

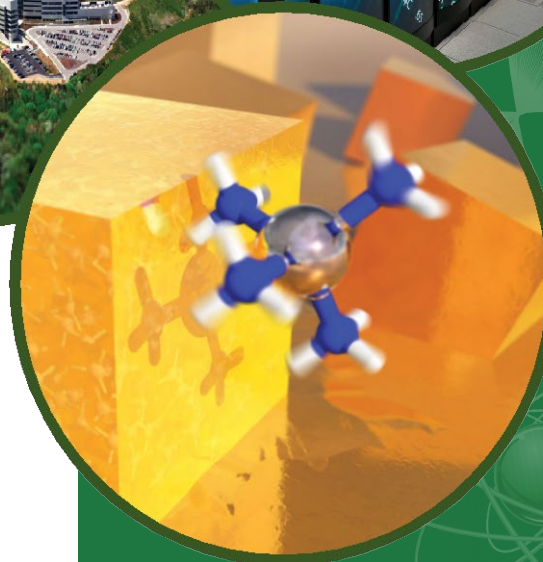
Neutron Vibrational Spectroscopy

2019 National School on
Neutron and X-ray Scattering

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Spectroscopy Group
Neutron Scattering Division
Oak Ridge National Laboratory

Acknowledgement to the VISION team (Luke Daemen and Timmy Ramirez-Cuesta) and users.



What is neutron vibrational spectroscopy

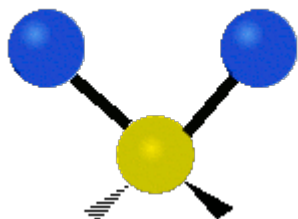
- Neutron vibrational spectroscopy (NVS)
- Chemists
- Organic/inorganic compounds
- Molecular systems
- Normal modes
- Intramolecular modes
- Intermolecular modes
- Librational modes
- Translational modes (phonons)
- cm^{-1}
- Inelastic neutron scattering (INS)
- Physicists
- Condensed matter
- Phonons
- meV

NVS focuses on applications of INS in chemistry

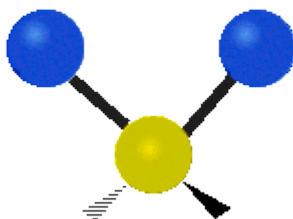
Molecular vibration

- Structure and **dynamics**

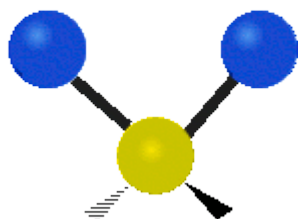
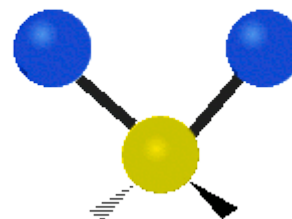
Symmetric stretching



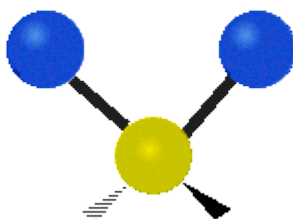
Asymmetric stretching



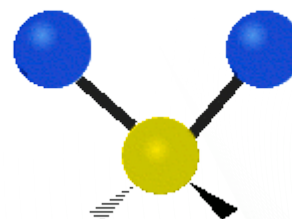
Scissoring (Bending)



Rocking



Wagging

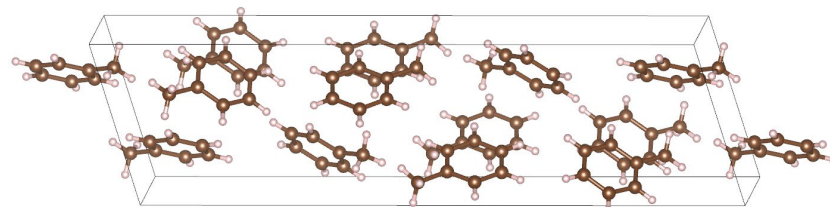
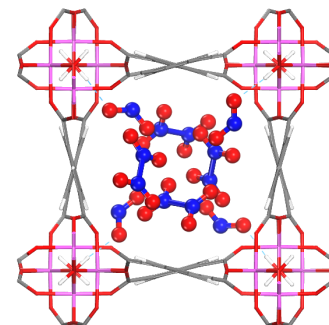
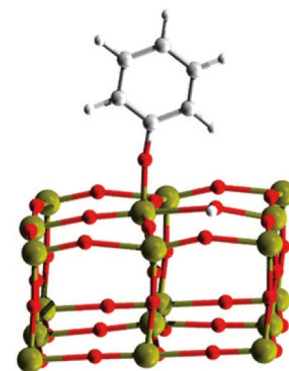


Twisting

Molecules dance in their own characteristic ways.

Vibration of molecules in different environment

- Gas (non-interacting, internal vibration)
- Surface (chemi/physi-adsorbed)
- Pores (restricted/confined motion)
- Solid (molecular crystals)



The vibrational behavior of a molecule is determined by:

- 1) internal structure (bond type, functional groups, etc.)
- 2) local environment (intermolecular forces)

What can we learn from molecular vibration?

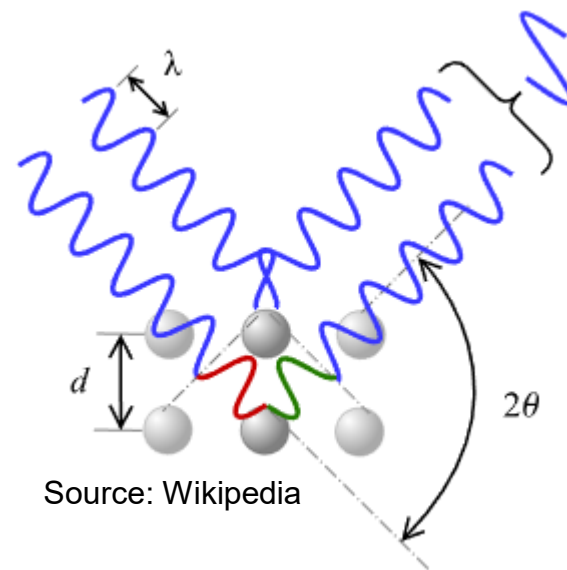
- Molecular and crystal structure
- Binding site and orientation (adsorption)
- Electronic structure (charge transfer)
- Thermodynamic properties (free energy, phase diagram, specific heat capacity and conductivity)
- Transport properties (diffusion and relaxation)
-

One of the most important vital signs of molecules

How to measure molecular vibration: Vibrational spectroscopy

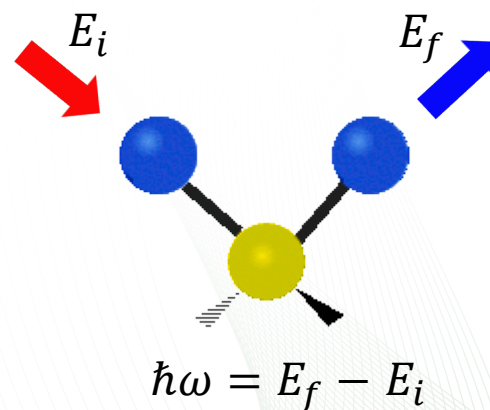
Crystallographers use diffraction of some form of radiation (light, electron, x-ray, neutron,...) to obtain information on the periodic arrangement of atoms in space. The wavelength of the radiation is comparable to interatomic distances.

Wavelength
Scattering angle



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.

Incident energy
Final energy
(Scattering angle)



Interpreting vibrational spectra

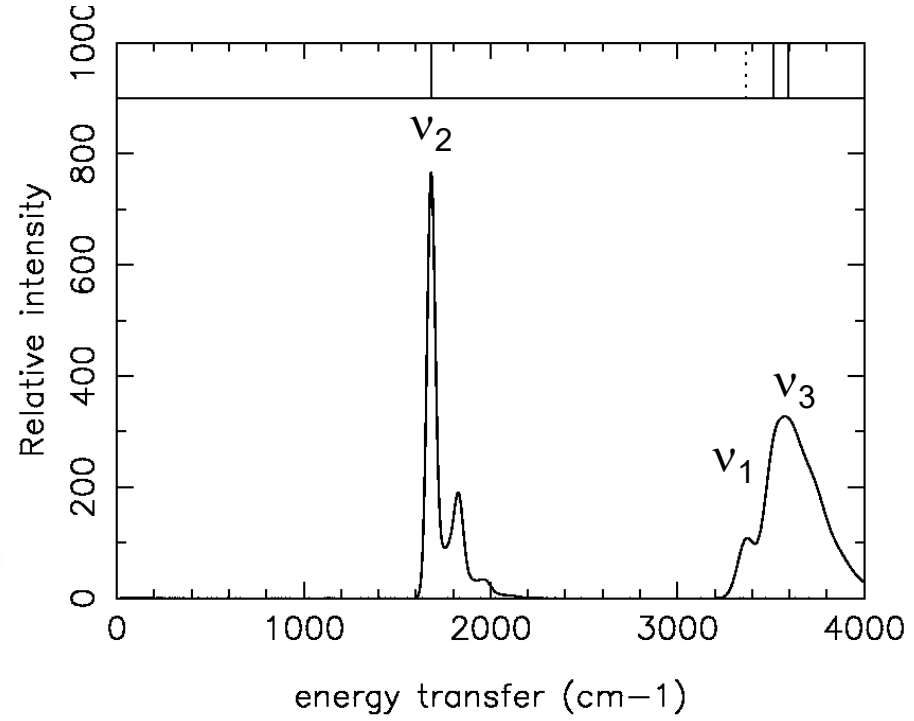
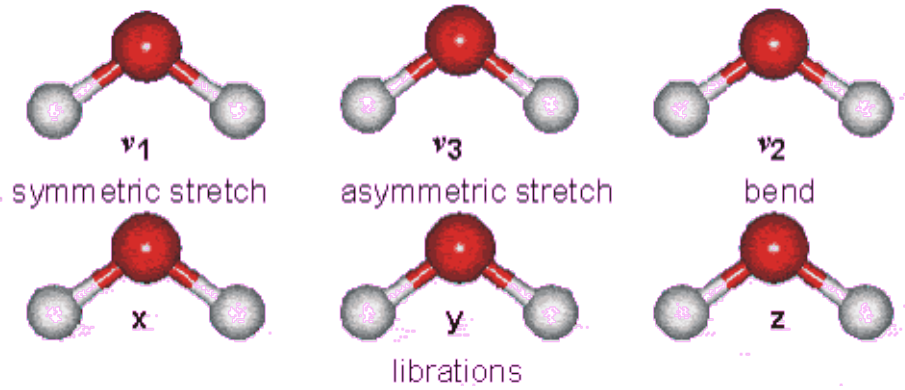
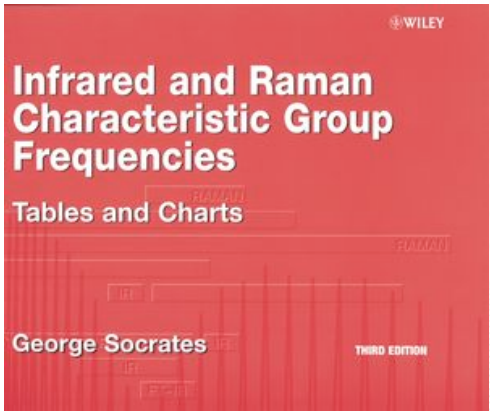


Table 1 Absorption frequencies of some common bonds (shown in bold type)

bond	type of compound	frequency
-C-H (stretch)	alkanes	2800-3000
=C-H (stretch)	alkenes, aromatics	3000-3100
≡C-H (stretch)	alkynes	3300
-O-H (stretch)	alcohols, phenols	3600-3650 (free) 3200-3500 (H-bonded) (broad)
-O-H (stretch)	carboxylic acids	2500-3300
-N-H (stretch)	amines	3300-3500 (doublet for NH ₂)
-C-H (stretch)	aldehydes	2720 and 2820
-C=C- (stretch)	alkenes	1600-1680
-C=C- (stretch)	aromatics	1500-1600
-C≡C-H (stretch)	alkynes	2100-2270
-C=O (stretch)	aldehyde, ketones, carboxylic acids	1680-1740
-C≡N (stretch)	nitriles	2220-2260
C-N (stretch)	amines	1180-1360
-C-H (bending)	alkanes	1375 (methyl)
-C-H (bending)	alkanes	1460 (methyl and methylene)
-C-H (bending)	alkanes	1370 and 1385 (isopropyl split)

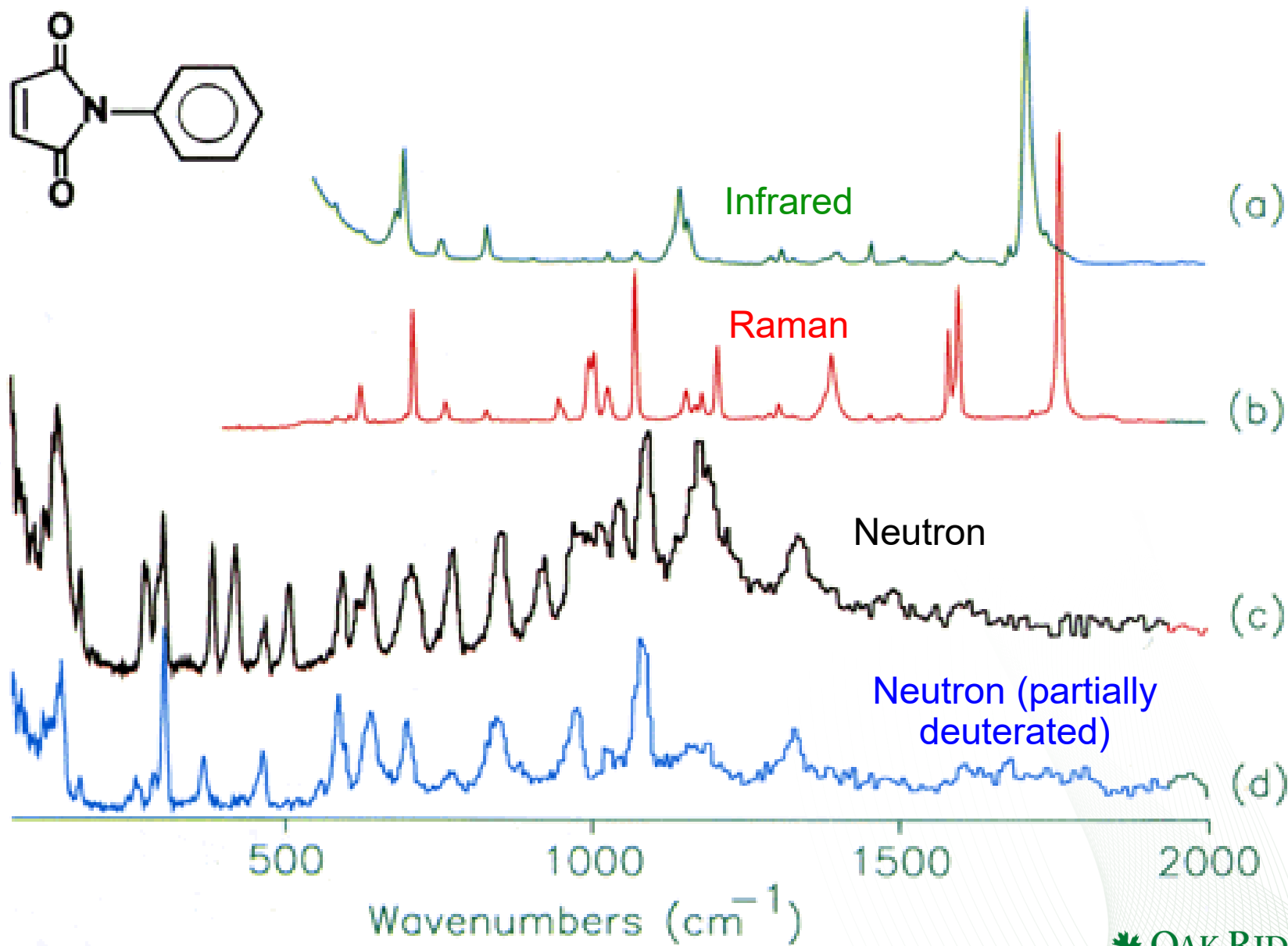
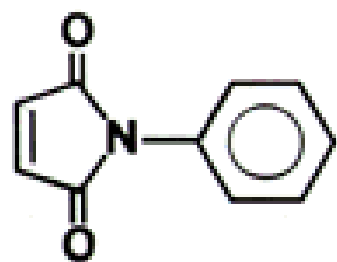


