Neutron Vibrational Spectroscopy

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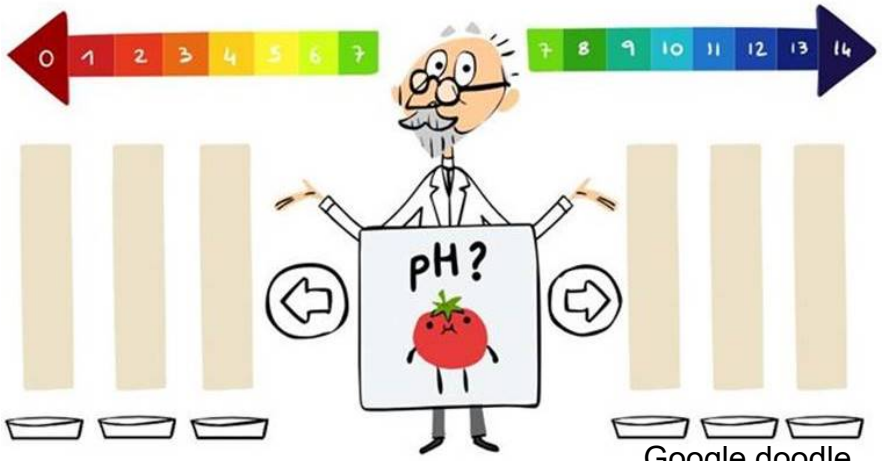
2022 National School on
Neutron and X-ray Scattering

Outline

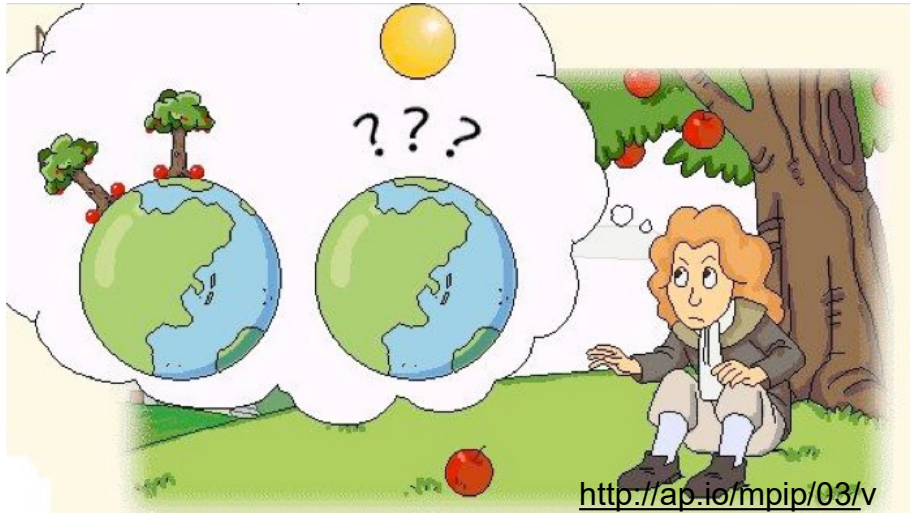
- Background and instrumentation
- Data analysis and modeling
- Applications
- Q&A

What is neutron vibrational spectroscopy (NVS)?

Neutron vibrational spectroscopy (NVS)	Inelastic neutron scattering (INS)
Chemists	Physicists
Molecular systems Organic/inorganic compounds	Condensed matter
Intramolecular modes Intermolecular modes	Phonons Magnons
S(ω) in cm^{-1}	S(Q,E) in meV
Indirect geometry instrument	Direct geometry instrument



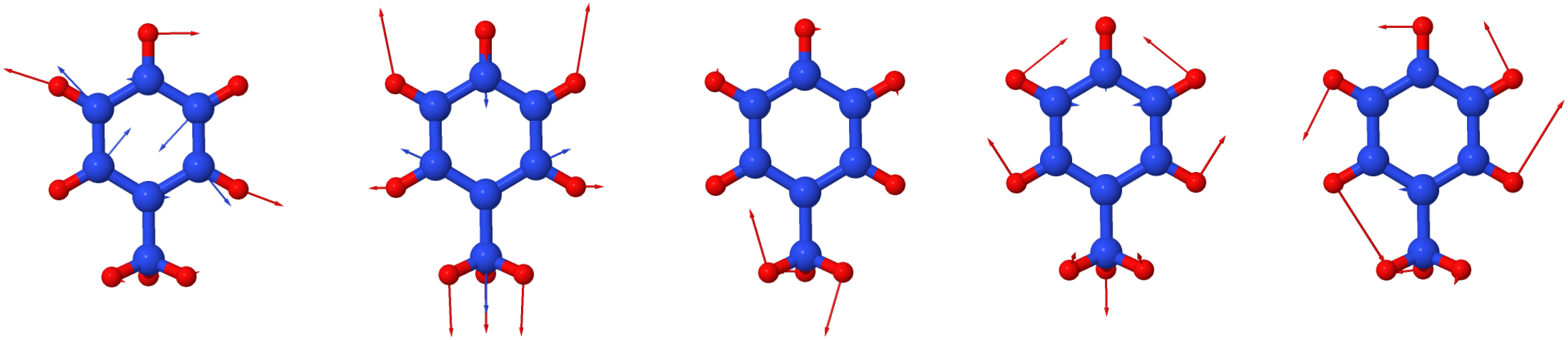
Google doodle



http://ap.io/mpip/03/v

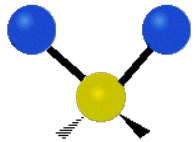
NVS focuses on applications of INS in chemistry

Molecular vibration: the eternal dance of molecules

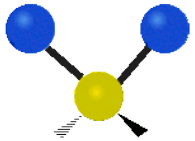


Each molecular vibration has its own "pace" and "motion".

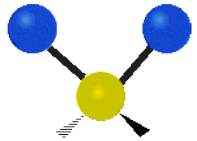
Symmetric stretching



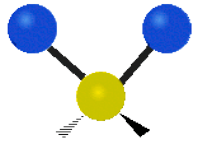
Asymmetric stretching



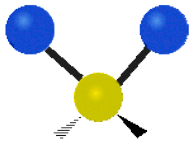
Scissoring (Bending)



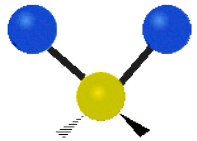
Rocking



Wagging

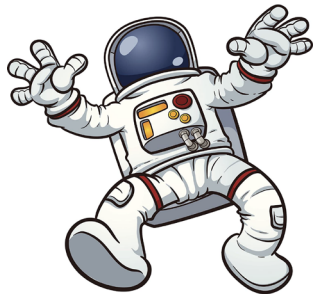


Twisting



https://en.wikipedia.org/wiki/Molecular_vibration

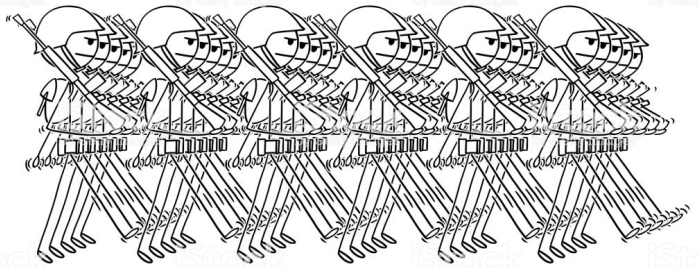
Vibration of molecules in different environment



Isolated (gas, non-interacting)

On surface (chemi/physi-adsorbed)

In pores (restricted/confined)

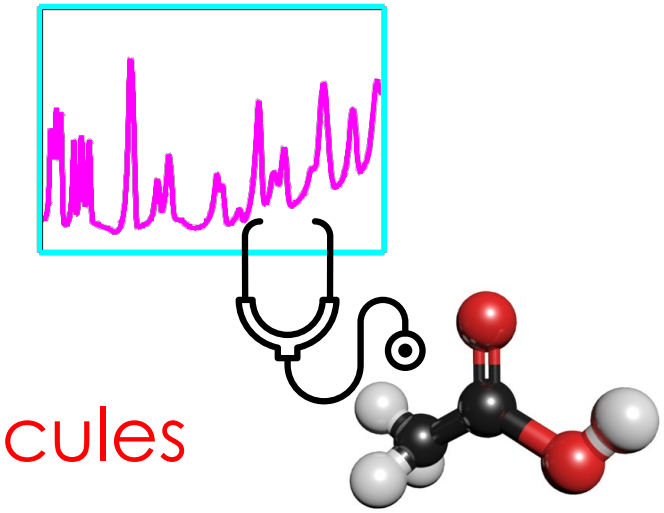


Self-assembled (solid)

The vibrational behavior of a molecule is determined by:
1) What it is (internal structure, bond type, functional groups, etc.)
2) Where it is (local environment, intermolecular forces)

What can we learn from molecular vibrations?

- Molecular and crystal structure (intermolecular interactions)
- Binding site and orientation (adsorption and catalysis)
- Electronic structure (charge transfer and ion/dipole interactions)
- Thermodynamic properties (free energy, stability, phase diagram, specific heat capacity and conductivity)
- Transport properties (diffusion and relaxation)
- ……

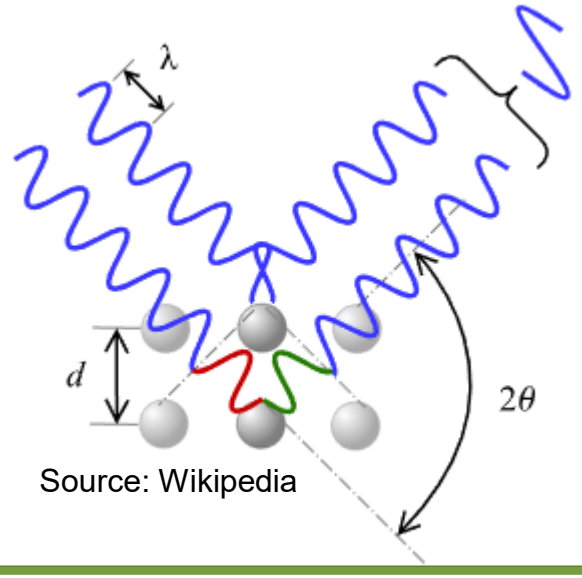


One of the most important vital signs of molecules

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.

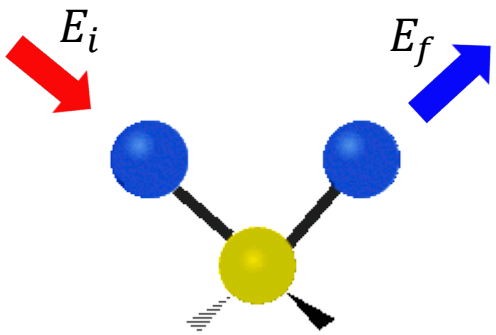
Wavelength
Scattering angle



Source: Wikipedia

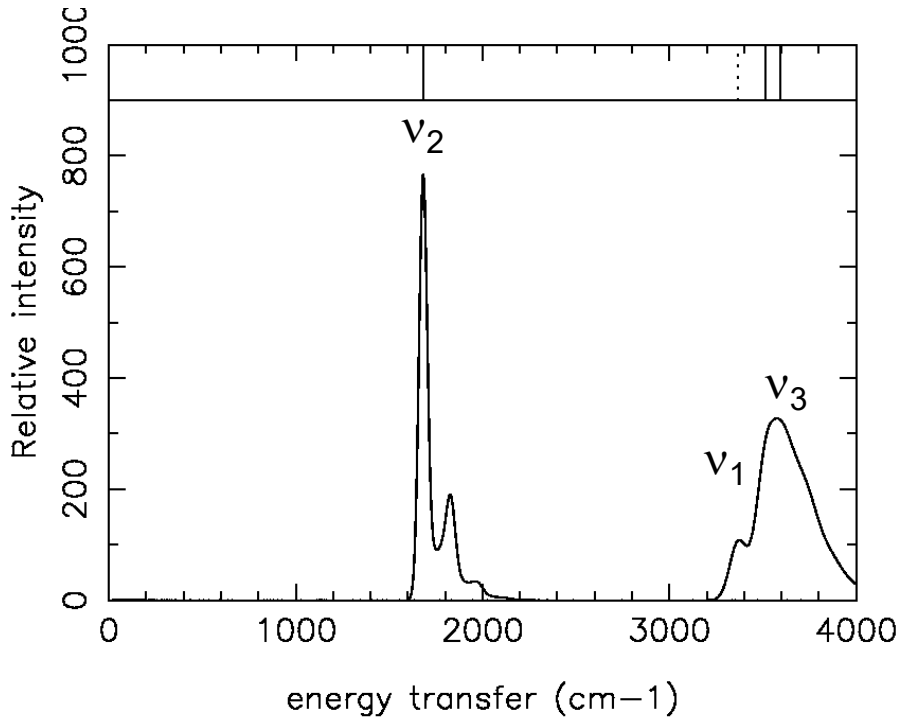
Spectroscopists use (inelastic) scattering of radiation (light, x-ray, neutron,...) to excite vibrational modes. The energy of the radiation is comparable to the energy associated with the vibrational excitations.

Incident energy
Final energy
(Scattering angle)



$$\hbar\omega = E_f - E_i$$

Interpretation of vibrational spectra: peak assignment



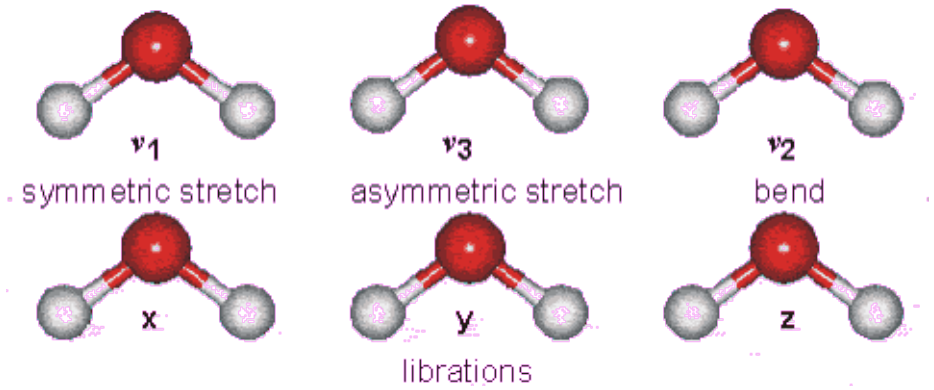
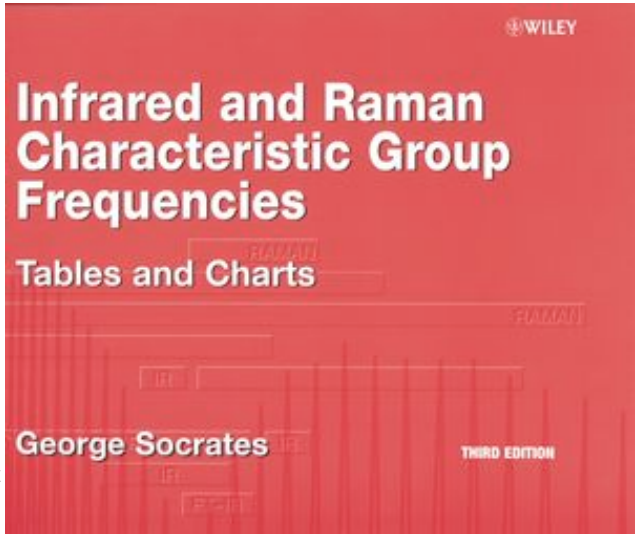


Table 1 Absorption frequencies of some common bonds (shown in bold type)

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(=O)–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)



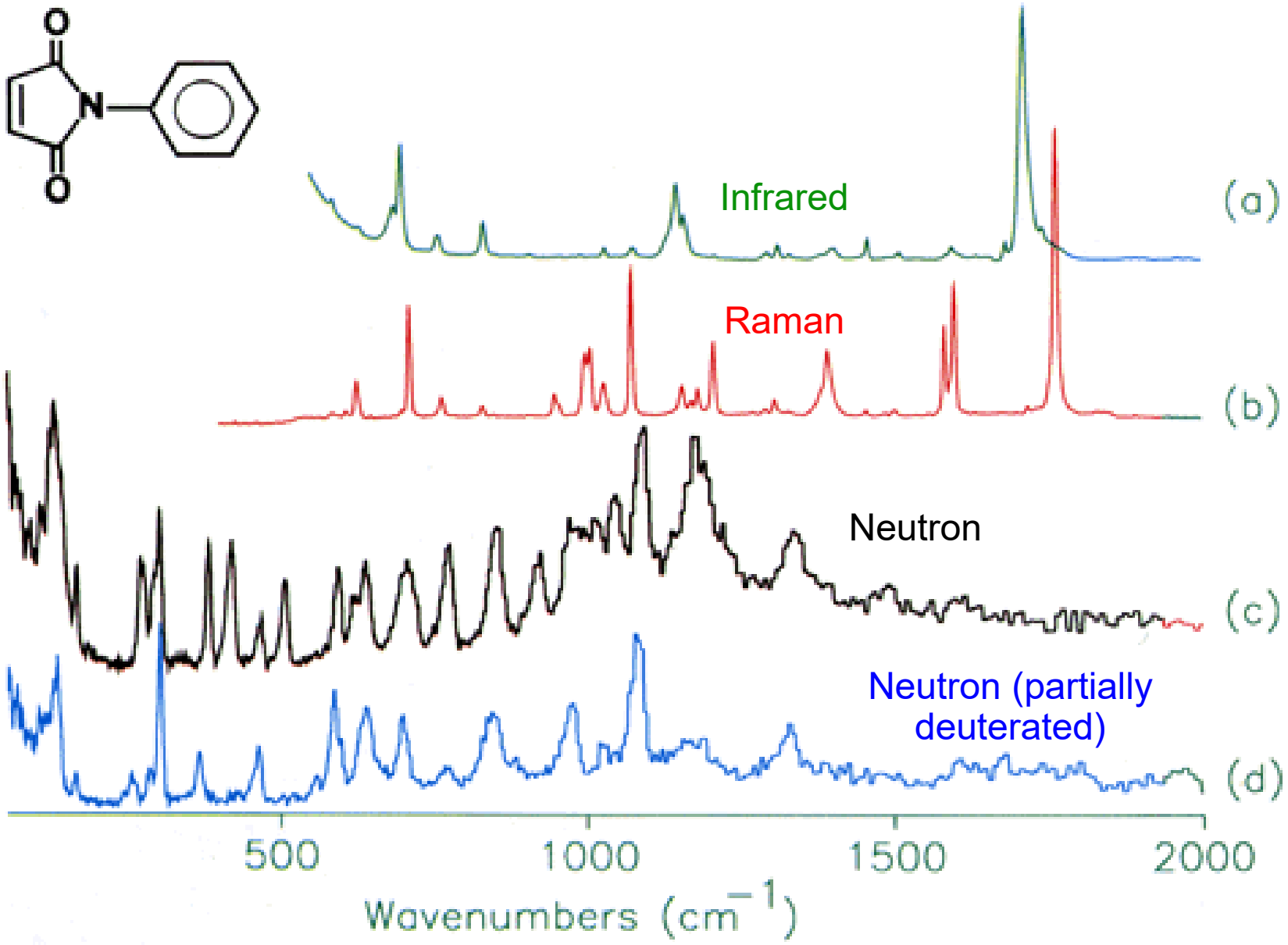
Vibrational spectroscopy with neutrons: pros and cons

