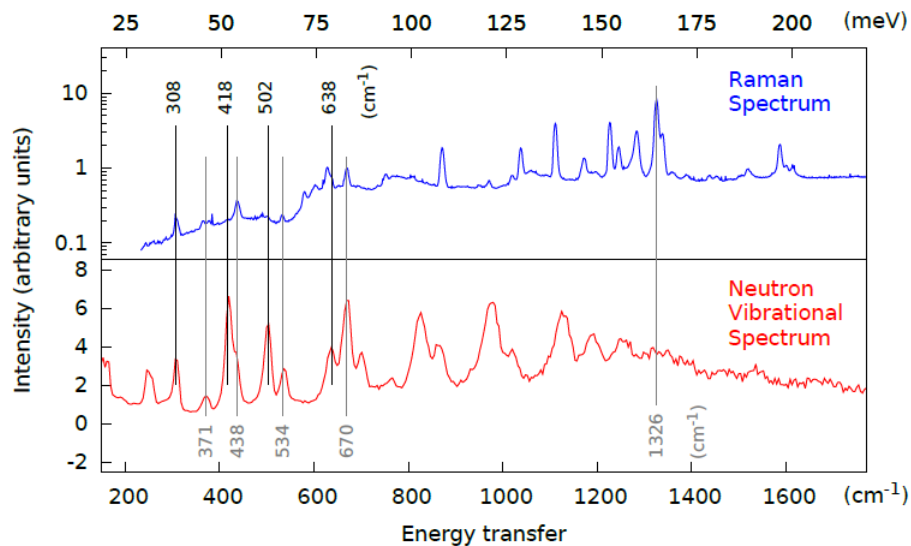
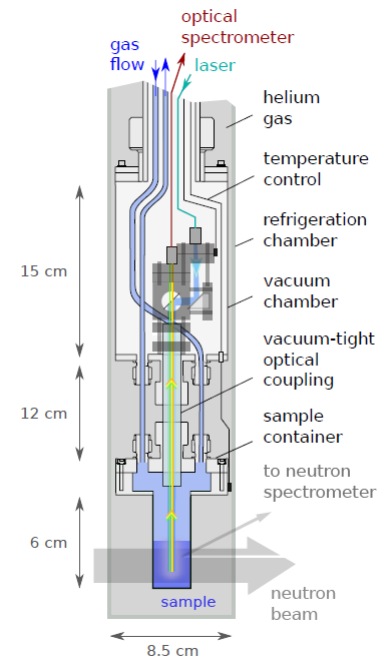
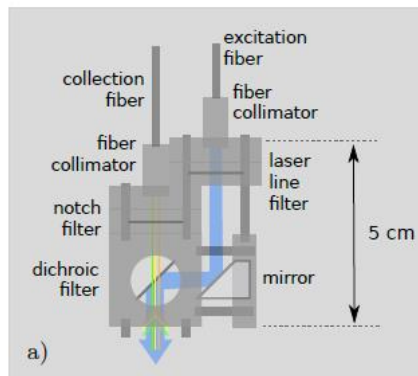
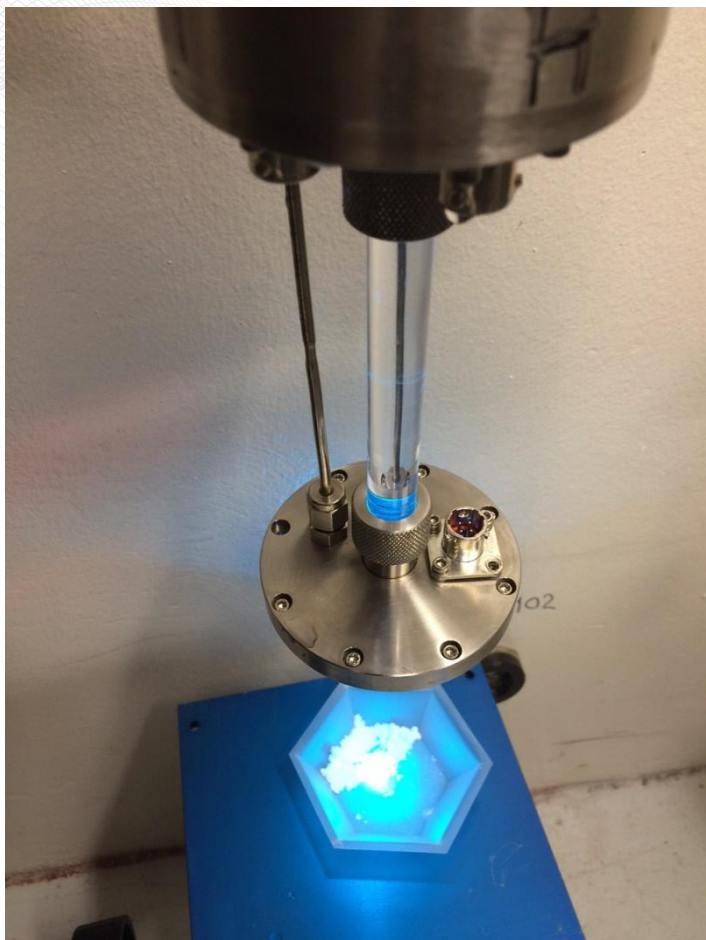
As long as we have a way to determine E_i and E_f and the number of particles with energy E_i and E_f , we can determine the number of excitations (vibrational modes) created with an energy of $\hbar\omega = E_i - E_f$. The result is the vibrational spectrum:



Vibrational spectroscopy

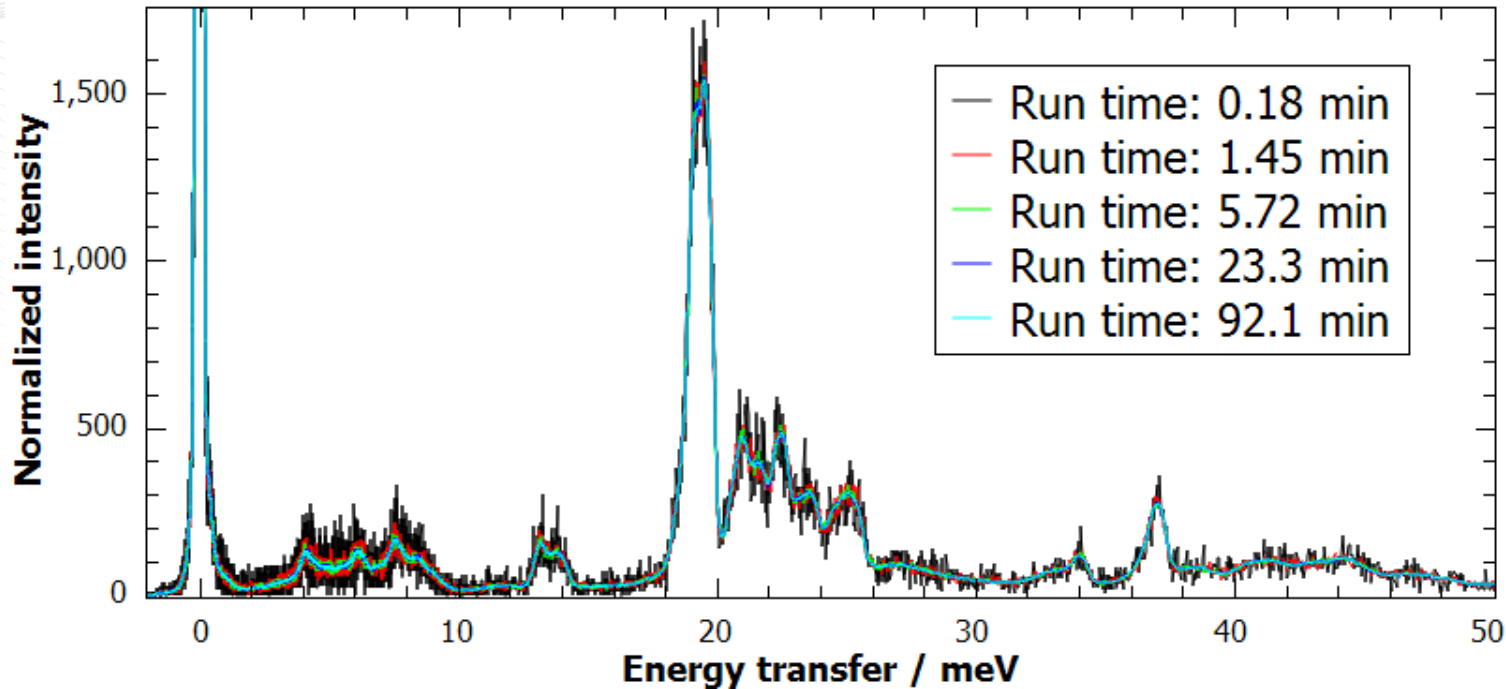
VISION (INS)	Raman/Infrared
Measures dynamics of nuclei (direct)	Measures response of electrons (indirect)
No selection rules	Selection rules apply
Great sensitivity to H	Cannot always see H
High penetration (bulk probe)	Low penetration (surface probe)
Easy access to low energy range (librational and translational modes)	Low energy cutoff applies (on the order of 100 cm^{-1})
Q trajectories in the (ω, Q) map; averaging over the Brillouin zone	Gamma point only
Weighted by neutron scattering cross section	Weighted by change in polarizability or dipole moment
Easy to simulate/calculate	Difficult to simulate/calculate
No energy deposition in sample	Heating, photochemistry, ...

Vibrational spectroscopy

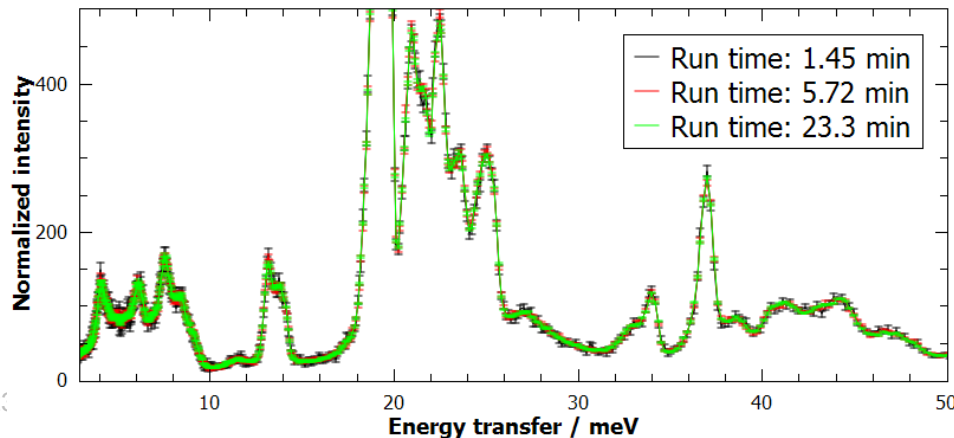


High throughput: INS in minutes

OctaMethyl POSS (1 gm) Measured at VISION



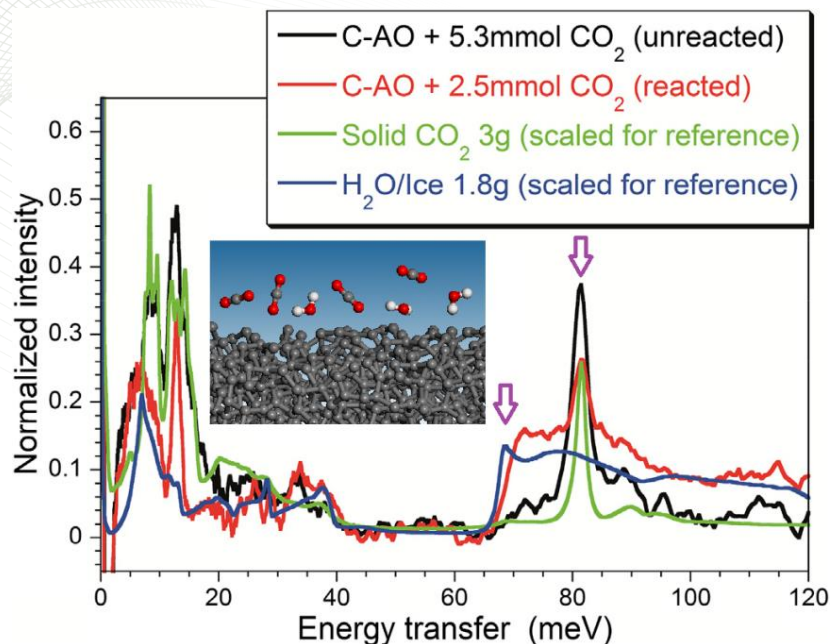
OctaMethyl POSS (1 gm) Measured at VISION



With 14 inelastic banks and 16 diffraction banks, VISION has the highest data rate (up to millions of events per second) among all neutron beam lines in the world.

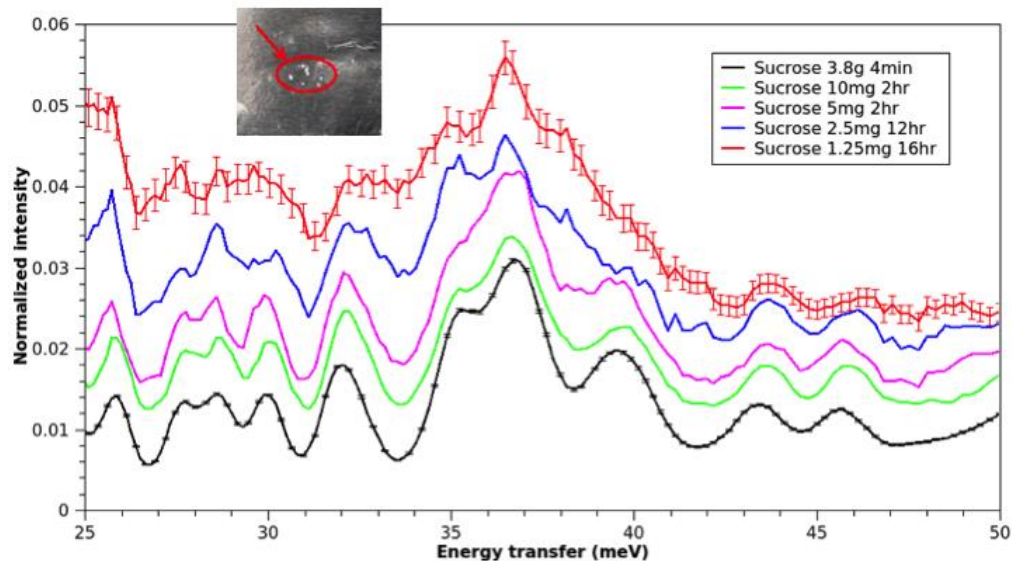
- INS database
- Parametric studies
- INS study of kinetics

High sensitivity: milligrams of samples



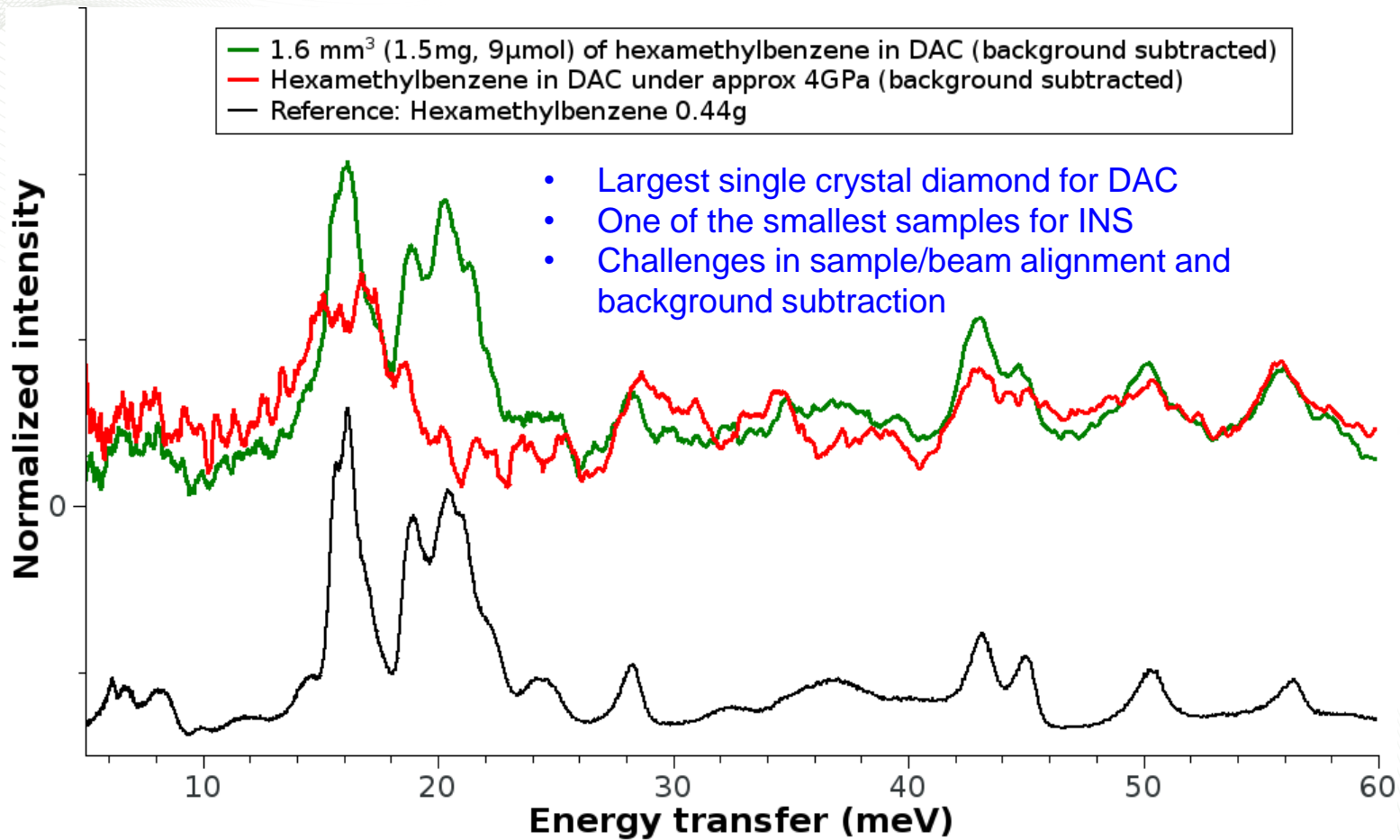
Very small amount of CO₂ (2.5 mg). In situ observation of surface reactions. Surface science, catalysis, gas capture and storage.