Vibrational spectroscopy with neutrons

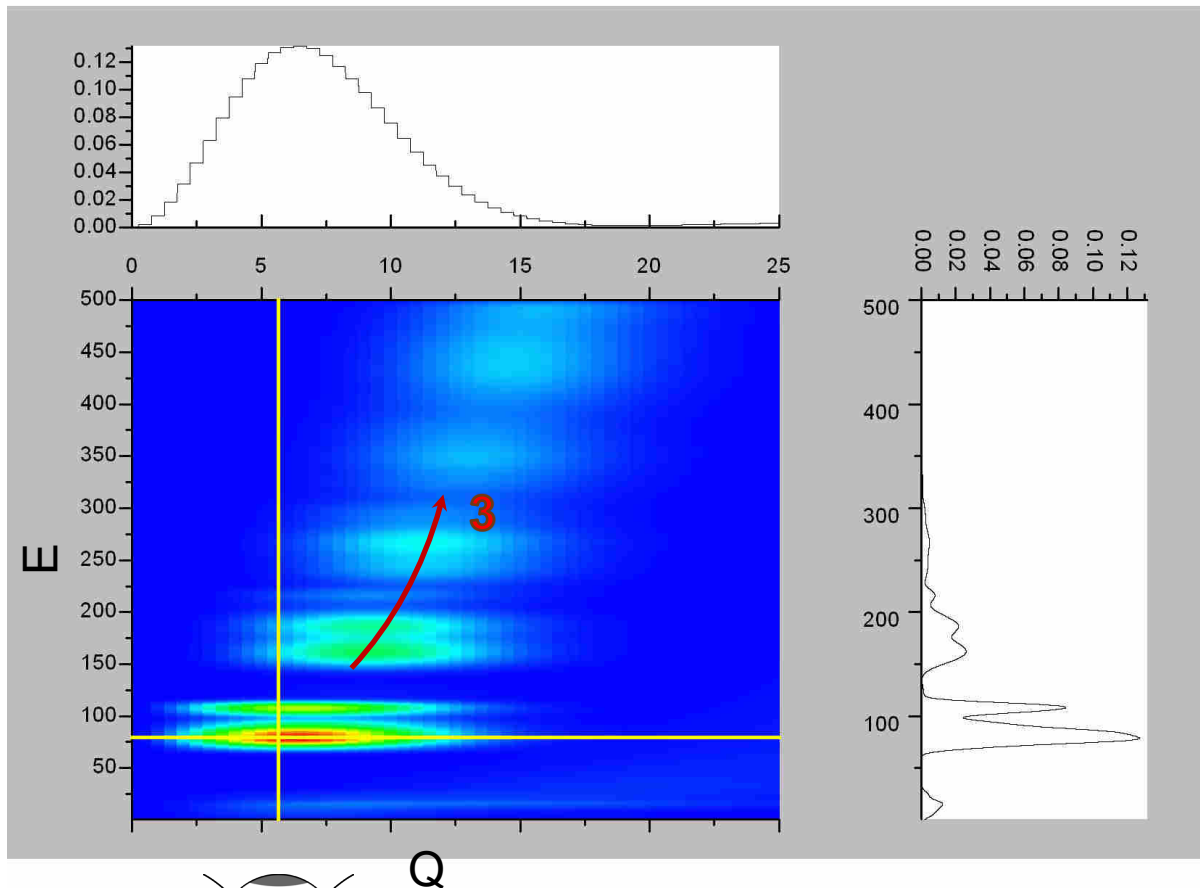
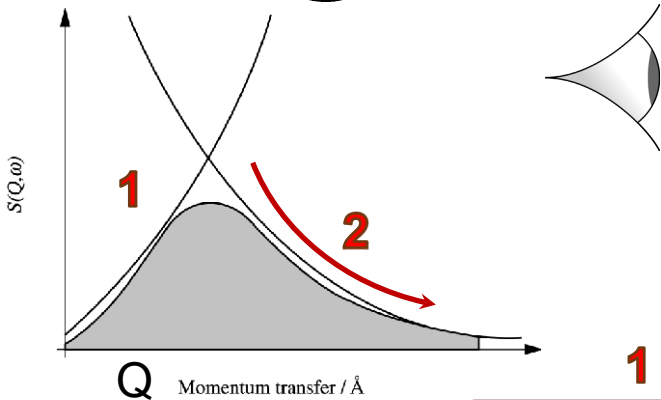
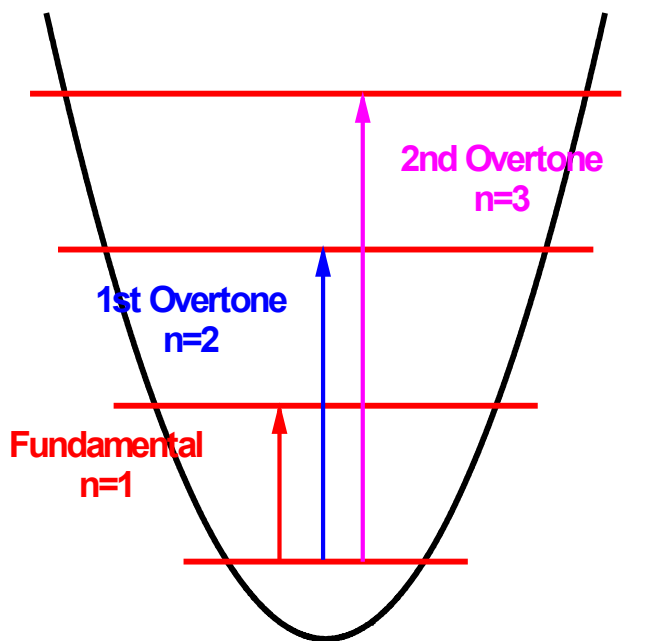
VISION (INS/NVS)	Raman/Infrared
Measures dynamics of nuclei (direct)	Measures response of electrons (indirect)
Can see Raman/Infrared-inactive modes	Selection rules apply
Great sensitivity to H	Cannot always see H
High penetration (bulk probe)	Low penetration (surface probe)
Easy access to low energy 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, ...

Complementary tools to study molecular vibration

Complementary tools to study molecular vibration



The $S(Q, \omega)$ map of molecular vibration

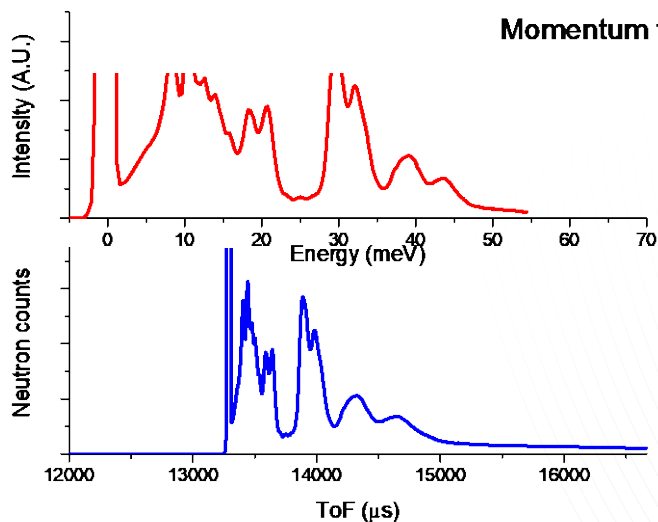
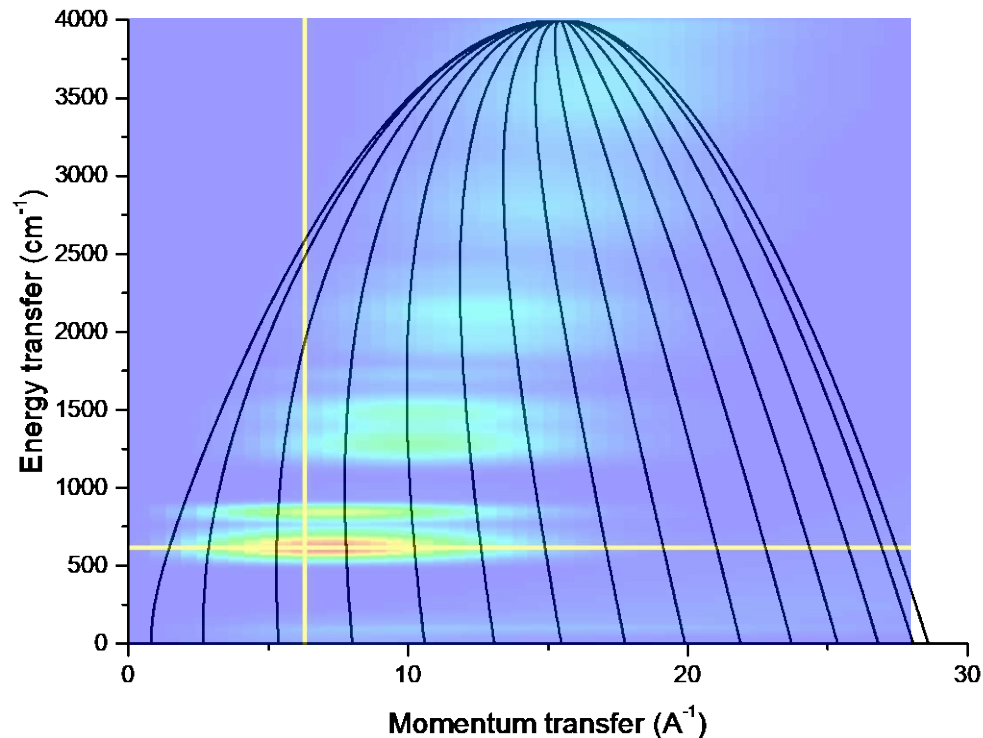
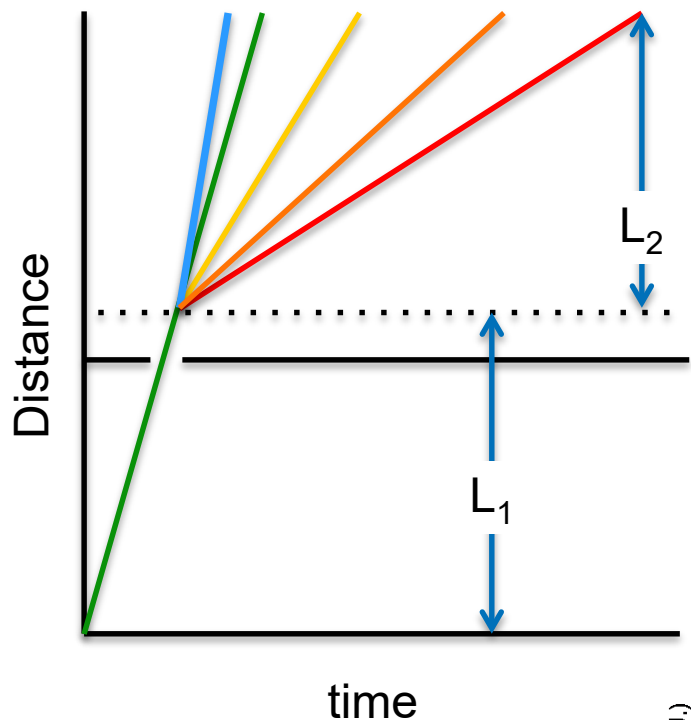


$$S(Q, n\omega_s) = \frac{(\mathbf{Q} \cdot \mathbf{U}_s)^{2n}}{n!} \exp[-(\mathbf{Q} \cdot \mathbf{U}_{total})^2]$$

$$\mathbf{U}_s = \sqrt{\frac{\hbar}{2m\omega_s}} e^{ds}$$



Instrument geometry: direct

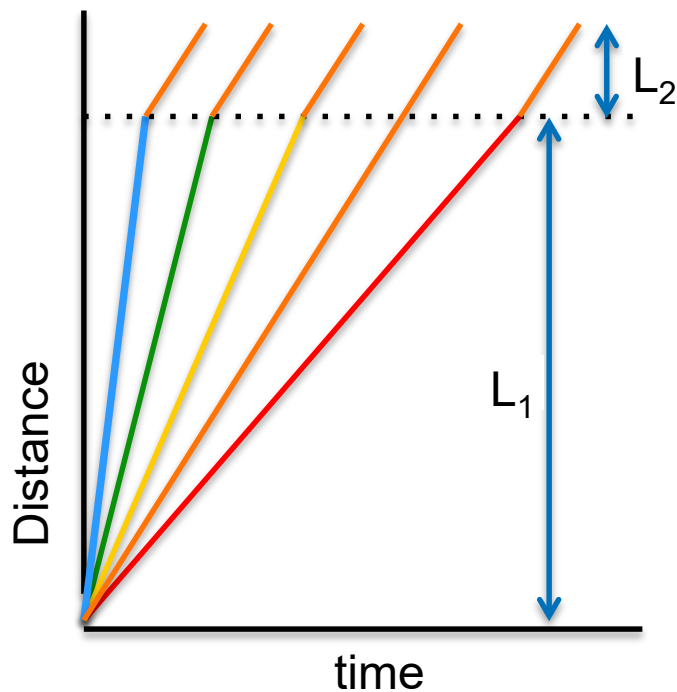


Fixed incident energy,
measure final energy and
scattering angle.

Examples: ARCS, CNCS,
HYSPEC, SEQUIOA

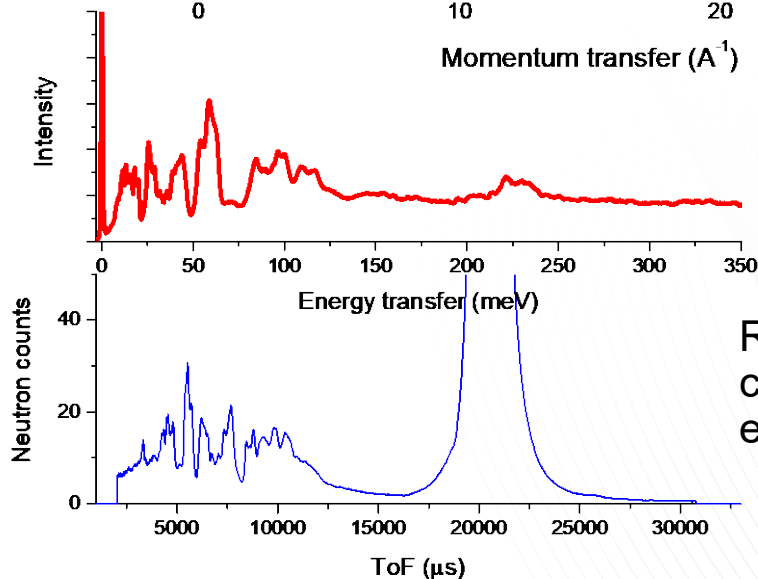
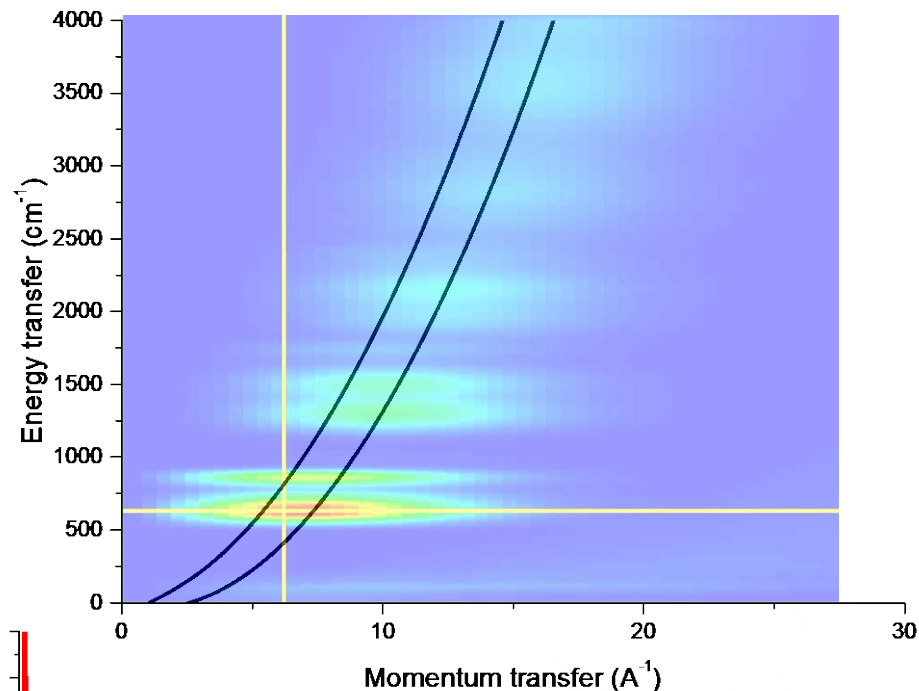
Resolution is almost a
constant fraction of
incident energy

Instrument geometry: indirect



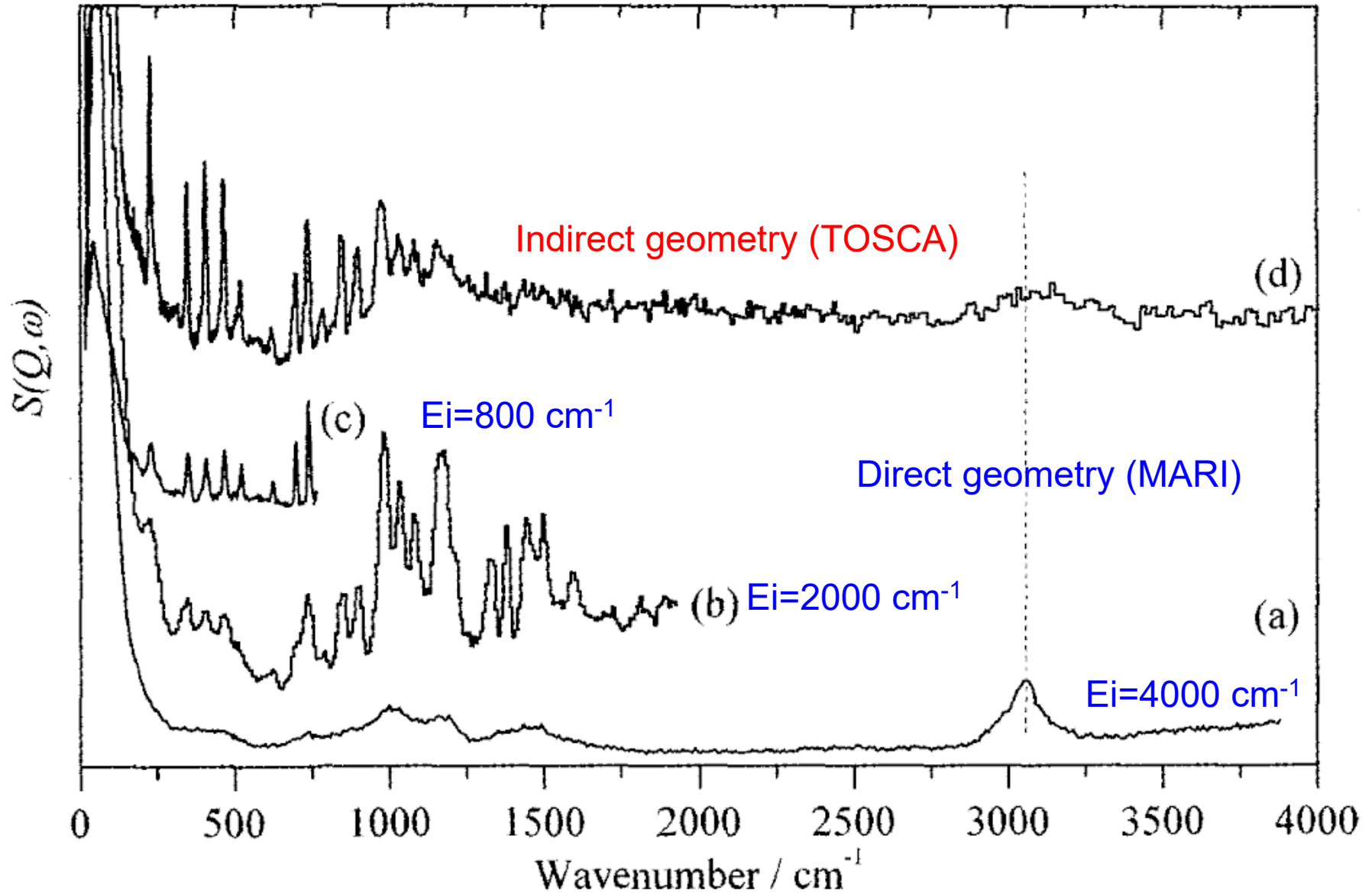
White incident beam,
fixed final energy,
calculate initial energy.