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 (Q,ω) 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, …

Main challenges: amount of sample, measurement time, energy/spatial resolution, temperature

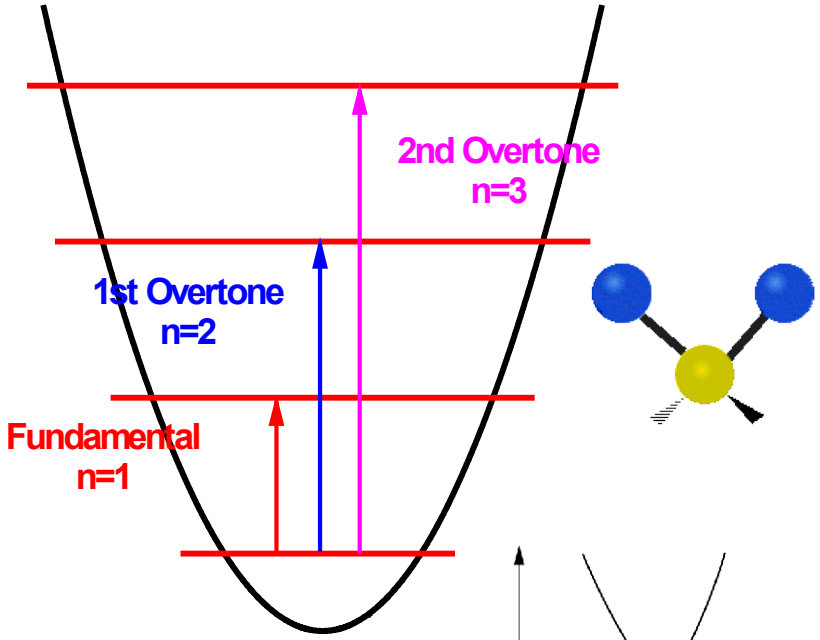
Complementary tools to study molecular vibration

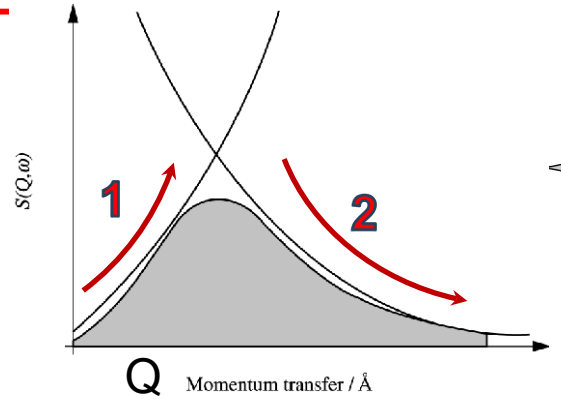
Complementary tools to study molecular vibration

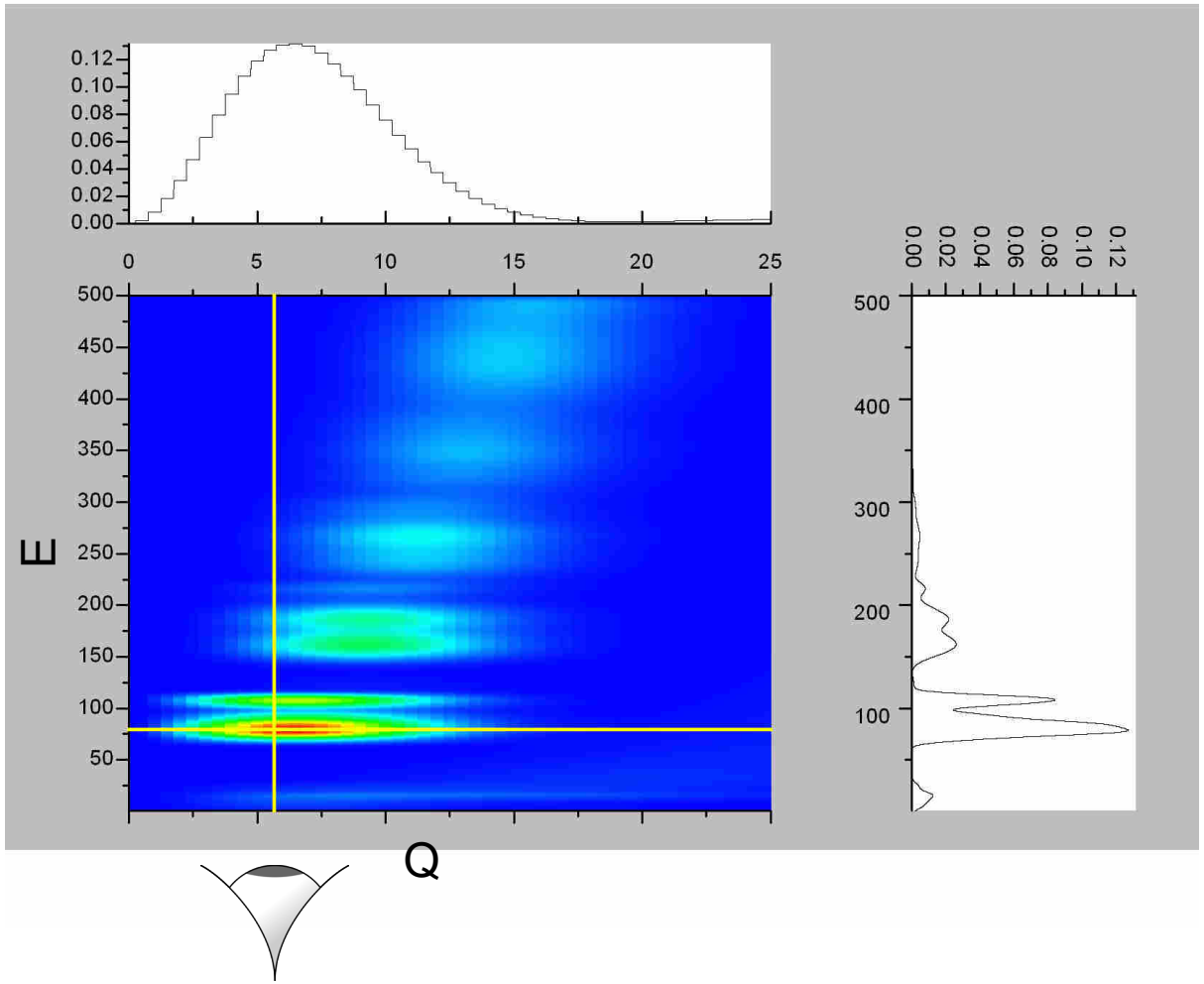


S.F. Parker, *Int.J. Vib. Spect.*, **2**, 1, 6-22 (1998)

A simple S(Q,ω) map of molecular vibration: key features



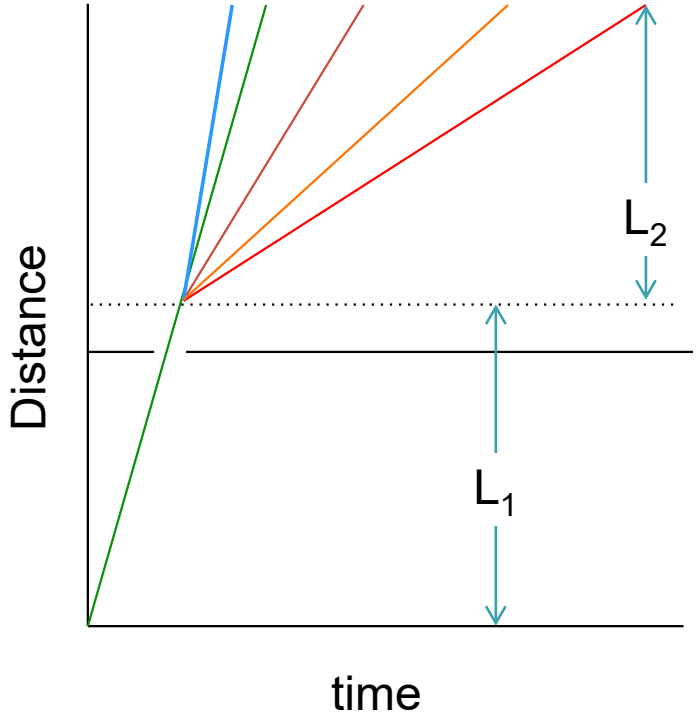




$$S(\boldsymbol{Q}, n\omega_s) = \frac{(\boldsymbol{Q}\cdot\boldsymbol{U}_s)^{2n}}{n!}\exp[-(\boldsymbol{Q}\cdot\boldsymbol{U}_{total})^2] \qquad \boldsymbol{U}_s = \sqrt{\frac{\hbar}{2m\omega_s}}\,\boldsymbol{e}_{ds}$$

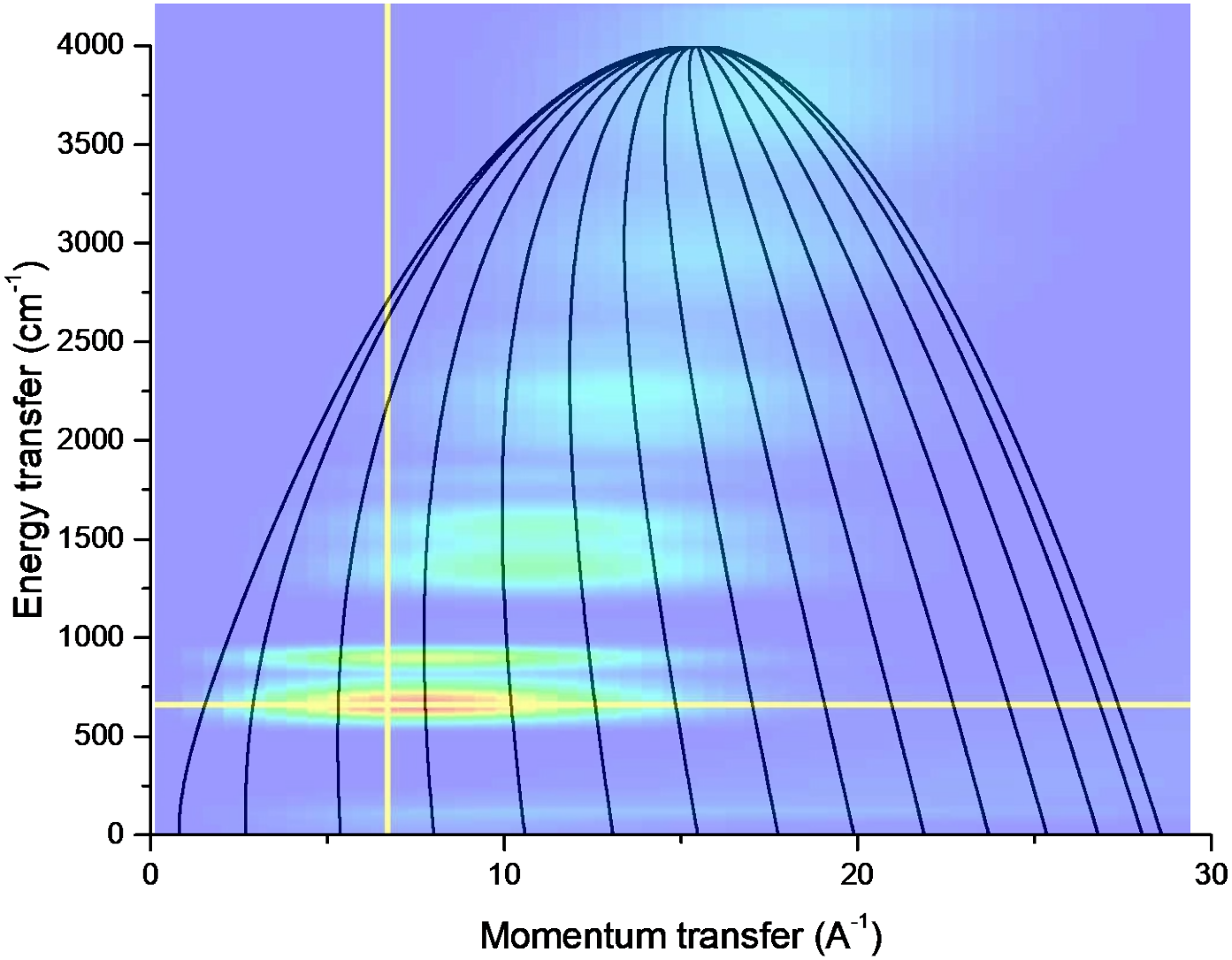
1 2

Choice of instrument for NVS: direct geometry

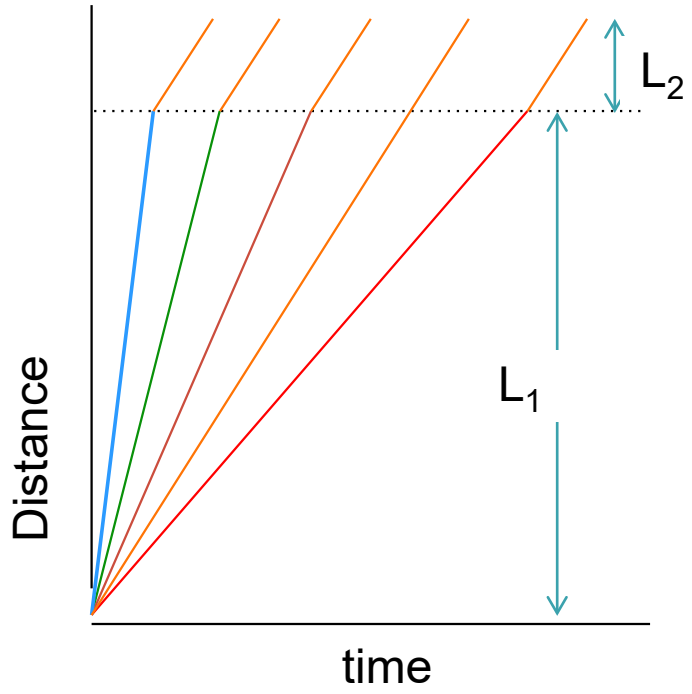


Fixed incident energy, measure final energy and scattering angle.