1.25 mg of table sugar



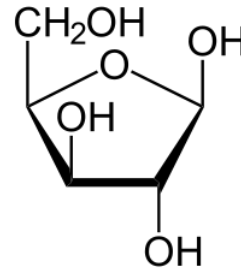
Extraordinary sensitivity, this is the smallest amount of sample ever measured using INS. Diamond anvil cells will be used in VISION

High sensitivity: milligrams of samples

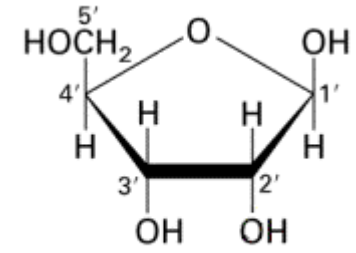


Conformation: aldopentoses

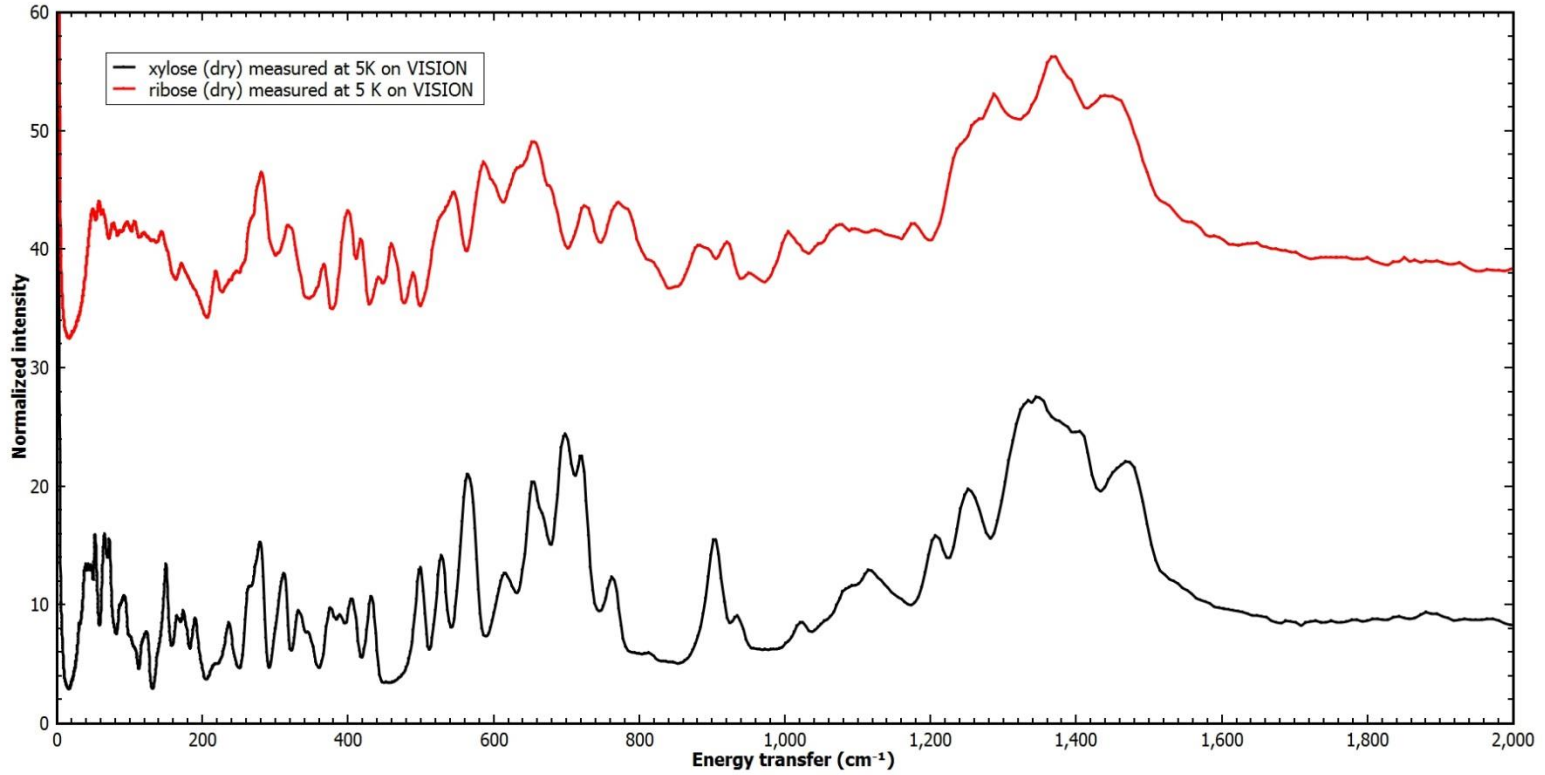
The vibrational spectrum is sensitive to differences in molecular conformations



Xylose

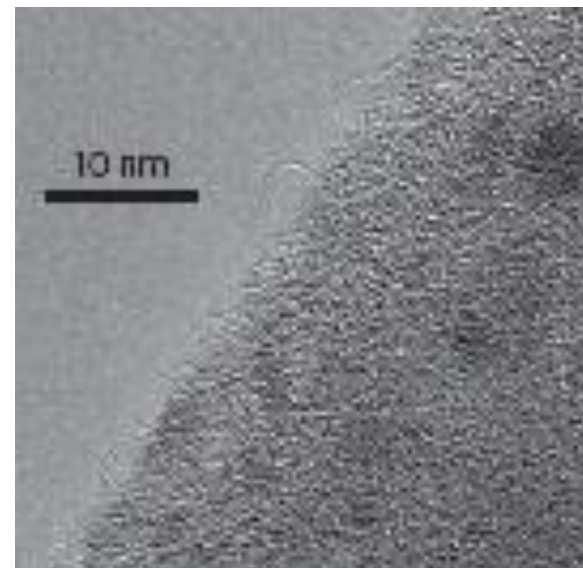
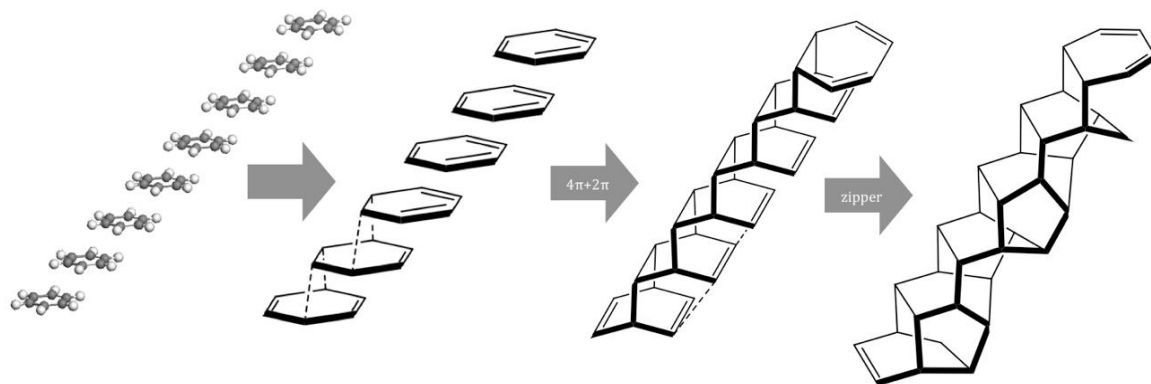


Ribose



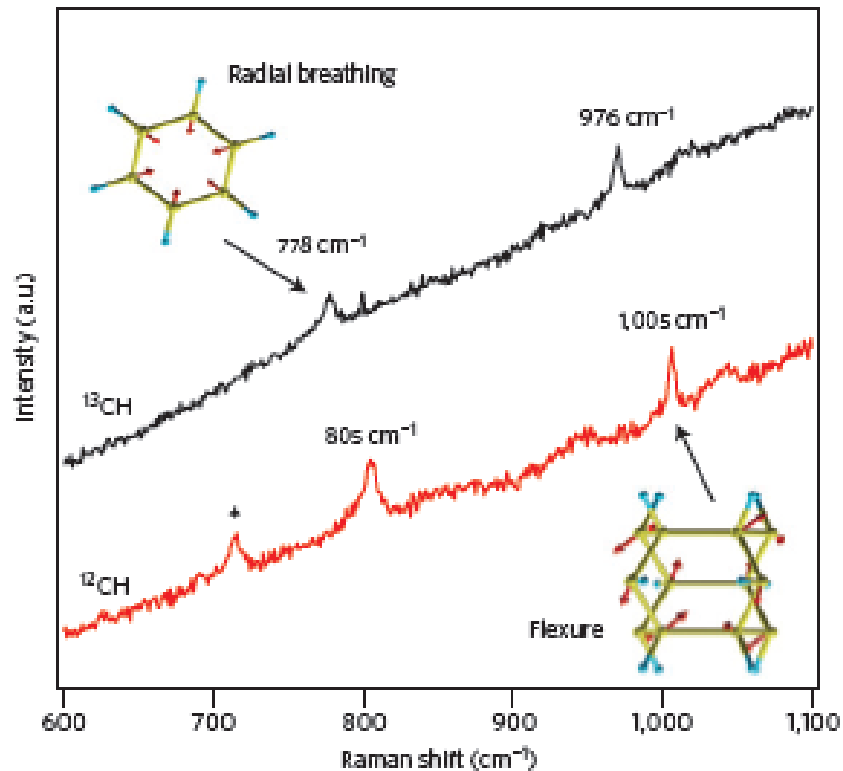
Model validation: Polybenzene nanothreads synthesized at high pressure

Benzene samples were compressed to 20 GPa at room temperature, maintained at this pressure for one hour, and slowly released to ambient pressure at an average rate of 2 GPa /hr to recover a solid white product.



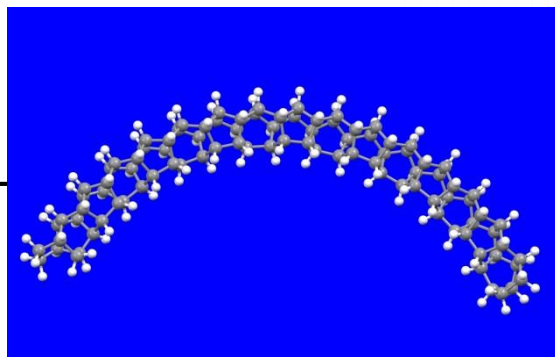
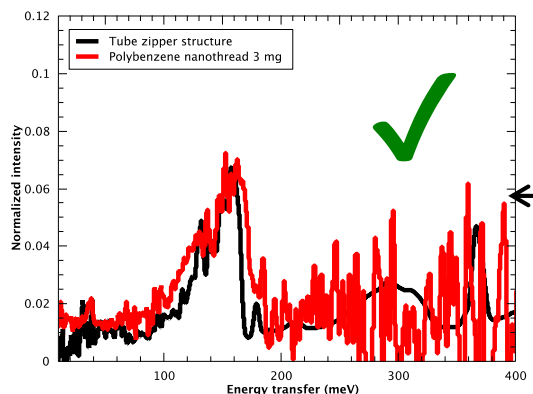
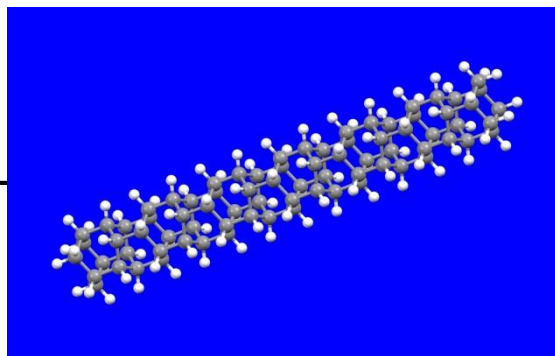
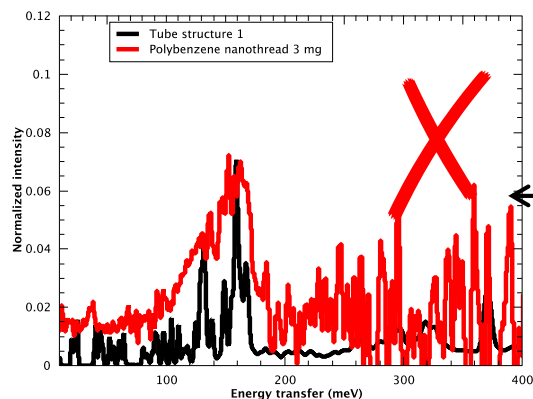
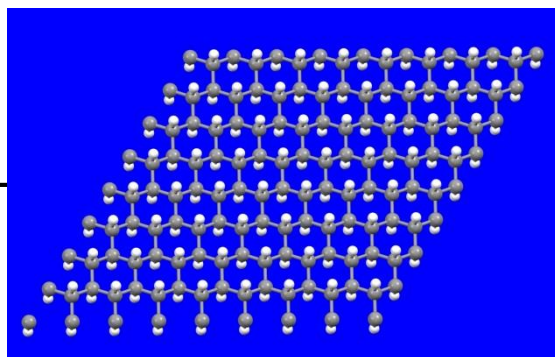
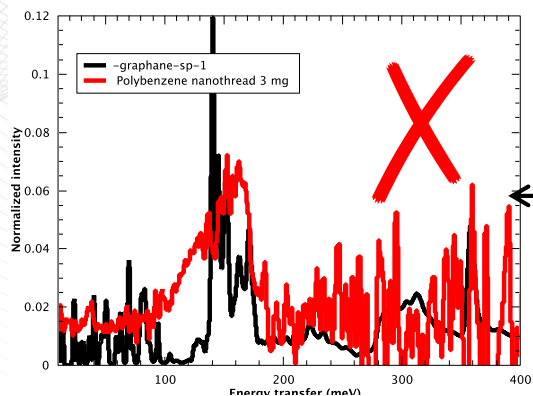
Collaboration with Malcolm Guthrie, John Badding, Vin Crespi
Original publication on carbon nanothreads: *Nature Materials*, **14**, 43 (2014)

Polybenzene nanothreads



The Raman spectrum is not particularly informative

Polybenzene nanothreads



- 3 mg sample synthesized on SNAP in diamond anvil cells and measured on VISION.

- Comparison of the experimental data from VISION and a series of DFT calculations of hypothetical structures that contain sp^3 carbon and the correct stoichiometry (C:H ratio 1:1) allows us to determine which structure corresponds to the measured spectra.

- top = graphane,
- middle = tubular structure
- bottom = zipper

The zipper structure provides the better agreement between calculation and experiment.