Examples: VISION, TOSCA



Resolution is almost a
constant fraction of
energy transfer

Choice of instrument for molecular vibration



VISION

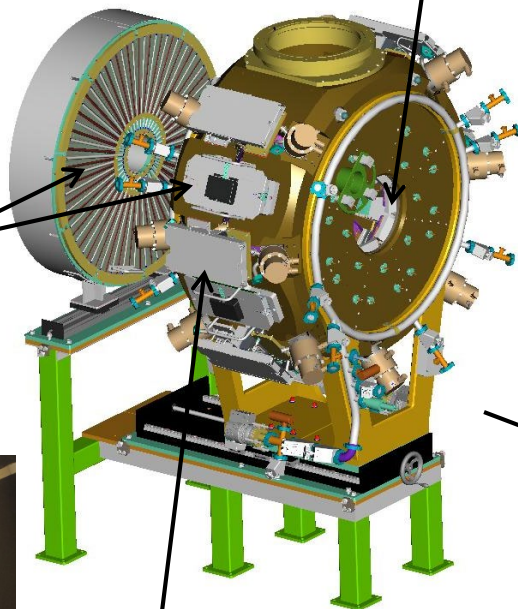
neutron beam



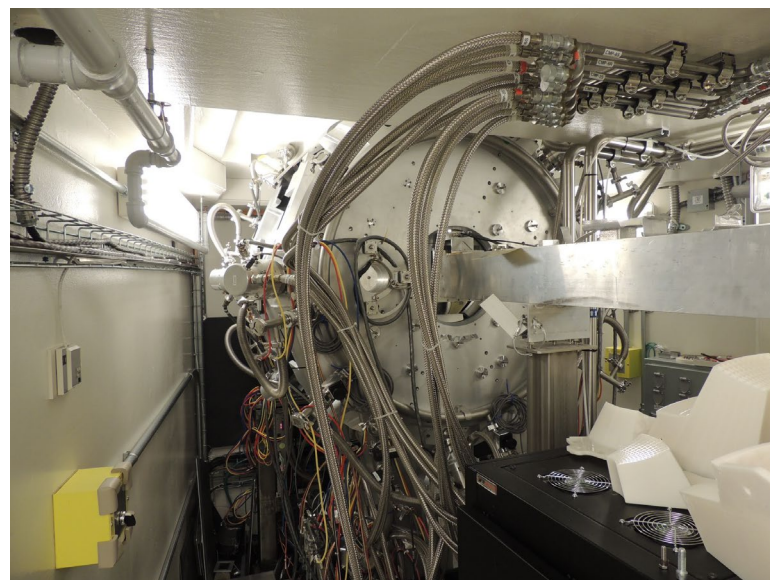
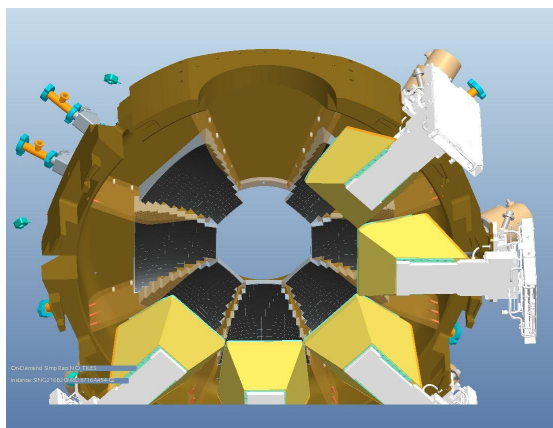
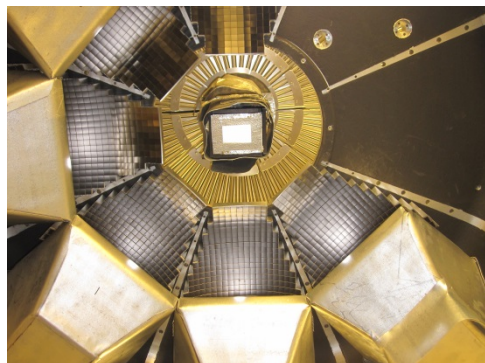
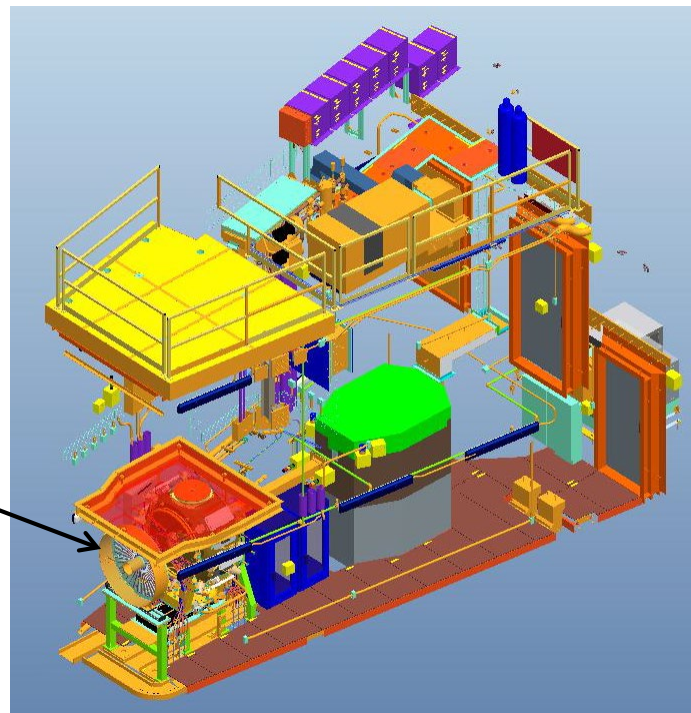
diffraction detectors



analyzers

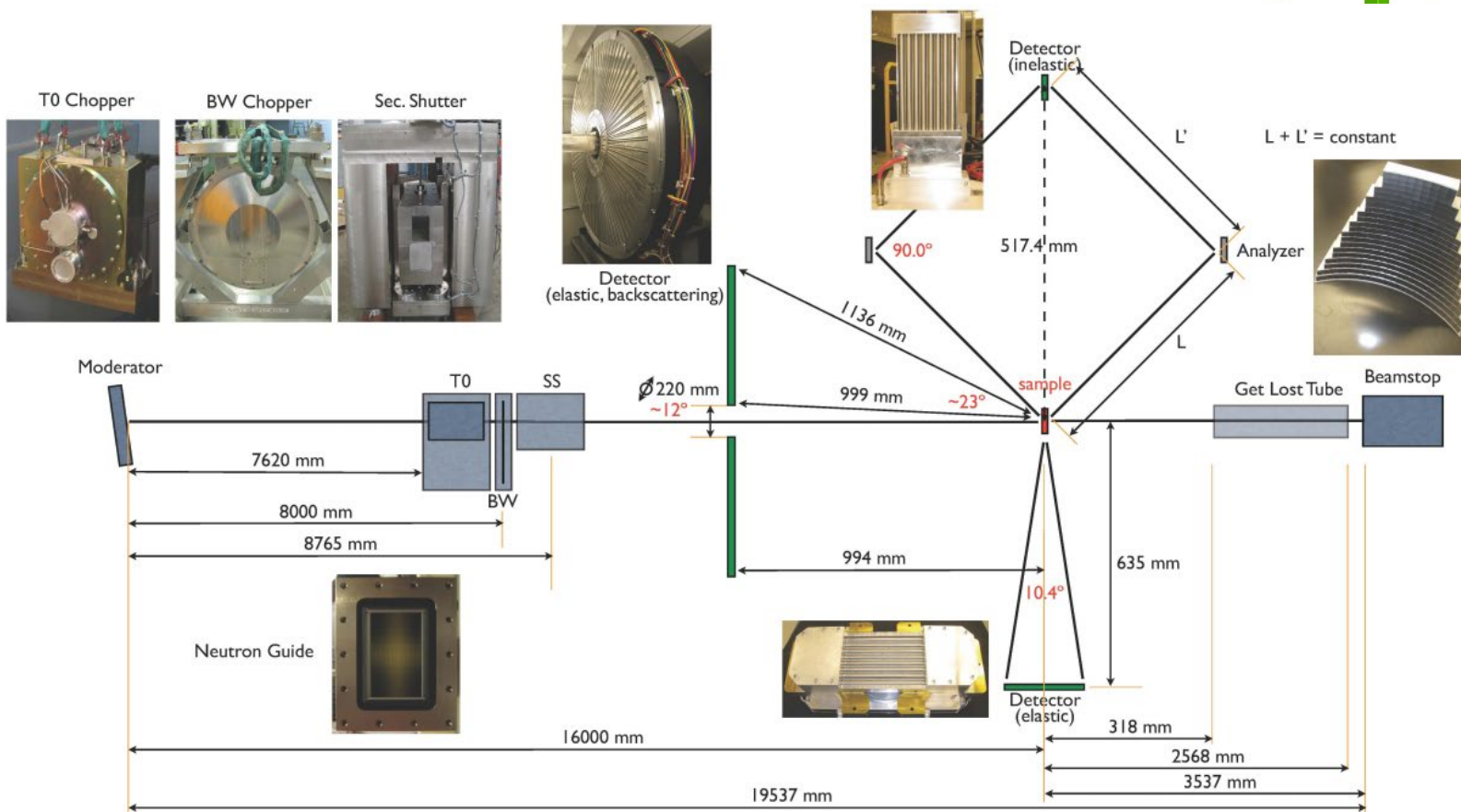
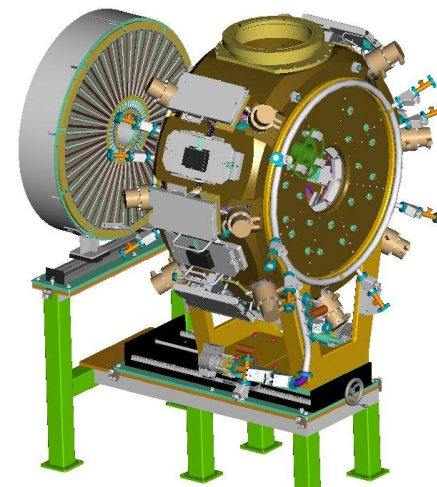


inelastic detectors

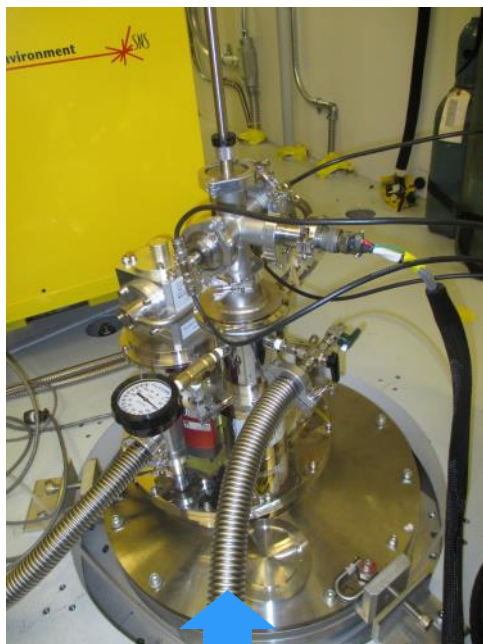


The VISION instrument

- 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 HMFW $\sim 150 \mu\text{s}$
- Backward and 90° diffraction banks



Sample environment

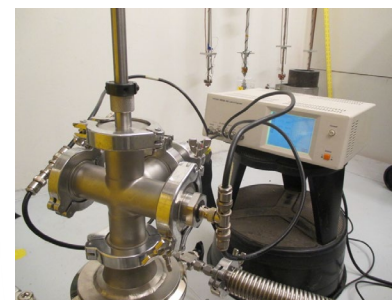
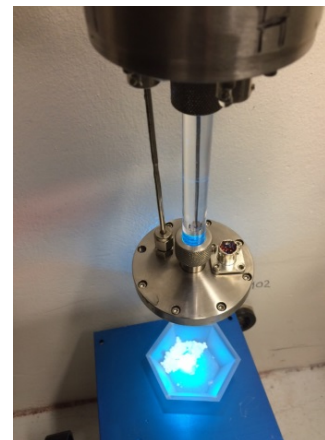


JANIS closed-cycle refrigerator (5-700K)



Pressure cells (piston, gas, diamond anvil).

In-situ Raman

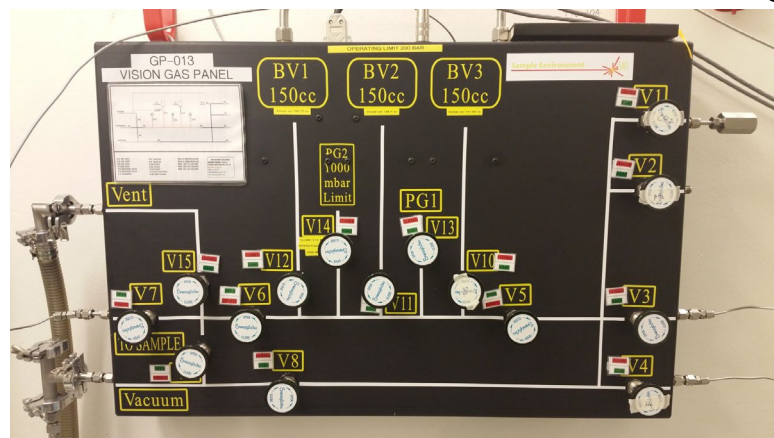


In-situ EIS

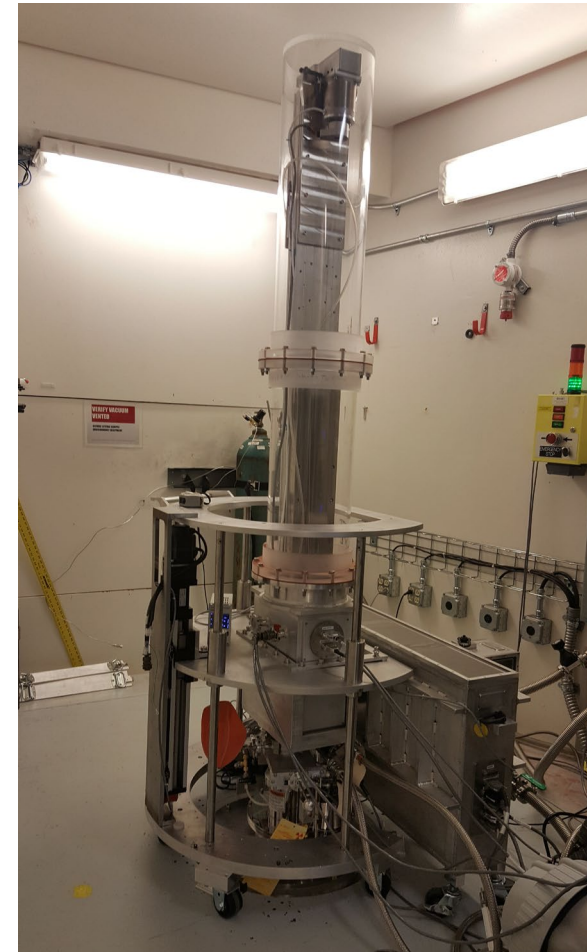
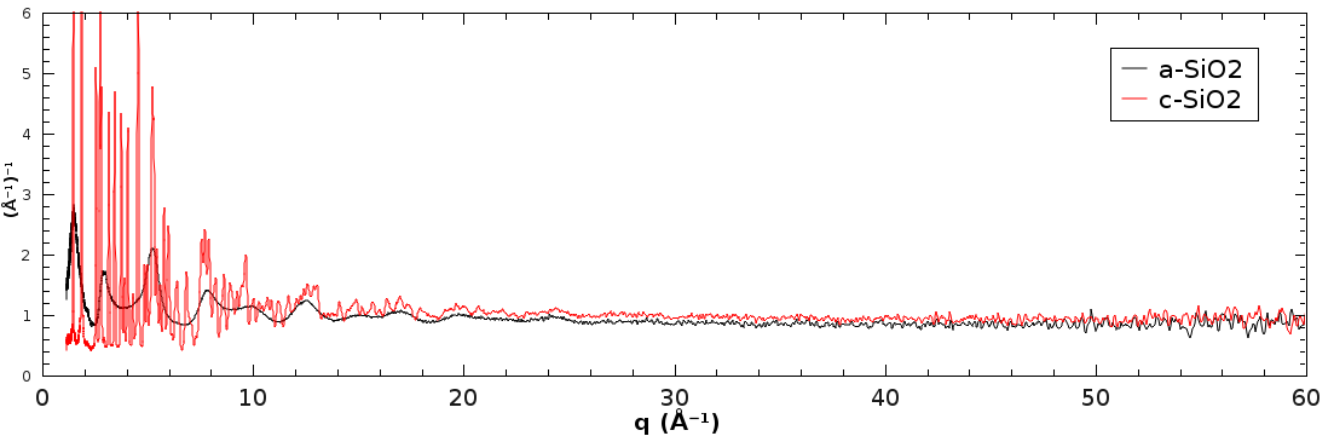
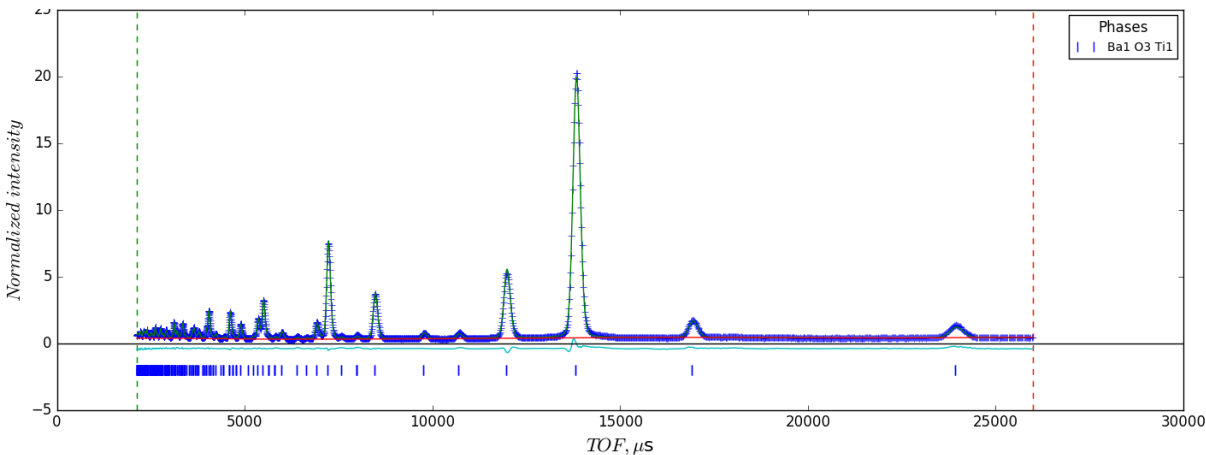
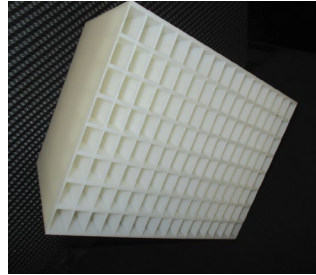
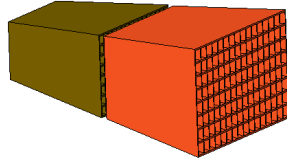
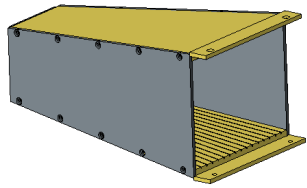


ortho/para H₂ converter

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

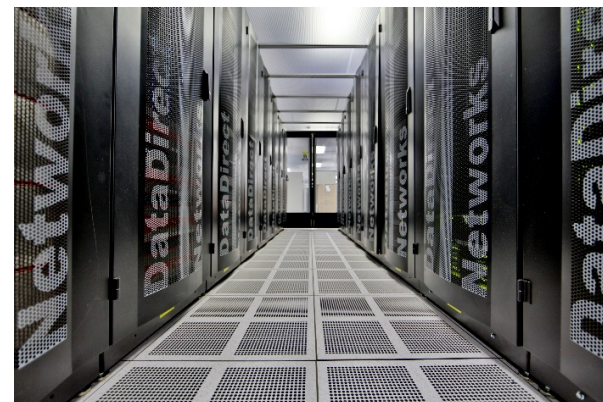
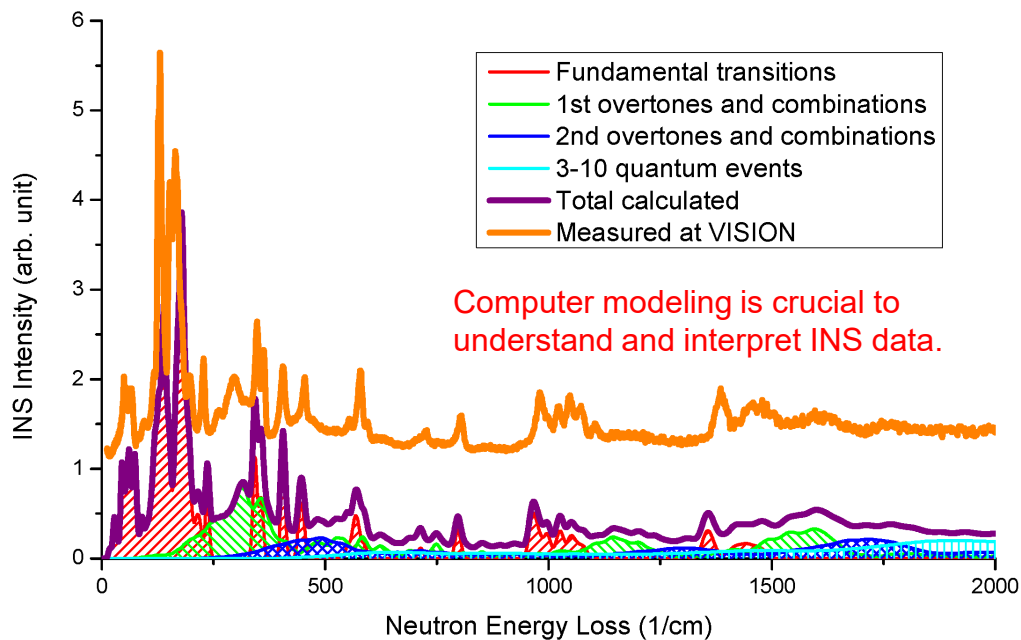


VISION diffraction banks and sample changer



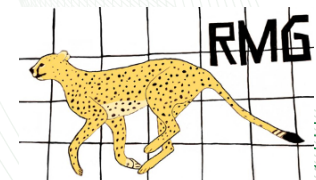
An automatic sample changer has been built for VISION. It can be operated continuously and has a 48-sample magazine that can be reloaded without the need to remove the changer from the instrument. A mail-in program is now available.