Examples: ARCS, CNCS, HYSPEC, SEQUOA, MARI

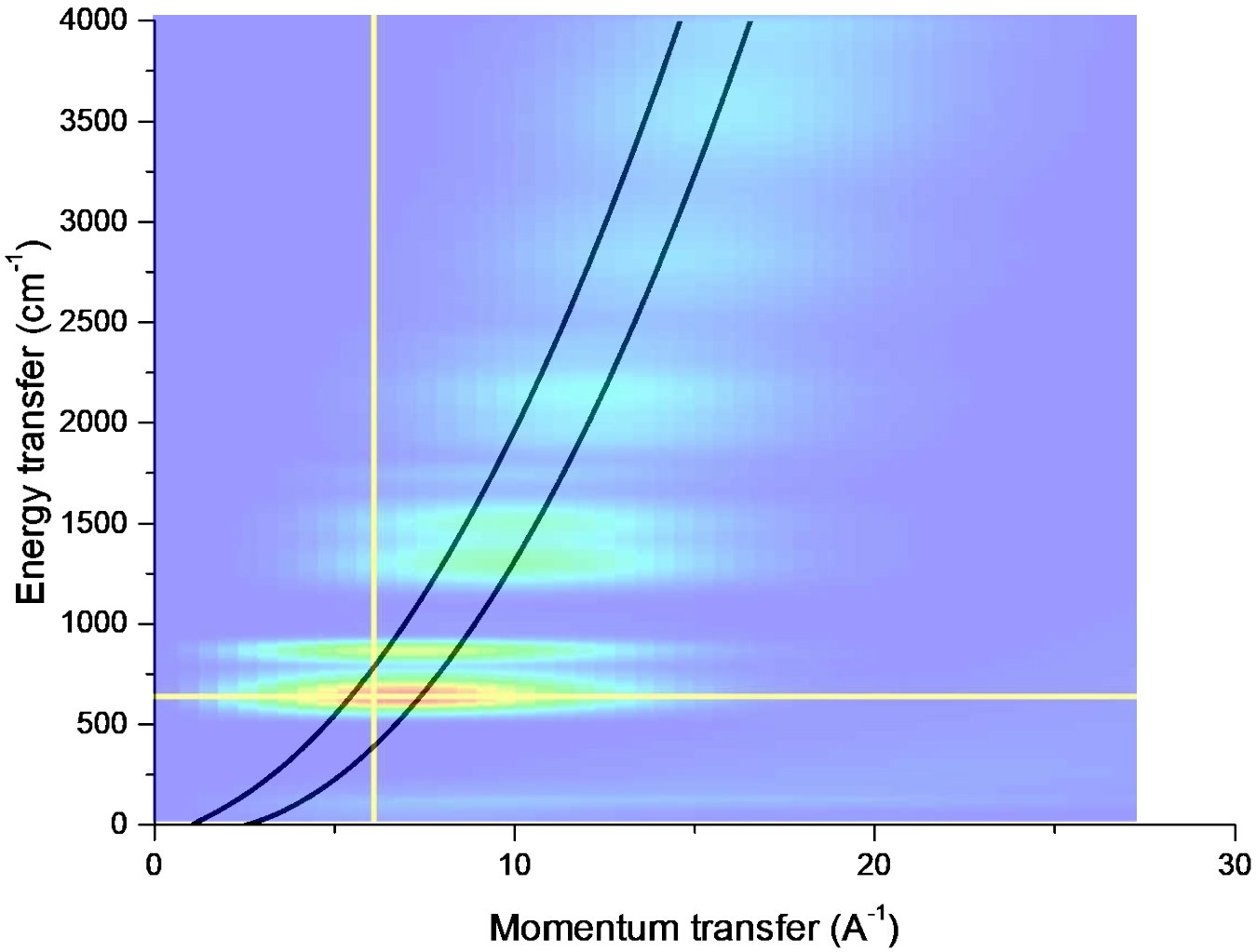


Choice of instrument for NVS: indirect geometry

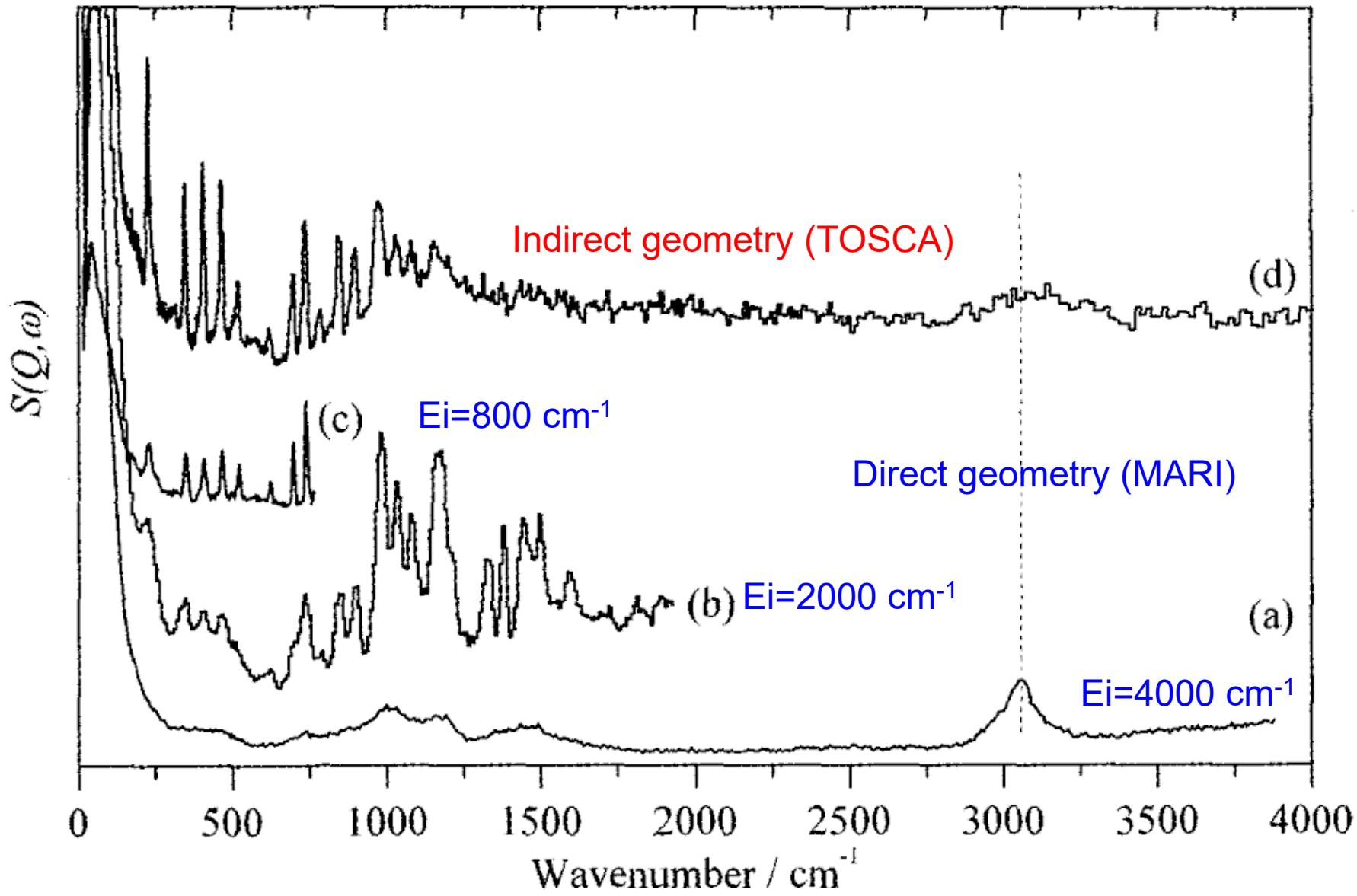


White incident beam,
fixed final energy,
calculate initial energy.

Examples: VISION, TOSCA



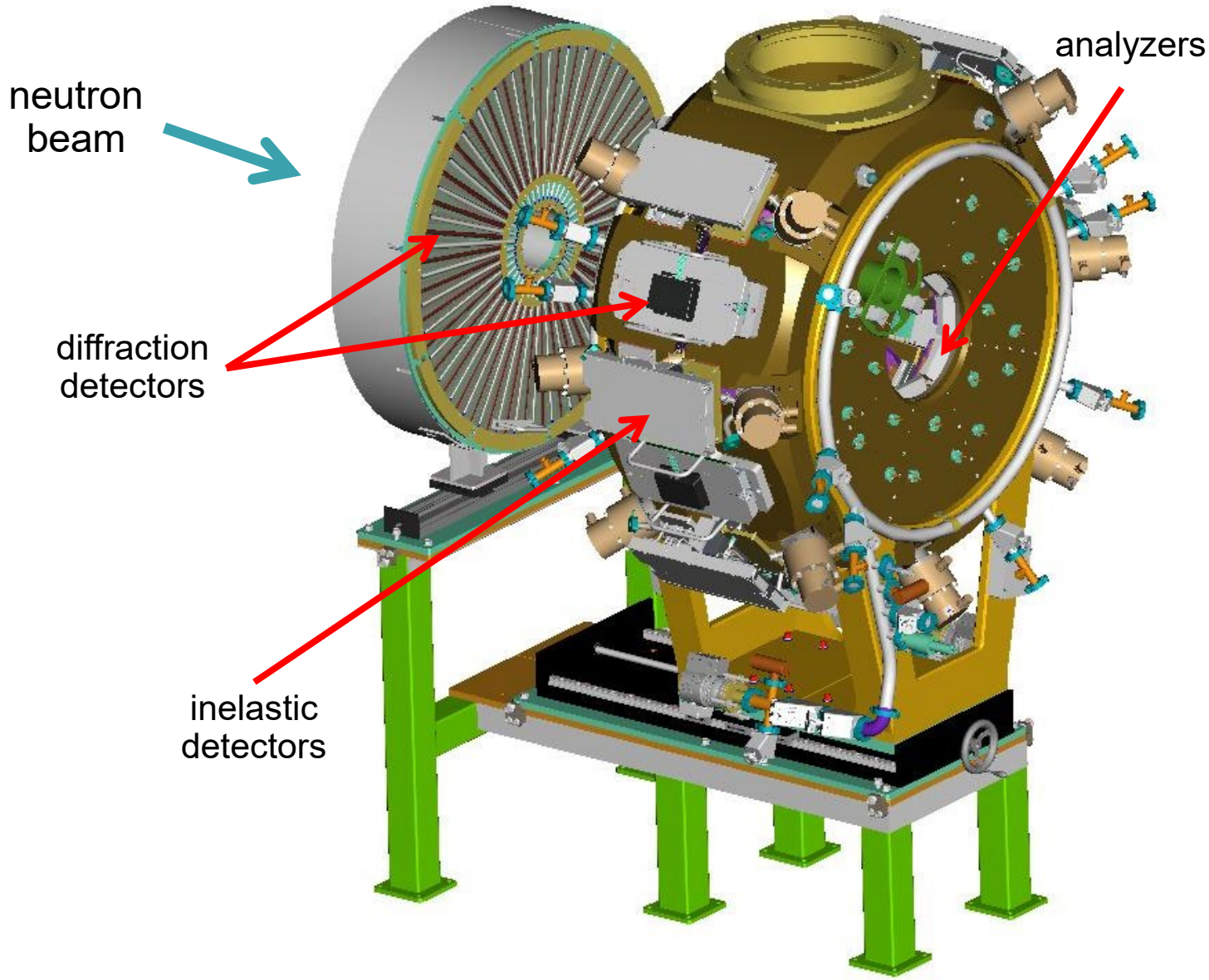
Choice of instrument for NVS: comparison



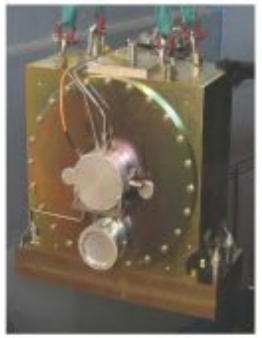
Mitchell et al. Vibration Spectroscopy with Neutrons, World Scientific 2005

VISION@SNS

- White incident beam, fixed final energy (indirect geometry)
- High flux and double-focusing
- Broadband (-2 to 1000 meV at 30Hz, 5 to 500 meV at 60 Hz)
- Constant dE/E throughout the spectrum (~1.5%)
- Elastic line HMFW ~150 μeV
- Backward and 90° diffraction banks



VISION@SNS


T0 Chopper


BW Chopper

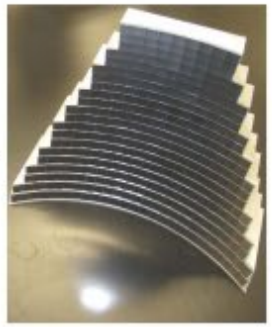

Sec. Shutter


Detector (elastic, backscattering)


Detector (inelastic)

L'

L + L' = constant


Analyzer

90.0°

517.4 mm

1136 mm

L

Moderator

T0

SS

Ø220 mm

~12°

999 mm

~23°

sample

Get Lost Tube

Beamstop

7620 mm

BW

8000 mm

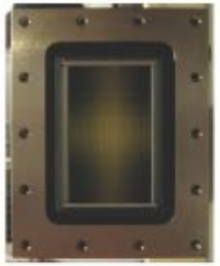
8765 mm

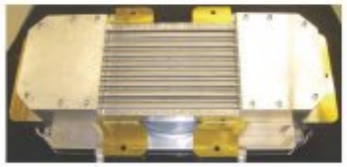
994 mm

635 mm

10.4°

Neutron Guide





Detector (elastic)