Diffraction at VISION

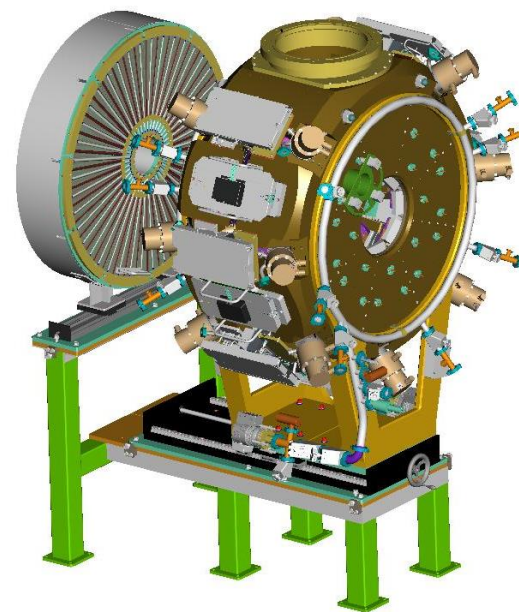
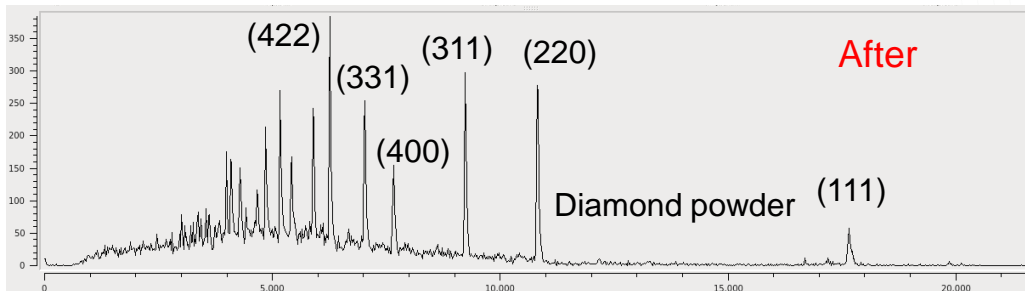
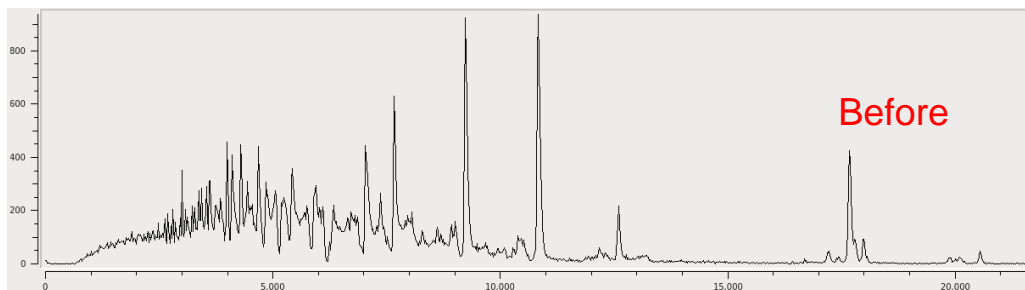
Simultaneous diffraction and inelastic neutron scattering



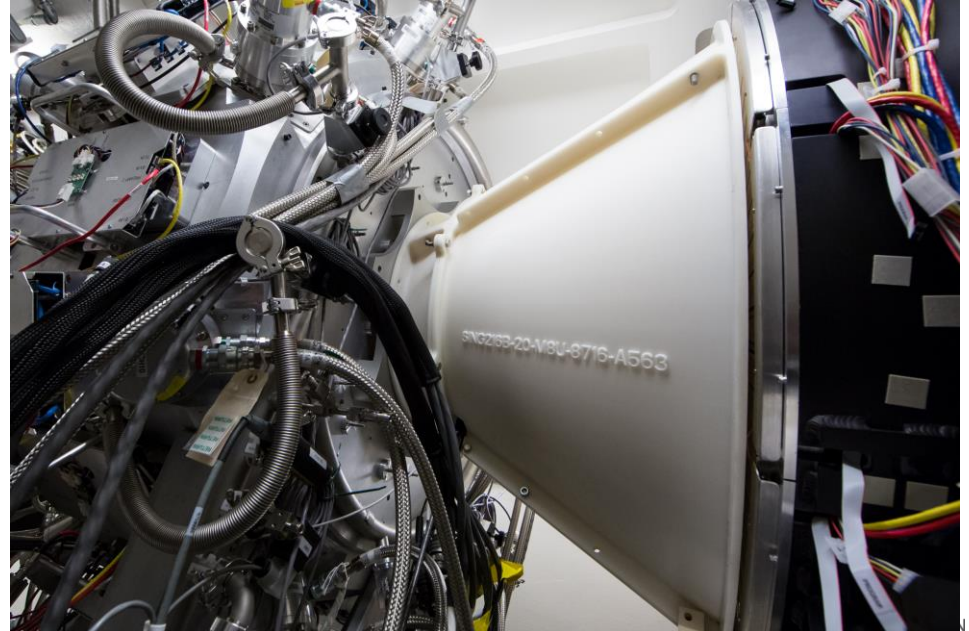
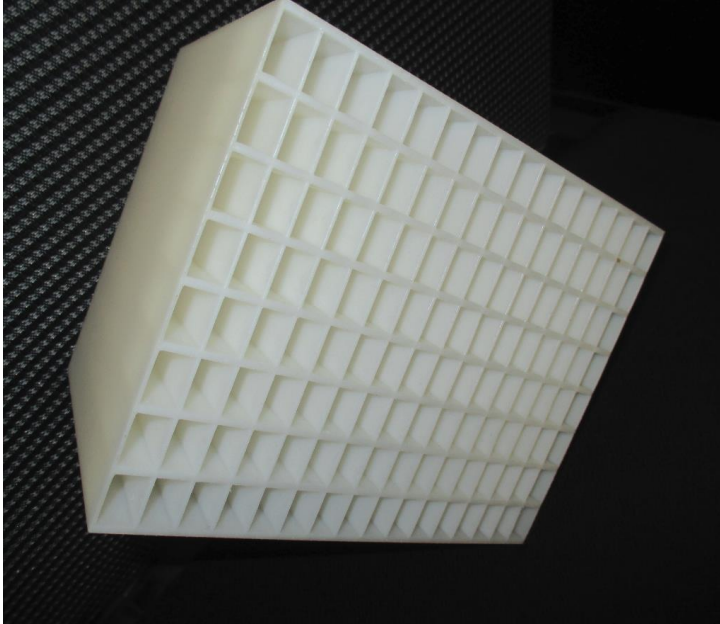
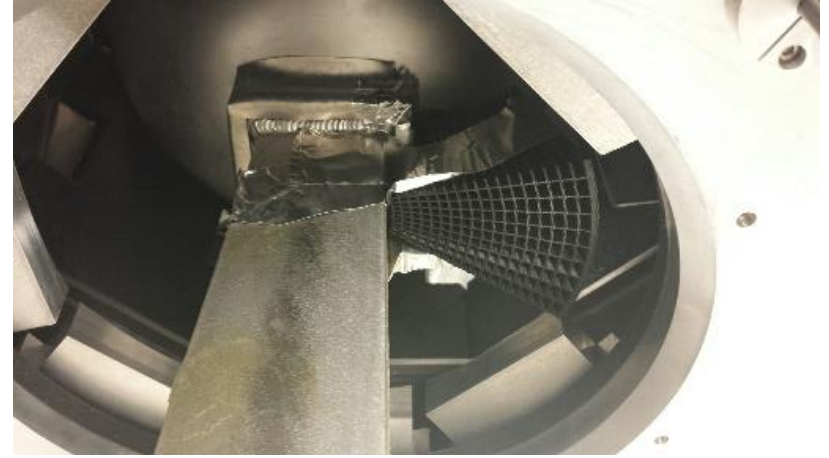
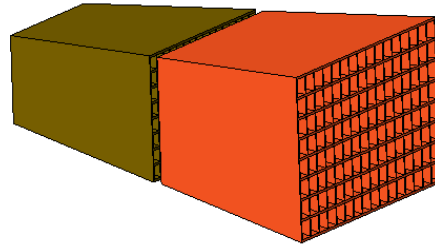
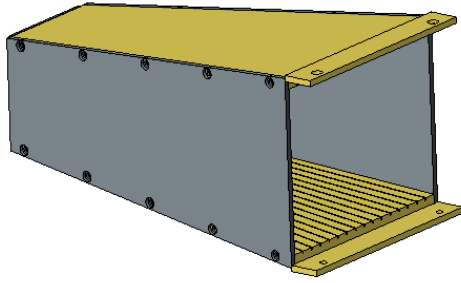
3D printed collimators have been tested for VISION to be used in the backscattering diffraction bank.

The reduction of the spurious peaks from the sample is very much noticeable.

Data collected in histogram or event mode

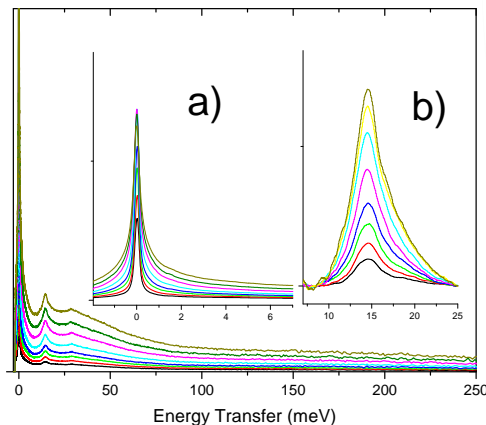
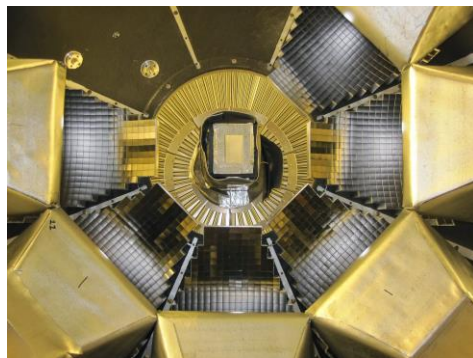
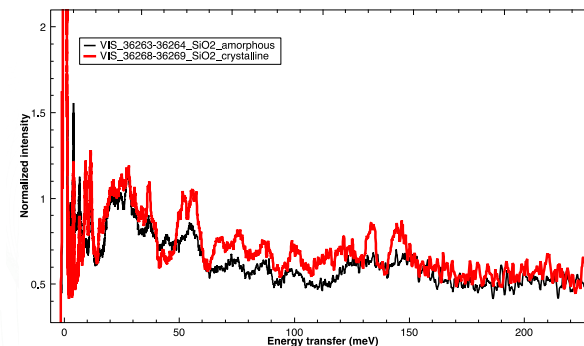
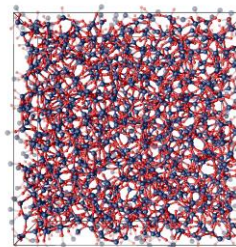
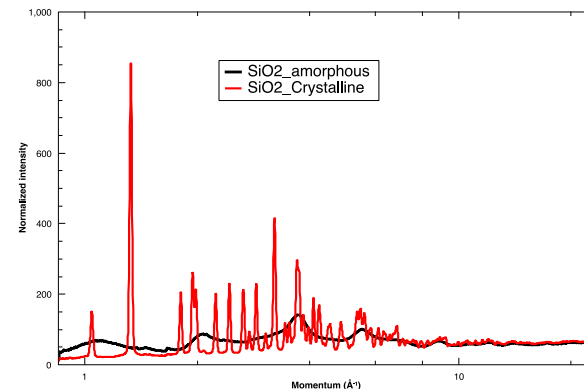


VISION pioneered the use of 3D printed collimators

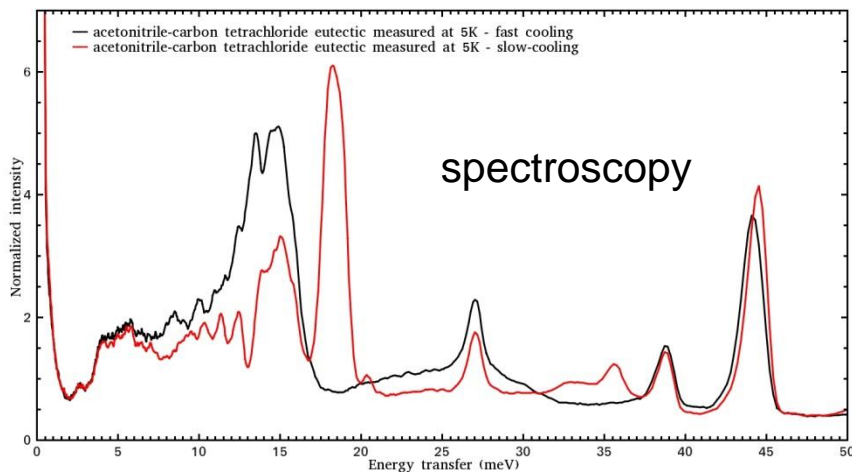


VISION: Inelastic, Diffraction and QENS

- Chemistry Oriented INS spectrometer
- White incident beam, fixed final energy (indirect geometry)
- High flux ($\sim 5 \times 10^7$ neutrons/cm²/s) and double-focusing
- Broadband (-2 to 1000 meV at 30Hz, 5 to 500 meV at 60 Hz)
- Constant $\Delta E/E$ throughout the spectrum ($\sim 1.5\%$)
- Elastic line HMF_W $\sim 120 \mu\text{eV}$
- Backward and 90° diffraction banks
- 4000 x its predecessor



Structure and dynamics of liquids and solutions



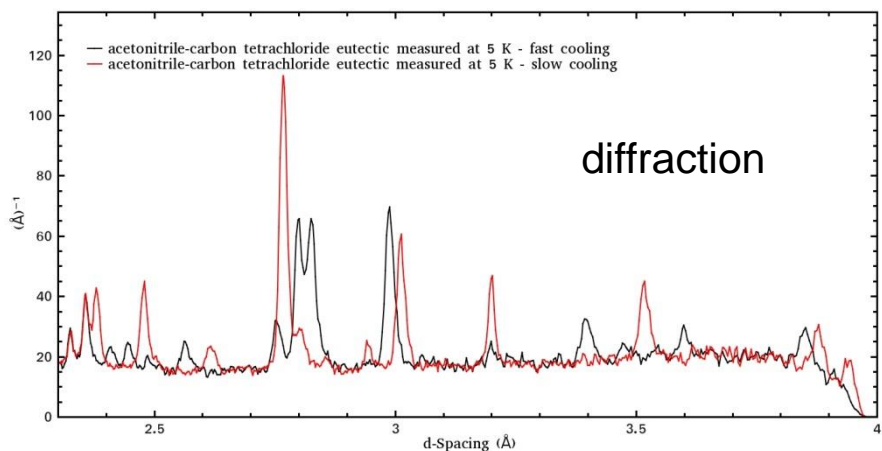
- CD₃CN-CCl₄ (deep) eutectic system

- $T_E = 210$ K; $x(\text{CD}_3\text{CN})$ at eutectic composition is 0.75

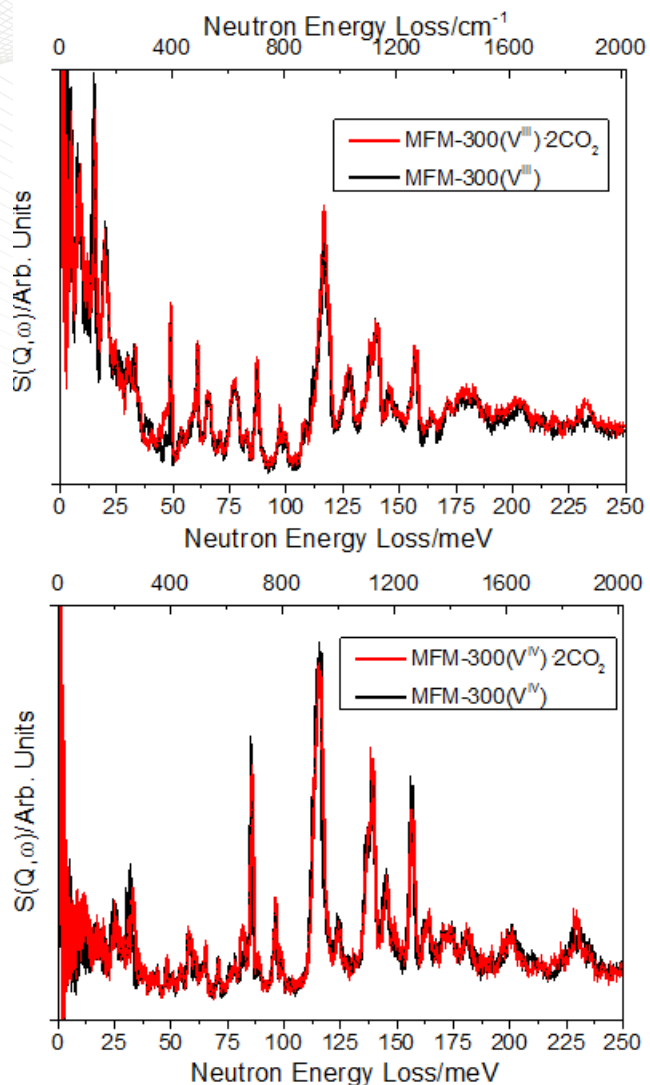
- no hydrogen bonding, but highly non-ideal system with $\Delta H_{\text{excess}} = -800$ J/mol)

- eutectic structure differs when liquid is cooled quickly or slowly from room temperature

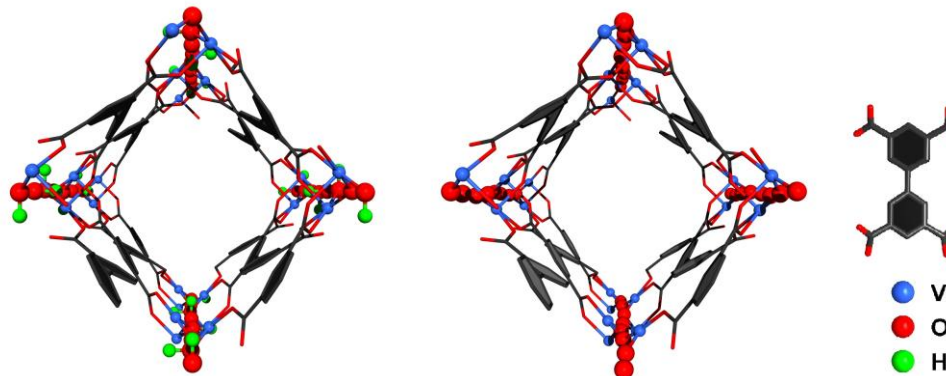
- simultaneous diffraction/spectroscopy is invaluable



Analysis of results



Spectroscopy provides a wealth of information, but this comes at the price of complex data sets, particularly in large systems.



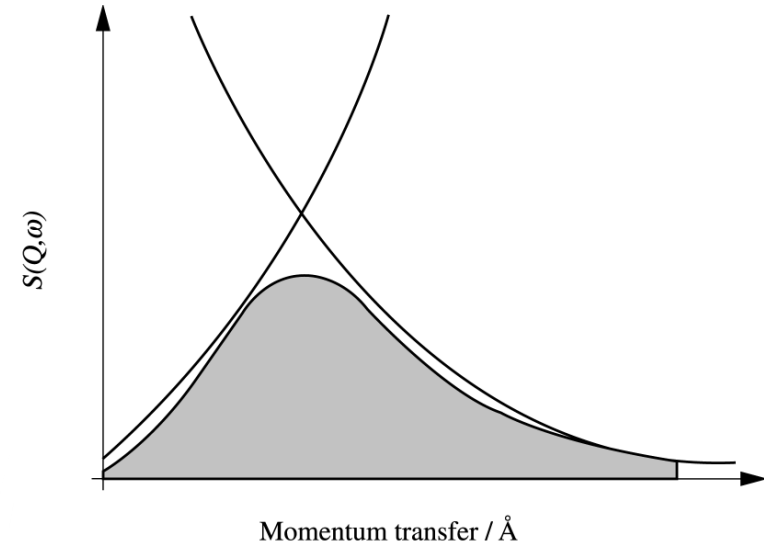
How do we interpret the results?