Integrated modeling for data interpretation



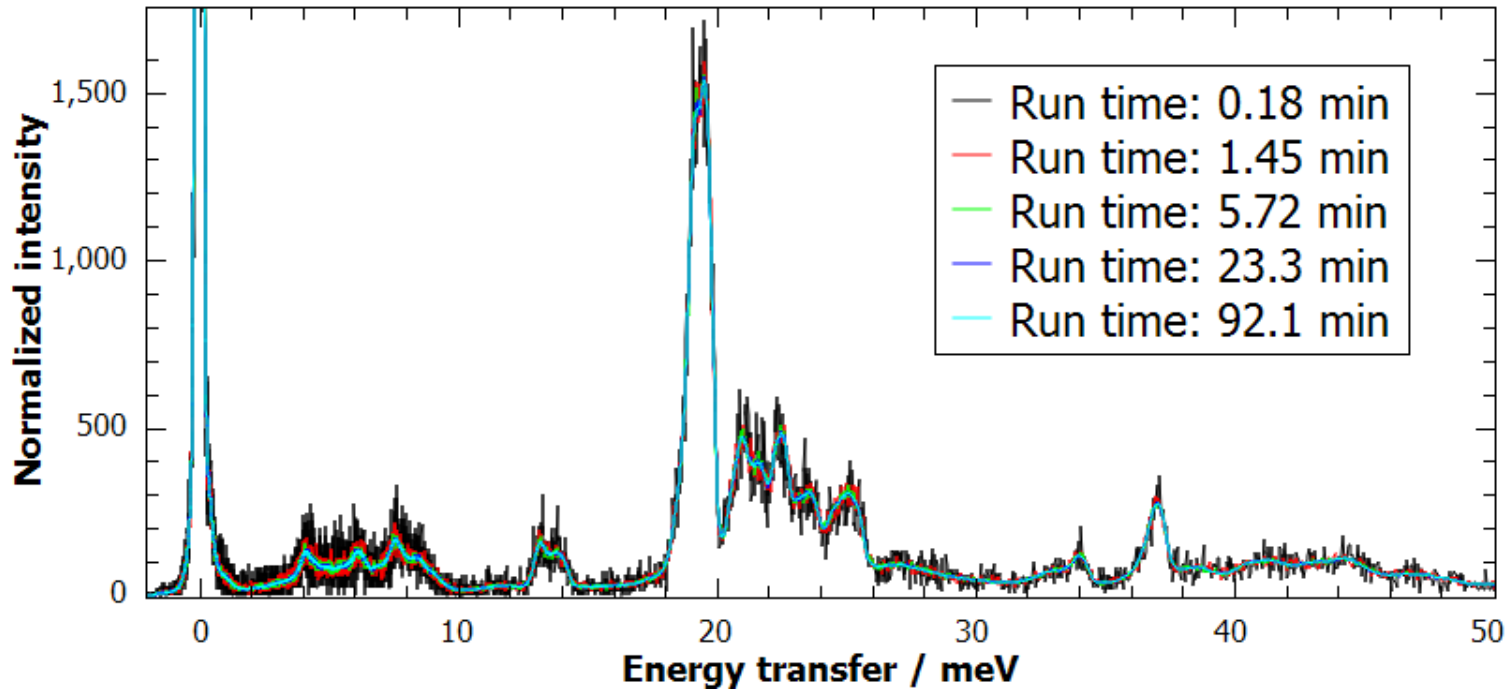
- Dual 16 core Intel Haswell E5-2698v3 3.2 GHz Processors per node
- 50 compute nodes, 1600 (non-hyperthreaded) cores
- 128 GB memory/node, 6.4 TB Total memory
- Each node has 10Gbe and Infiniband networking for connectivity.
- Installed as part of the ORNL Compute and Data Environment for Science (CADES)

VirtuES cluster

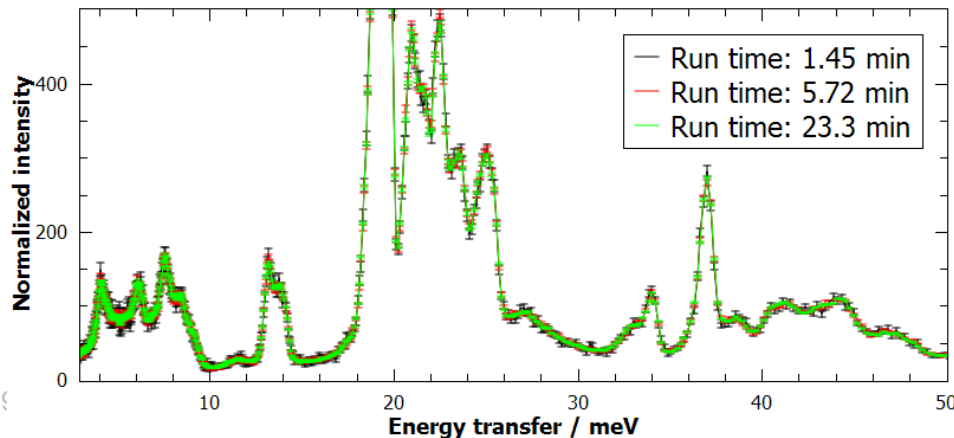


High throughput: INS in minutes

OctaMethyl POSS (1 gm) Measured at VISION



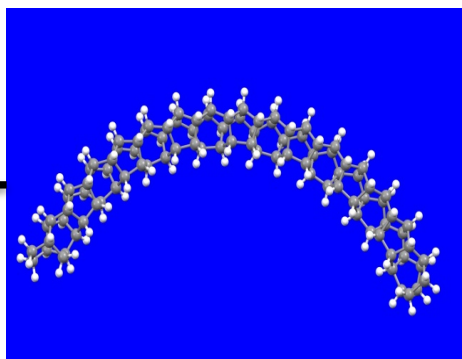
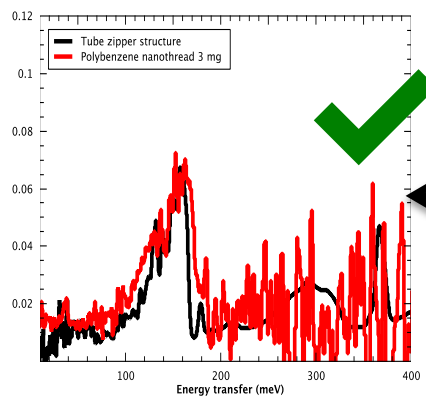
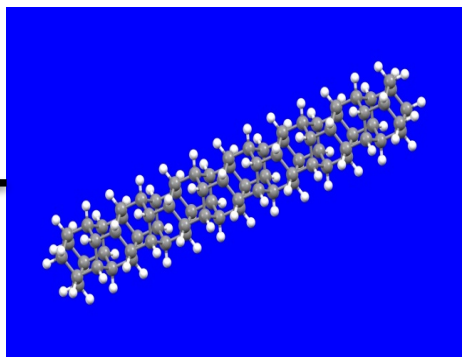
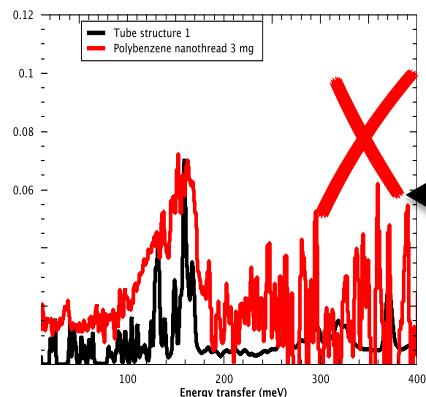
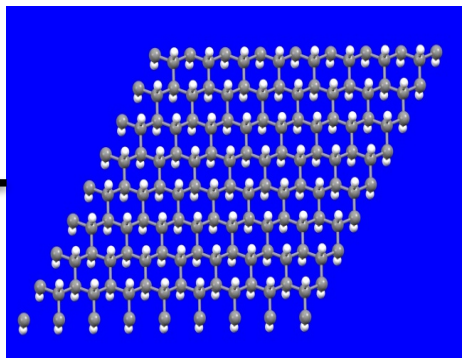
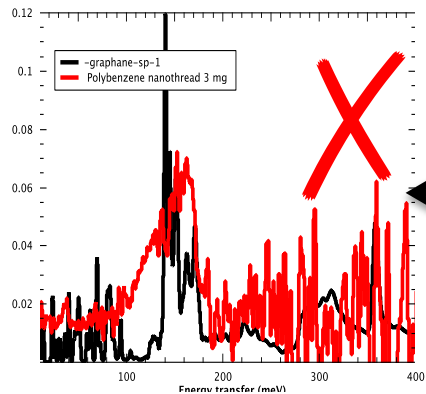
OctaMethyl POSS (1 gm) Measured at VISION



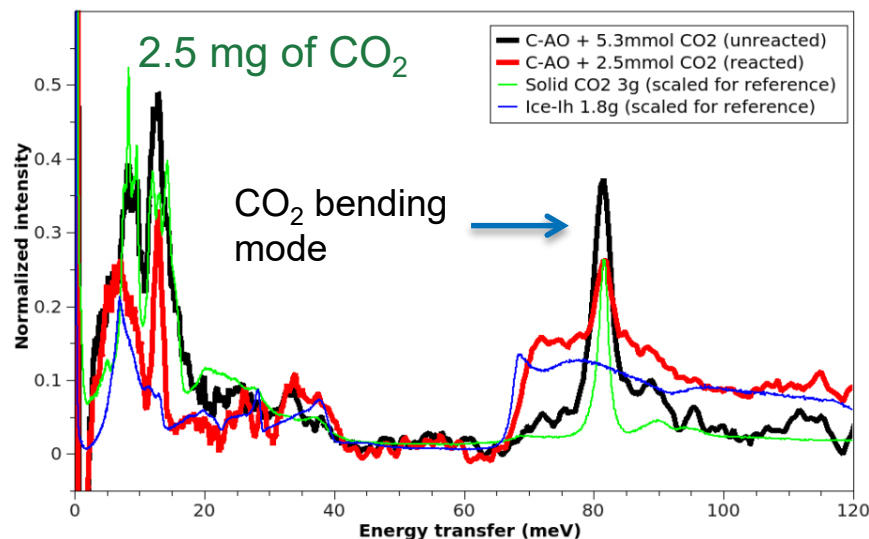
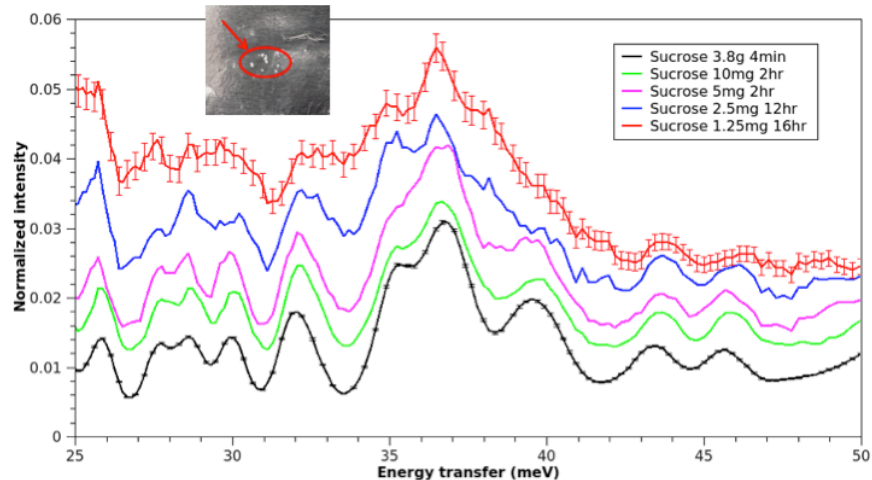
With 14 inelastic banks and 16 diffraction banks, VISION has the highest data rate (up to millions of events per second) among all neutron beam lines in the world.

- INS database
- Parametric studies
- INS study of kinetics

High sensitivity: milligrams of samples



1.25 mg of table sugar

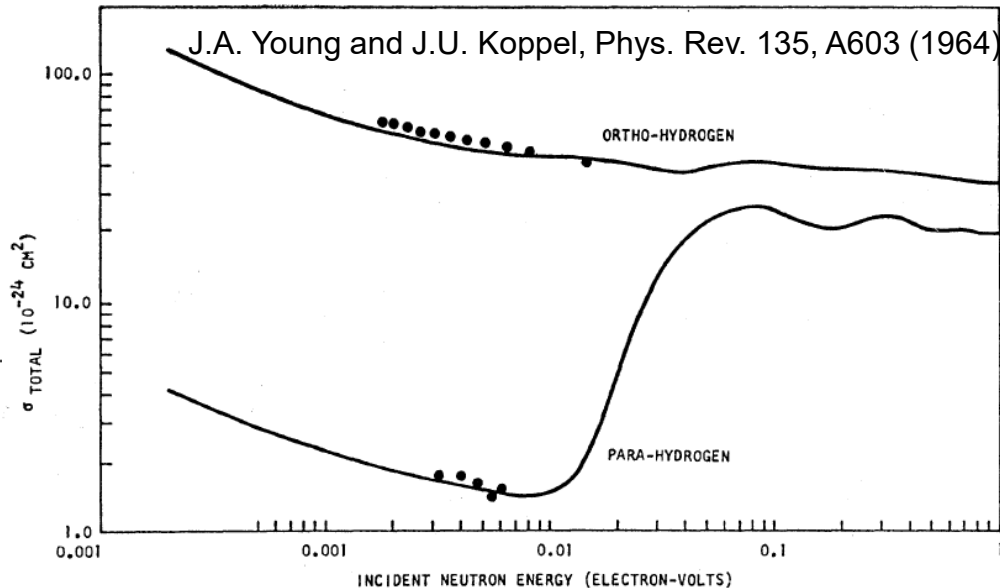
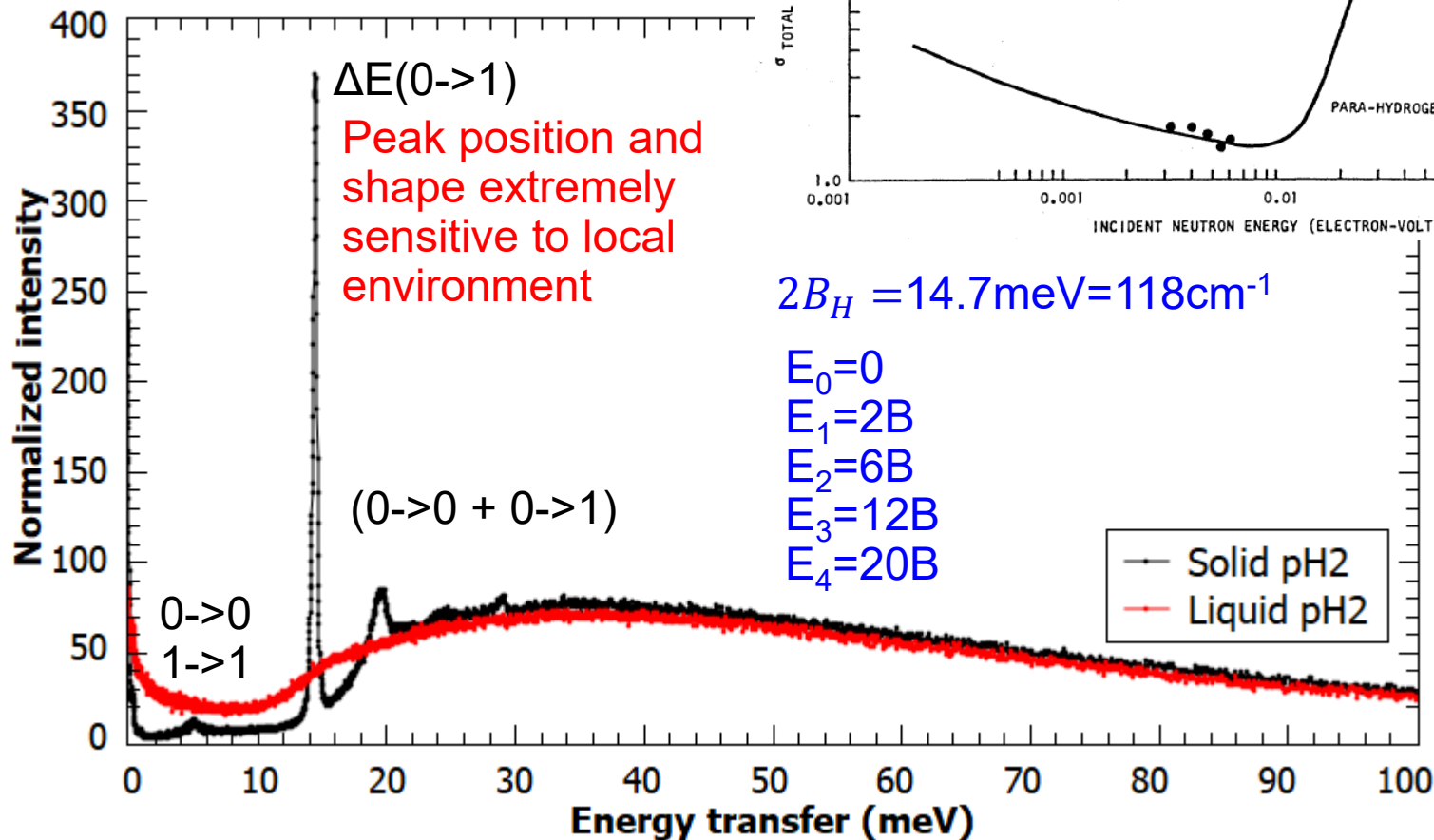
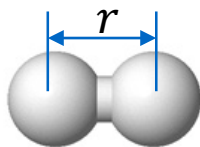