318 mm

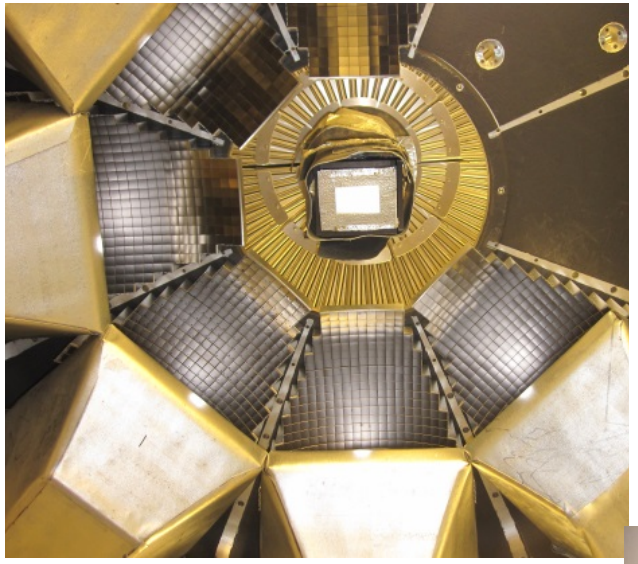
16000 mm

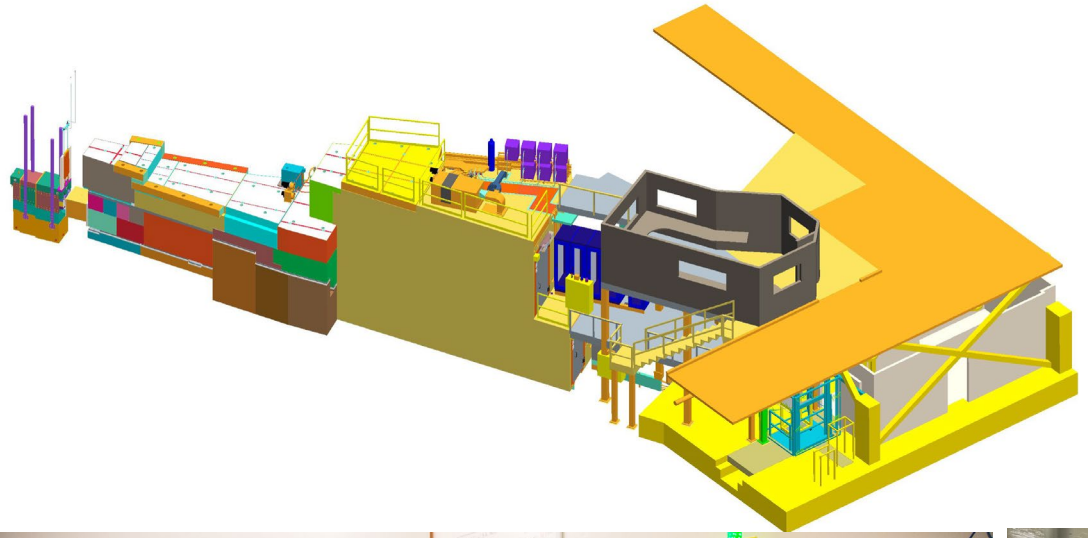
2568 mm

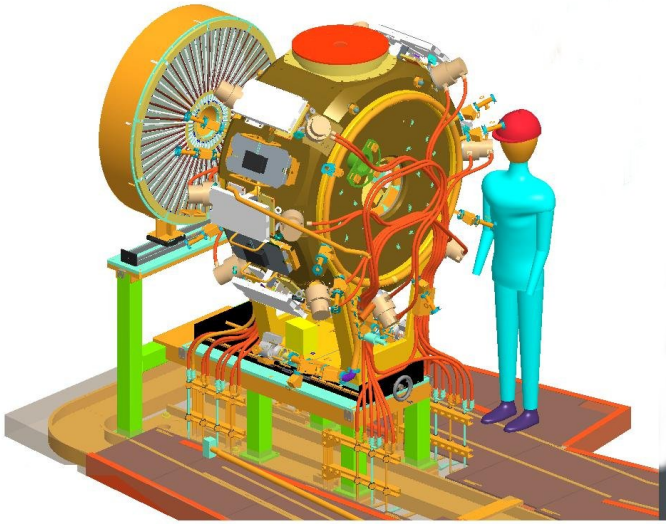
3537 mm

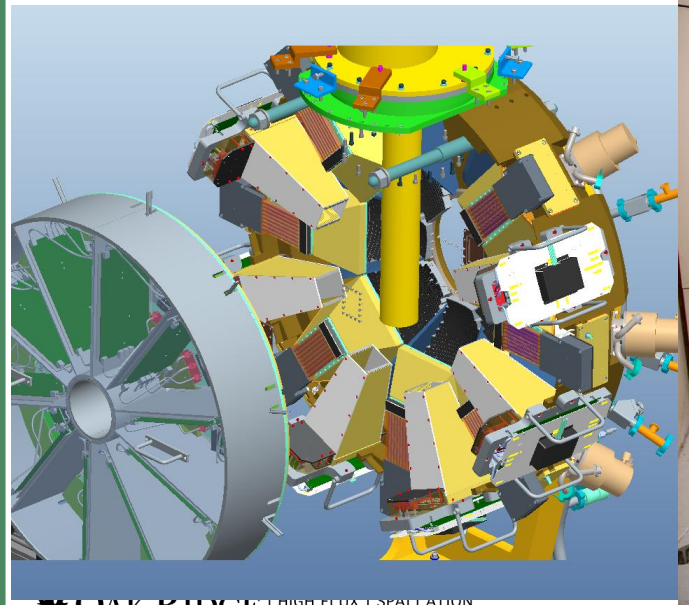
19537 mm

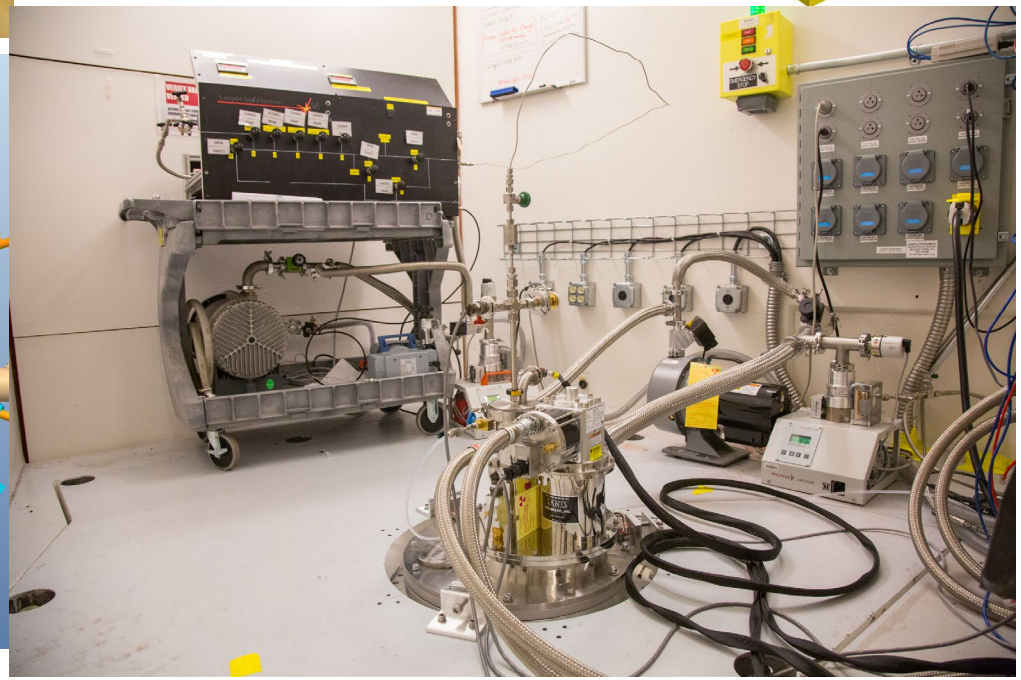
VISION@SNS: a gallery

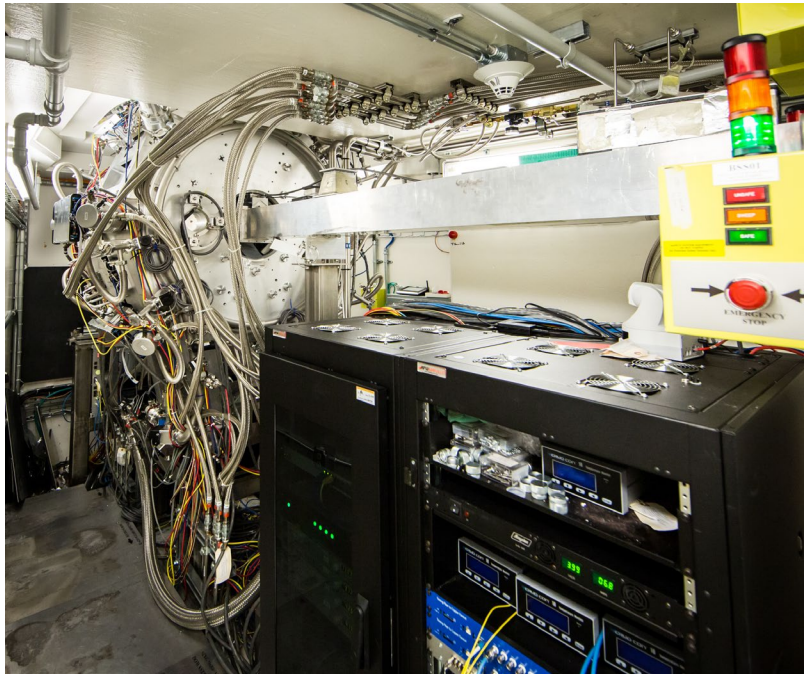




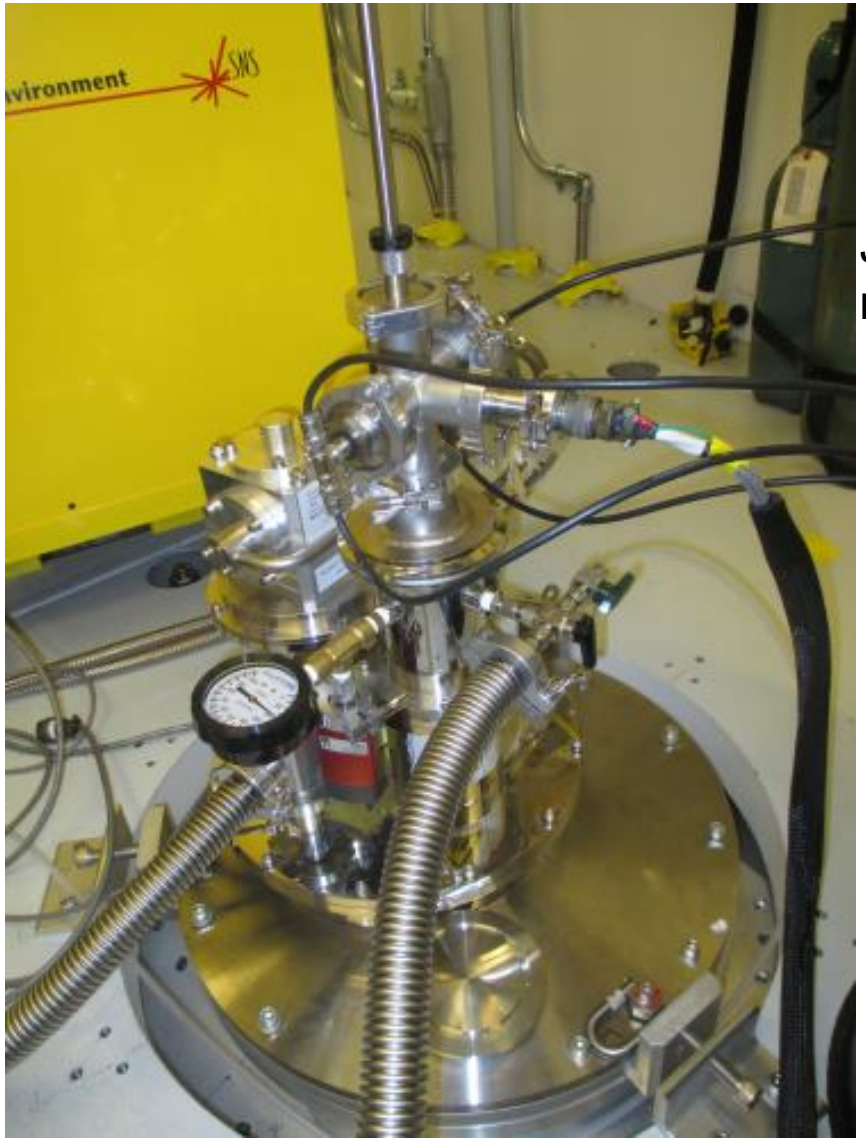




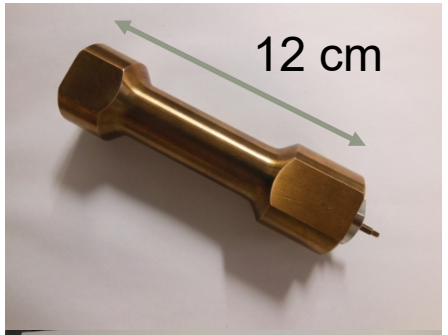




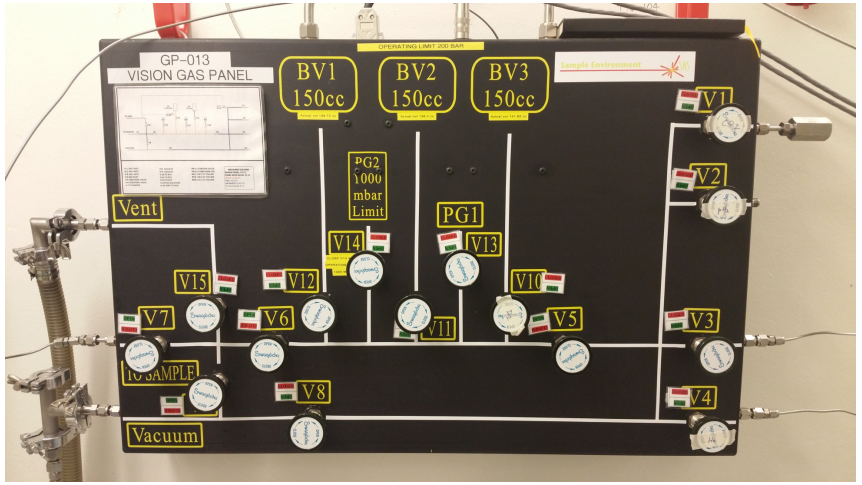
Sample environment at VISION



JANIS closed-cycle refrigerator (5-600K)

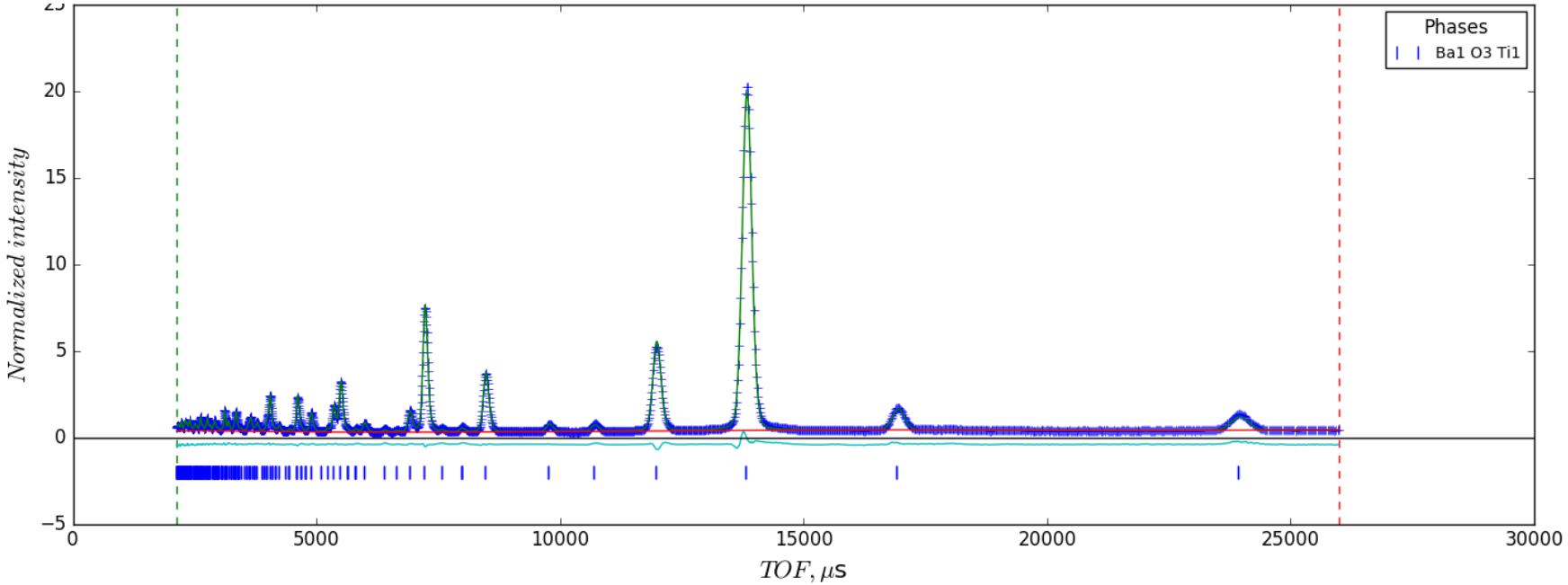


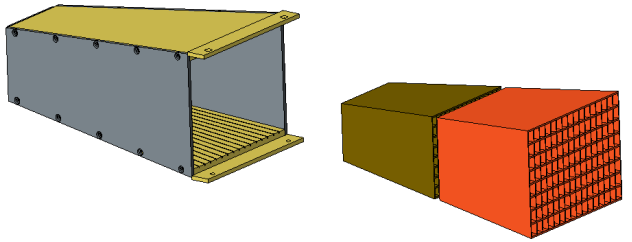
Pressure cells (piston, gas, diamond anvil).

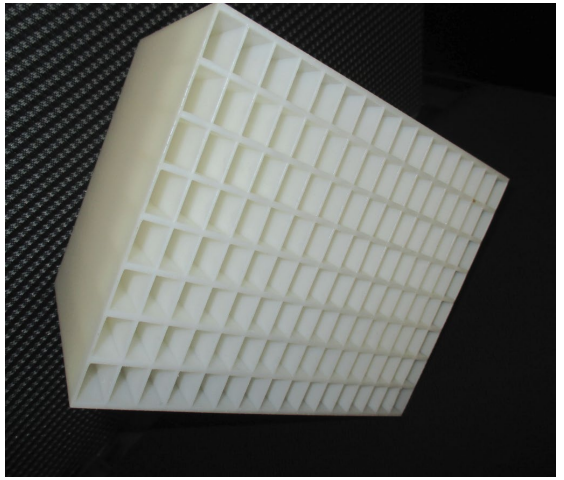


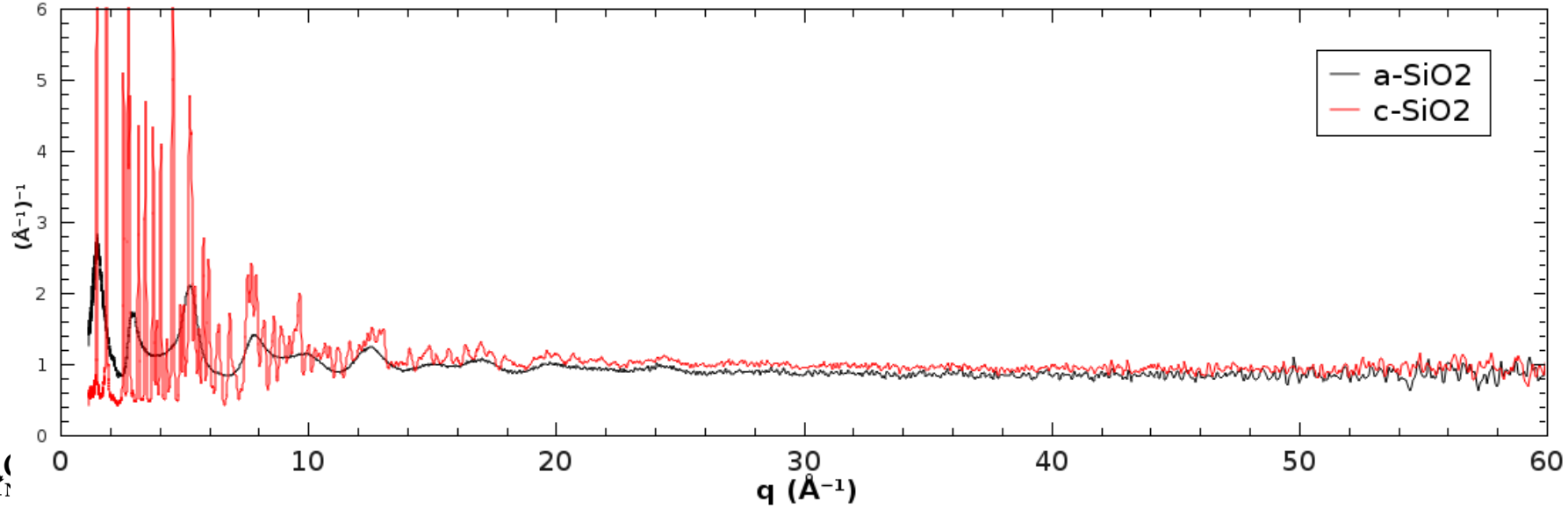
Gas handling panel for gas dosing, mixing, flow, adsorption (vacuum to 200 bar)

VISION diffraction banks

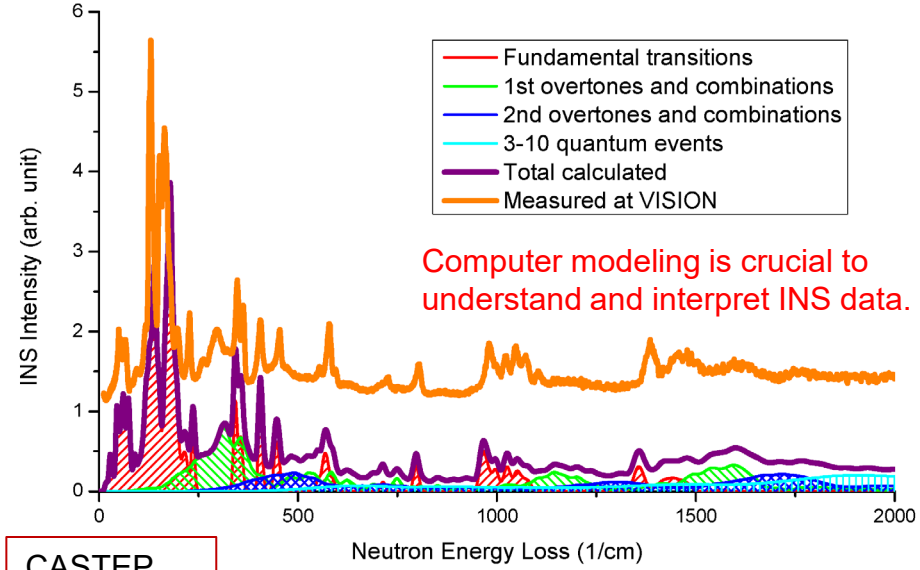








Integrated modeling for data interpretation



Computer modeling is crucial to understand and interpret INS data.

- 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

CASTEP
VASP
QE
CP2K
Gaussian

→ Vibrational modes and frequencies → INS simulation (OClimax) → Simulated INS spectra

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

Data reduction and analysis (Mantid) → 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

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

- Interpret neutron data
  - assigning peaks to vibrational modes

What

- Obtain insight on fundamental properties
  - understanding interatomic interactions, anharmonicity, complex excitations, phase transitions, chemical reactions

How

- Connect theory and experiment
  - simulation is a virtual experiment and an *in silico* implementation of theory

Why

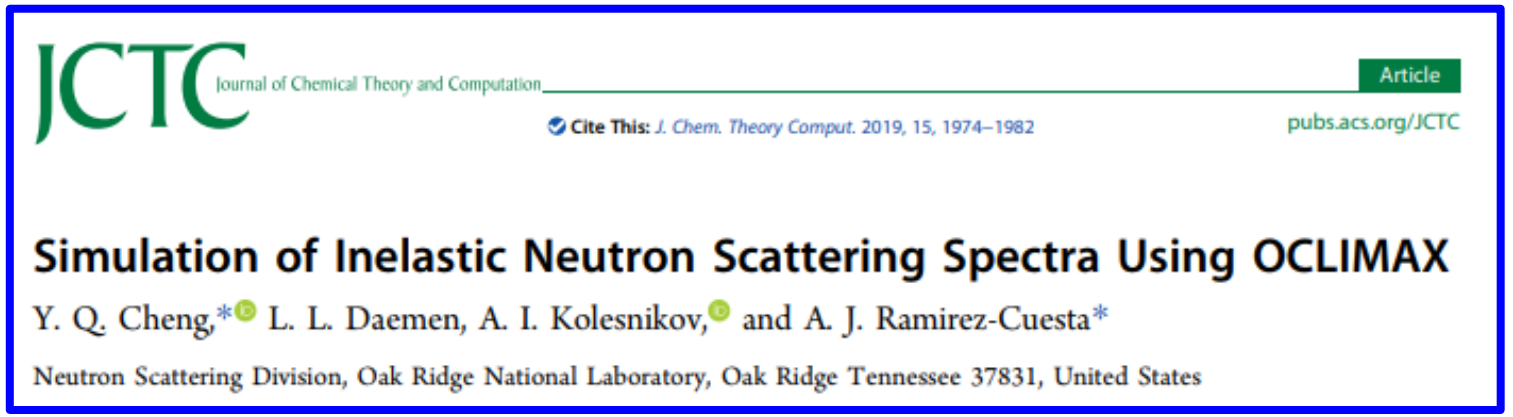
We can measure it.  We do understand it.