Inelastic Neutron Scattering

- 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.
- Simple interaction: $V = \sigma \cdot \delta(r - R)$
- For incoherent inelastic neutron scattering, the spectral intensity is given by:

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

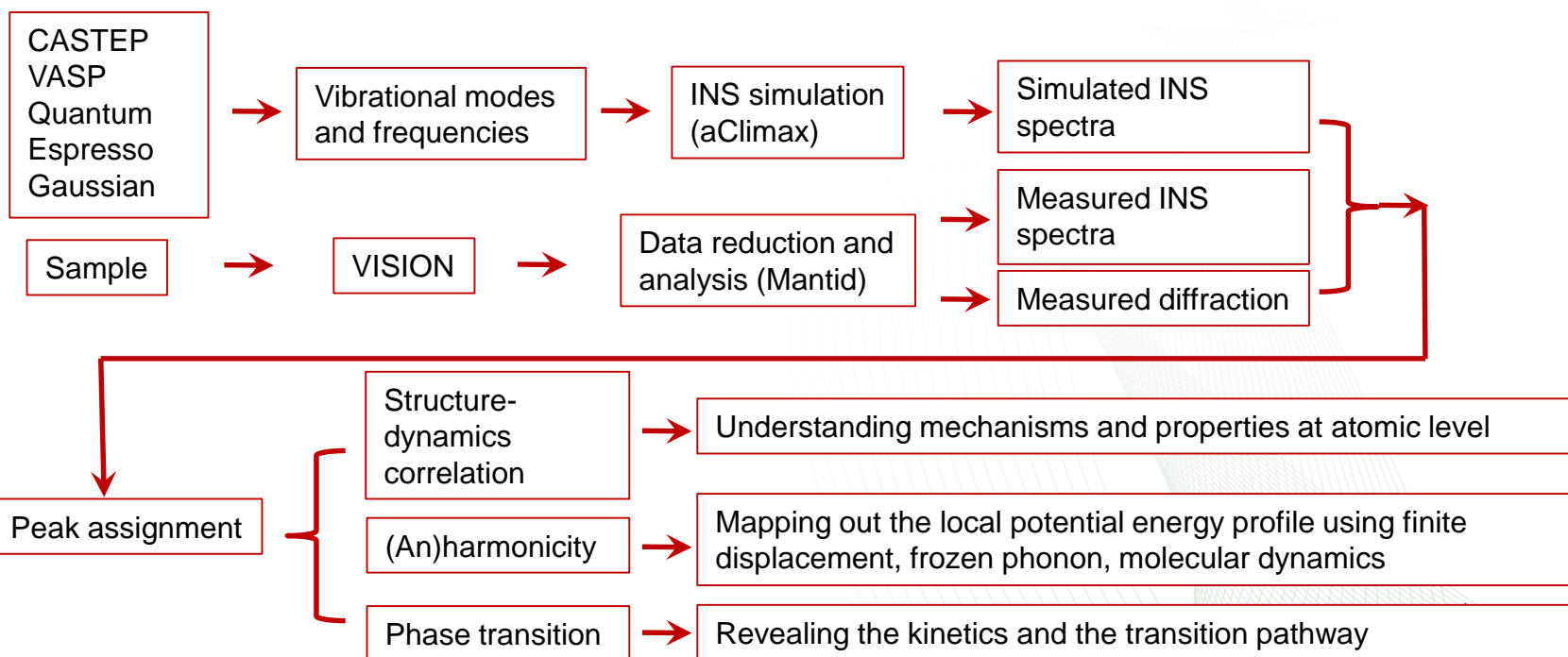
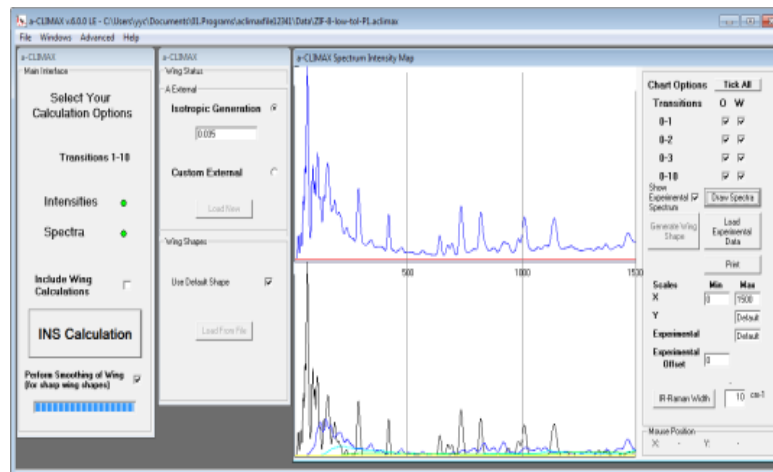
Frequencies and displacements can be calculated from a known structure (DFT, MD, molecular mechanics, etc). With this information $S(\mathbf{Q}, \omega)$ can be calculated for comparison with inelastic neutron scattering data.



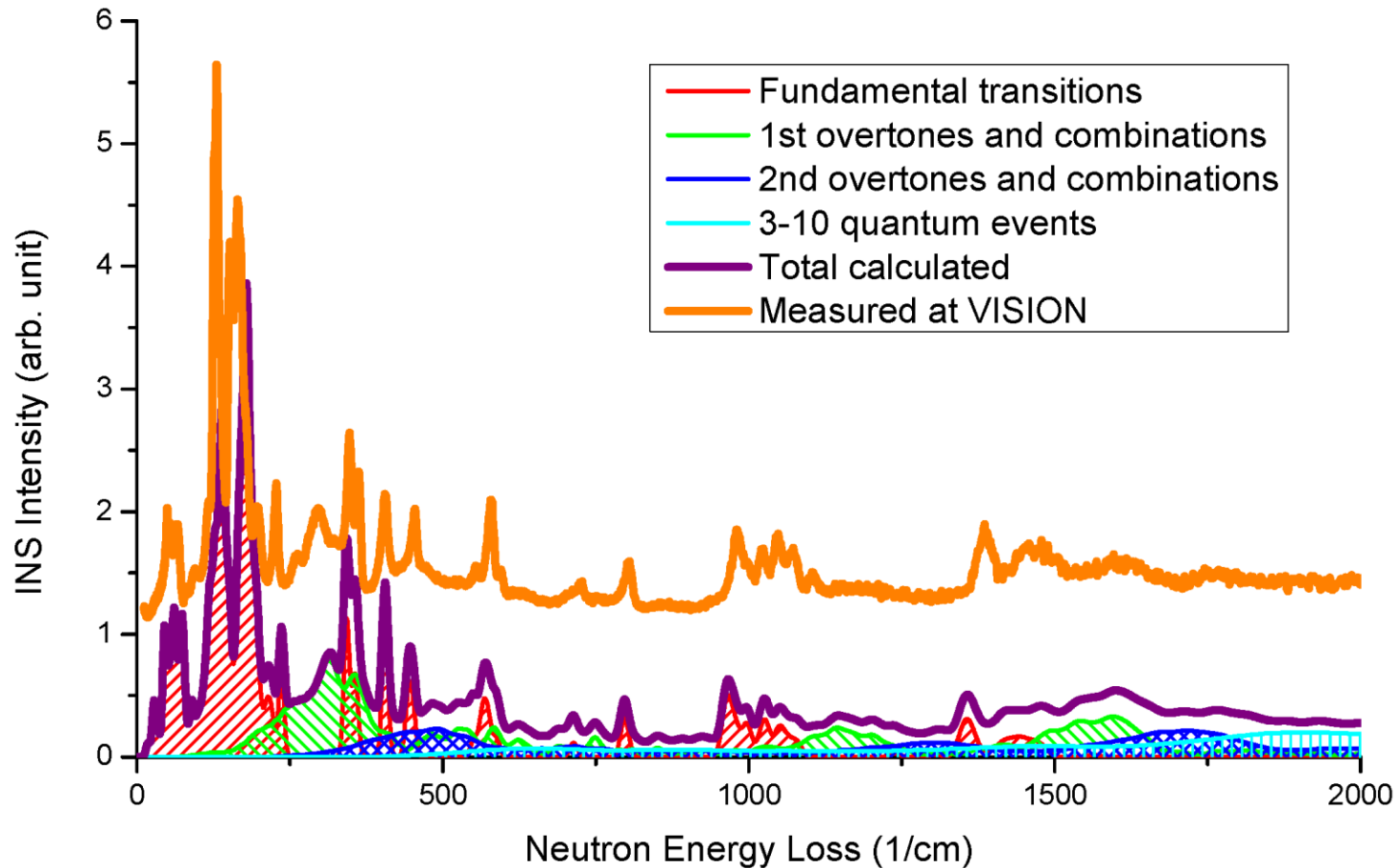
➡ More difficult to do for Raman (e-photon interaction)

Integrated modeling for data interpretation

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

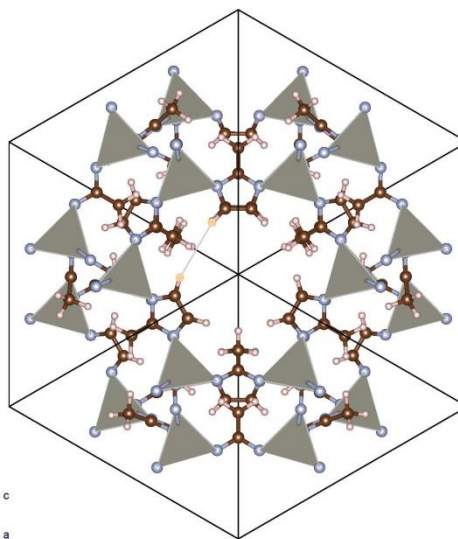
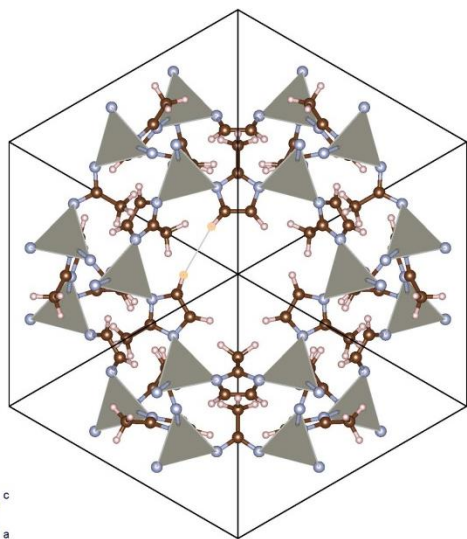
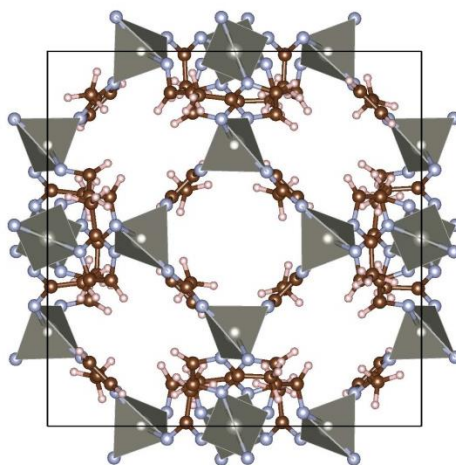
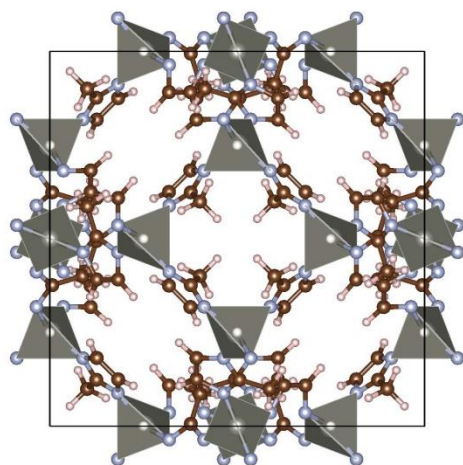


Comparison



sample is hexamethybenzene

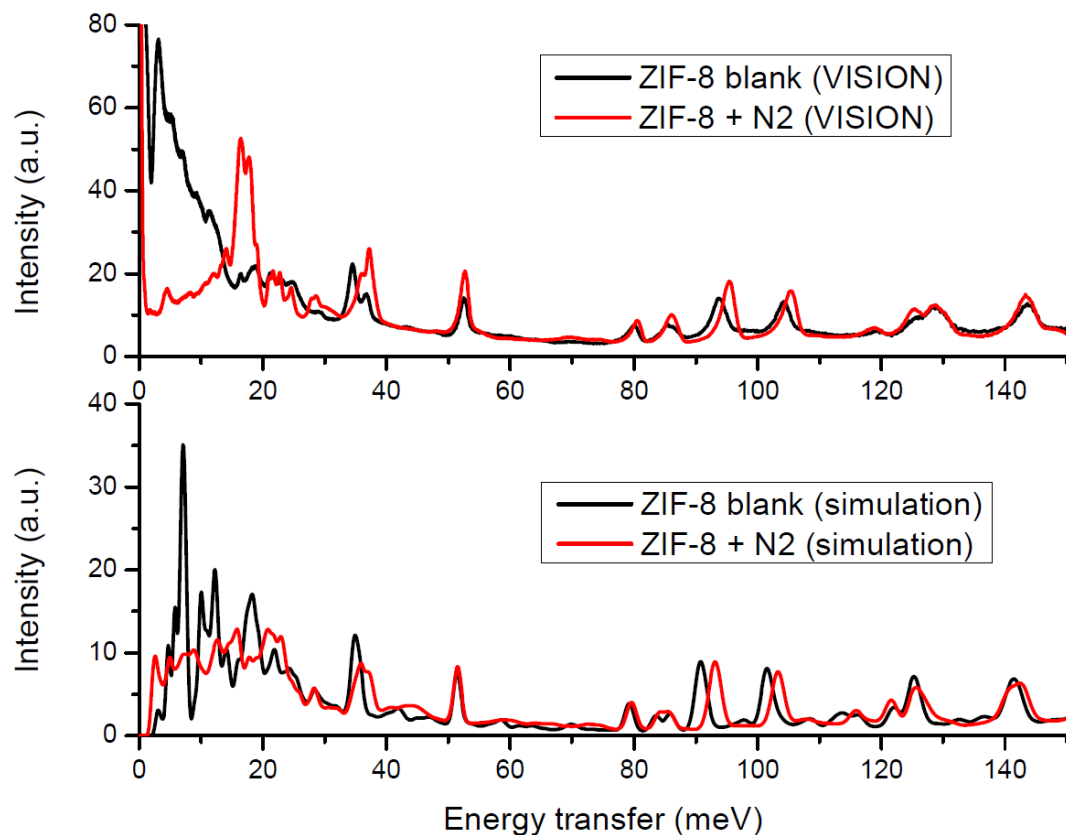
Gate-opening in a metal-organic framework



Structure of blank ZIF-8 and ZIF-8 loaded with N₂. The rotation of the methyl groups and the swinging of the imidazolate rings associated with the gate opening can be seen by comparing the marked areas

For clarity the N₂ molecules are not shown.