Molecular hydrogen solid

Quantum diatomic rotor

$$E_{rot} = J(J + 1)B_{rot}$$

$$B_{rot} = \frac{\hbar^2}{2I} = \frac{\hbar^2}{mr^2}$$

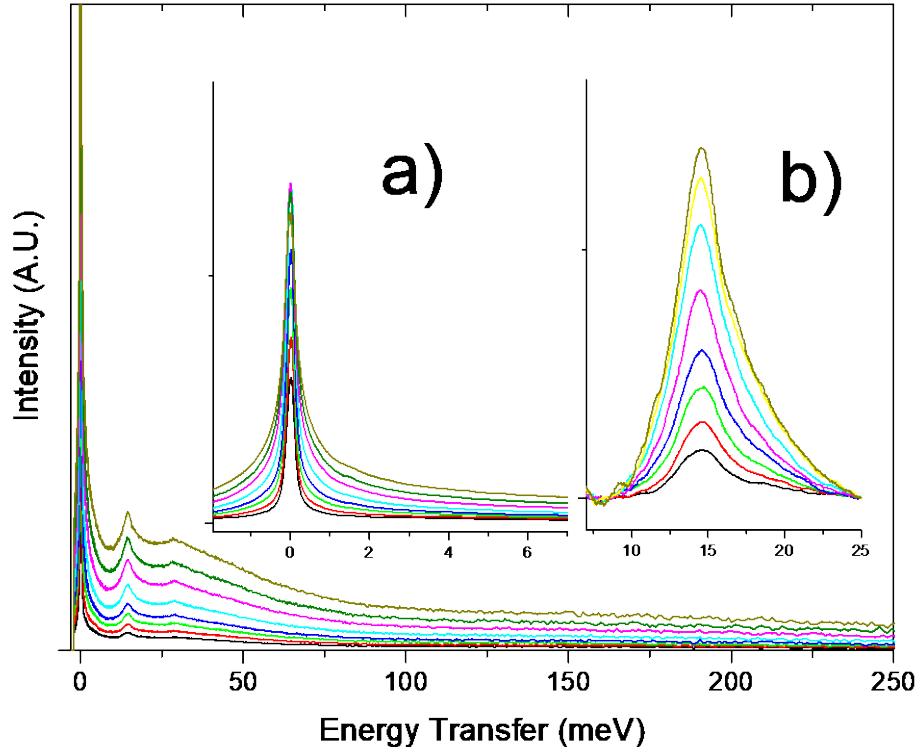


$$2B_H = 14.7 \text{ meV} = 118 \text{ cm}^{-1}$$

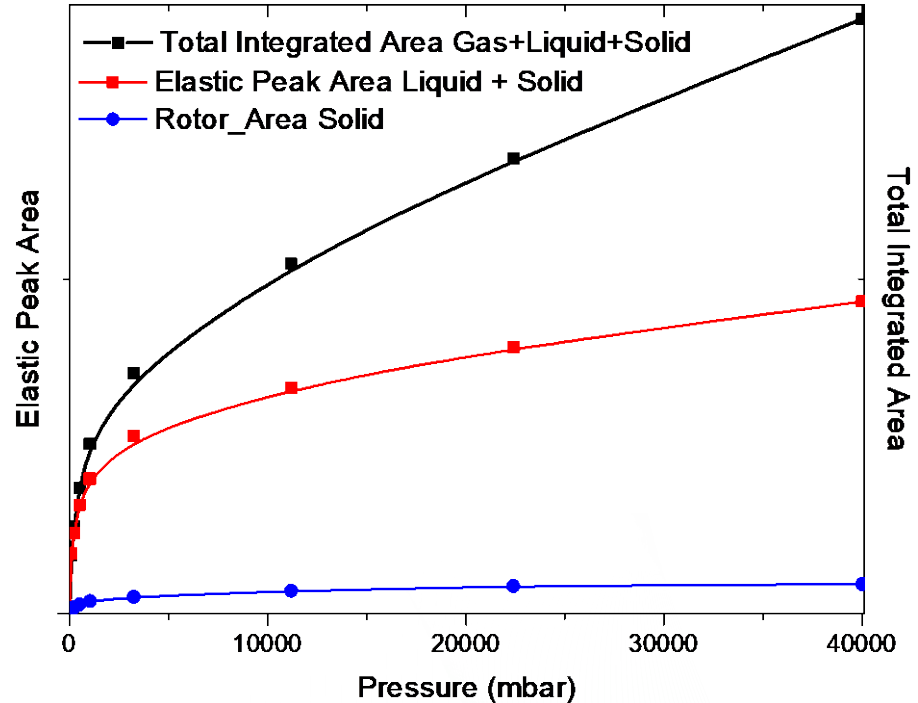
- $E_0 = 0$
- $E_1 = 2B$
- $E_2 = 6B$
- $E_3 = 12B$
- $E_4 = 20B$

Hydrogen adsorption: being precise and quantitative

Hydrogen adsorption on ultra-porous carbon



The INS (VISION) spectra of hydrogen at 77K as function of pressure. From 0.1 bar to 40 bar. a) the elastic line of hydrogen, b) the rotational line.

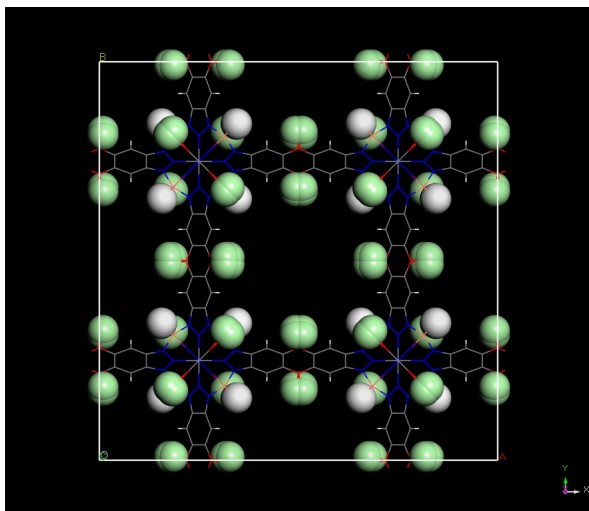


The integrated intensities for the

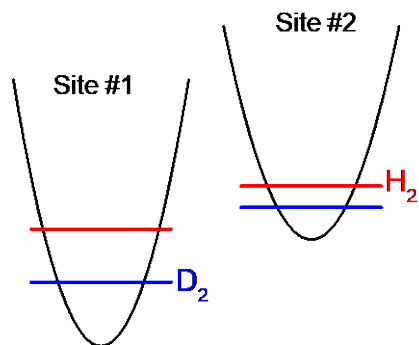
- total spectra (gas+liquid+solid, black),
- elastic intensity (liquid+solid, red),
- rotor line solid hydrogen (blue trace).

INS can quantify the relative amount of molecular hydrogen phases when adsorbed in porous materials

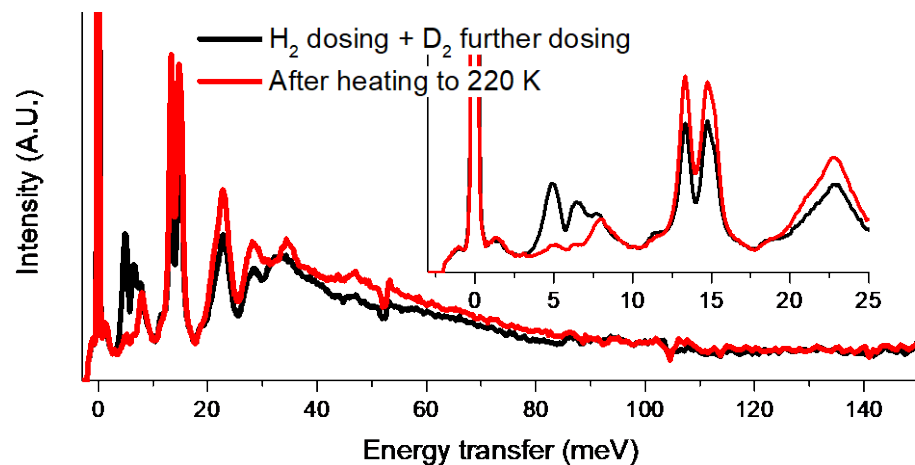
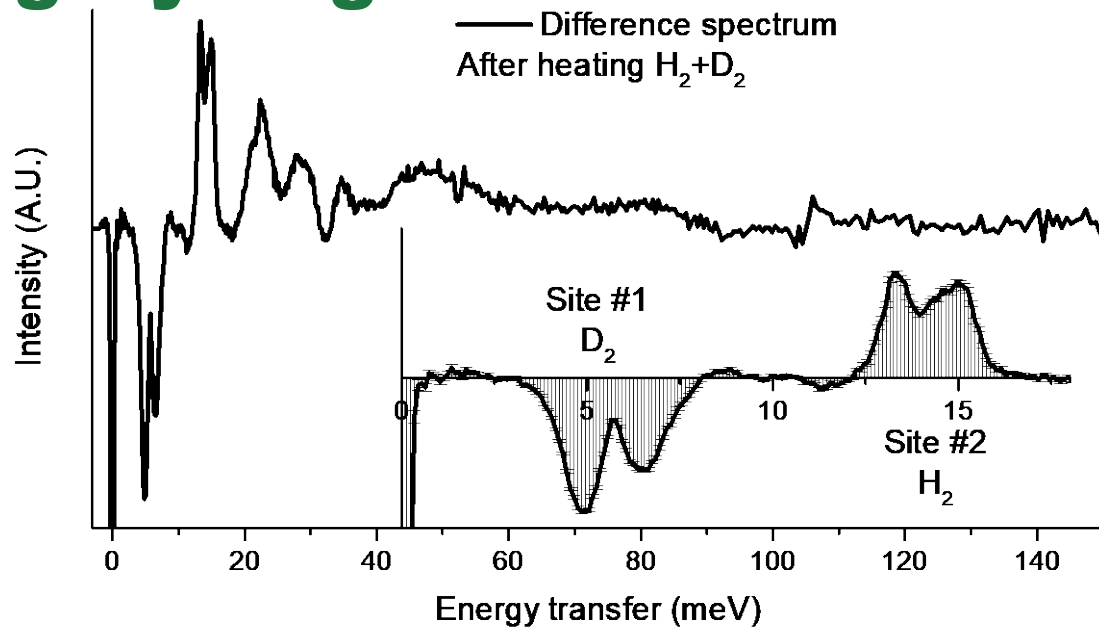
Quantum Sieving Hydrogen in a MOF



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.



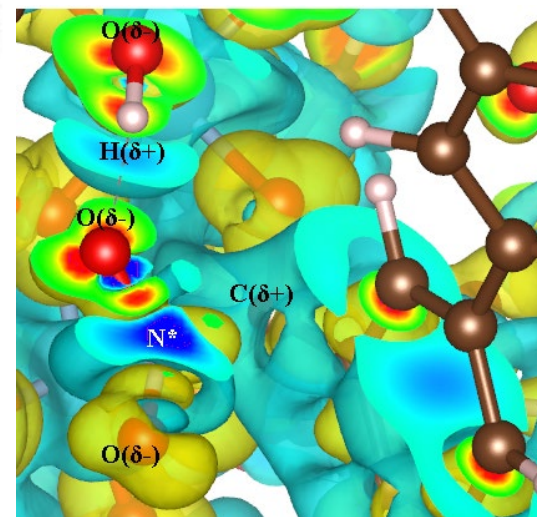
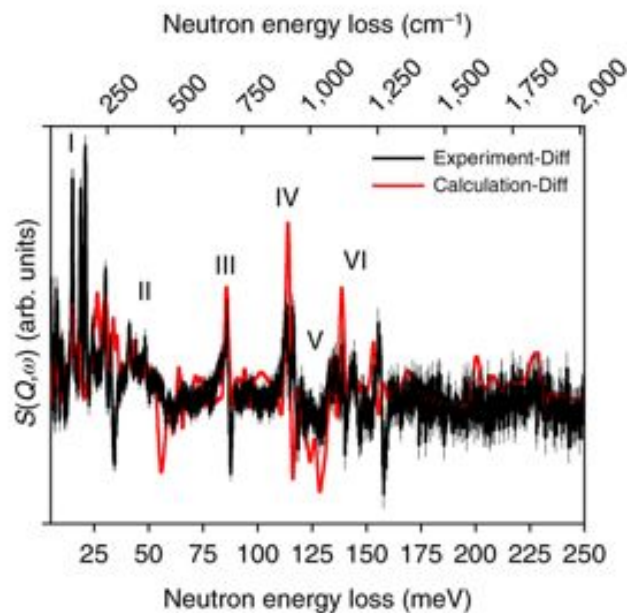
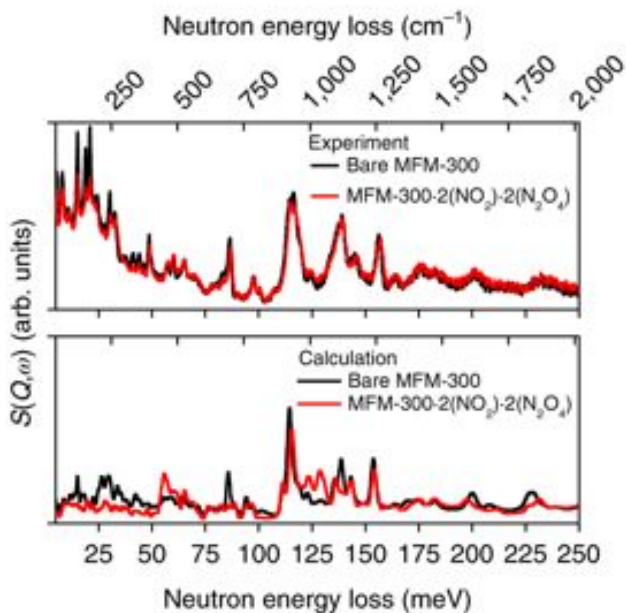
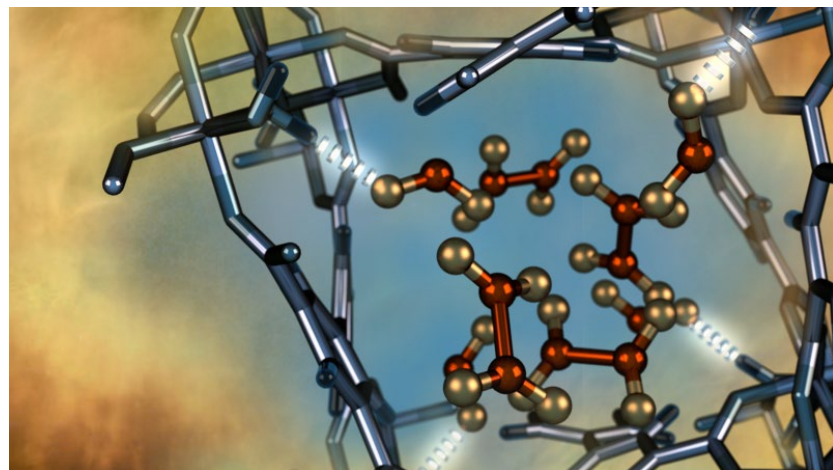
Hydrogen is dosed first, so it mostly takes the lower energy site (Site #1), afterwards deuterium gas is added and has to go to the available site (Site #2)



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

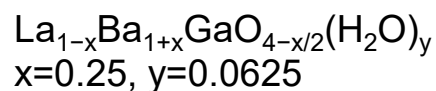
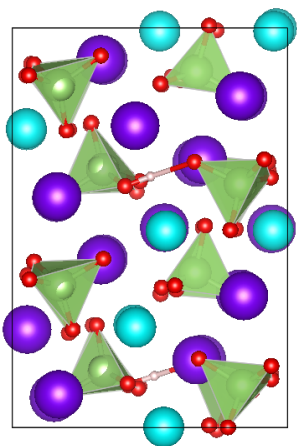
Fundamental mechanism behind small differences

- Reversible and selective adsorption of NO_2 with high uptake of 14.1 mmol g^{-1}

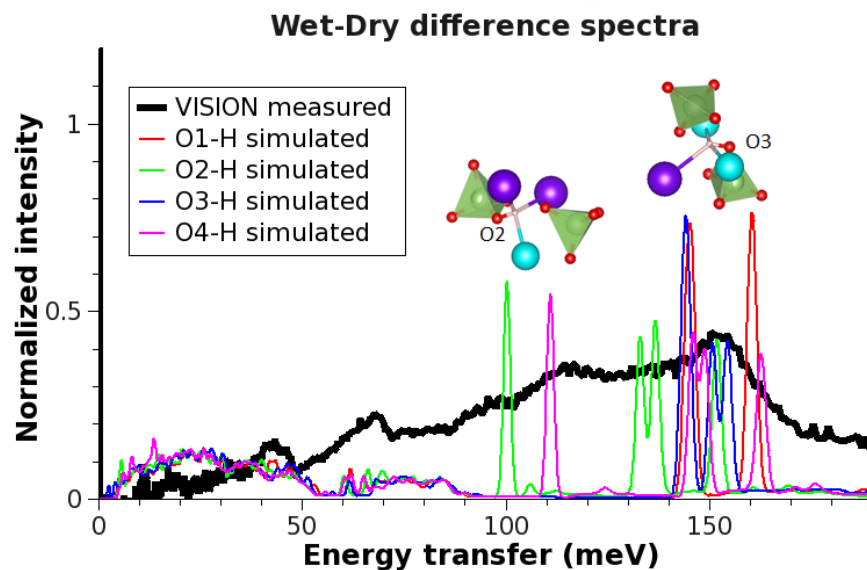
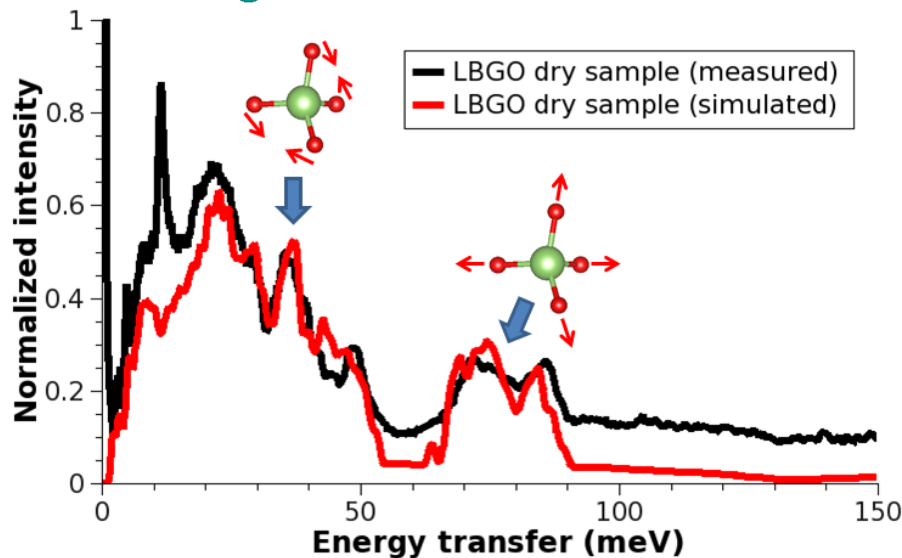
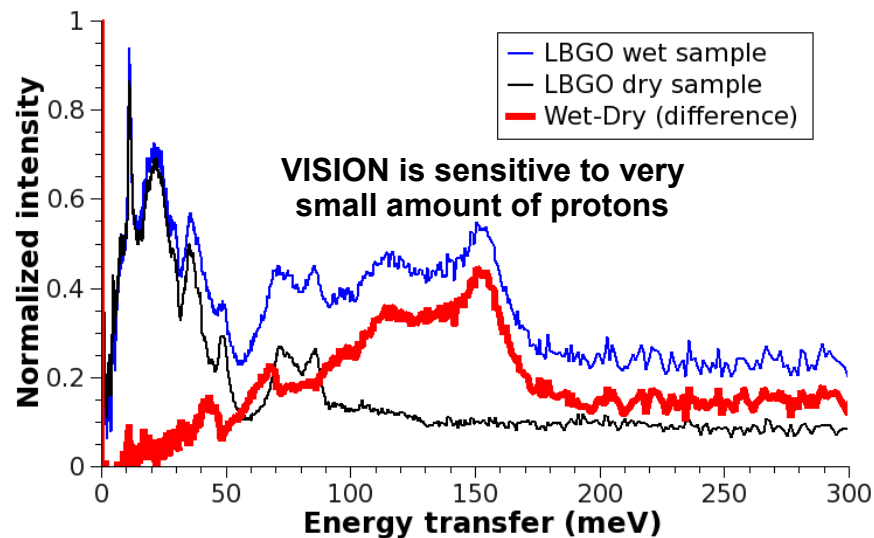