Development of OCLIMAX

- Started 2016
- First version released 2017
- Paper published 2019
- Used to analyze data from VISION and multiple other neutron spectrometers

Features:

- ❖ Full scattering (coherent, incoherent, elastic, inelastic)
- ❖ Powders and single crystals
- ❖ Temperature effects
- ❖ Multiphonon excitations
- ❖ Arbitrary instrument geometry and resolution
- ❖ Arbitrary cuts in 4-dimensional Q-E space
- ❖ Interface with atomistic modeling tools (e.g. DFT codes)
- ❖ Interface with INS data analysis tools (e.g. DAVE and Mantid)
- ❖ User-friendly (multiple platform, easy to use, fast on PCs)
- ❖ Parameter-free thermal neutron scattering cross-sections
- ❖ Molecular dynamics trajectories to INS spectra


JCTC Journal of Chemical Theory and Computation
Article
Cite This: J. Chem. Theory Comput. 2019, 15, 1974−1982
pubs.acs.org/JCTC

Simulation of Inelastic Neutron Scattering Spectra Using OCLIMAX

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

OCLIMAX bridges theory and INS experiments

Common atomistic modeling tools

QUANTUMESPRESSO

b-initio VASP ienna ackage imulation

CASTEP

CP2K

a computational tool for solid state chemistry and physics CRYSTAL

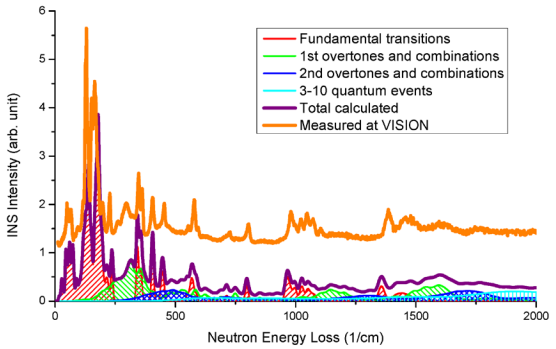
ORCA

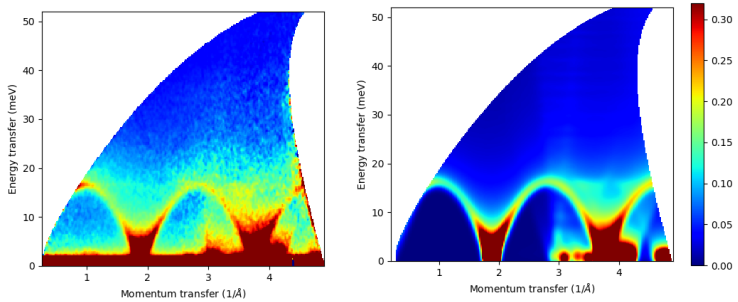
NWCHEM HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

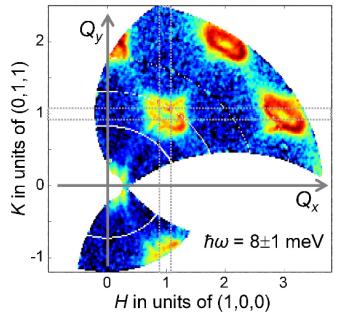
RMG

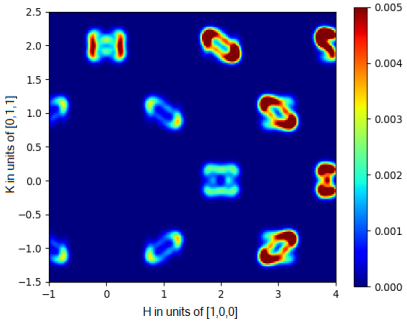
pymatgen 2.0.0

OCLIMAX



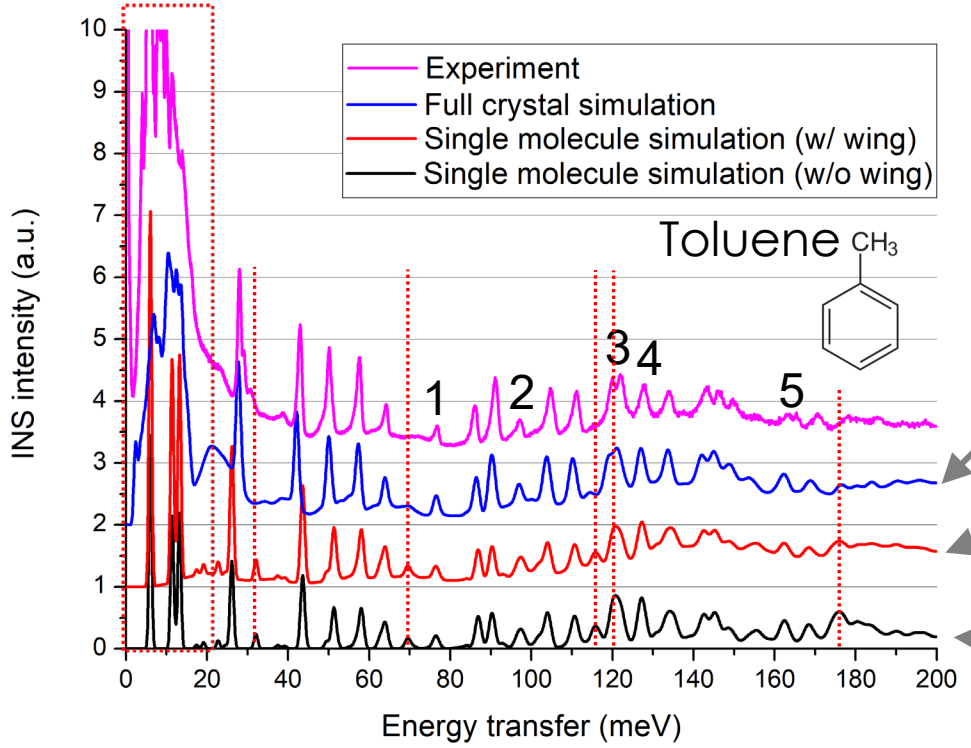


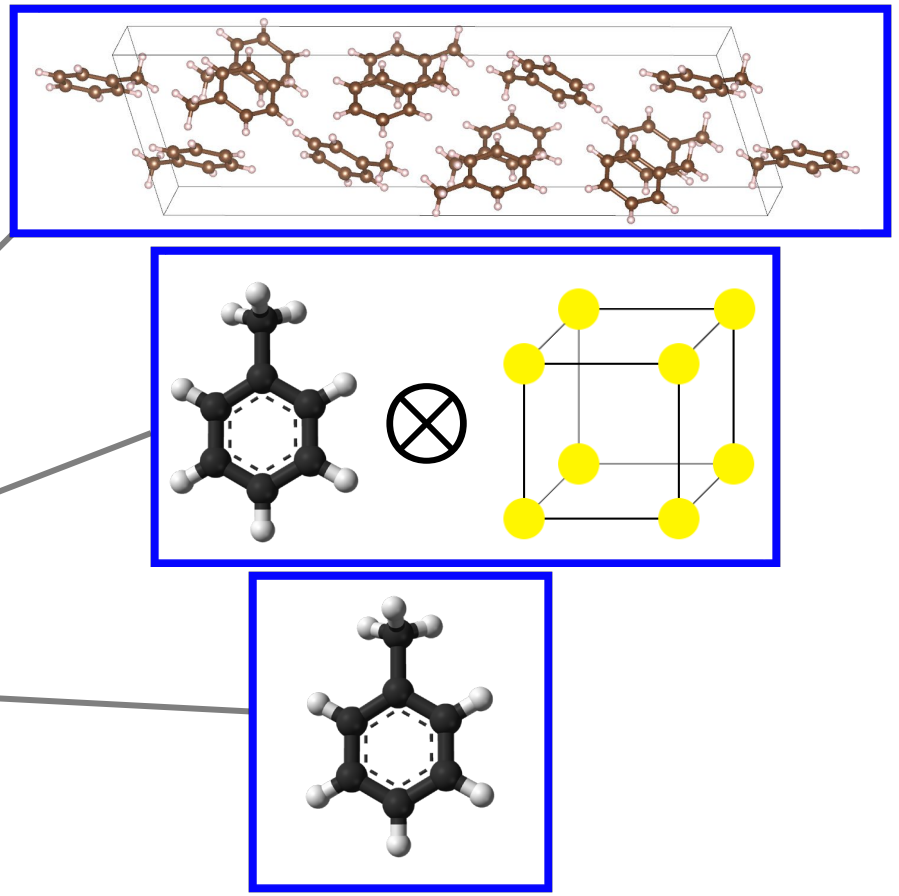


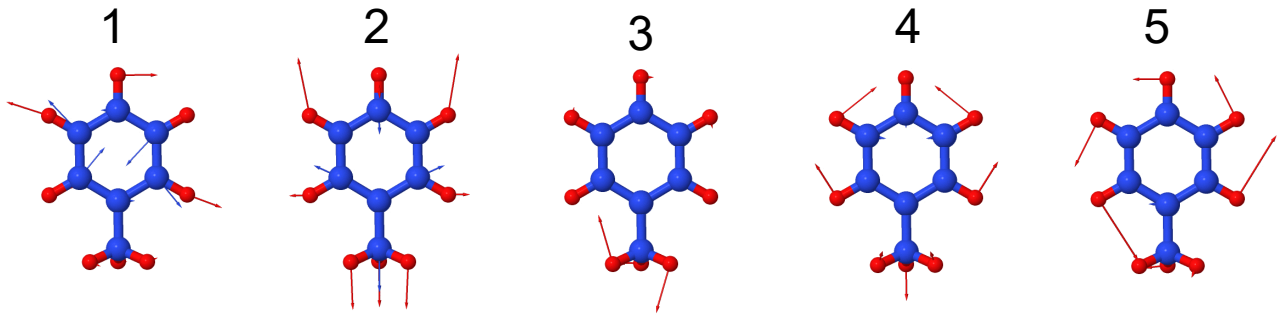


VISION, CNCS, HYSPEC, SEQUOIA, ARCS and many other neutron spectrometers.

OCLIMAX example: From single molecule to solid

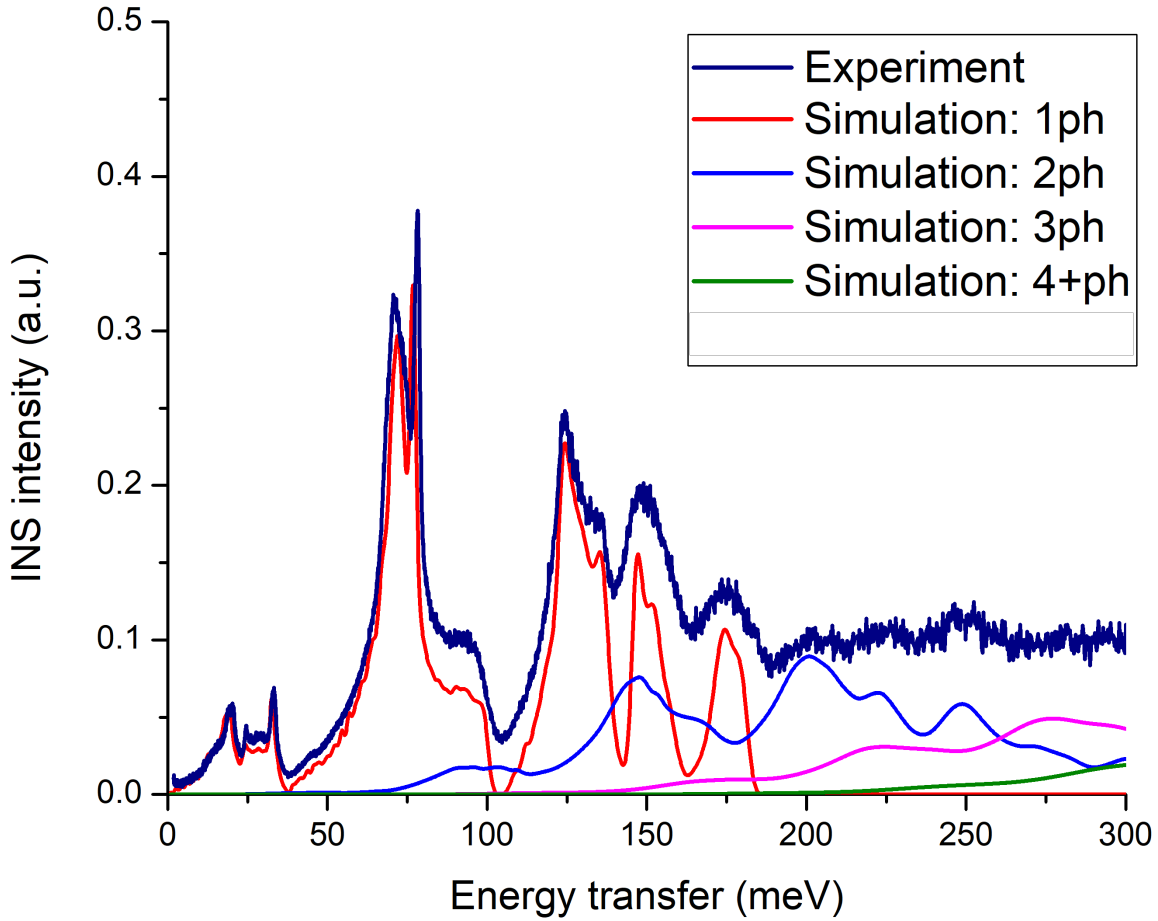


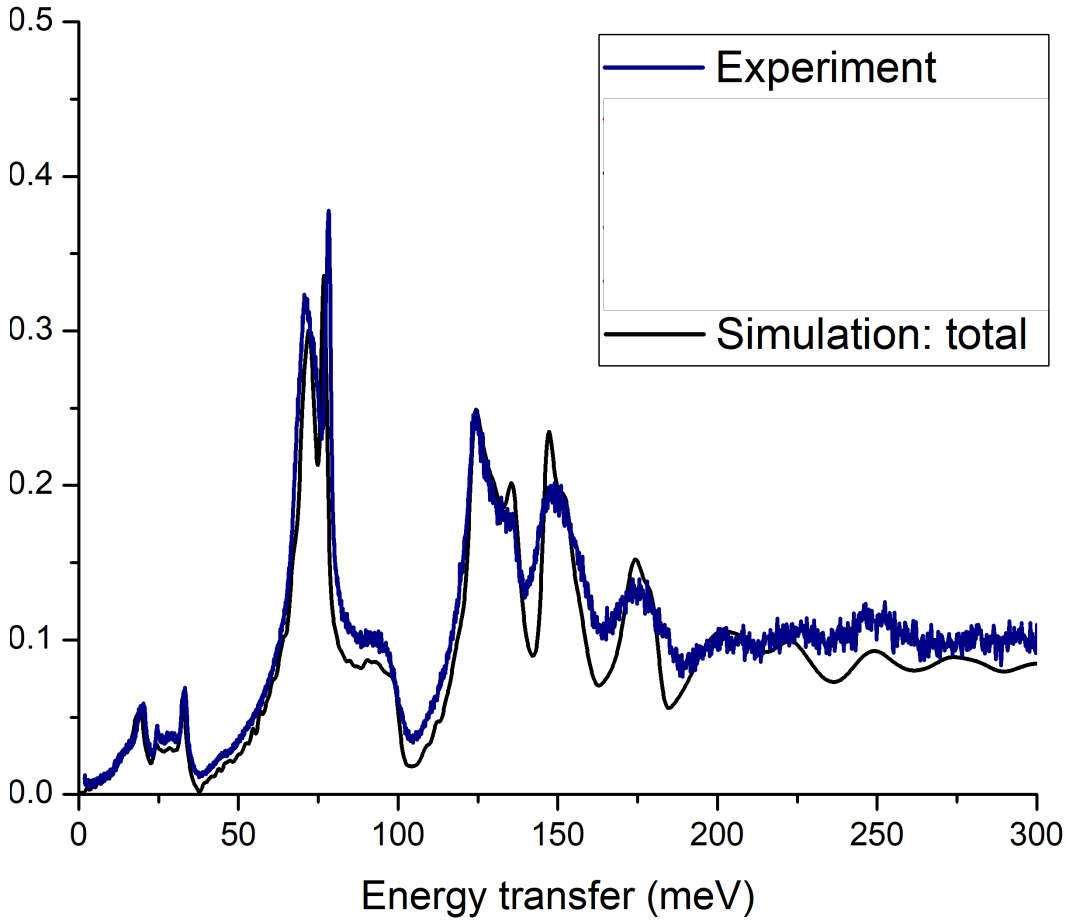




- ✓ Understanding intermolecular interactions (van der Waals forces, hydrogen bonding, charge transfer)

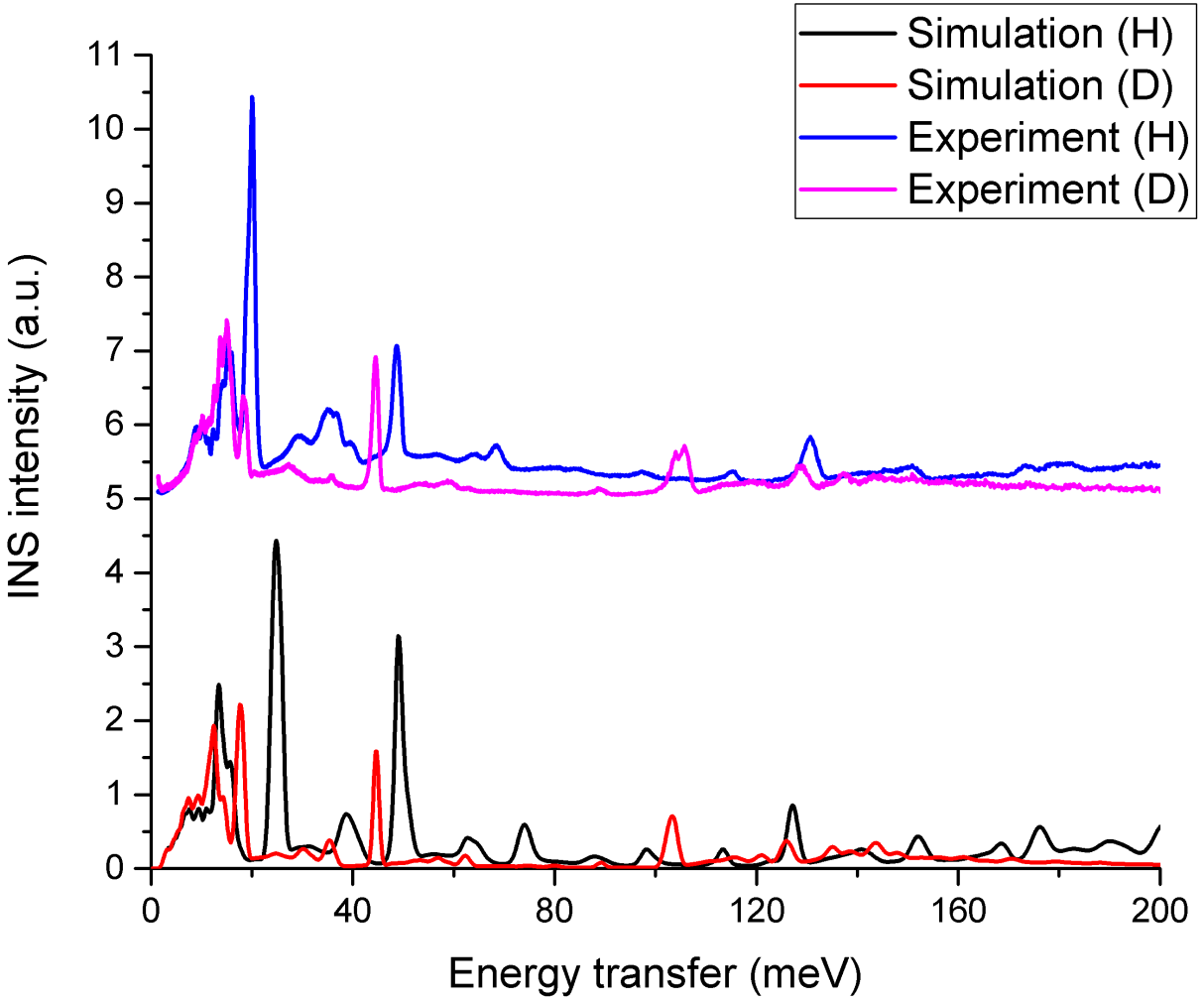
OCLIMAX example: Multiphonon excitations

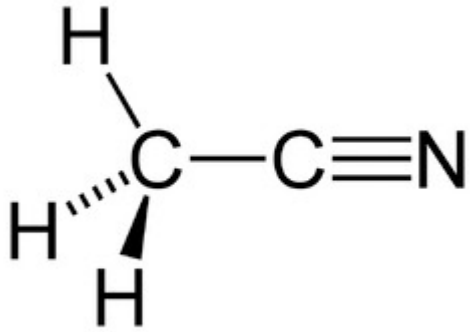




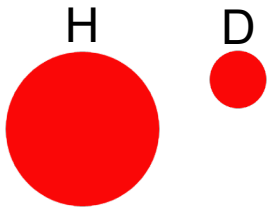
- ✓ Solving phonon density of states
- ✓ Understanding anharmonicity and potential energy landscape