Gate-opening in a metal-organic framework

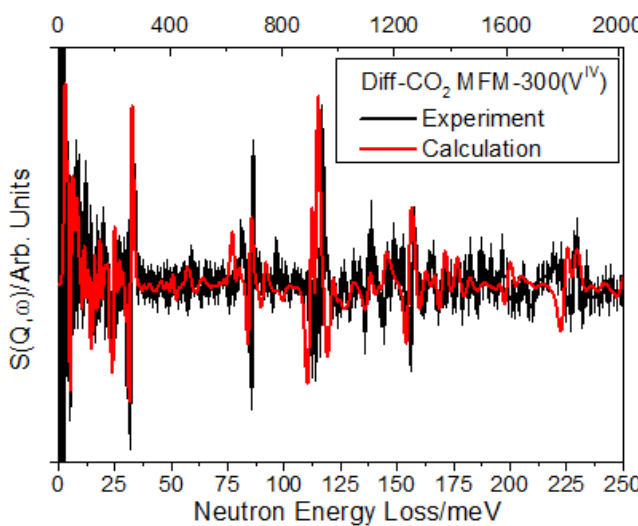
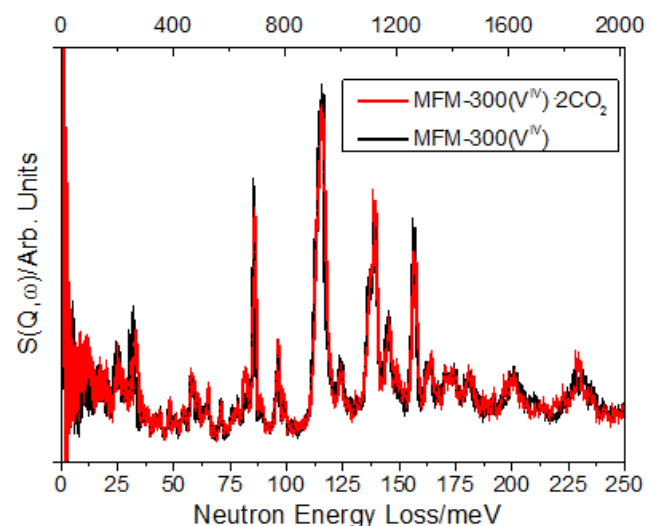
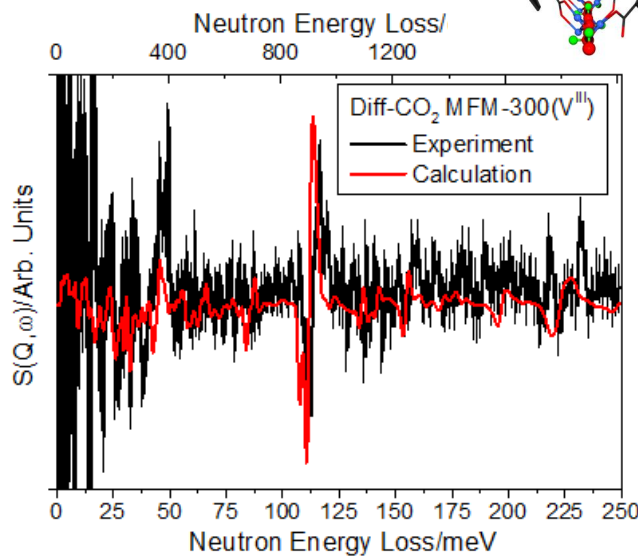
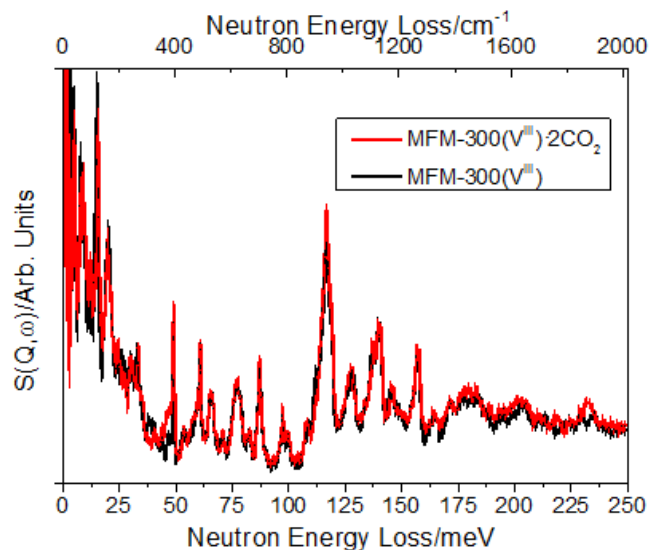
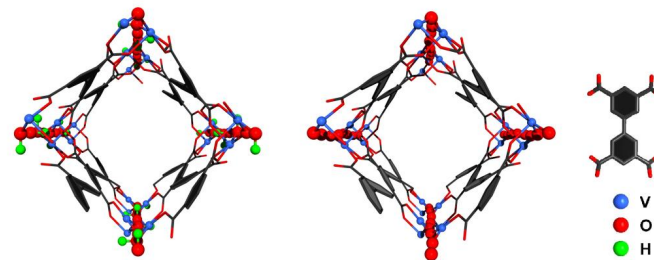


Measured (upper panel) and simulated (lower panel) INS spectra of blank ZIF-8 and ZIF-8+N₂.

The strong peaks are mainly due to vibrational modes involving large displacement of hydrogen (in the methyl groups and the imidazolate rings)

Casco, M. E. et al. Gate-opening effect in ZIF-8: the first experimental proof using inelastic neutron scattering. *Chemical Communications*, v. 52, n. 18, p. 3639-3642, 2016

INS signature of CO₂ capture

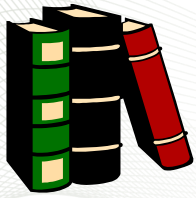


This study combining NPD, INS and modelling has unambiguously determined the CO₂ binding sites and structural dynamics for MFM-300(VIII) and MFM-300(VI). It is confirmed that the proton on the hydroxy group can not only attract and localise adsorbed CO₂ molecules via direct formation of hydrogen bonds, but also affects the macroscopic packing and arrangement of CO₂ molecules in the extended channel.

Studying H₂ adsorption in Porous Materials & Surfaces with INS

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

**Characterization of the interaction
strength**



The Theory



- H₂ ground state ($J=0$) parahydrogen (p-H₂) antisymmetric nuclear spin wavefunction ($\uparrow\downarrow$) and symmetric rotational wavefunction.
- The first rotational state, ($J=1$) orthohydrogen (o-H₂) symmetric nuclear spin wavefunction ($\uparrow\uparrow$) and antisymmetric rotational wavefunction.
- Transitions p-H₂ \leftrightarrow o-H₂ are detected with neutrons because neutrons exchange spin states with the H₂ molecule.

In solid dihydrogen, H₂ 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.

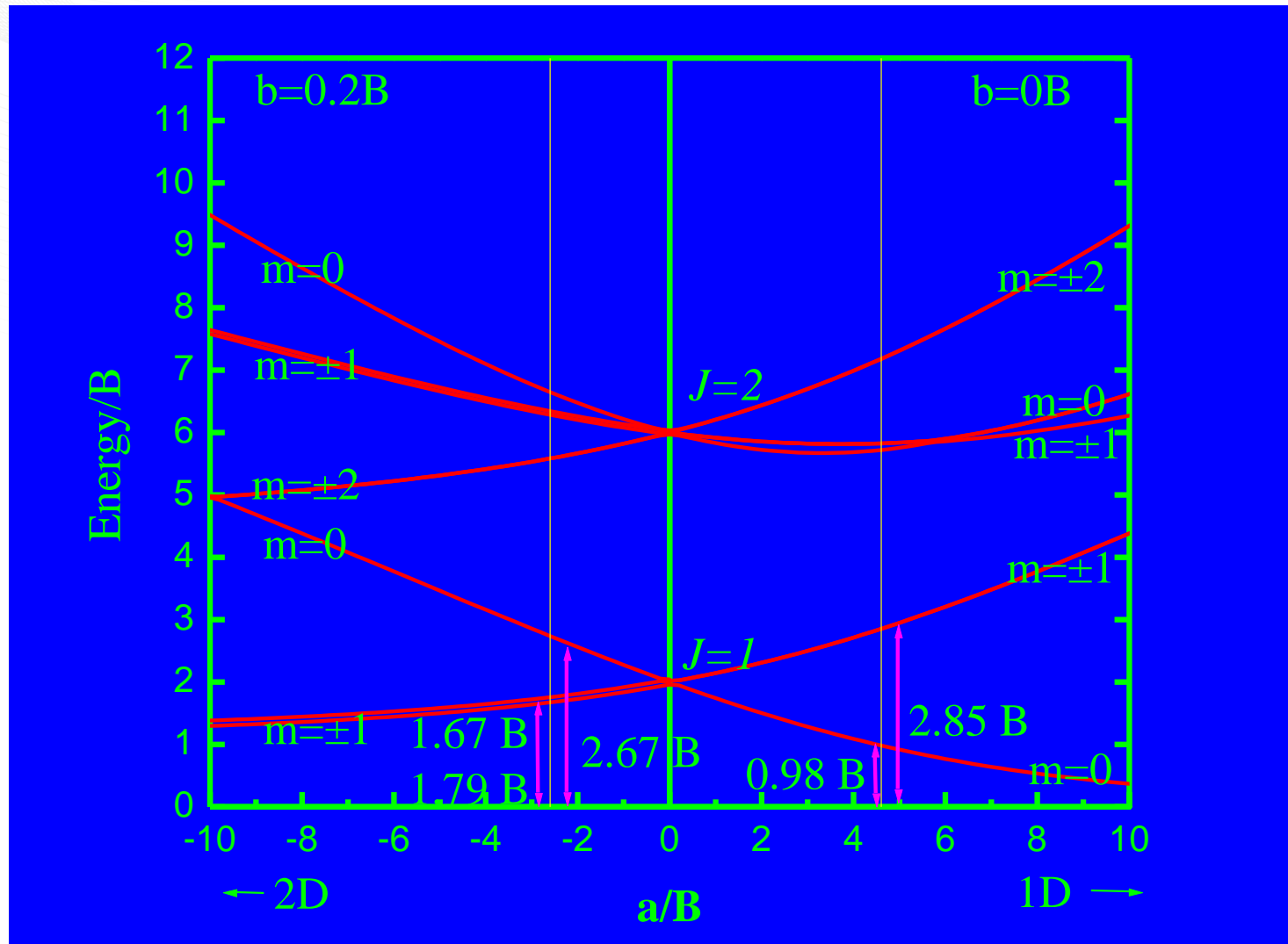
The potential that governs the motion of a H_2 molecule on a surface may be expressed as

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

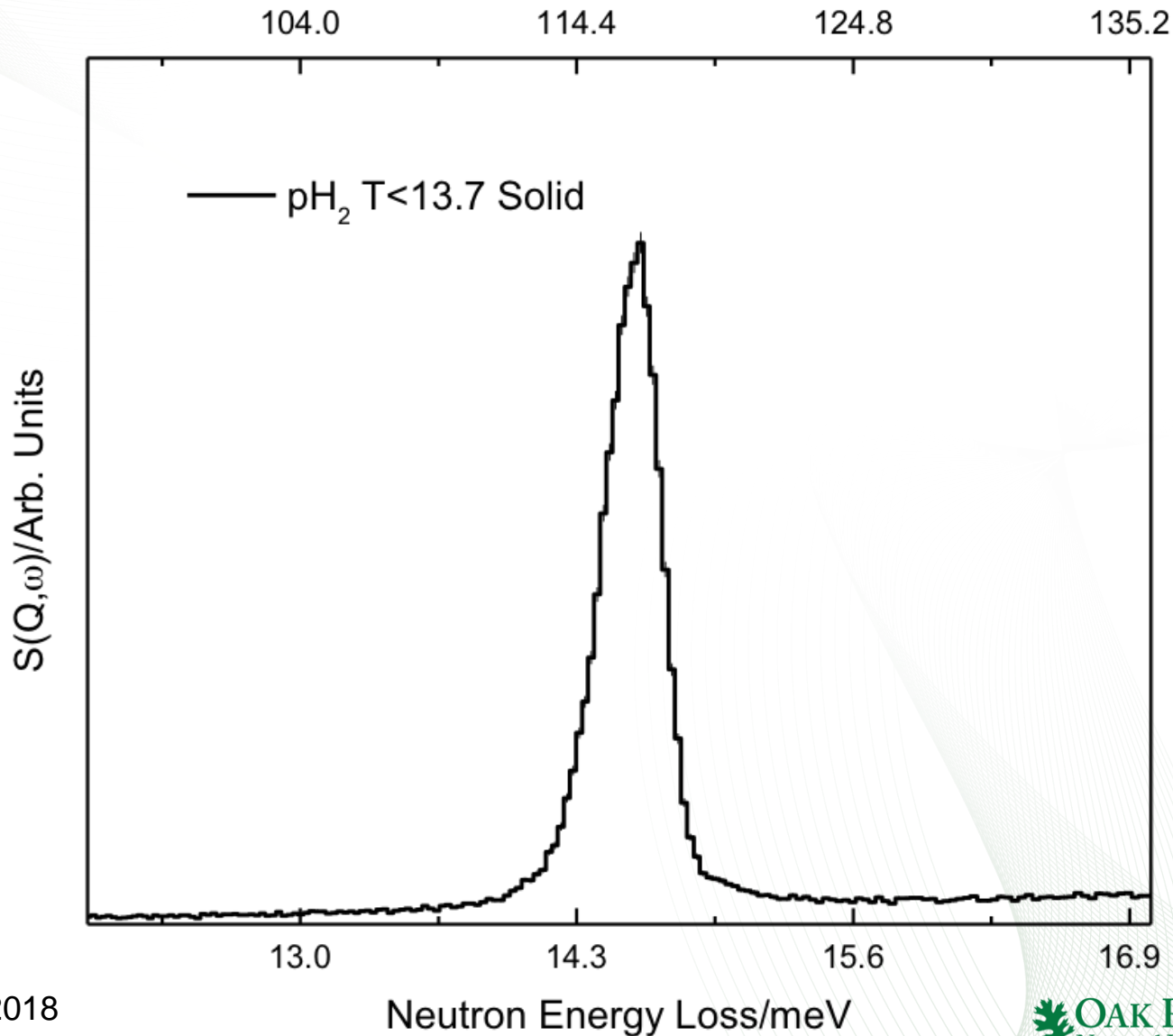
- $a > 0$ the molecule is aligned to an axis (1D case).
- $a < 0$ the molecule is constrained in a plane (2D case)
- The splitting between levels is $1B$ if a is large and negative, because the energy levels are:

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

The Energy Levels

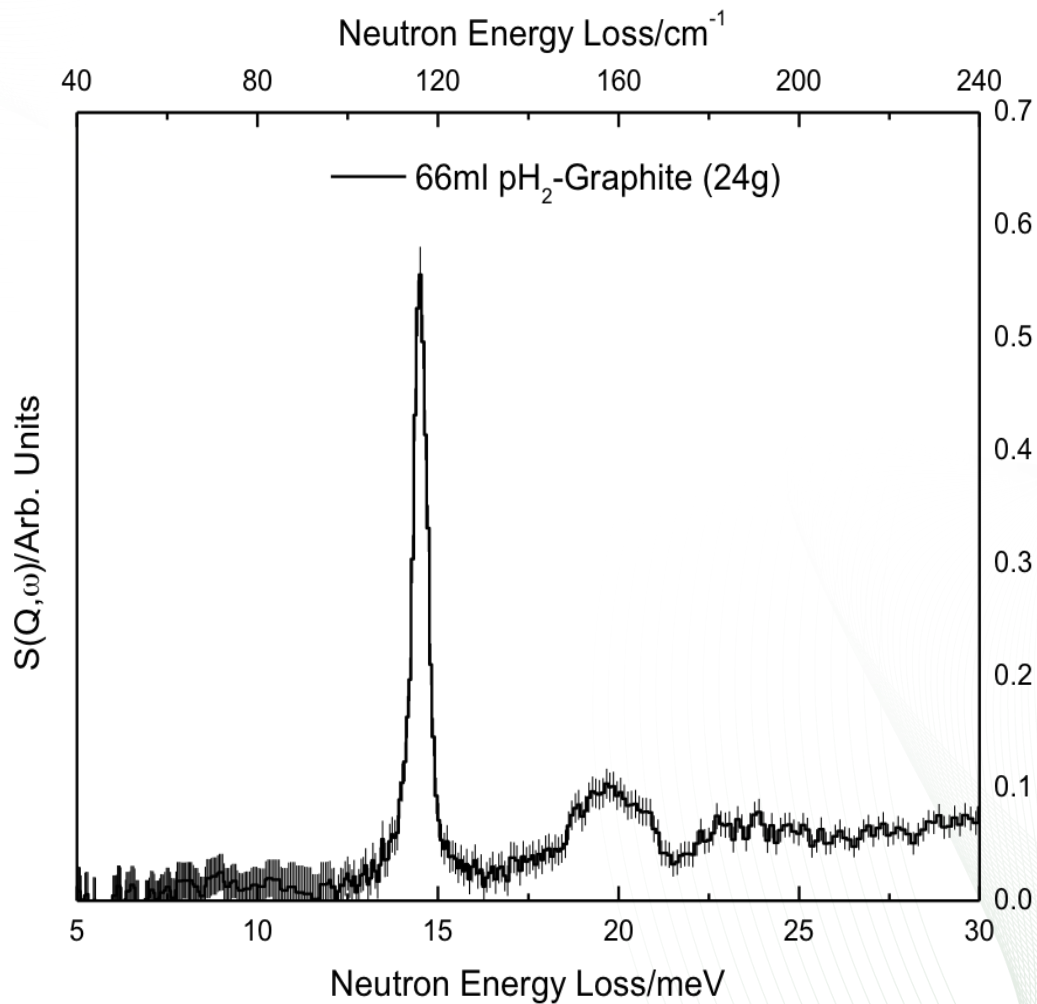


What are we expecting?



