OAK RIDGE National Laboratory

Neutron Vibrational Spectroscopy

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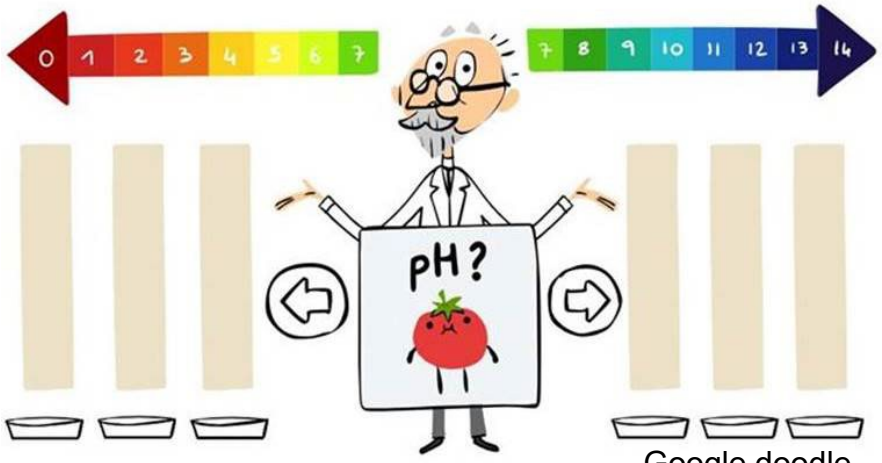
U.S. DEPARTMENT OF ENERGY

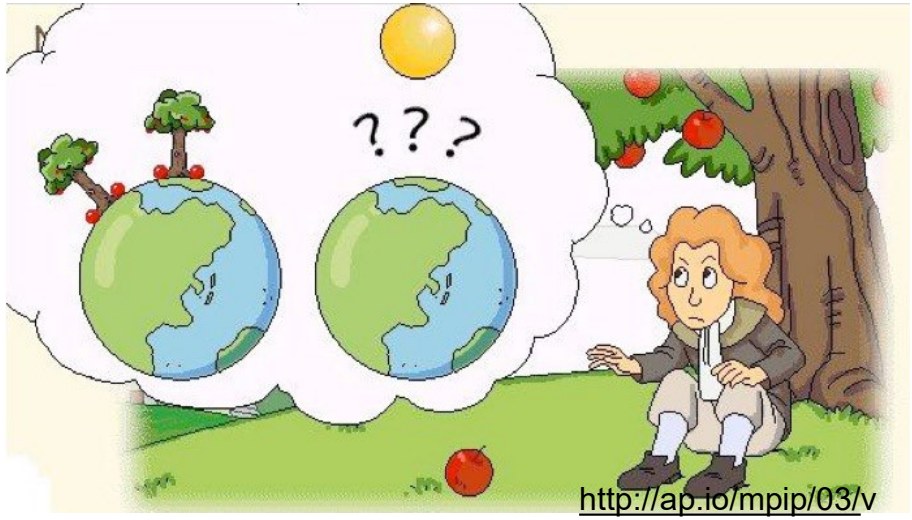
2024 National School on
Neutron and X-ray Scattering

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 and $Å^{-1}$
Indirect geometry instrument	Direct geometry instrument