Isotope substitution: acetonitrile





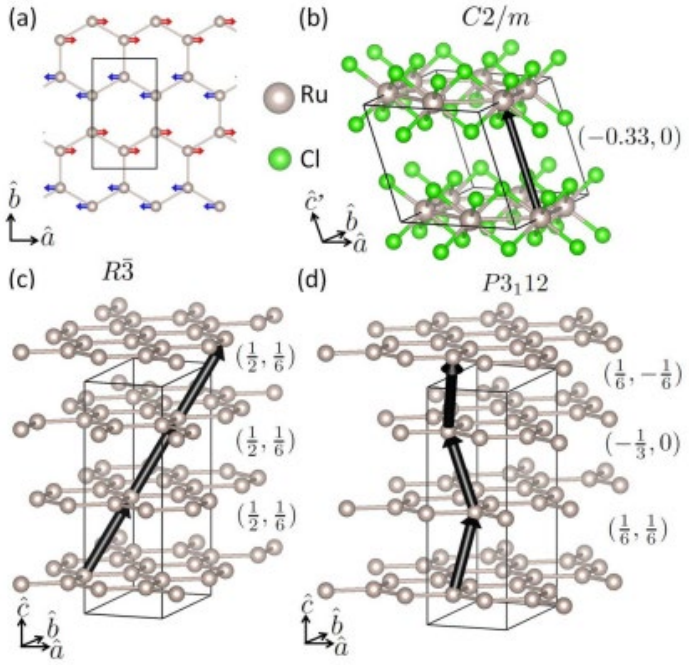
$$\omega = \sqrt{\frac{k}{m}}$$



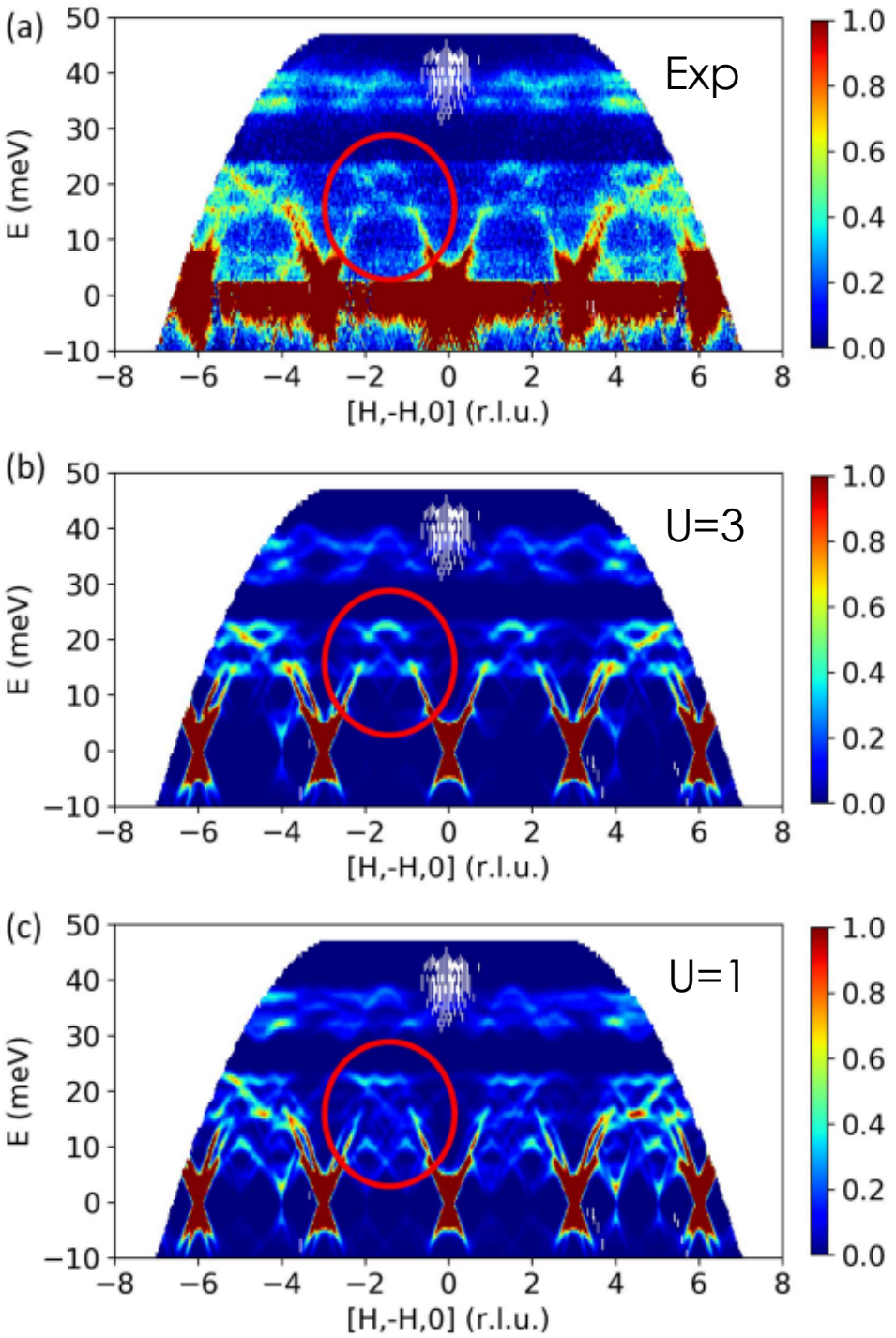
- ✓ Virtual experiment for doping effects and isotope labeling
- ✓ Breaking down the total intensity into partial contributions from individual species or atoms

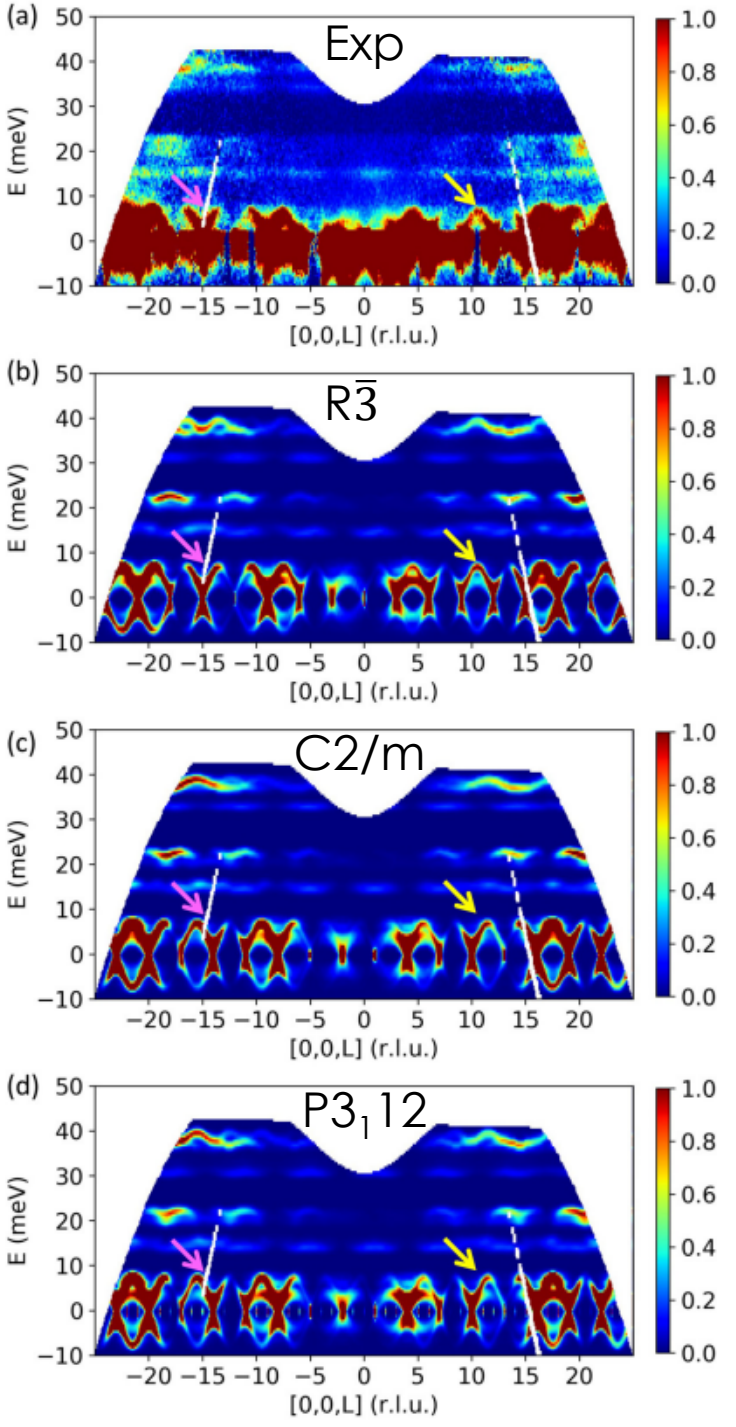
Single crystal $RuCl_3$

Using experiment to correct theory



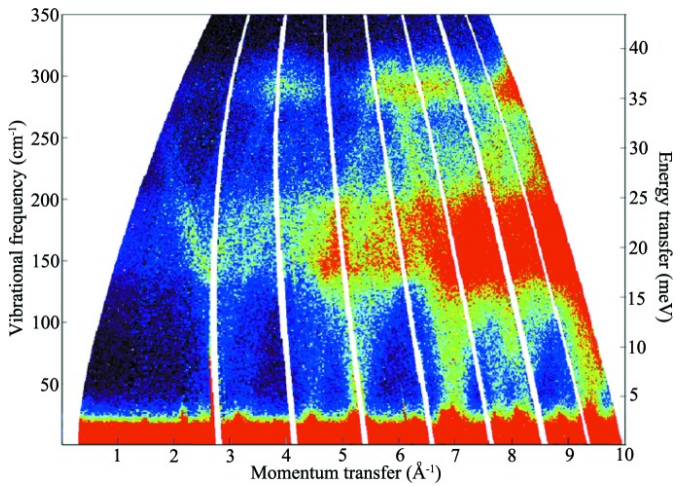
S. Mu et al. Phys. Rev. Res., **4**, 013067 (2022)



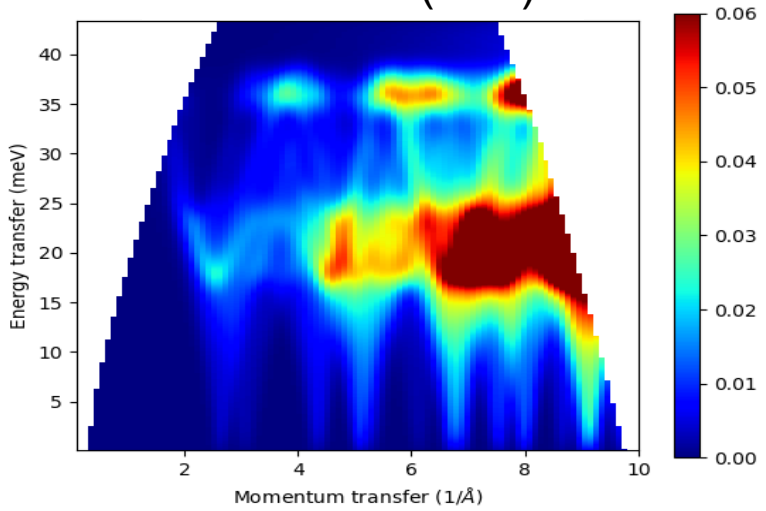


Coherent effects in powder spectra: aluminum

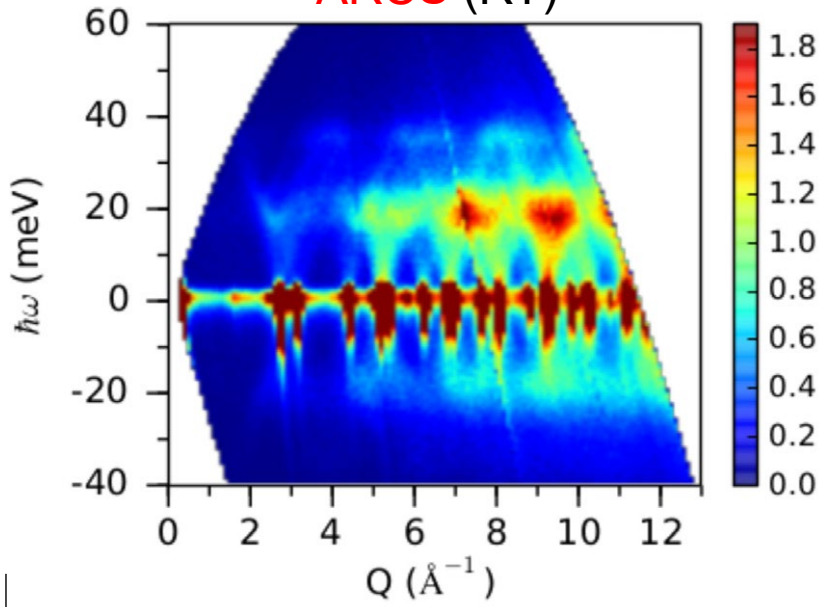
MARI (10K)



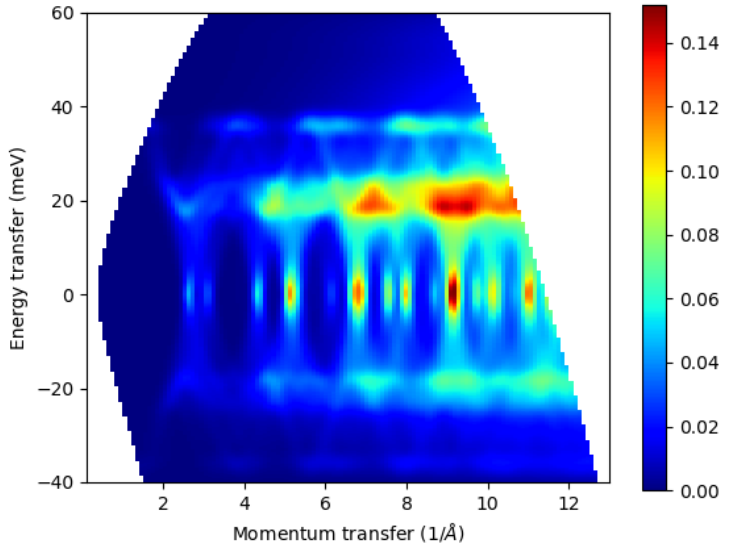
OCLIMAX (10K)



ARCS (RT)

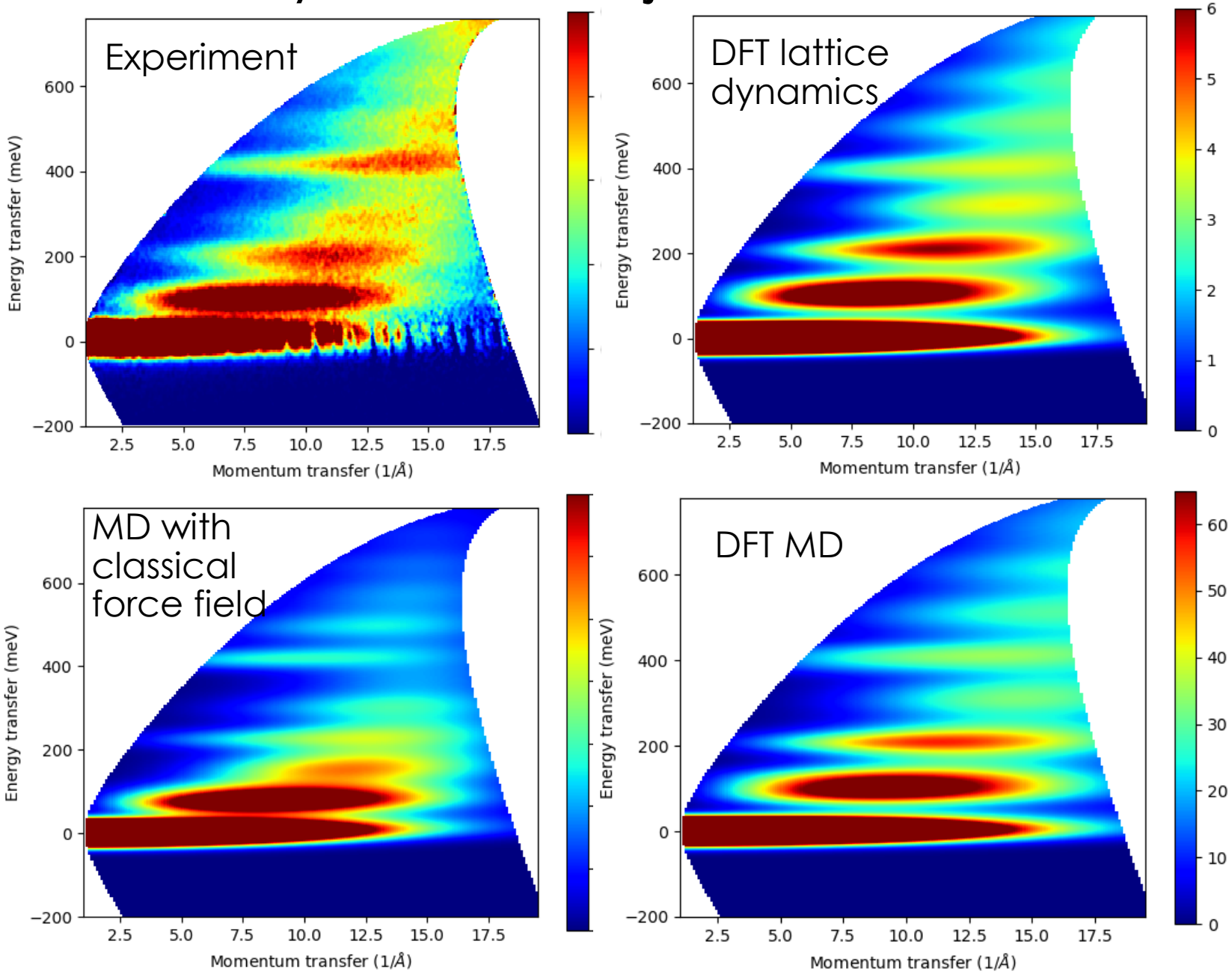


OCLIMAX (RT)



MARI data from: D. L. Roach et al. J. Appl. Cryst. **46**, 1755-1770 (2013).
ARCS data from: Lin et al. Nucl. Instrum. Methods Phys. Res., Sect. A 2016, 810, 86–99.