New insight based on but beyond INS data

- Mechanism of proton conductivity in solid electrolyte for fuel cells

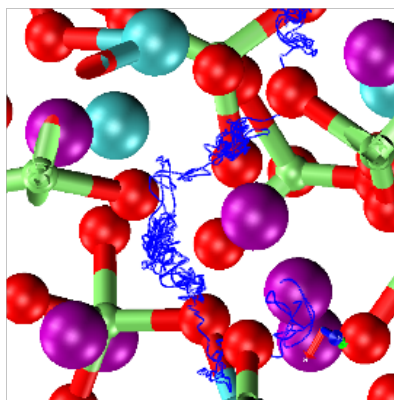


La: cyan
Ba: purple
Ga: green
O: red

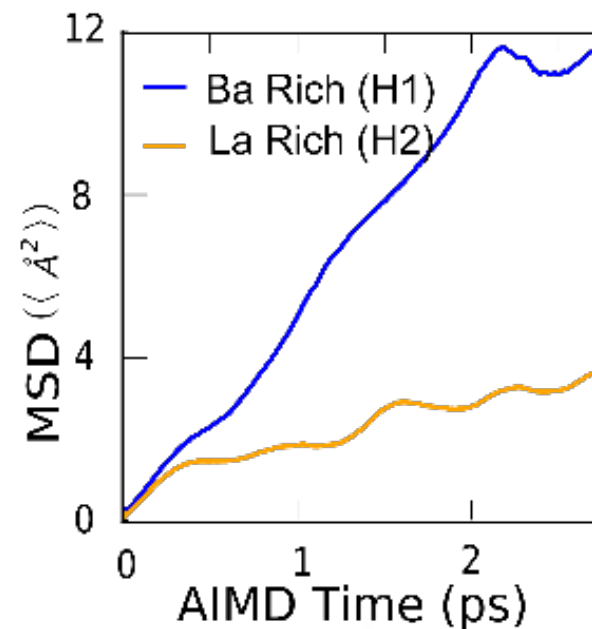
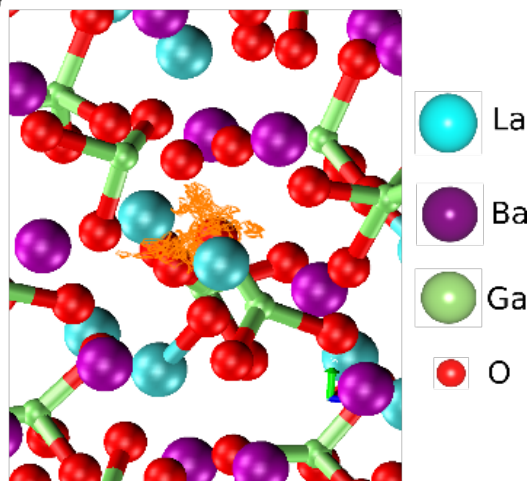


New insight based on but beyond INS data

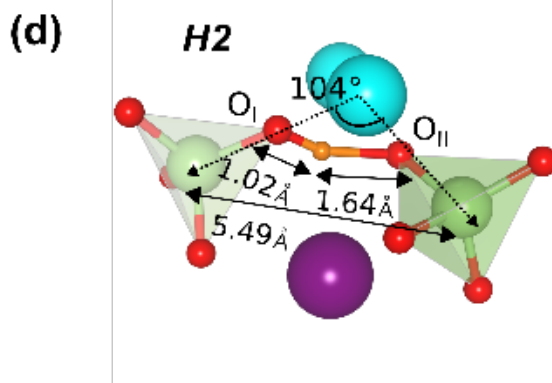
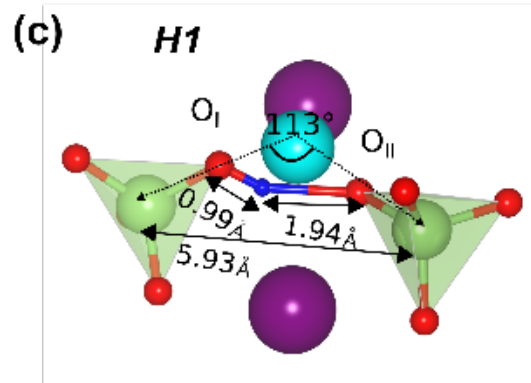
(a) **Ba-rich (H1)**



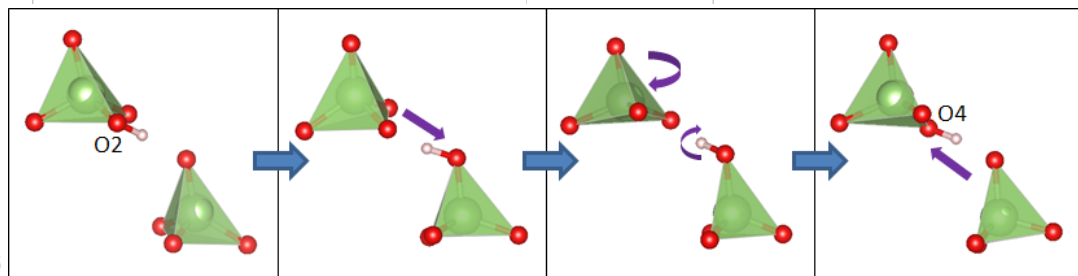
(b) **La-rich (H2)**



(c)



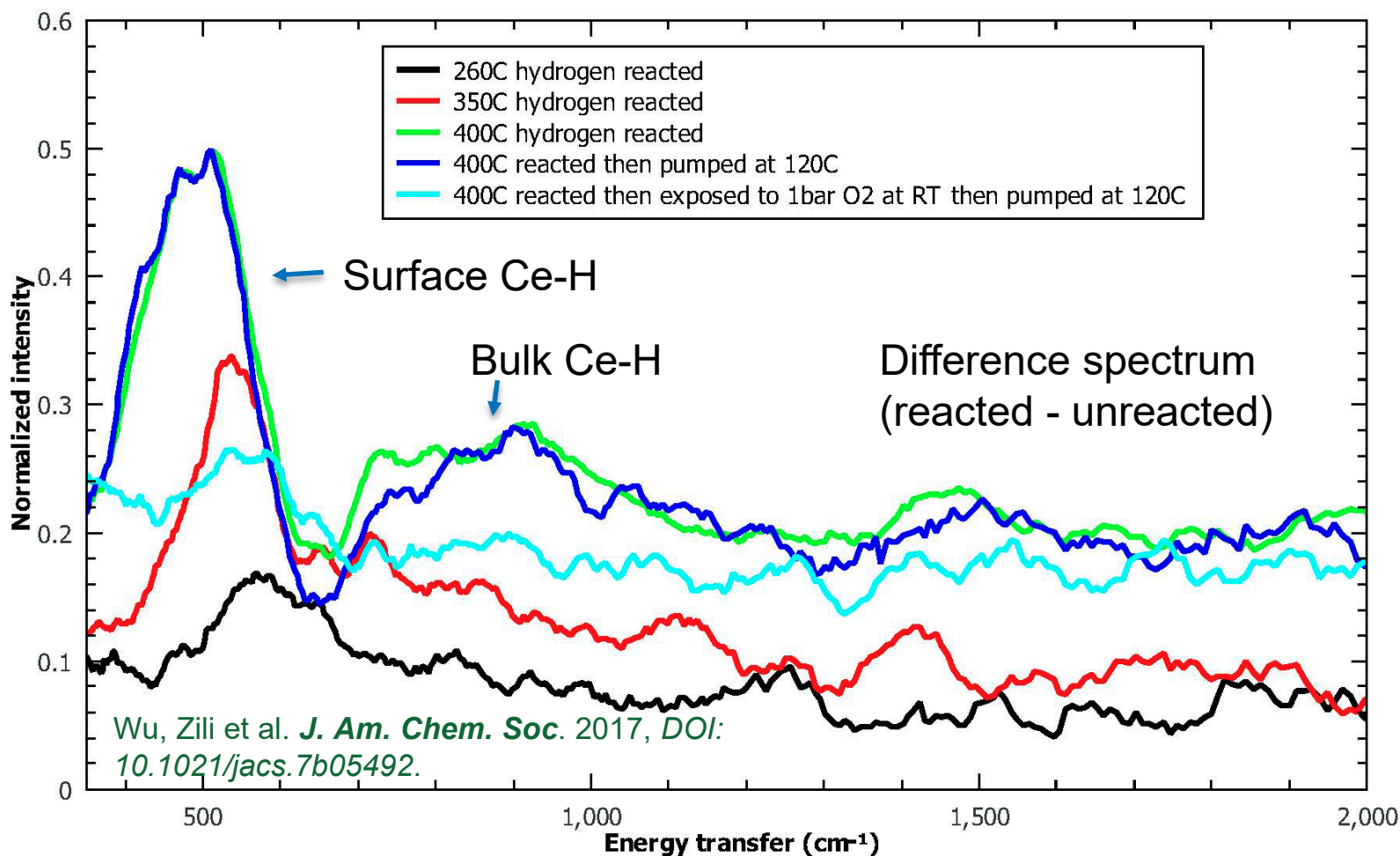
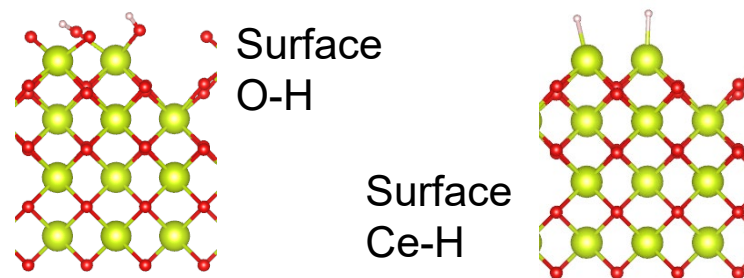
Cheng Y.Q., Balachandran J., Bi Z., Bridges C.A., Paranthaman M.P., Daemen L.L., Ganesh P., Jalarvo N., *Journal of Materials Chemistry A*, 5, 15507–15511 (2017).



VISION+modeling identifies various local chemical environment for the protons, and reveals the proton transport mechanism

First evidence of Ce-H formation on CeO₂

- A key step to understand the hydrogen activation mechanism and in turn the hydrogenation performance of this material.




Simulation of INS and OCLIMAX



Why do we need simulations for NVS (or INS in general)?

- Interpret neutron data
 - assigning peaks to vibrational modes
- Obtain insight on fundamental properties
 - understanding interatomic interactions, anharmonicity, complex excitations, phase transitions, chemical reactions
- Connect theory and experiment
 - simulation is a virtual experiment and an *in silico* implementation of theory

We can measure it.  We do understand it.

What to simulate for INS?

- Double differential cross-section

$$\frac{d^2\sigma}{d\Omega dE'} = \text{(number of neutrons scattered per second into a small solid angle } d\Omega \text{ in the direction } \theta, \phi \text{ with final energy between } E' \text{ and } E' + dE') / \Phi d\Omega dE',$$

- Fermi's golden rule

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\lambda \rightarrow \lambda'} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar^2} \right) |\langle k' \lambda' | V | k \lambda \rangle|^2 \delta(E_\lambda - E_{\lambda'} + \hbar\omega) \propto \frac{k'}{k} S(Q, \omega)$$

V : potential describing the interaction between neutrons and the system

$\hbar\omega$: fundamental excitation in the system

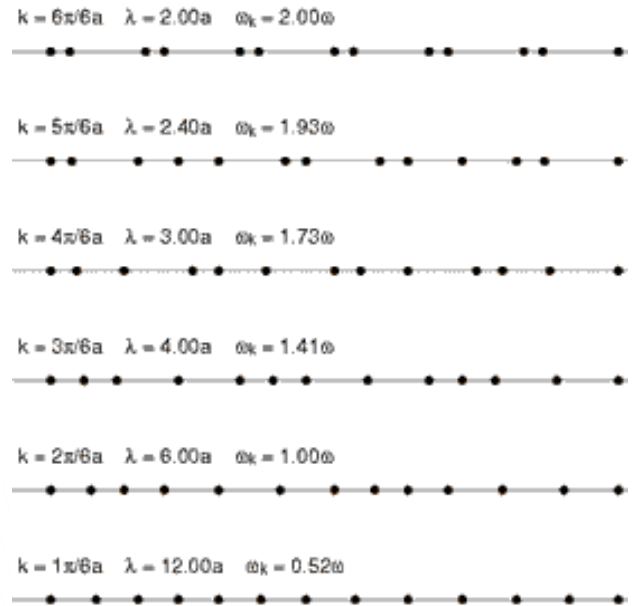
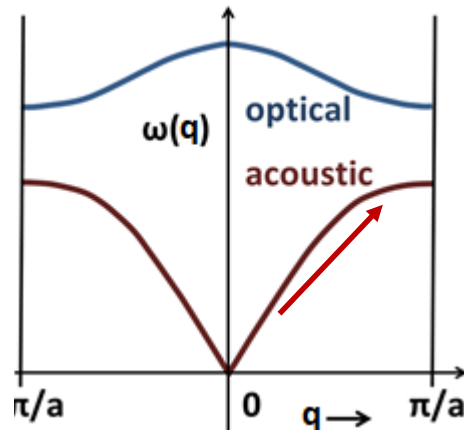
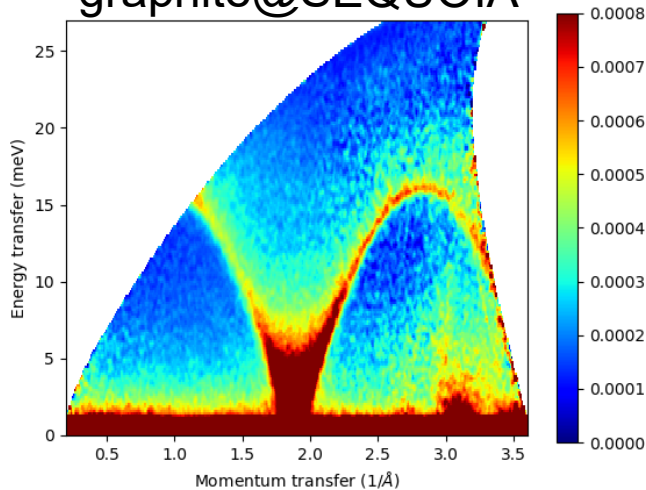
- The goal is to formulate the interaction between neutrons and the system, so that $S(Q, \omega)$ can be expressed by the excitations of interest.