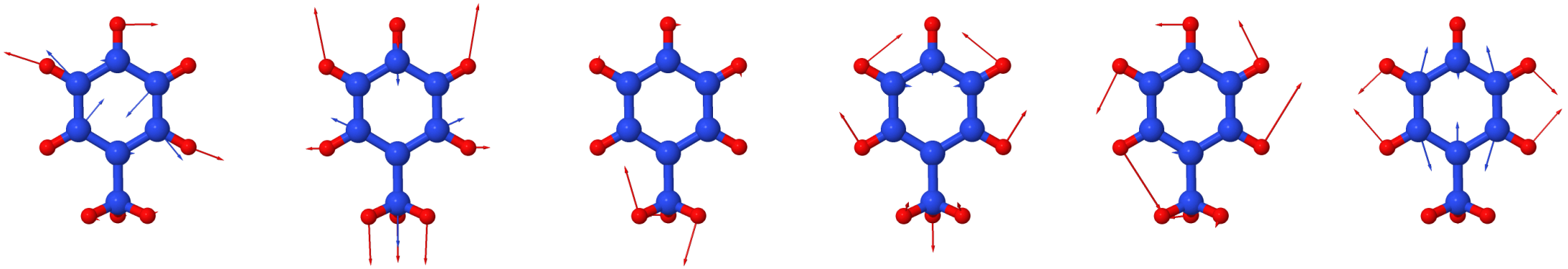
Google doodle



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

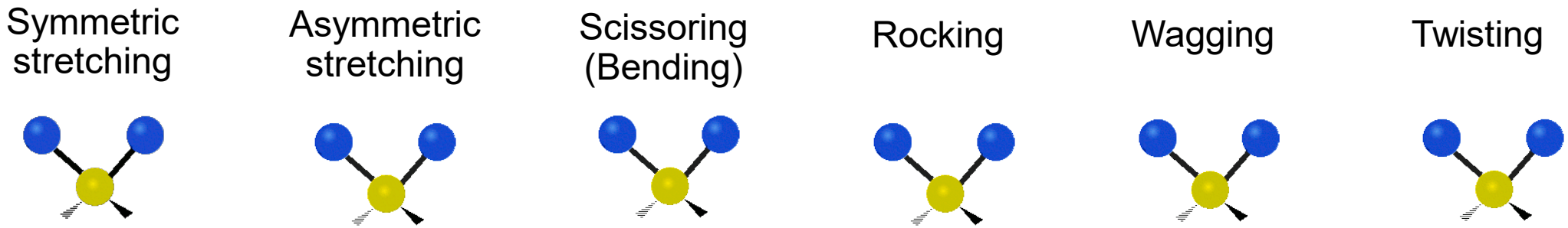
NVS focuses on applications of INS in chemistry. It can be considered a neutron version of Raman/IR spectroscopy

Molecular vibration: the eternal dance of molecules



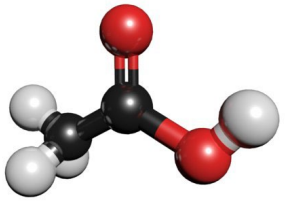
Note: the actual frequency is 40000000000000 faster!

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

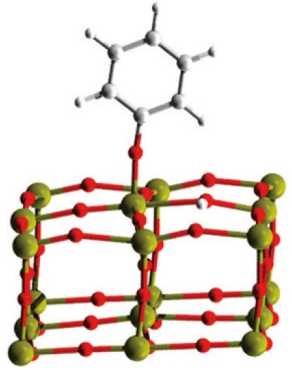


https://en.wikipedia.org/wiki/Molecular_vibration

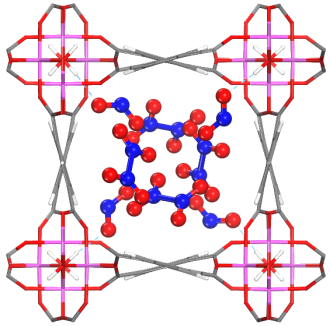
Vibration of molecules in different environment



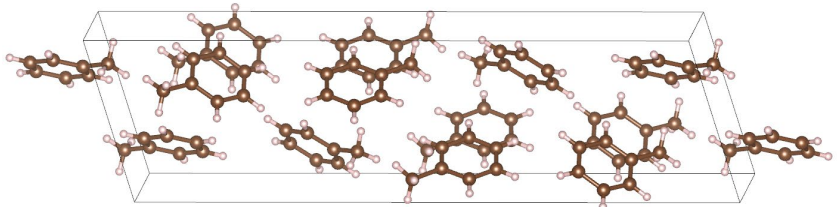
Isolated (gas, non-interacting)



On surface (chemi/physi-adsorbed)



In pores (restricted/confined)