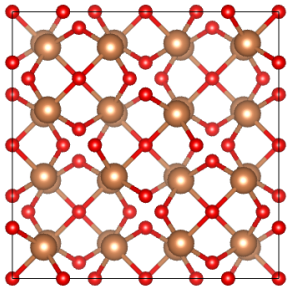
Molecular dynamics trajectories to INS: ice Ih



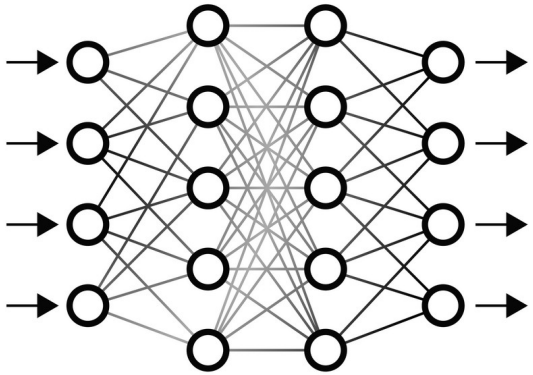
- ✓ Lattice dynamics only feasible for small/crystalline systems
- ✓ MD much more efficient for large/complex systems such as amorphous or biological materials
- ✓ MD not limited by harmonic approximation

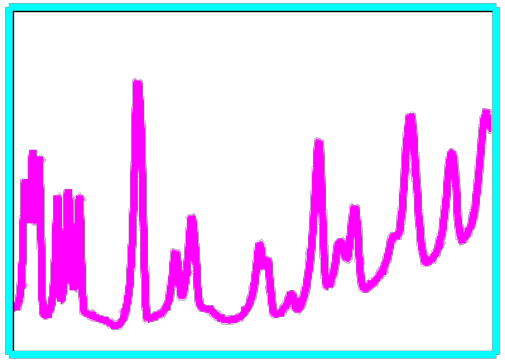
Neural networks connecting structure and neutron scattering data

- Challenge: The modeling is not easy enough for users
  - Computing resources (hardware, software)
  - Expertise (learning curve)
- Can we bypass the modeling step altogether?



Atomic structure

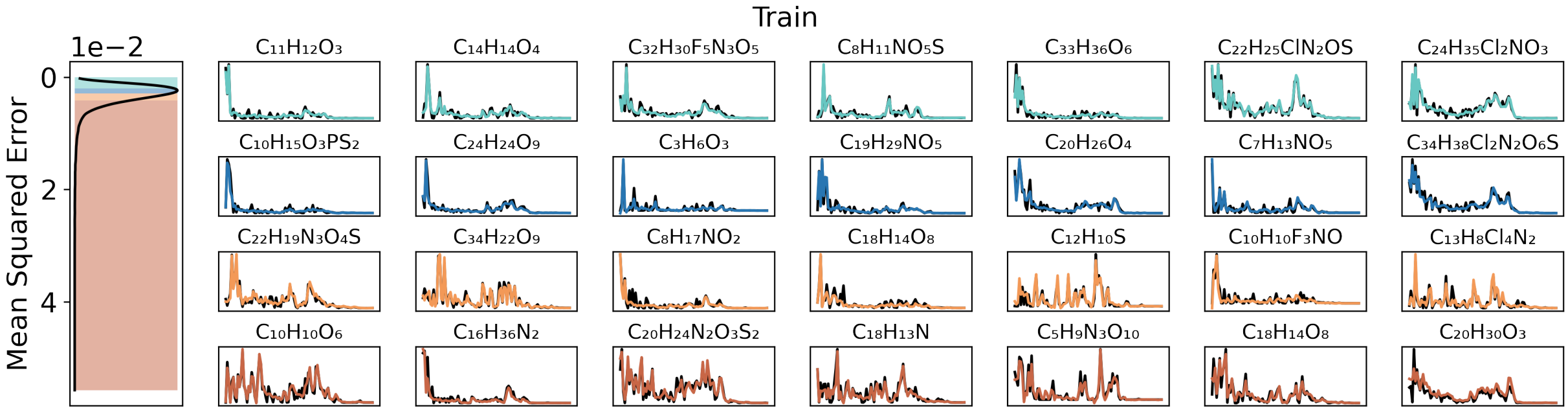




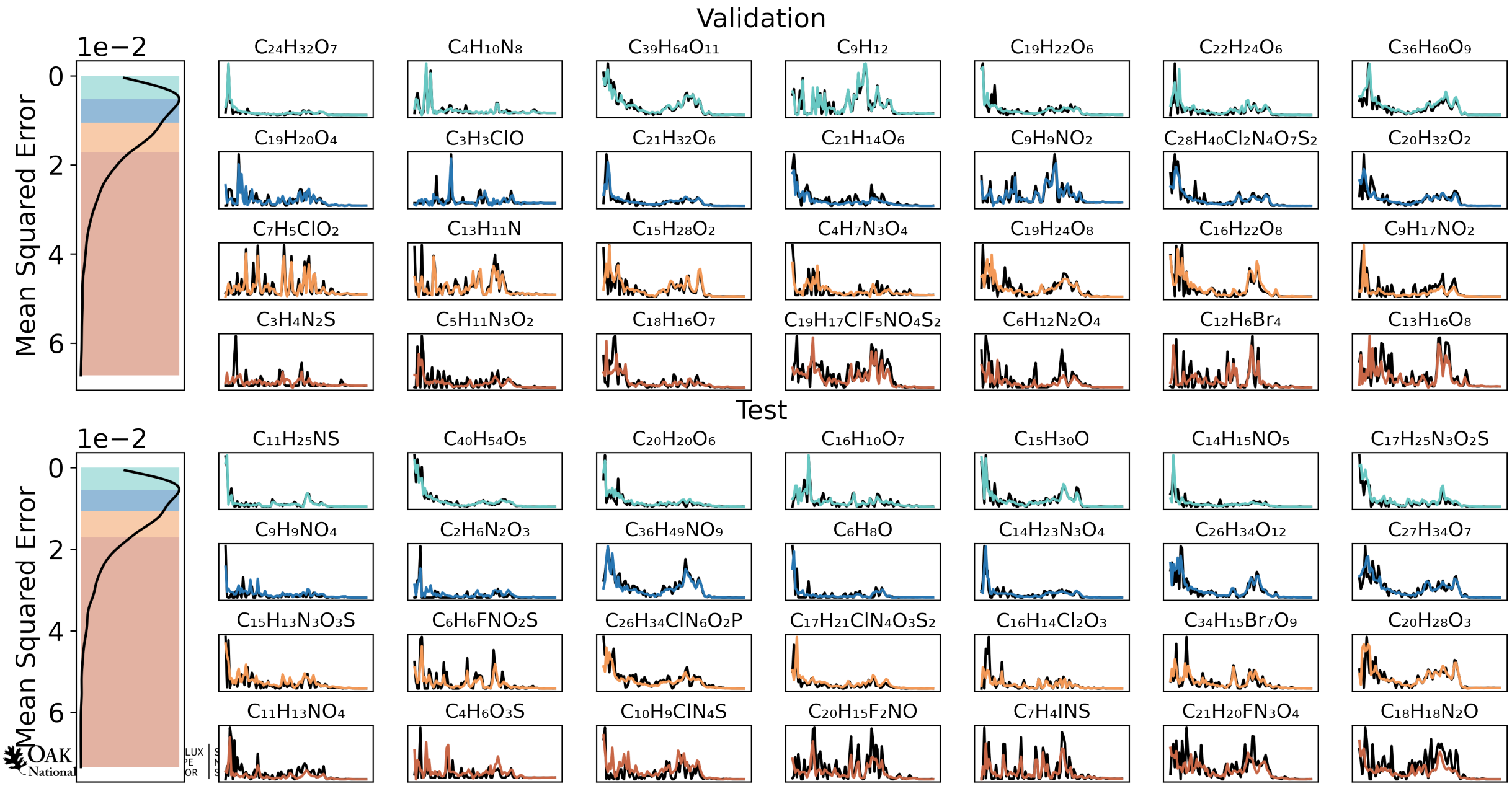
Neutron scattering spectra

Direct prediction from structure to spectra

- PubChem Organic Chemicals (~45,000 molecules, 90% training, 5% validation, 5% testing)
- Simulated INS spectra were generated using Gaussian and OCLIMAX (80~2000cm^{-1}, 97 data points)



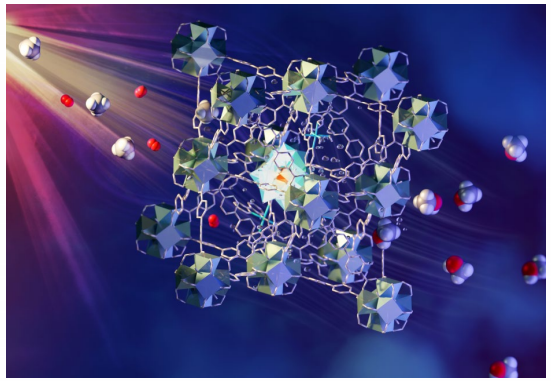
Direct prediction from structure to spectra



Applications

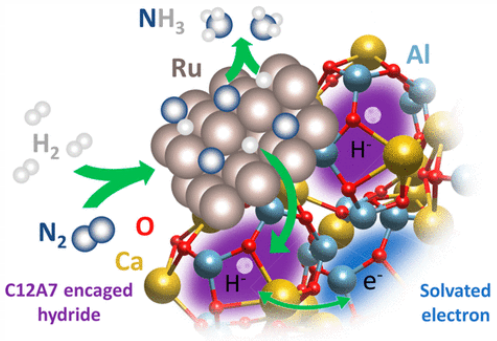
Metal-organic framework

- Strong interactions between methane molecules and mono-iron-hydroxyl sites in a MOF are revealed, which lead to weakened C-H bonds, facilitating methane to methanol conversion.
  - B. An et al., *Nature Materials* (2022)



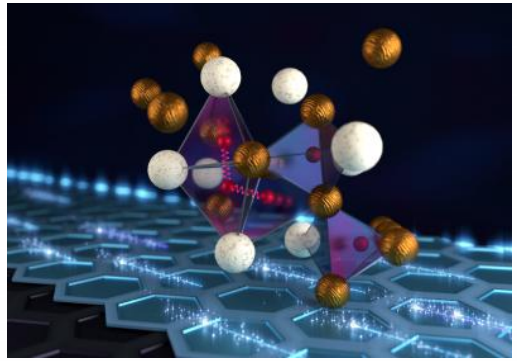
Nano-catalyst

- The reactive species involved in ammonia synthesis over Ru/C12A7 electride catalysts is surface adsorbed hydrogen, not encaged hydrogen.
  - Kammert J. et al. *JACS*, **142**, 7655-7667 (2020)



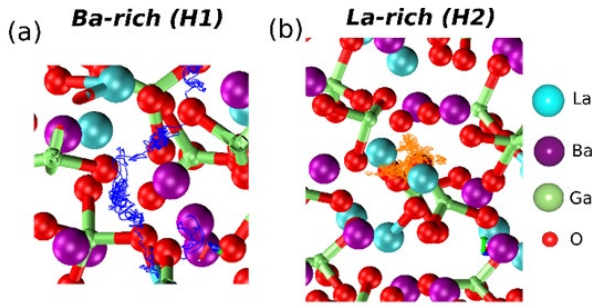
Complex hydride

- Unexpected short H-H distance is revealed in a metal alloy hydride by neutron scattering and large-scale parallel simulation. The anomaly has implications on high temperature superconductivity.
  - Borgschulte et al., *PNAS* **117**, 4021 (2020)



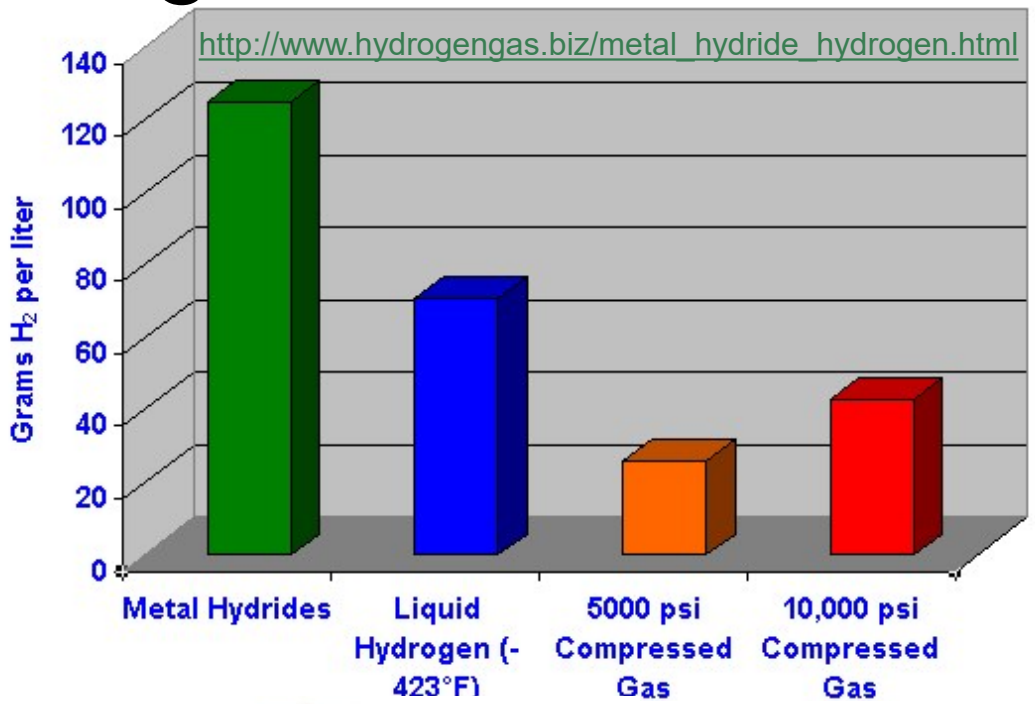
Ionic conductor

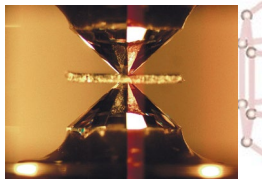
- The local structure origin underlying the proton conductivity is determined in an electrolyte material for solid-oxide fuel cells, guiding the design of novel ionic conductors.
  - Cheng et al., *J. Mater. Chem. A* **5**, 15507 (2017)

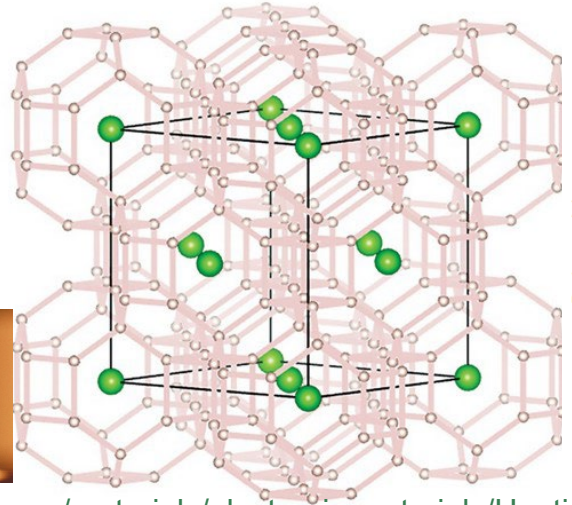


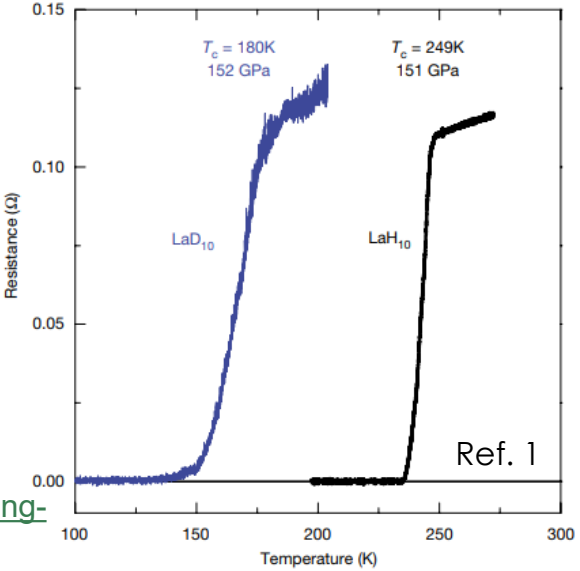
Metal hydrides: why putting hydrogen in metals?

- Hydrogen storage
  - Mg_2NiH_4, $LaNi_5H_5$, $NaAlH_4$
  - Reversibility at desired T/P
- High Tc superconductors
  - LaH_{10} (250K, 150GPa)[1]
  - YH_{10} (~300K, 250GPa, predicted[2])
  - Weak covalent bonds between H
- The Switendick criterion
  - H-H distance > 2.1 Å under ambient pressure[3]





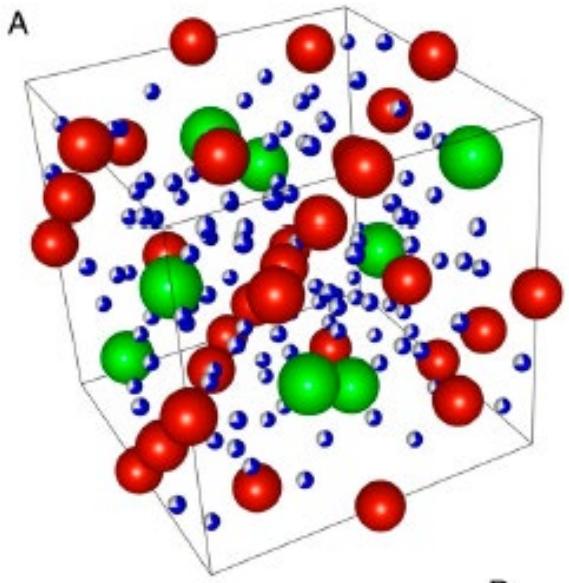




https://cen.acs.org/materials/electronic-materials/Hunting-next-high-temperature-superconductor/96/i39

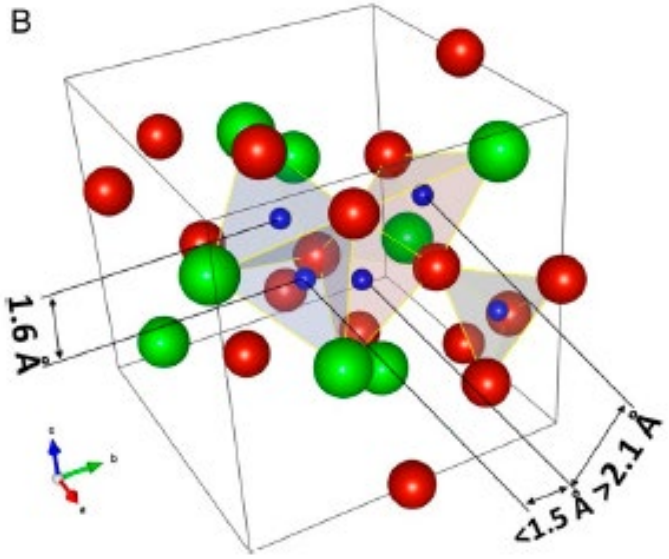
1. A. P. Drozdov et al. Nature 569, 528–531 (2019).
2. H. Liu et al. PNAS 114, 6990 (2017).
3. A. C. Switendick, Z. Phys. Chem. 117, 89–112 (1979).