Coherent inelastic scattering

- One-phonon $S(Q, \omega)$

$$S_{coh\pm 1}(\mathbf{Q}, \omega) = \frac{1}{2N} \sum_s \sum_{\tau} \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{m_d}} \exp(-W_d) \exp(i\mathbf{Q} \cdot \mathbf{r}_d) (\mathbf{Q} \cdot \mathbf{e}_{ds}) \right|^2 \times \langle n_s + \frac{1}{2} \pm \frac{1}{2} \rangle \delta(\omega \mp \omega_s) \delta(\mathbf{Q} \mp \mathbf{q} - \boldsymbol{\tau})$$

graphite@SEQUOIA



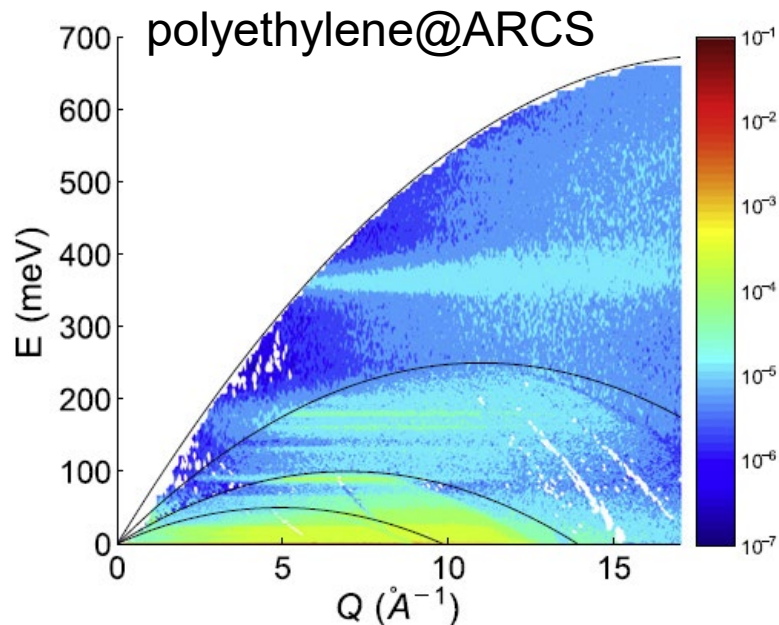
- **Peak position in energy depends on Q .**
- **Total intensity determined by not only how each atom moves, but also their relative phase.**

From: wikipedia

Incoherent inelastic scattering

- One-phonon $S(Q, \omega)$

$$S_{inc\pm 1}(\mathbf{Q}, \omega) = \sum_d \frac{1}{2m_d} \left\{ \bar{b}_d^2 - (\bar{b}_d)^2 \right\} \exp(-2W_d) \sum_s \frac{|\mathbf{Q} \cdot \mathbf{e}_{ds}|^2}{\omega_s} \left\langle n_s + \frac{1}{2} \pm \frac{1}{2} \right\rangle \delta(\omega \mp \omega_s)$$



Coherent



Incoherent

C.M. Lavelle et al. / Nuclear Instruments and Methods
in Physics Research A 711 (2013) 166–179

- **Peak position in energy does not depend on Q**
- **Each atom contributes to the total intensity independently.**

Incoherent approximation

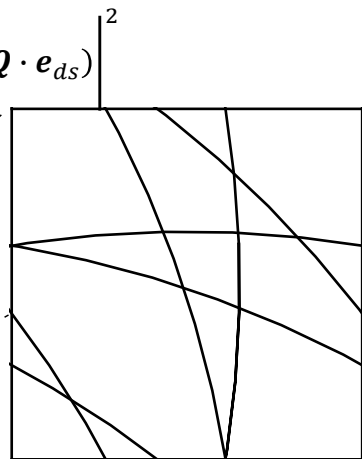
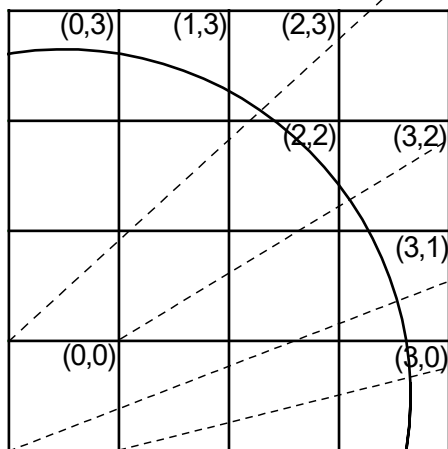
- When and why

- Elements/isotopes with large incoherent scattering cross-section (e.g., hydrogen, vanadium) – **The scattering itself is intrinsically incoherent.**
- High Q or large unit cell (small Brillouin zone), e.g. in low symmetry or disordered structure – **The scattering may be coherent, but the ruler is too big for the pattern to be resolved.**

$$S_{coh\pm 1}(\mathbf{Q}, \omega)$$

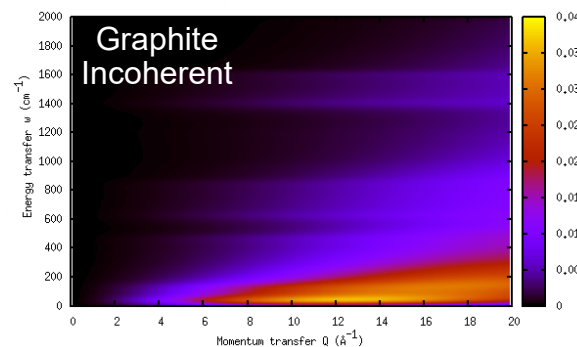
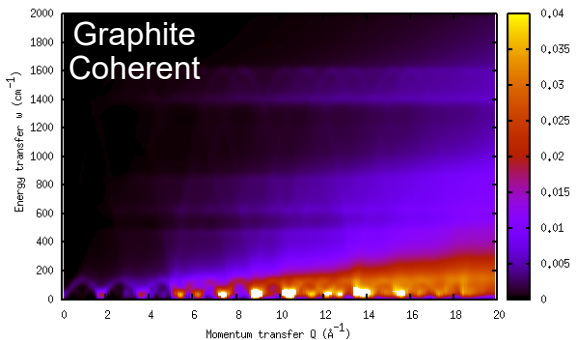
$$= \frac{1}{2N} \sum_s \sum_{\tau} \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{m_d}} \exp(-W_d) \exp(i\mathbf{Q} \cdot \mathbf{r}_d) (\mathbf{Q} \cdot \mathbf{e}_{ds}) \right|^2$$

$$\times \langle n_s + \frac{1}{2} \pm \frac{1}{2} \rangle \delta(\omega \mp \omega_s) \delta(\mathbf{Q} \mp \mathbf{q} - \boldsymbol{\tau})$$



Powder averaging

$$S(\mathbf{Q}, n\omega_s) = \frac{(\mathbf{Q} \cdot \mathbf{U}_s)^{2n}}{n!} \exp[-(\mathbf{Q} \cdot \mathbf{U}_{total})^2]$$



$$\mathbf{U}_s = \sqrt{\frac{\hbar}{2m\omega_s}} \mathbf{e}_{ds}$$

OCLIMAX: features

- INS calculation of powder and single crystal samples
- Full calculation (including coherent effects) and incoherent approximation
- Combinations and overtones
- Temperature effect
- Phonon wing calculation for single molecules
- Sampling trajectories in Q - ω space for indirect and direct geometry instruments
- Easy interface with common DFT programs

JCTC

Journal of Chemical Theory and Computation

Article

Cite This: *J. Chem. Theory Comput.* 2019, 15, 1974–1982

pubs.acs.org/JCTC

[Journal of Chemical Theory and Computation, 15, 3, 1974-1982 \(2019\).](#)

Simulation of Inelastic Neutron Scattering Spectra Using OCLIMAX

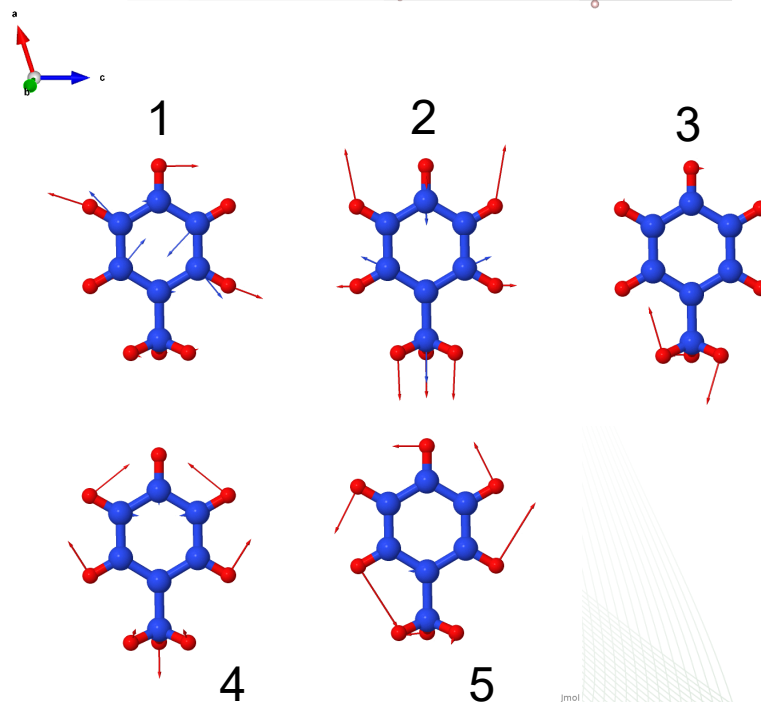
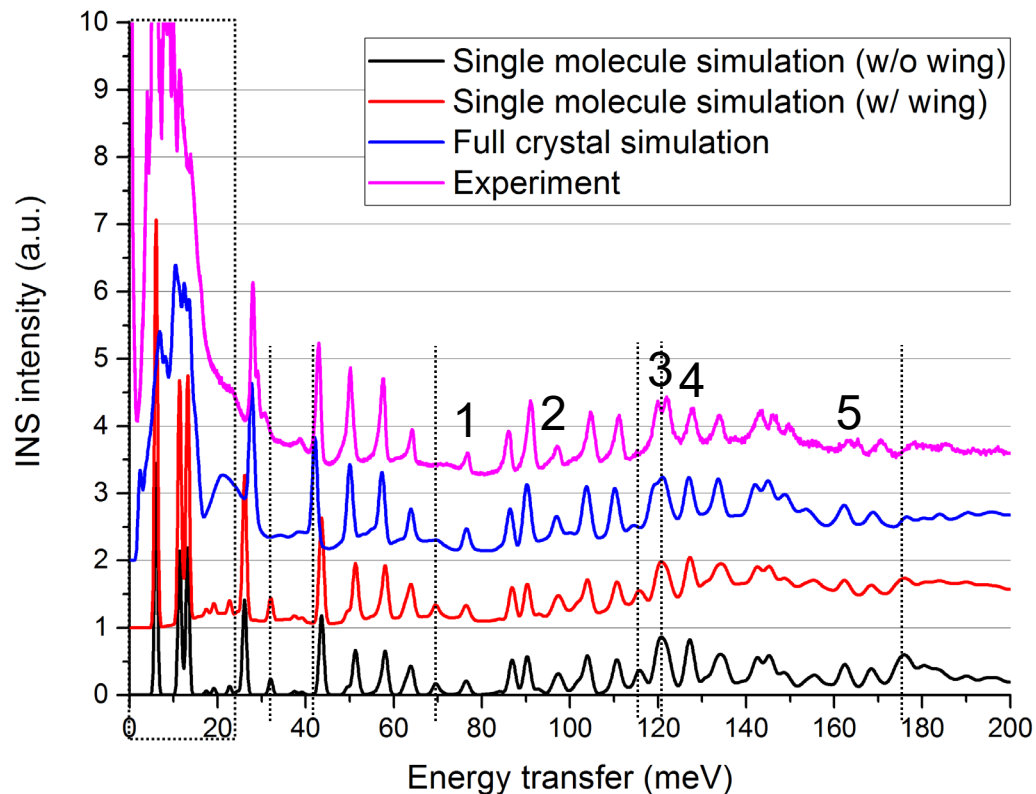
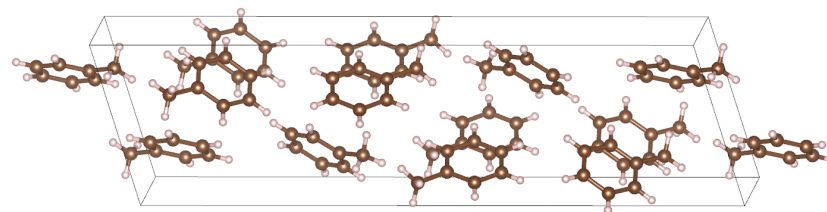
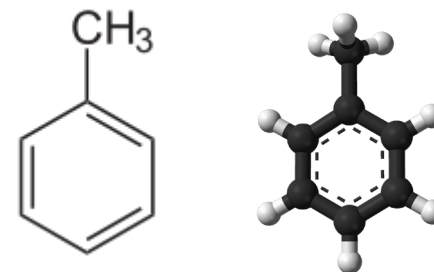
Y. Q. Cheng*,^{ORCID} L. L. Daemen, A. I. Kolesnikov,^{ORCID} and A. J. Ramirez-Cuesta*

Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge Tennessee 37831, United States

ORNL
laboratory

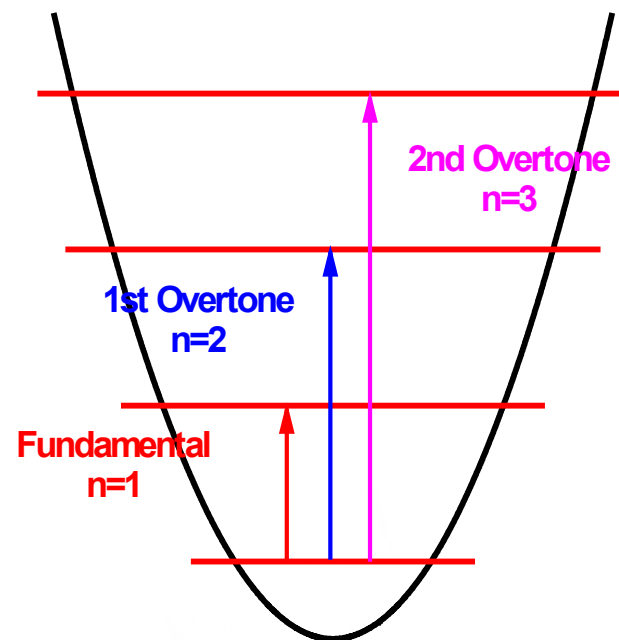
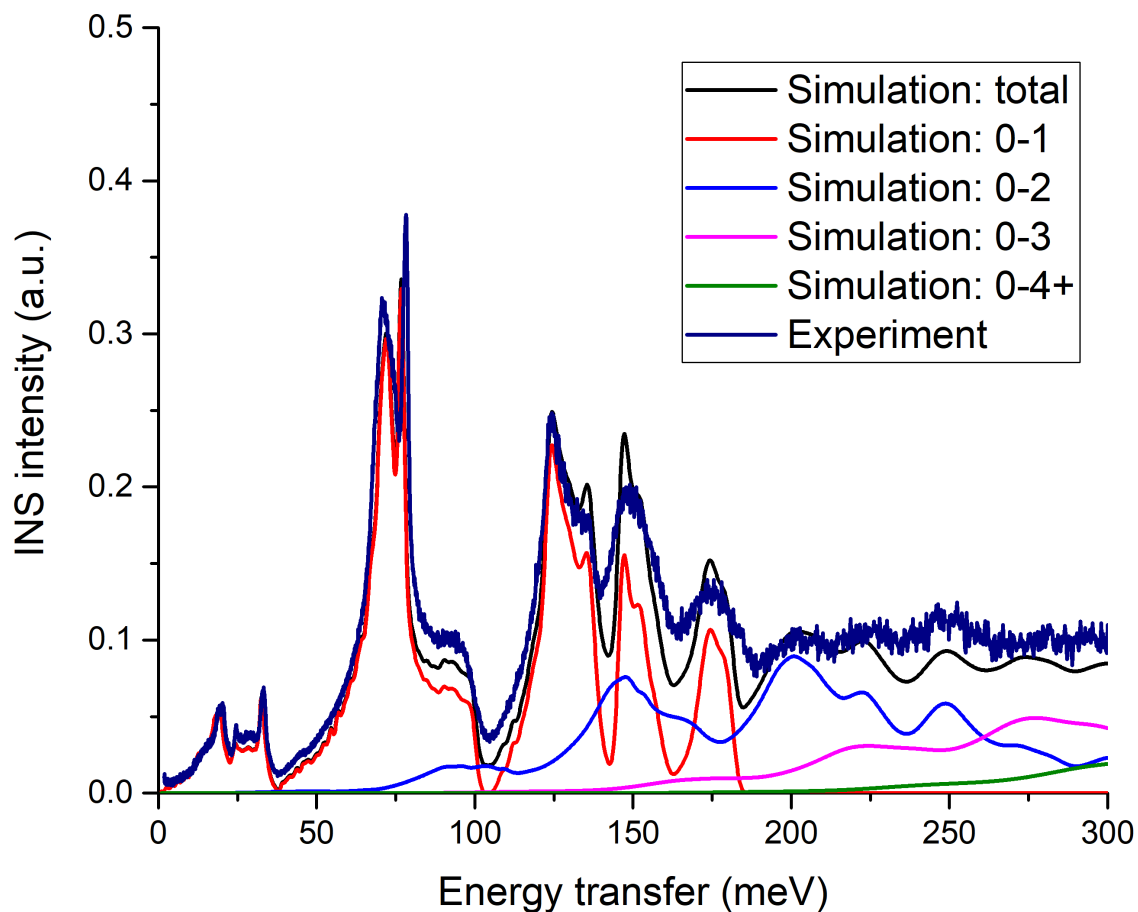
OCLIMAX example: toluene

- Single molecule
- Wing calculation
- Full crystal calculation
- Role of intermolecular interactions



OCLIMAX example: MgH2

- Higher order excitations

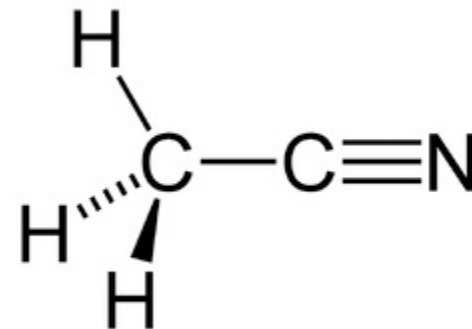
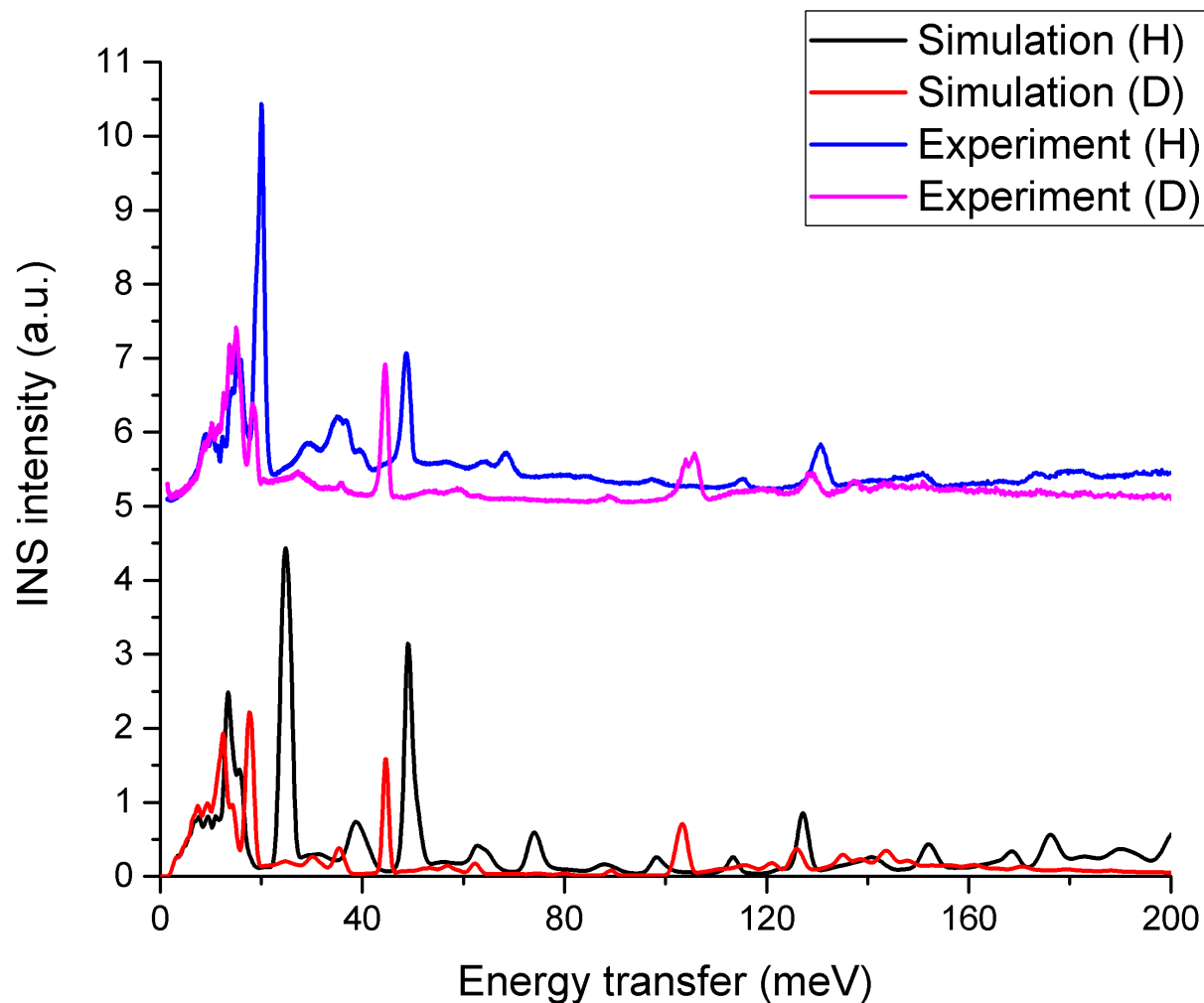