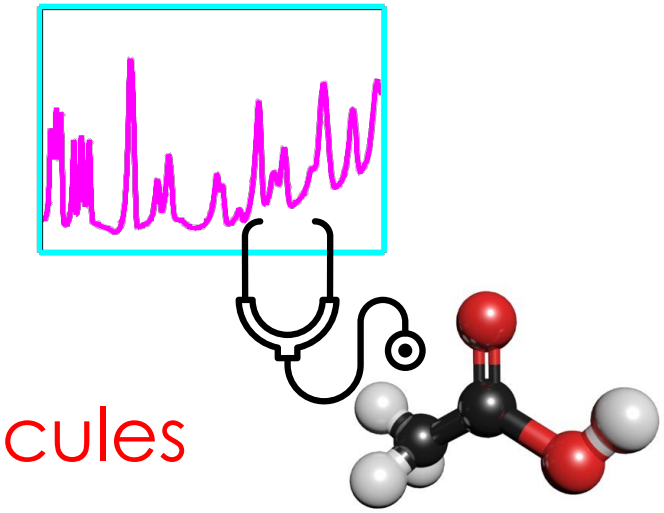


Self-assembled (solid)

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
- Binding site and binding mechanism in a host-guest system
- Charge transfer and ion/dipole interactions
- Thermodynamic properties (free energy, stability, phase diagram, specific heat capacity and conductivity)
- Transport properties (diffusion and relaxation)
- ……

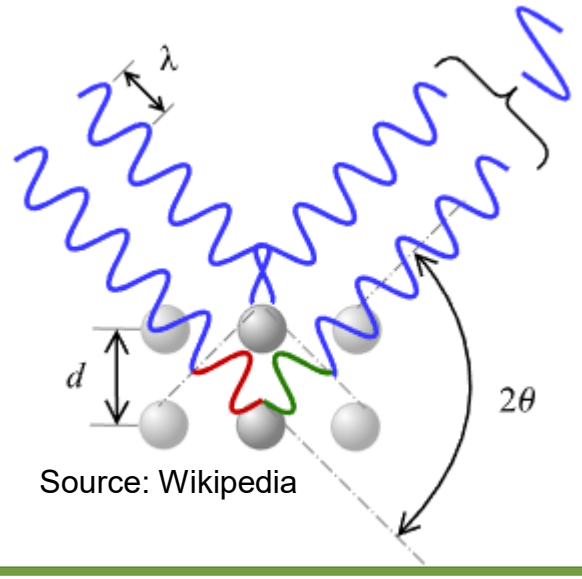


One of the most important vital signs of molecules

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.