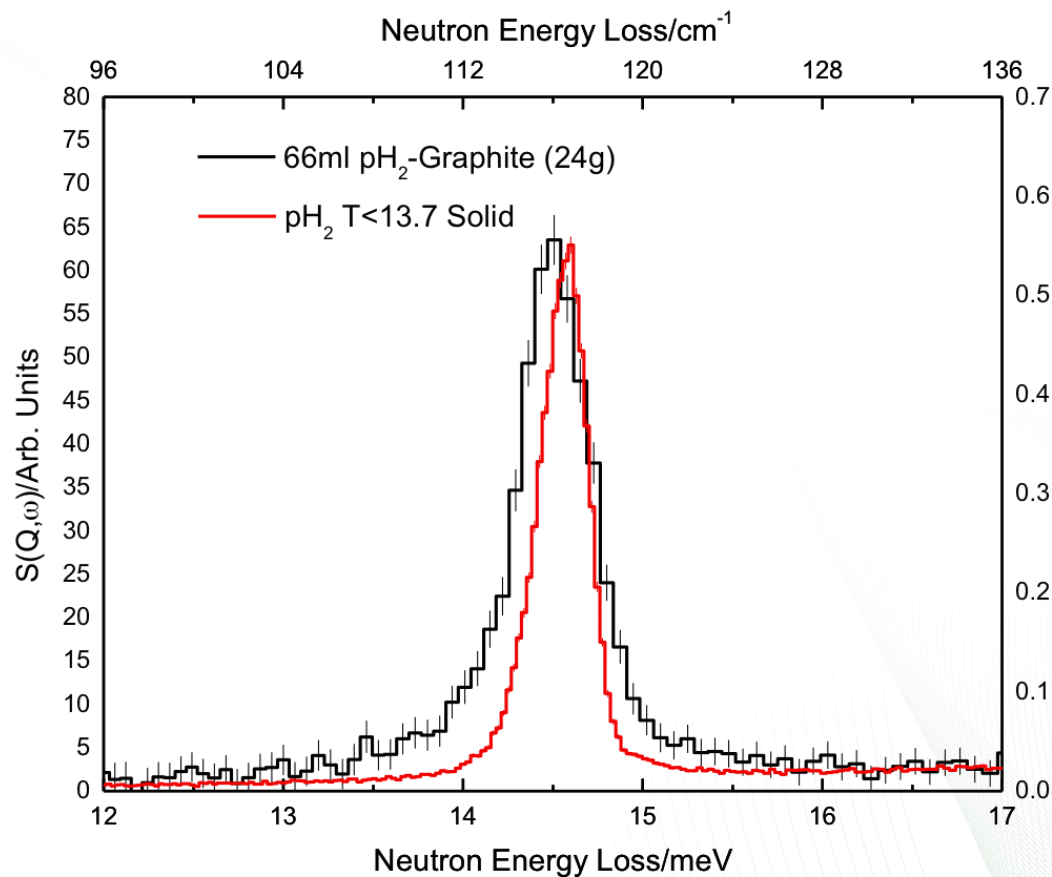
01 August 2018

Interaction of graphite with Hydrogen



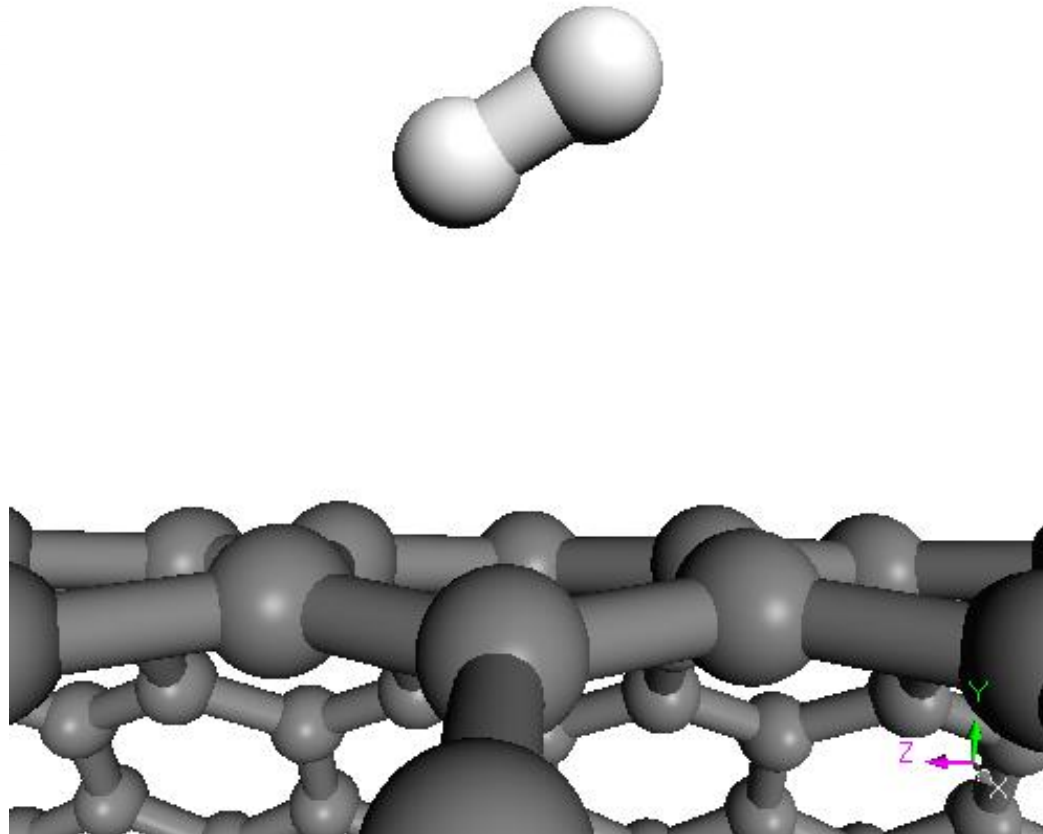
01 August 2018

Interaction of graphite with Hydrogen



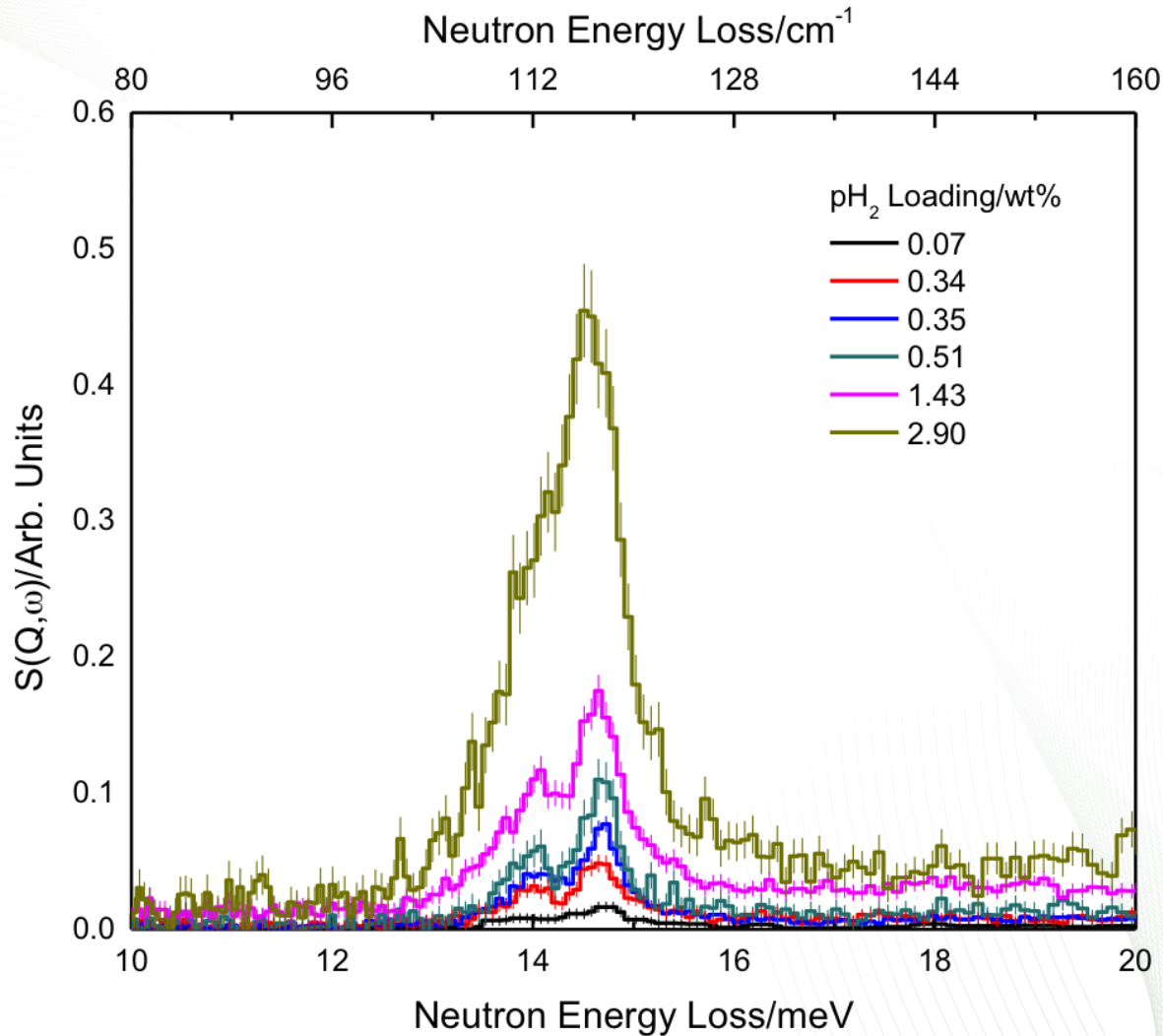
01 August 2018

Interaction of SWNT with Hydrogen



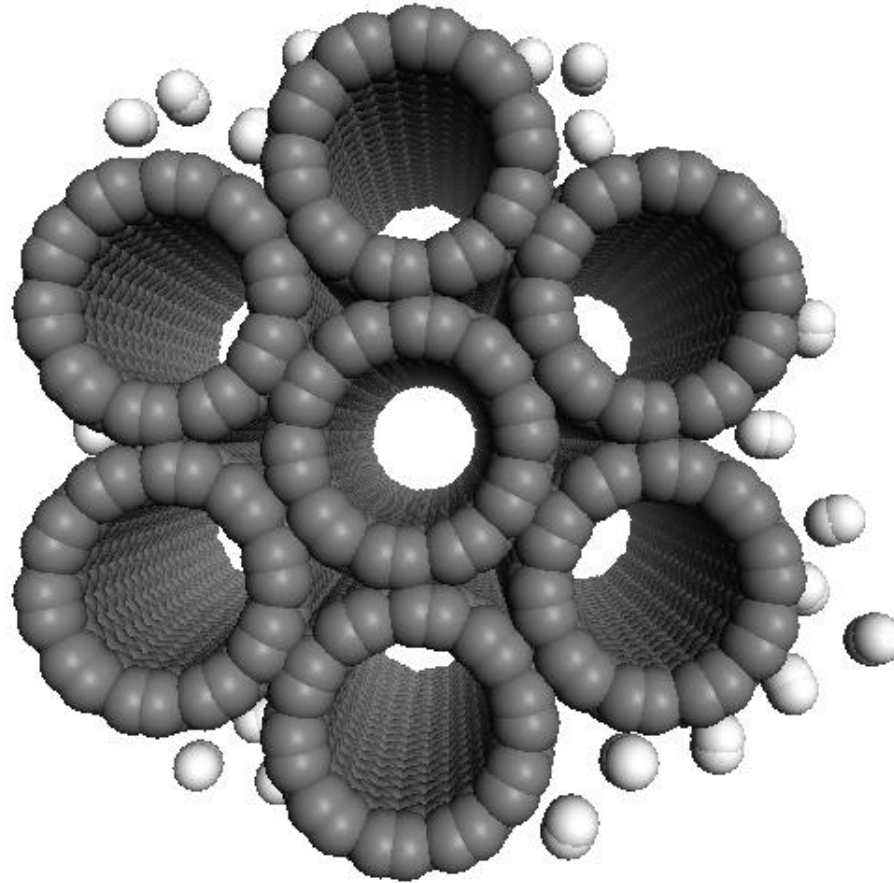
01 August 2018

Interaction of SWNT with Hydrogen



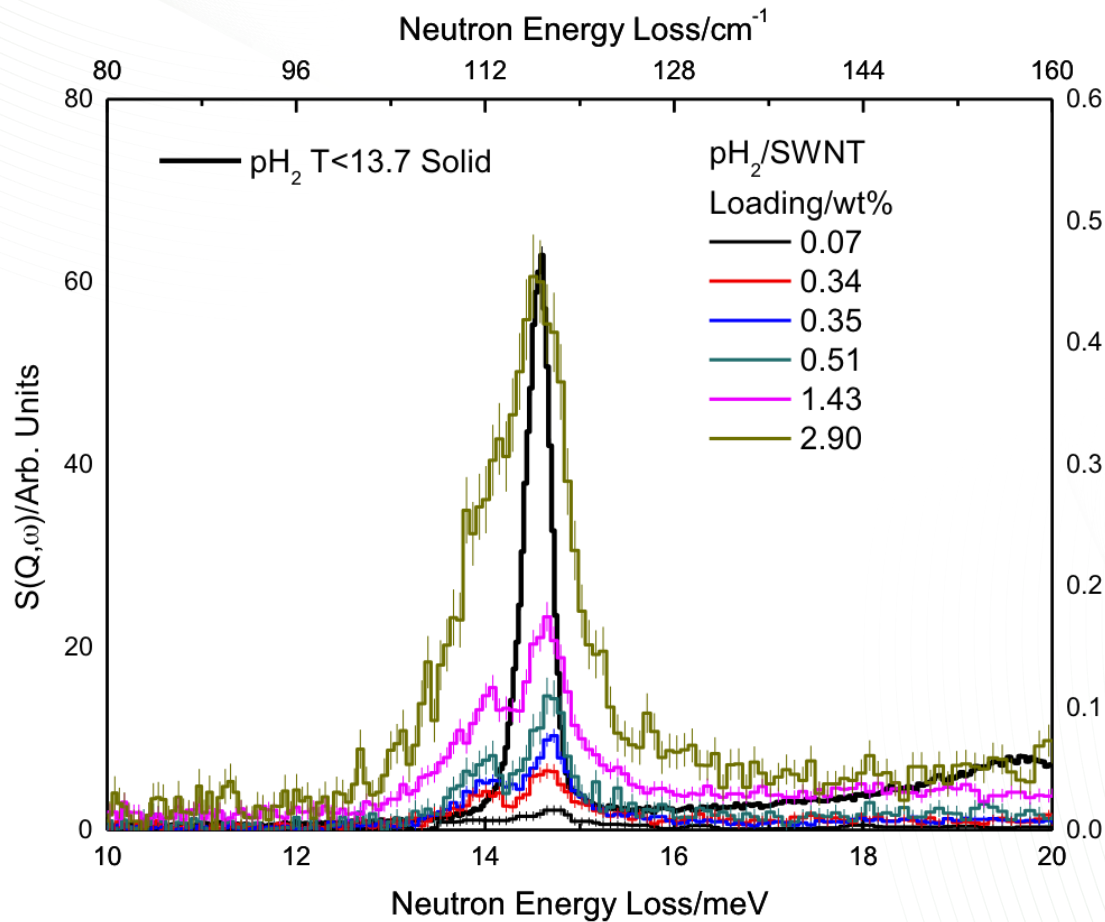
01 August 2018

Interaction of SWNT with Hydrogen



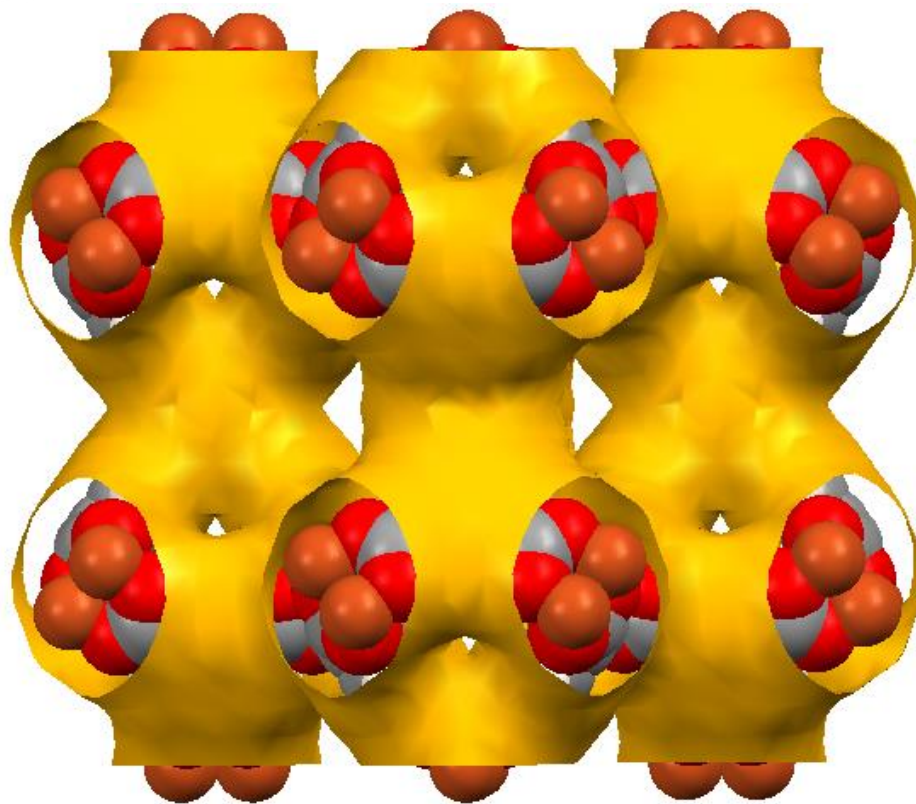
01 August 2018

Interaction of SWNT with Hydrogen



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

Example #1 H₂ in Cu-MOF

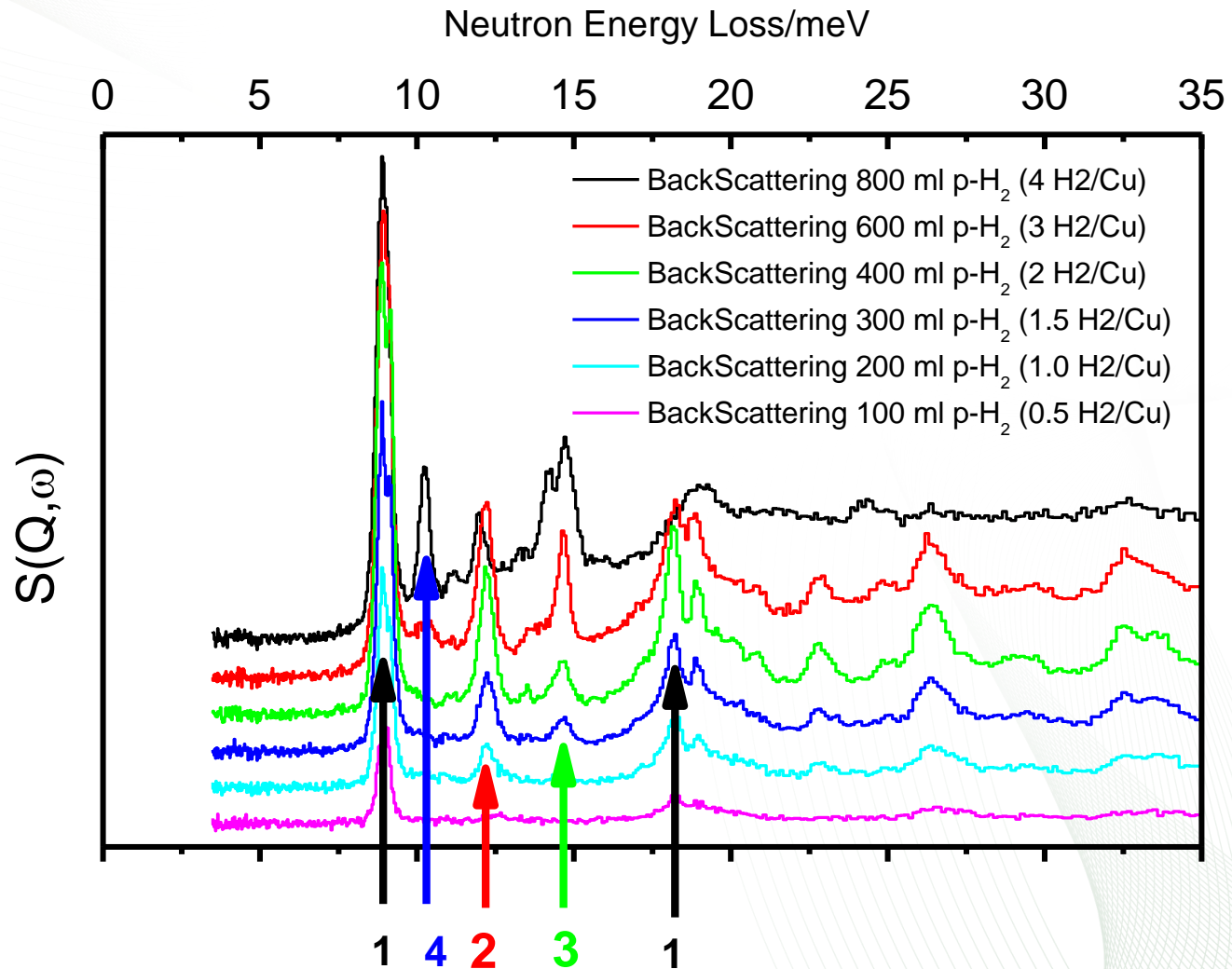