The mysterious peak at high H concentration

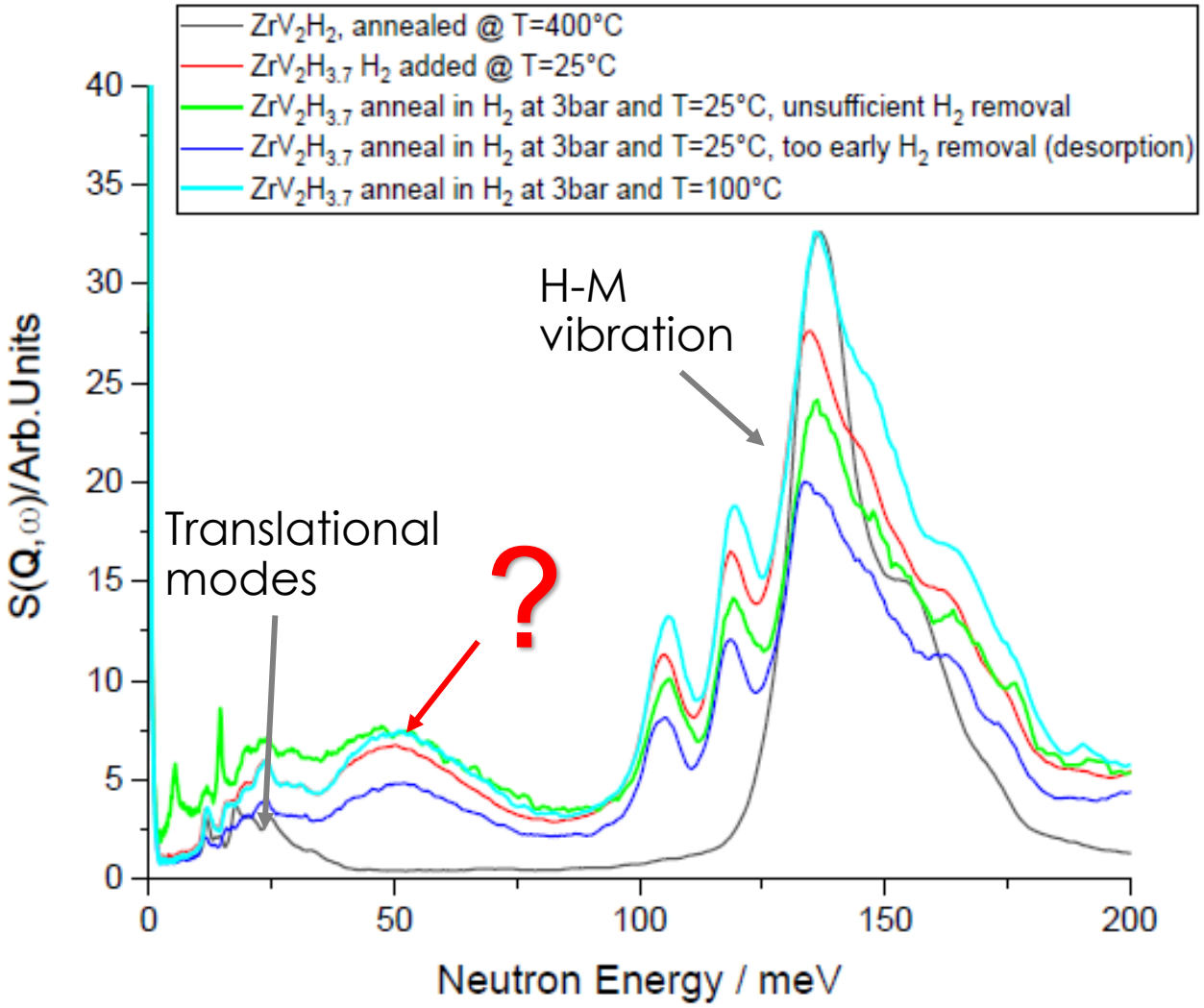


ZrV2Hx (0≤x≤4):
V: red
Zr: green
H: blue

Possible H sites in ZrV2Hx:
- 32e sites, 3V+1Zr (^{T}H)
- 96g sites, 2V+2Zr (^{O}H)
- 8a sites, 4V (unstable)



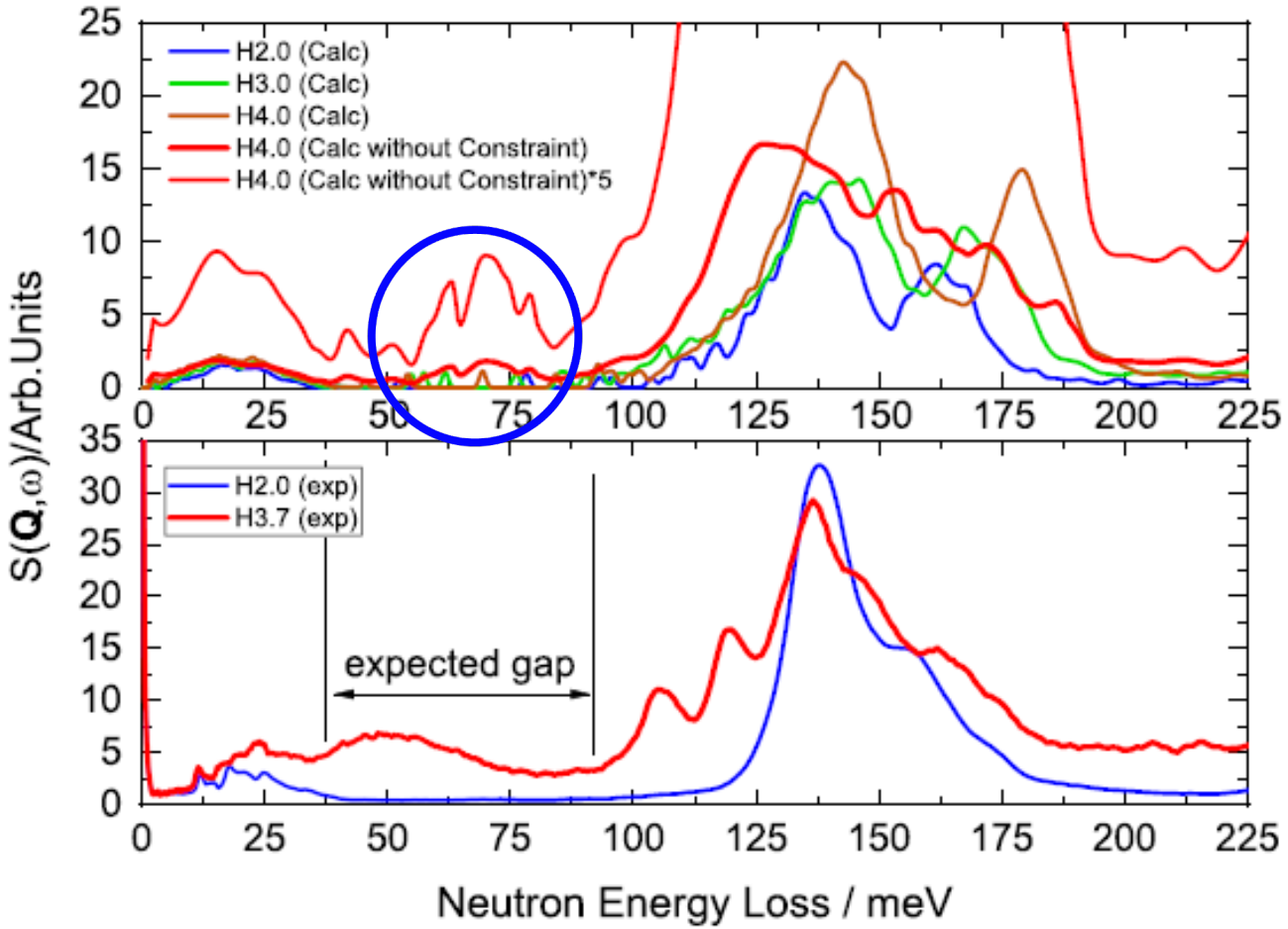
Possible H-H distances in ZrV2Hx:
- ^{T}H-^{T}H > 2.1Å
- ^{O}H-$^{O/T}$H ~ 1.6Å

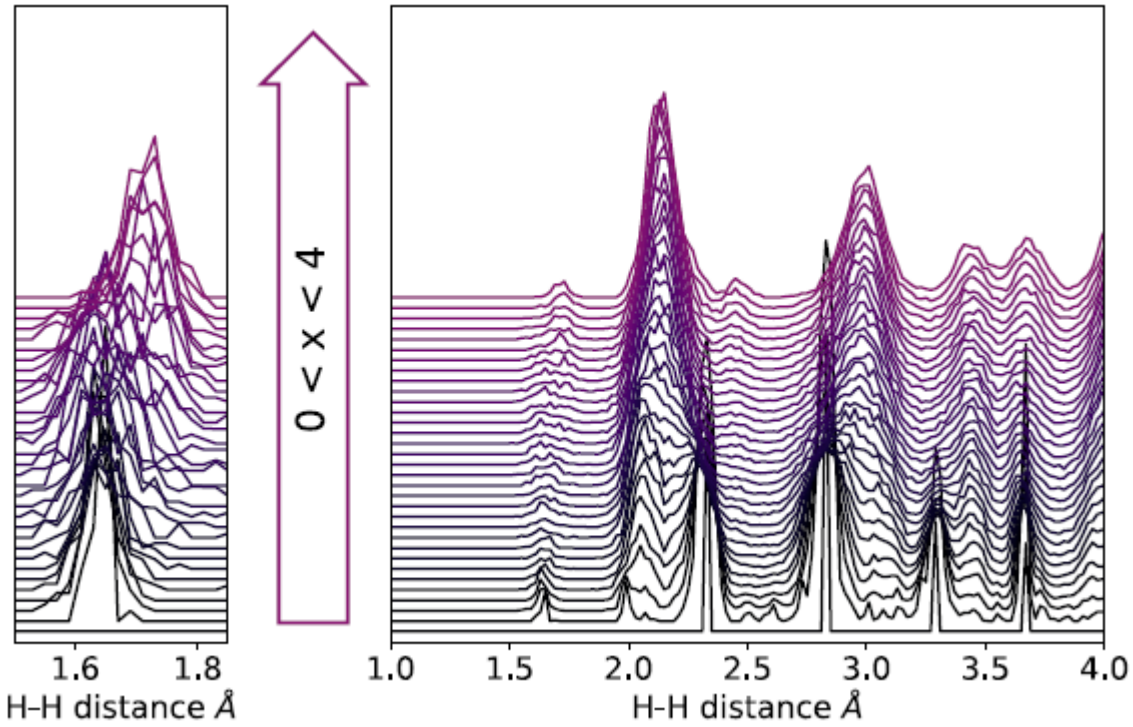


Borgschulte et al., *PNAS* **117,** 4021 (2020)

Violation of Switendick criterion under ambient pressure

- Origin of the unexpected peak



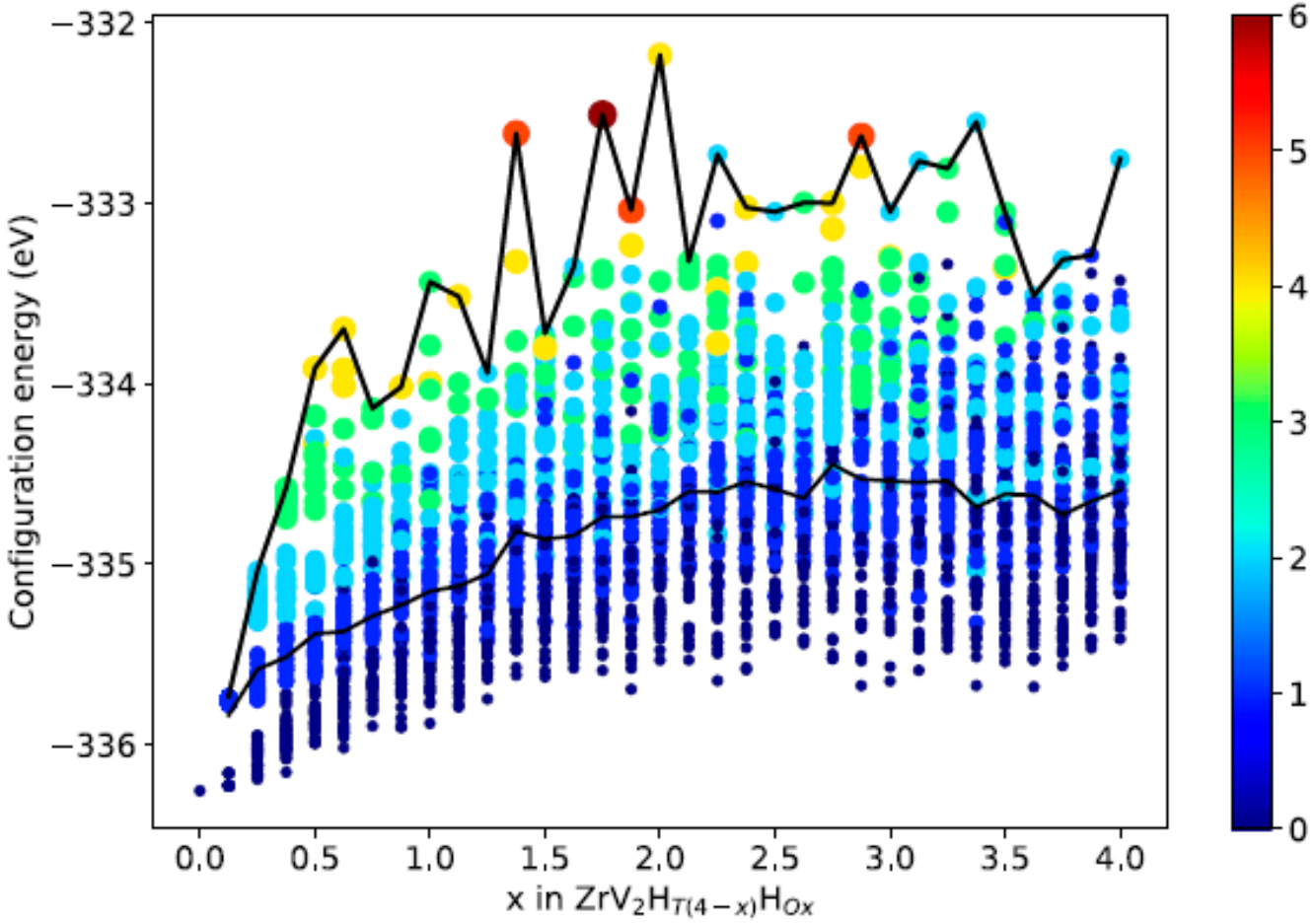


Pair distribution function of $ZrV_2{}^{T}H_{4-x}{}^{O}H_x$ from density functional theory (DFT)

Borgschulte et al., *PNAS* **117,** 4021 (2020)

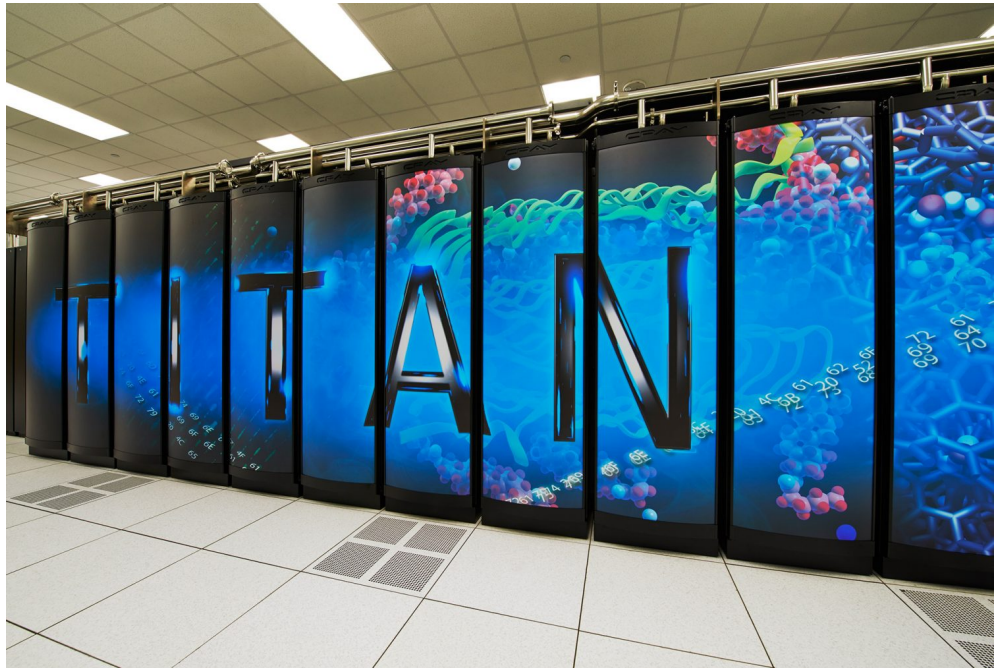
Thermodynamic basis for the violation

- Massive ensemble DFT calculations with TITAN



Potential energy penalty for having at least one violation: ~1.5 kJ/[mol H]

Compensated by configurational entropy



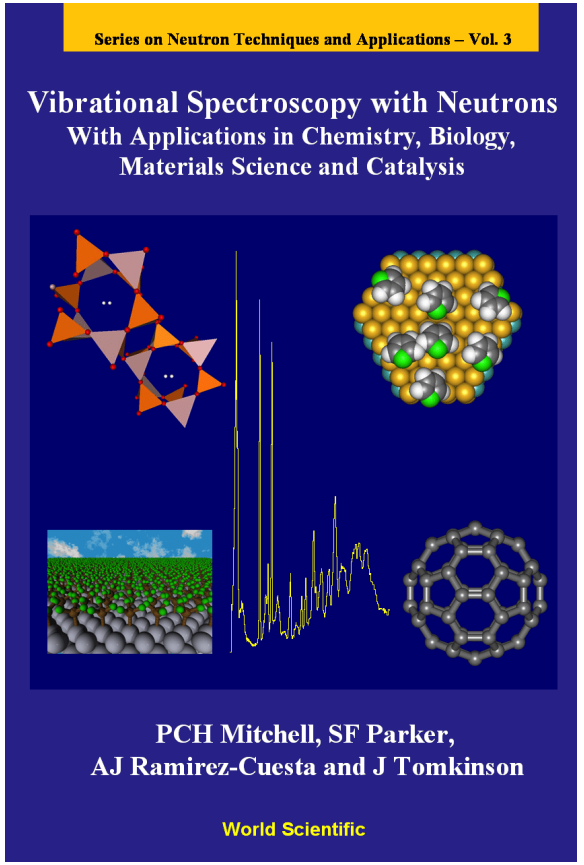
3,200 individual DFT simulations
17% of Titan for nearly a week

Borgschulte et al., *PNAS* **117,** 4021 (2020)

Acknowledgements

- VISION team
- VISION users
- LDRD funding
- CADES and OLCF

References



Stewart F. Parker, Anibal J. Ramirez-Cuesta, Luke Daemen, Vibrational spectroscopy with neutrons: Recent developments, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2018, 190, 518-523

Cheng, Y. Q.; Daemen, L. L.; Kolesnikov, A. I.; Ramirez-Cuesta, A. J. Simulation of Inelastic Neutron Scattering Spectra Using OCLIMAX. J. Chem. Theory Comput. 2019, 15 (3), 1974–1982

https://neutrons.ornl.gov/vision

Questions?

Neutron Vibrational Spectroscopy - Yongqiang Cheng

https://forms.office.com/g/arPm7mpAX2

chengy@ornl.gov