Quantum harmonic oscillator

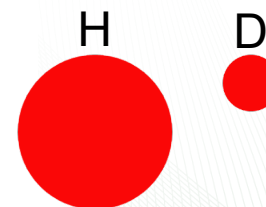
$$(n + \frac{1}{2})\hbar\omega$$

OCLIMAX example: acetonitrile

- Isotope substitution



$$\omega = \sqrt{\frac{k}{m}}$$



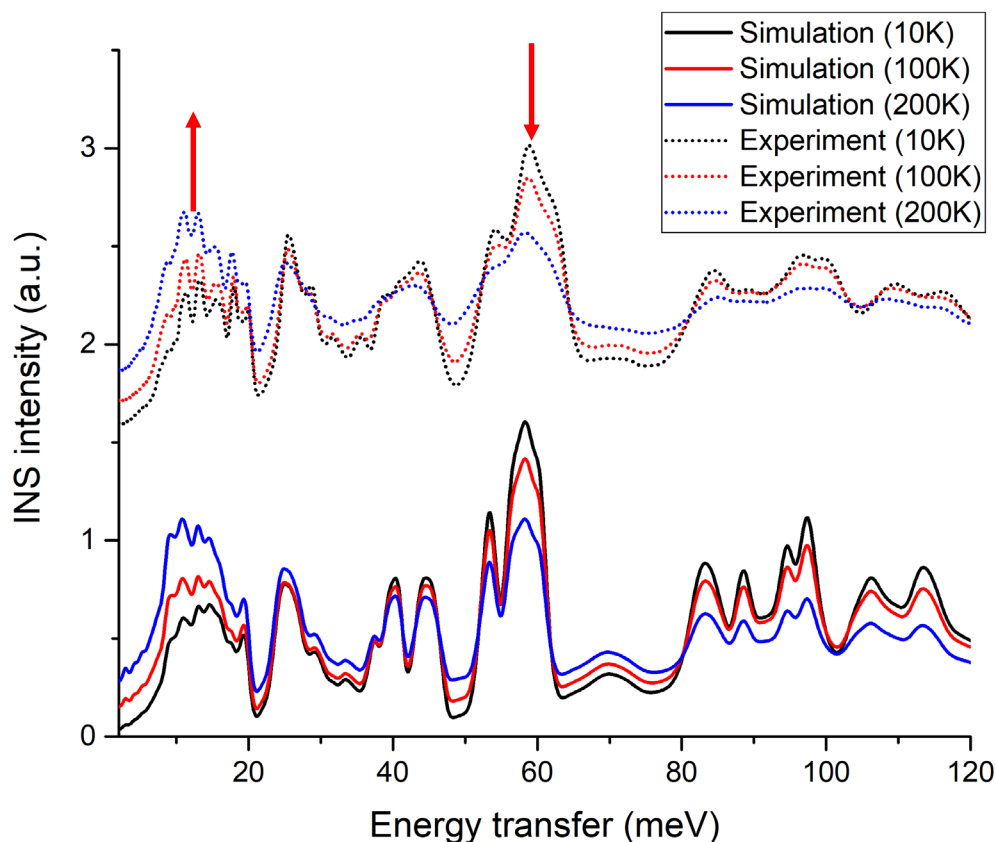
OCLIMAX example: alanate

- Temperature effects

- Phonon population
- Debye-Waller factor

$$W_d = \frac{\hbar}{4m_d N_q} \sum_s \frac{(\mathbf{Q} \cdot \mathbf{e}_{ds})^2}{\omega_s} (2n_s + 1)$$

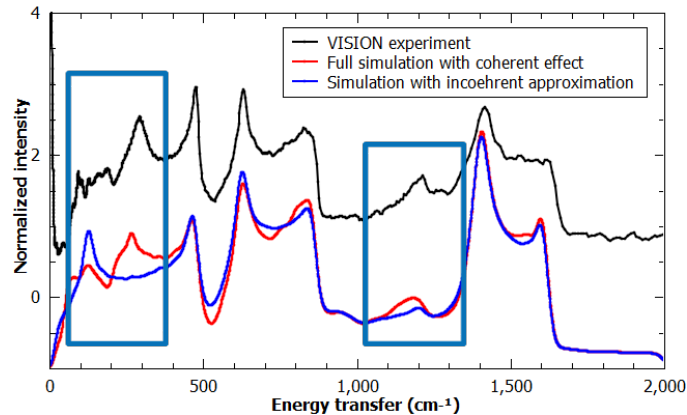
$$S_{inc\pm 1}(\mathbf{Q}, \omega) = \sum_d \frac{1}{2m_d} \left\{ \bar{b}_d^2 - (\bar{b}_d)^2 \right\} \exp(-2W_d) \sum_s \frac{|\mathbf{Q} \cdot \mathbf{e}_{ds}|^2}{\omega_s} \left\langle n_s + \frac{1}{2} \pm \frac{1}{2} \right\rangle \delta(\omega \mp \omega_s)$$



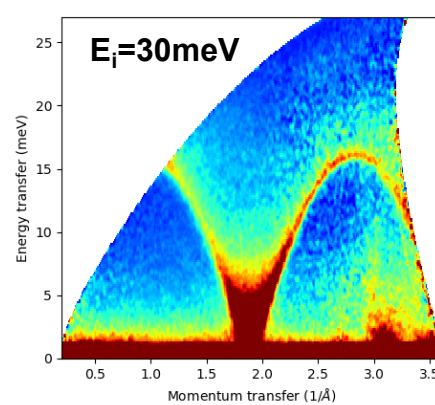
OCLIMAX example: graphite

- Coherent scattering
 - Powders
 - Single crystal
- Kinematics
 - Option to generate masks in the map

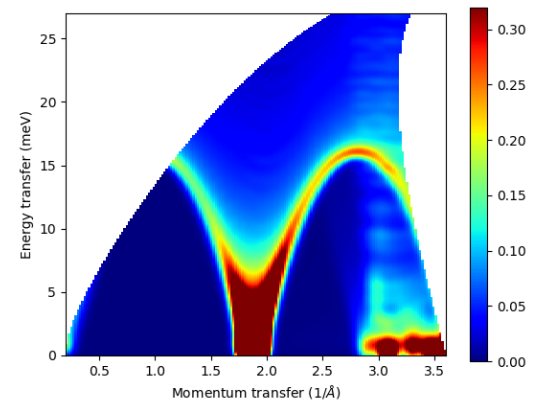
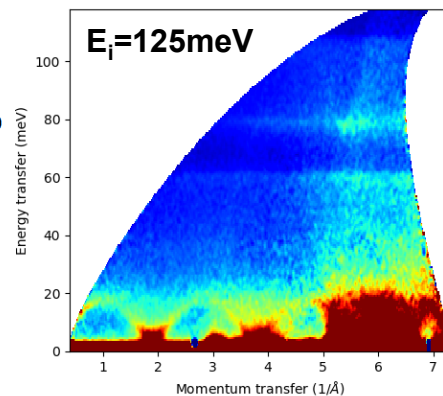
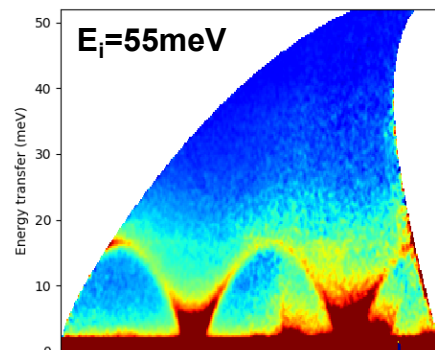
VISION



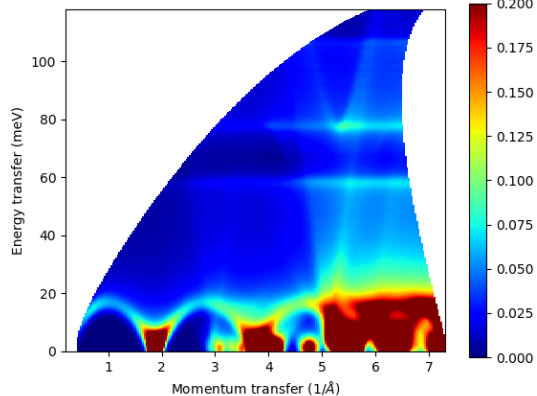
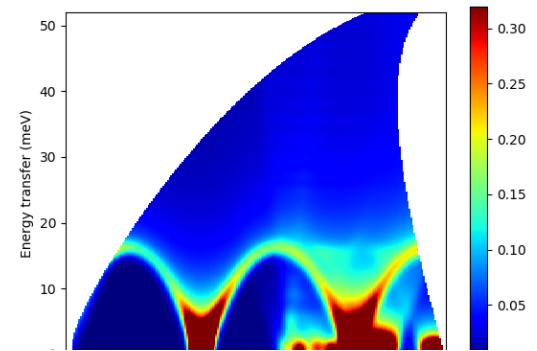
Full calculation versus incoherent approximation



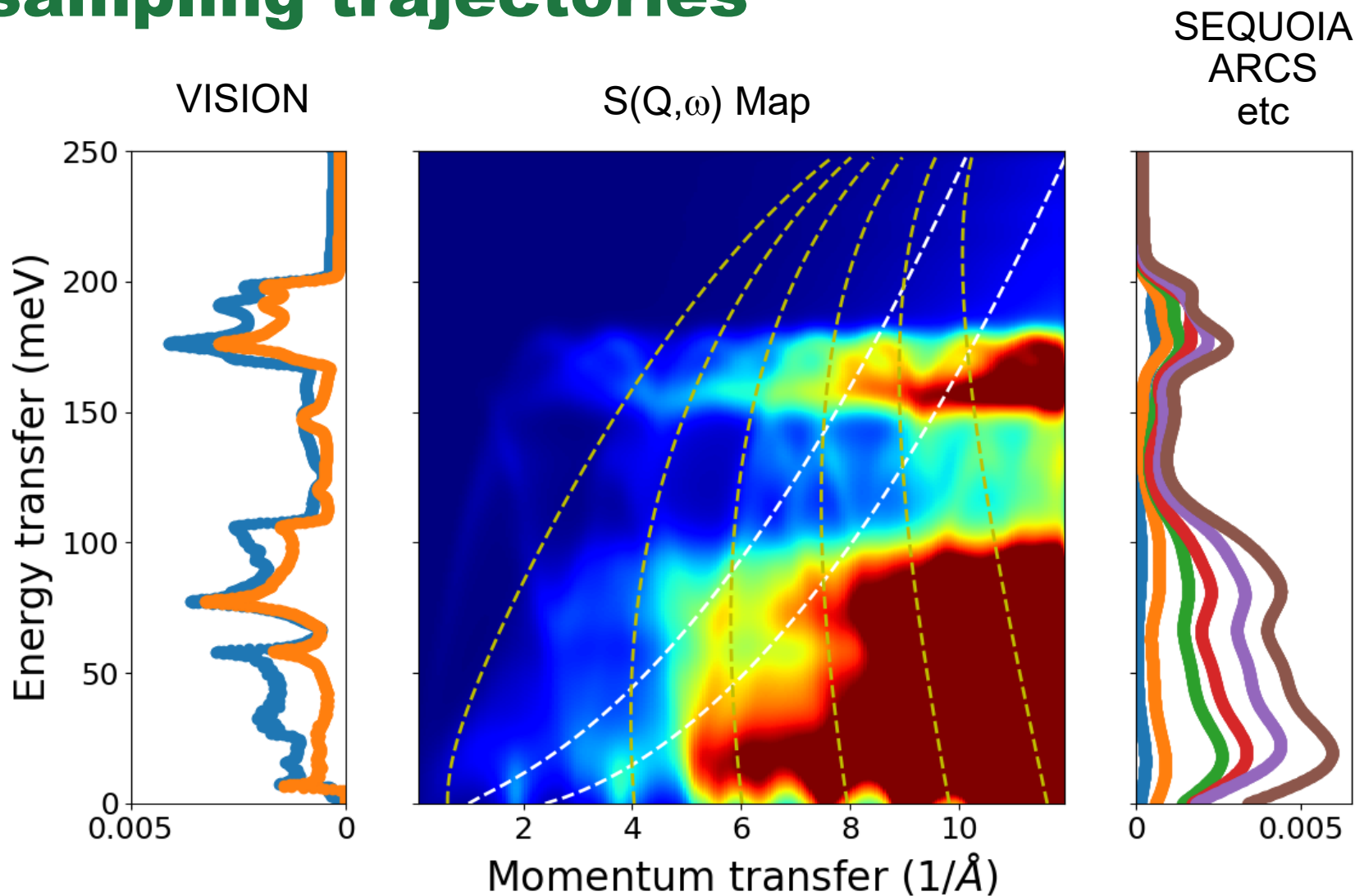
SEQUOIA



OCLIMAX

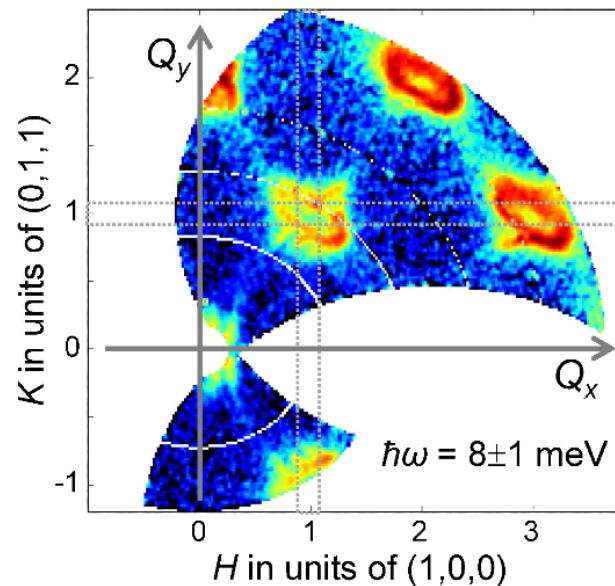
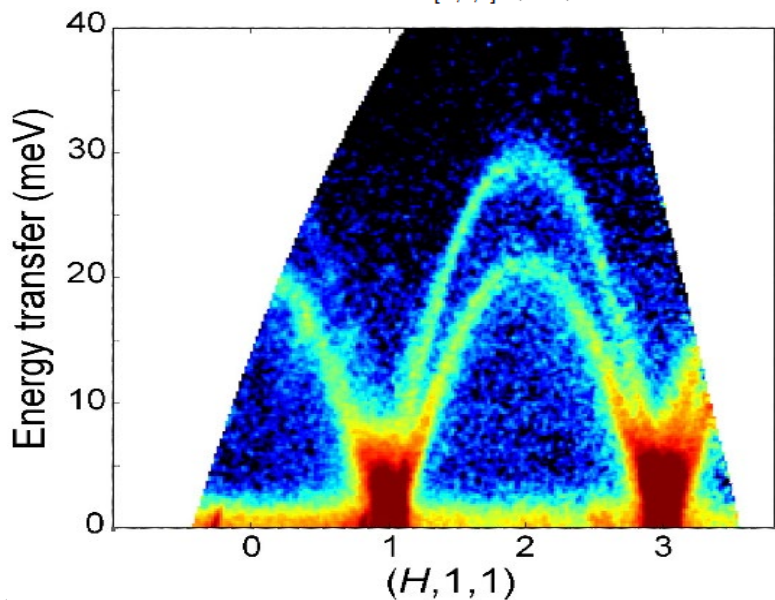
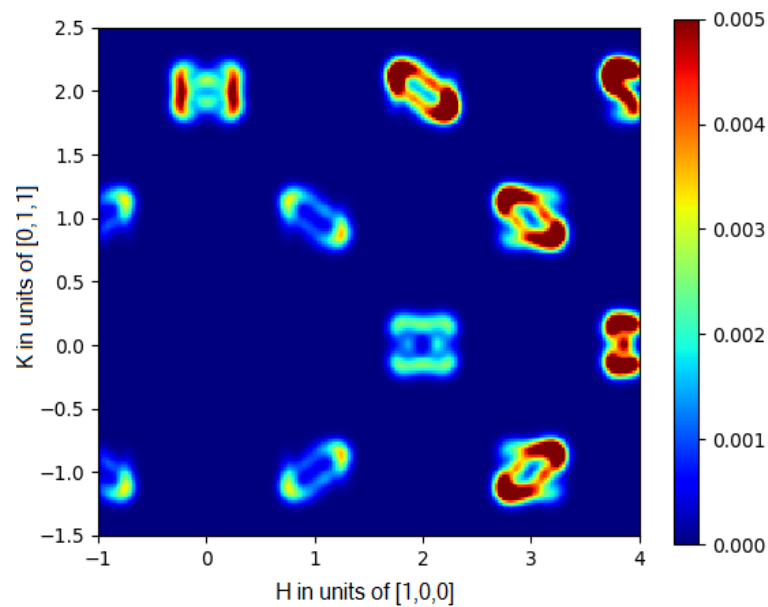
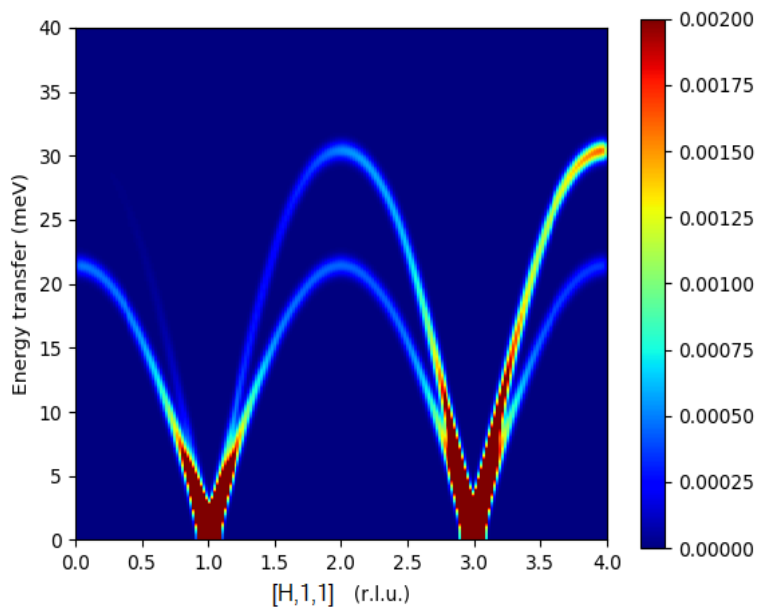


Calculated $S(Q, \omega)$ map and various sampling trajectories



Cheng Y.Q., Daemen L.L., Kolesnikov A.I., Ramirez-Cuesta A.J., "Simulation of inelastic neutron scattering spectra using OCLIMAX", *Journal of Chemical Theory and Computation*, 15, 3, 1974-1982 (2019).

OCCLIMAX example: single crystal



Questions?



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