Franck Millange, Sam Callear, Richard Walton, Timmy Ramirez-Cuesta
Chemical Physics 427 (2013) 9

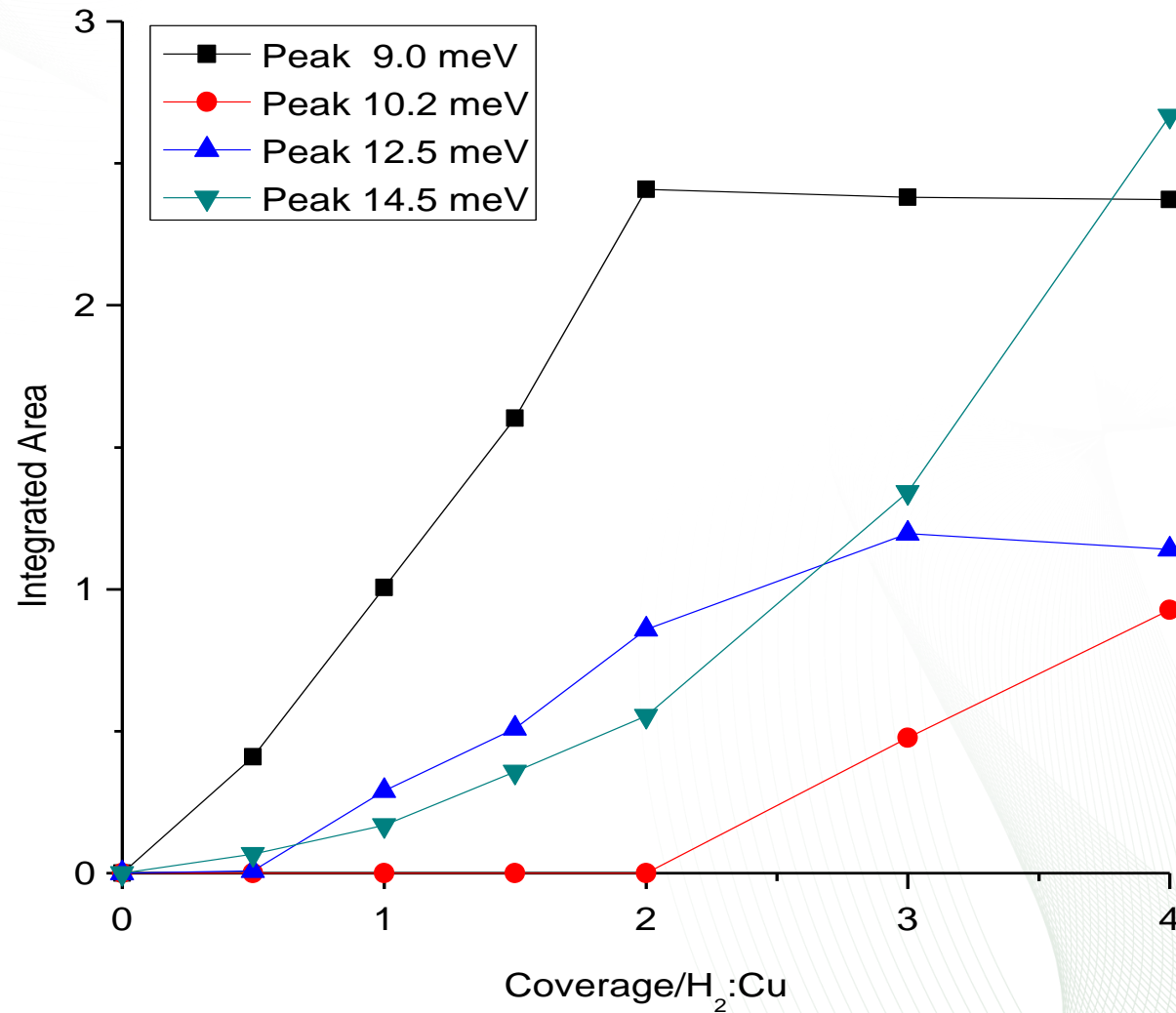
doi:<http://dx.doi.org/10.1016/j.chemphys.2013.07.020>.

01 August 2018

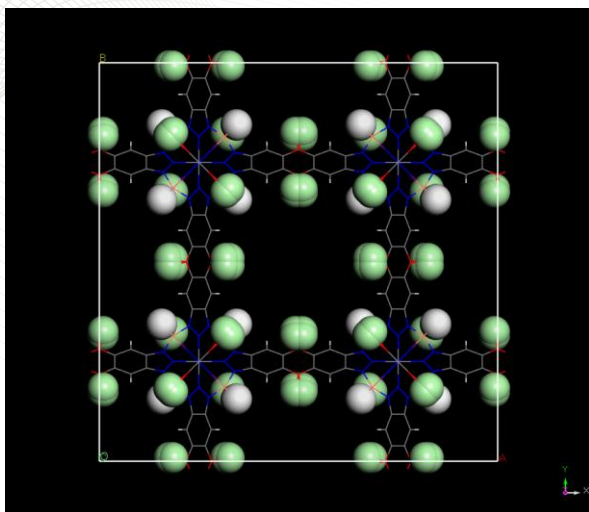
H₂ in Cu-MOF #1



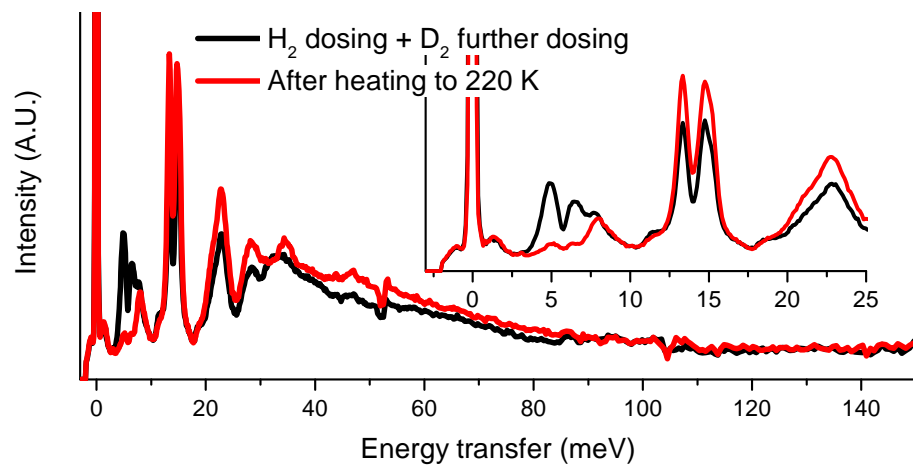
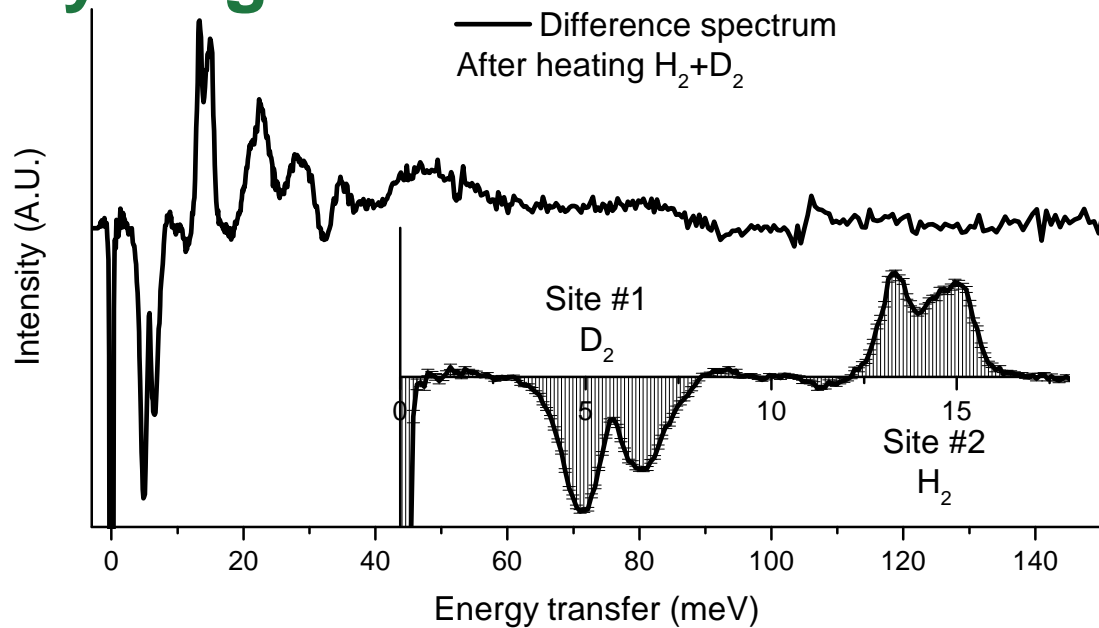
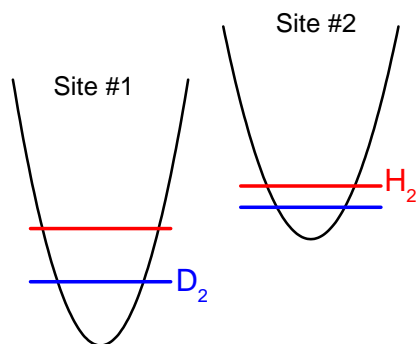
H₂ in Cu-MOF #1



Quantum Sieving Hydrogen in a MOF

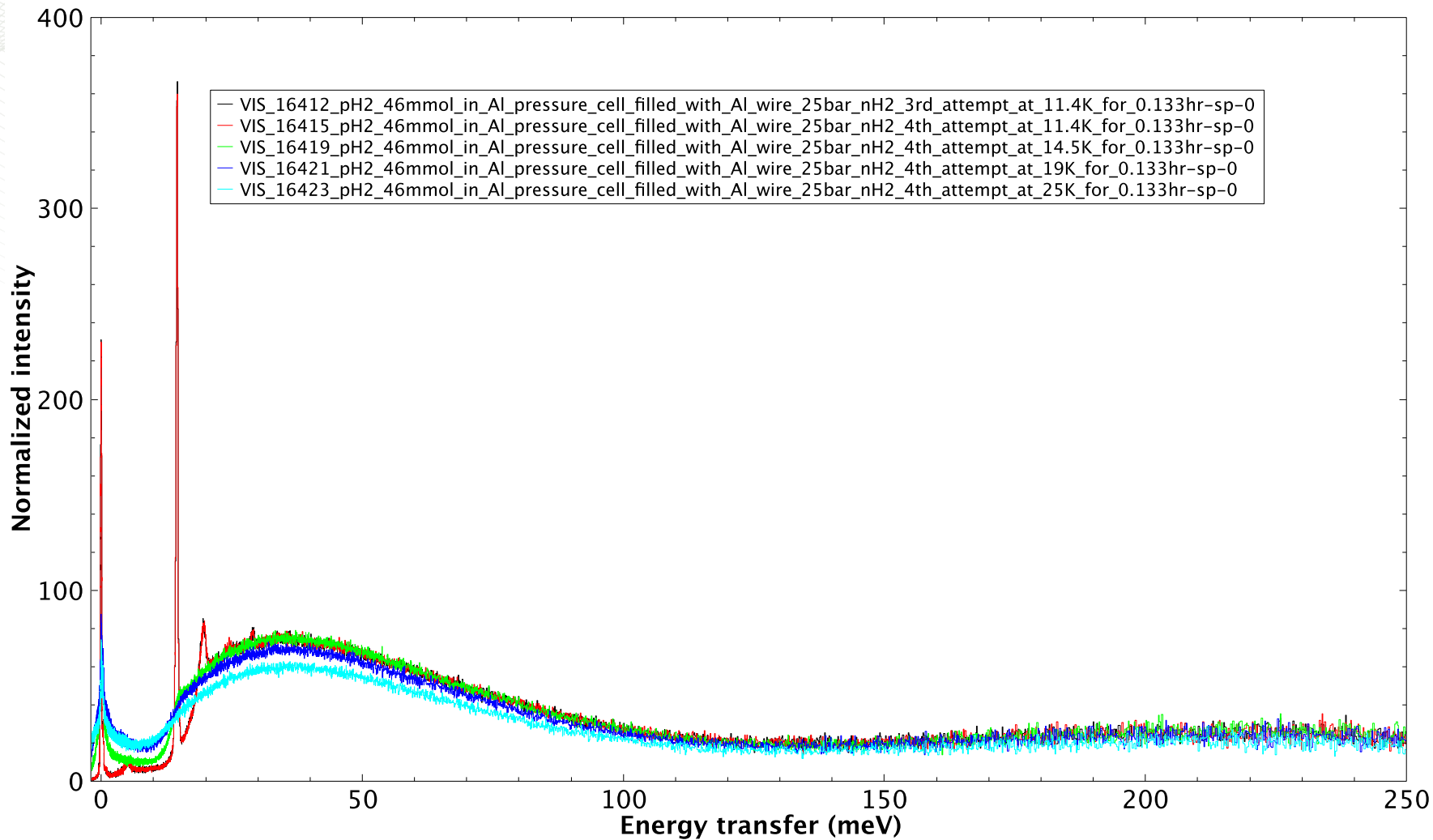


Quantum sieving is a technique for isotope separations; heavier isotopes induce favorable adsorption in nanoscale pores due to the difference in zero point energy of isotopes.

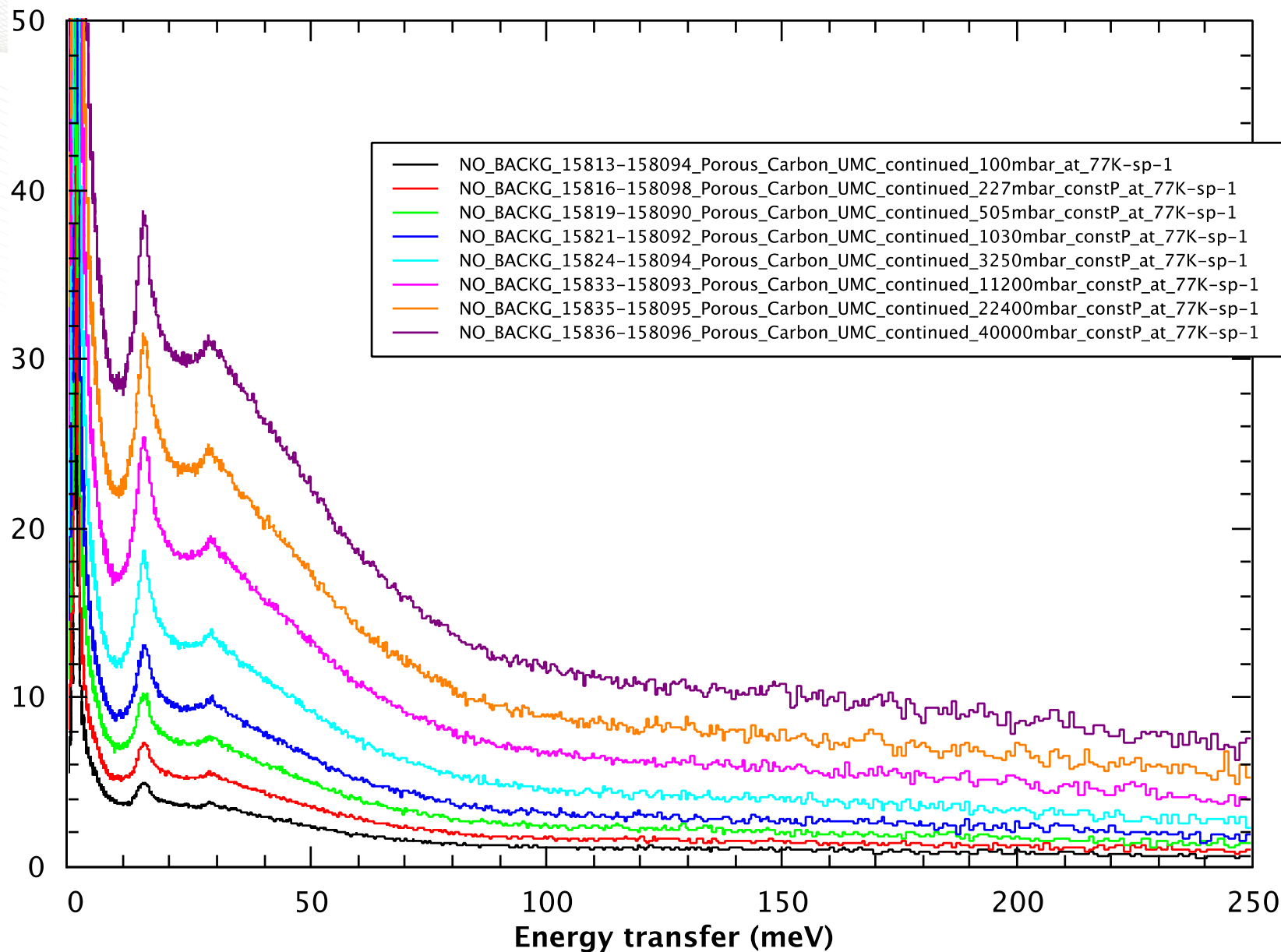


Black trace is hydrogen dosed at 77K and cooled down, further deuterium is added at 77K. Red trace is spectrum after warming sample to 220K and cool down. The hydrogen in site #1 has been displaced to site #2

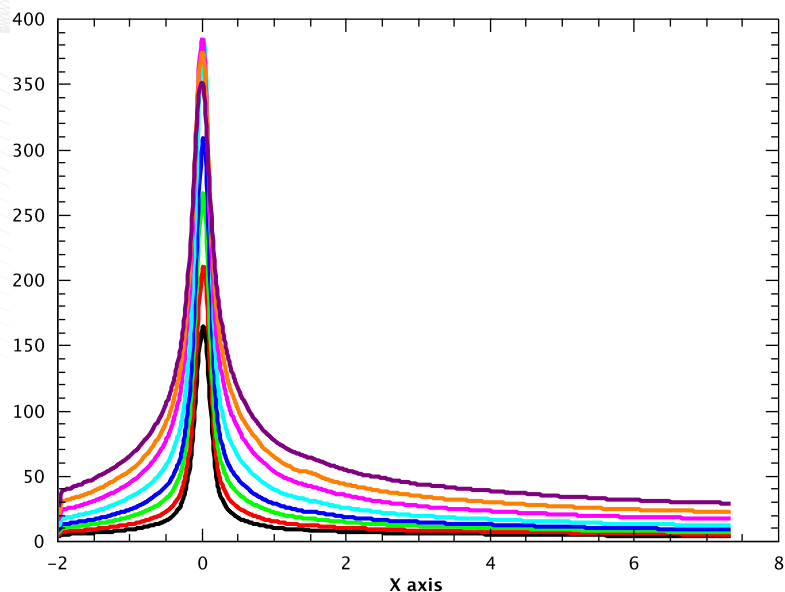
Molecular hydrogen solid



Molecular hydrogen in porous carbon



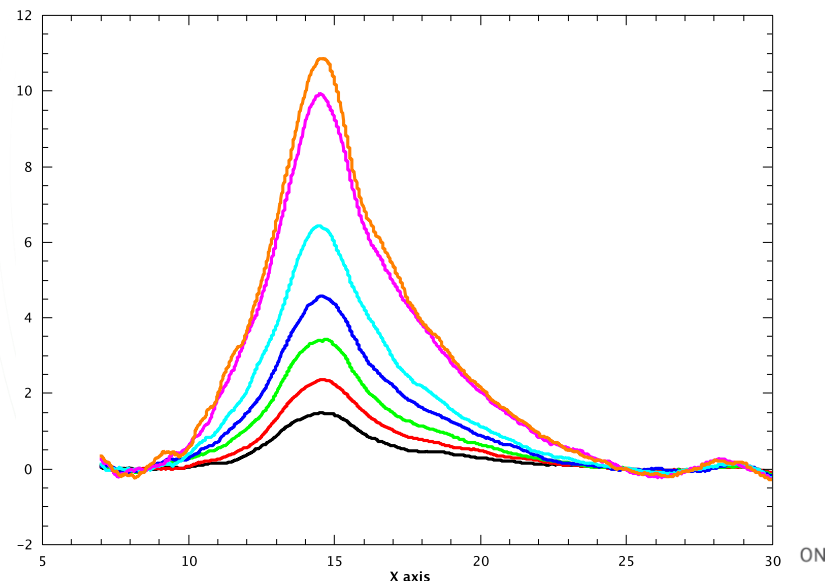
Molecular hydrogen in porous carbon



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.

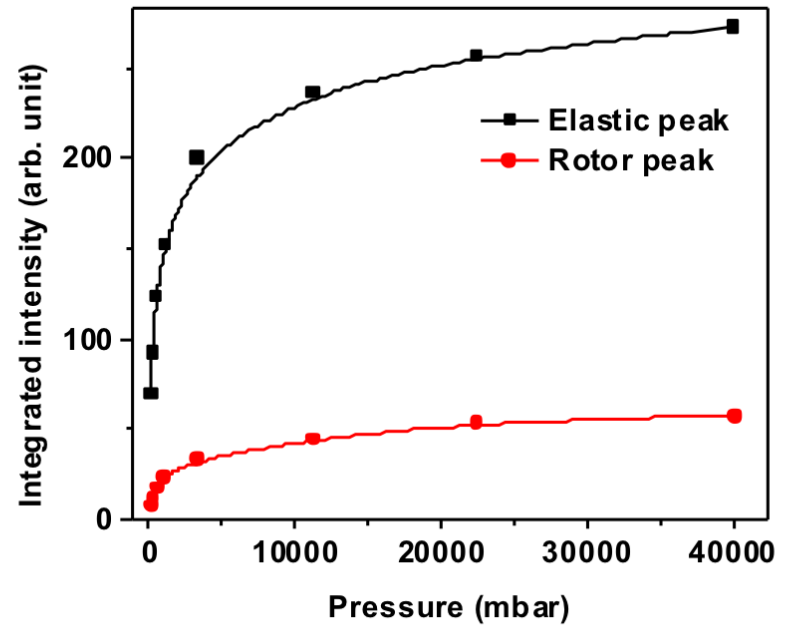
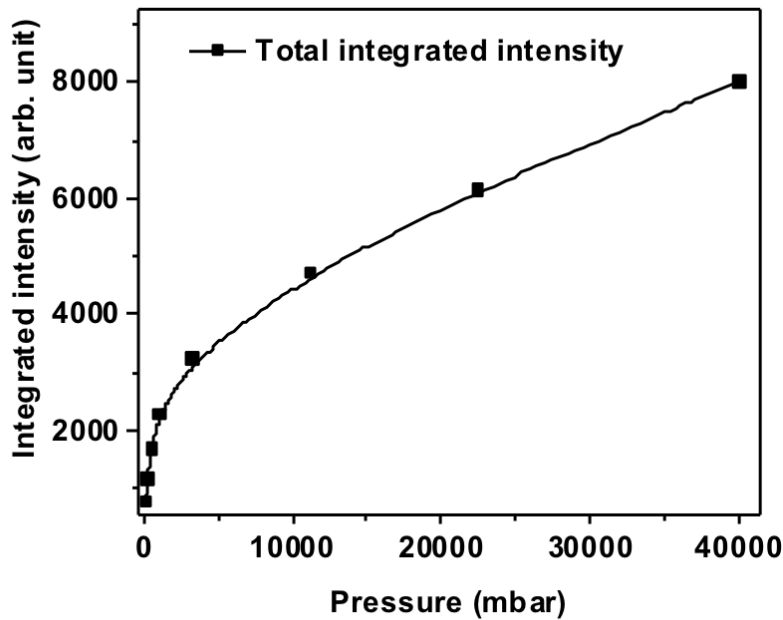
There is very little broadening of the rotor line, since the momentum transfer is larger than the corresponding one at the elastic line (dynamical trajectory of indirect geometry). The load keeps increasing even at 40 bar.

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.



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)



Summary

What is VISION

- It is the world's first high throughput inelastic neutron scattering instrument.
- Its overall count rate in the inelastic signal is three orders of magnitude greater than that of similar spectrometers currently available.
- It measures vibrational spectra in a broad energy range (1 meV to >500 meV)
- It records structural information using diffraction detectors in the backscattering position simultaneously with inelastic neutron scattering
- It has integrated modeling capability that helps to interpret the INS spectra

What can be studied with VISION

- Hydrogenous and non-hydrogenous materials
- Molecular vibration and phonon density of states
- Crystalline and disorder materials (powders)
- Nano materials
- Porous materials
- Surface (e.g., catalysis)

Capabilities

- In situ gas handling
- High pressure: gas cells, clamps cells, DAC
- Automatic sample changer
- Computer cluster for modeling and data analysis



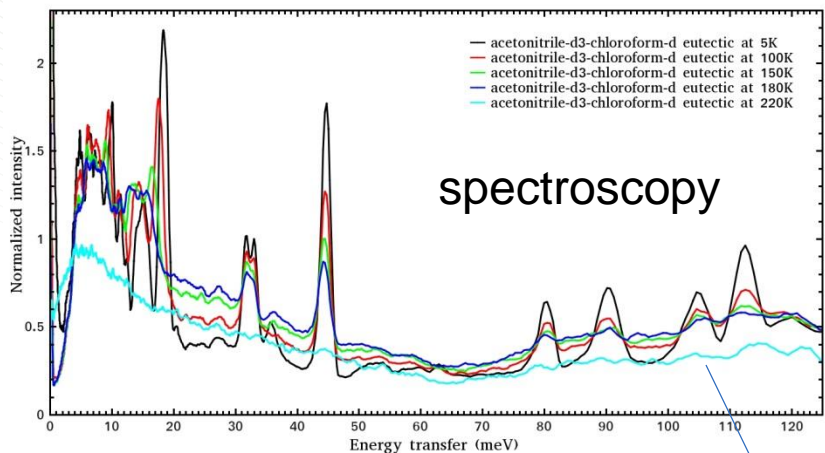
Intermolecular interactions: Deep Eutectic Solvents

- + Most chemistry takes place in solution of pure or mixed solvents
- + We have no predictive, quantitative, microscopic theory of solubility
- + Deep Eutectic Solvents (DES) are now very popular within the field of "Green Chemistry"
- + Our knowledge of the structure of liquids and solutions has improved over the past few decades. Our understanding of intermolecular forces between solvent(s) and solute(s) remains limited. Optical spectroscopy is of limited use, particularly in hydrogen-bonded systems.
- + The study of liquids and solutions has been historically problematic for inelastic neutron scattering because of the effect of Debye-Waller broadening (which requires low T and/or low Q) and recoil on the vibrational spectrum (which requires low Q)
- + **New approach to liquids and solutions and new, vast area of research for chemical spectroscopy with neutrons !**

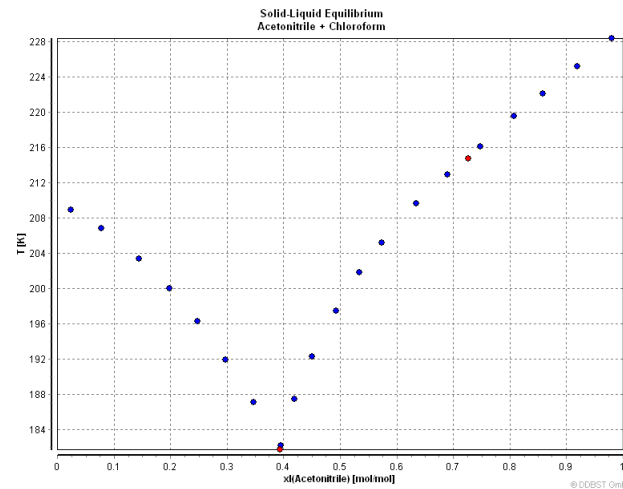
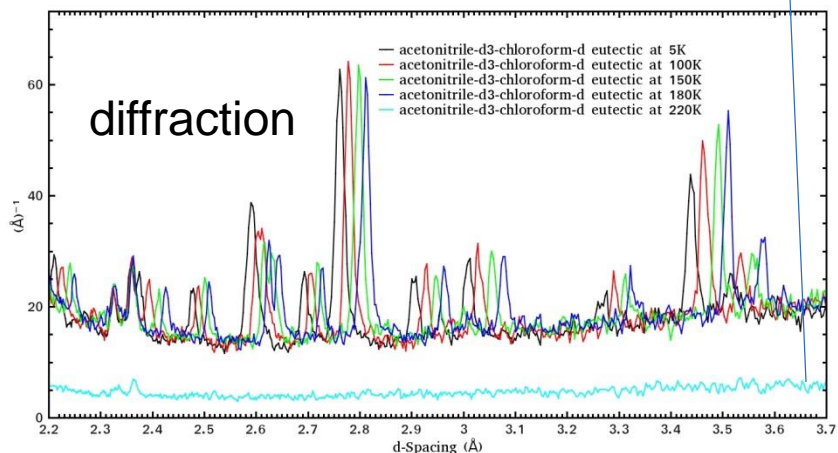
Structure and dynamics of liquids and solutions

What we can do today on VISION ...

simultaneous spectroscopy and diffraction



liquid

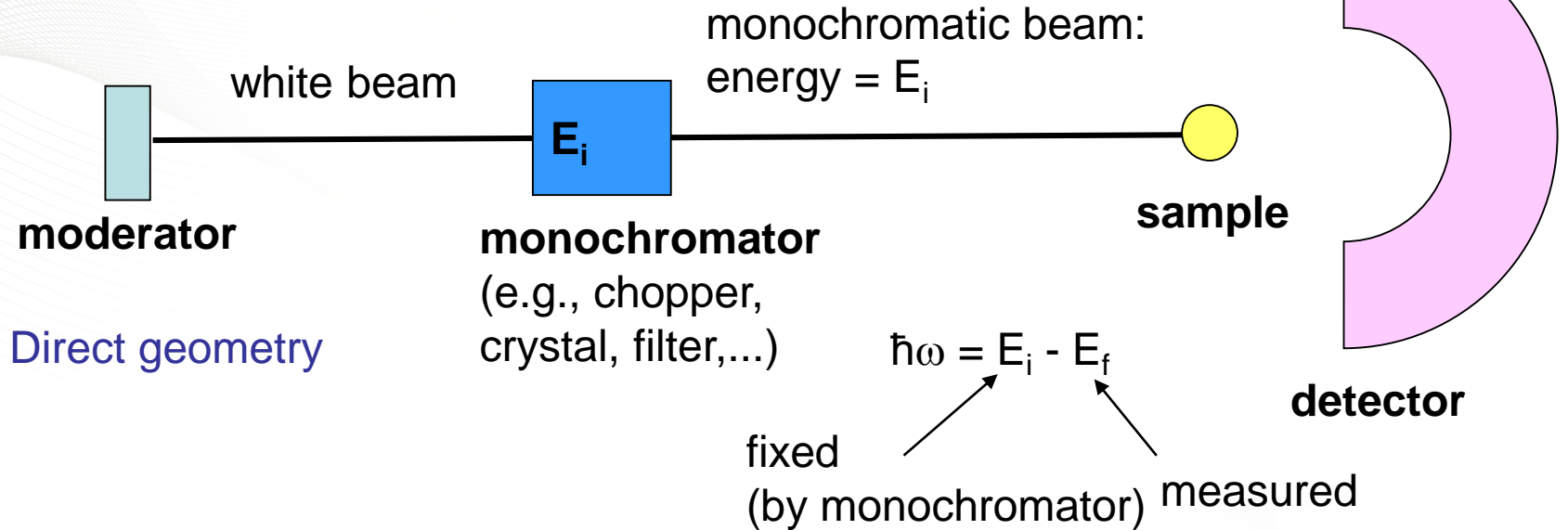


- model deep-eutectic system, acetonitrile-chloroform
- $T_E = 182$ K; $x(\text{CD}_3\text{CN}) = 0.4$ at eutectic composition
- strongly non-ideal system because of hydrogen bonding ($\Delta H_{\text{excess}} = 800$ J/mol)

What is the structure of the $(\text{CH}_3\text{CN})_2:(\text{CHCl}_3)_3$ molecular complex at the eutectic composition? \Rightarrow no model !

Instruments

Spectrometer configurations



Inverted geometry