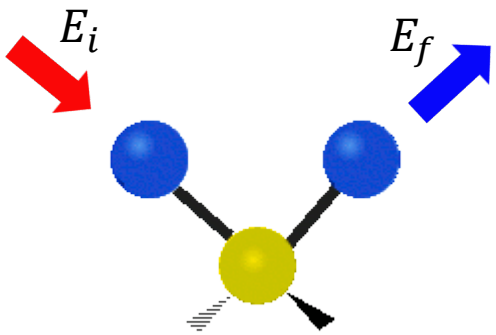
Wavelength
Scattering angle



Source: Wikipedia

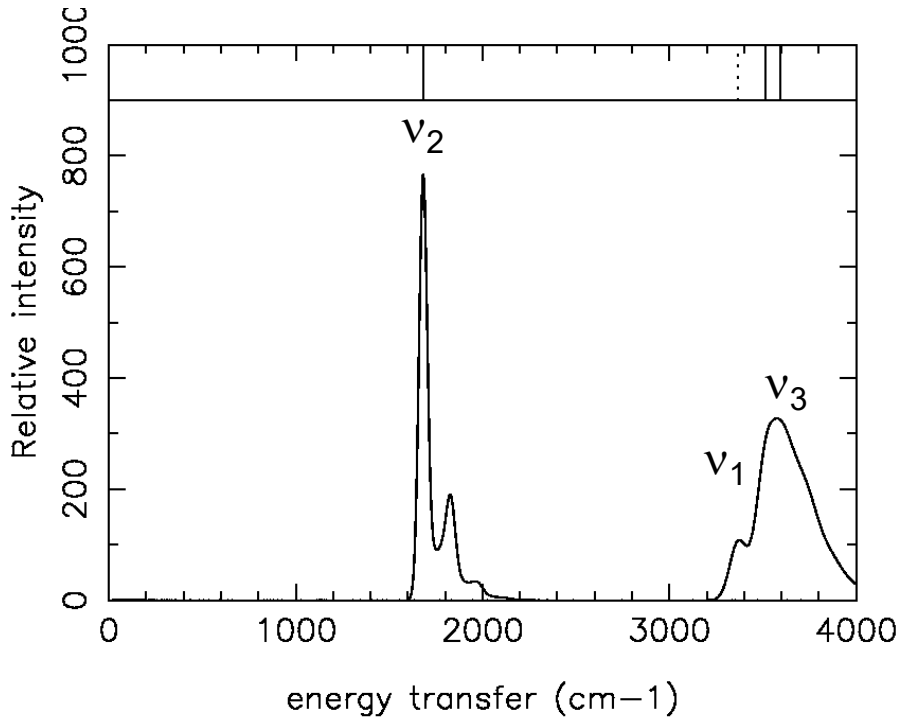
Spectroscopists use (inelastic) scattering of radiation (light, x-ray, neutron,...) to excite vibrational modes. The energy of the radiation is comparable to the energy associated with the vibrational excitations.

Incident energy
Final energy
(Scattering angle)



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

Interpretation of vibrational spectra: peak assignment



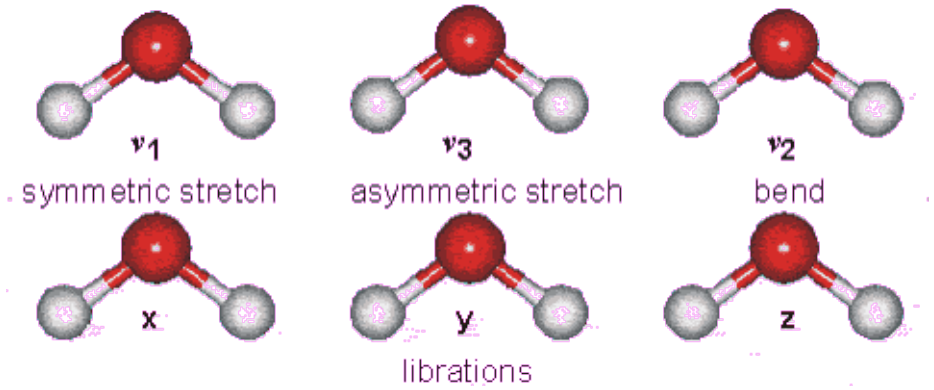
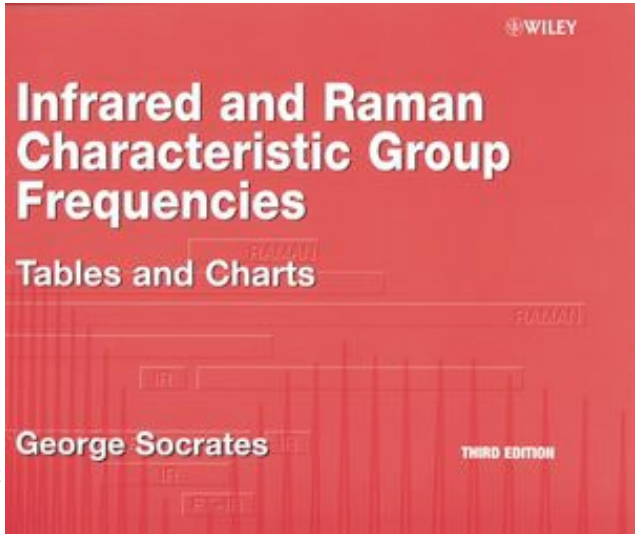


Table 1 Absorption frequencies of some common bonds (shown in bold type)

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)



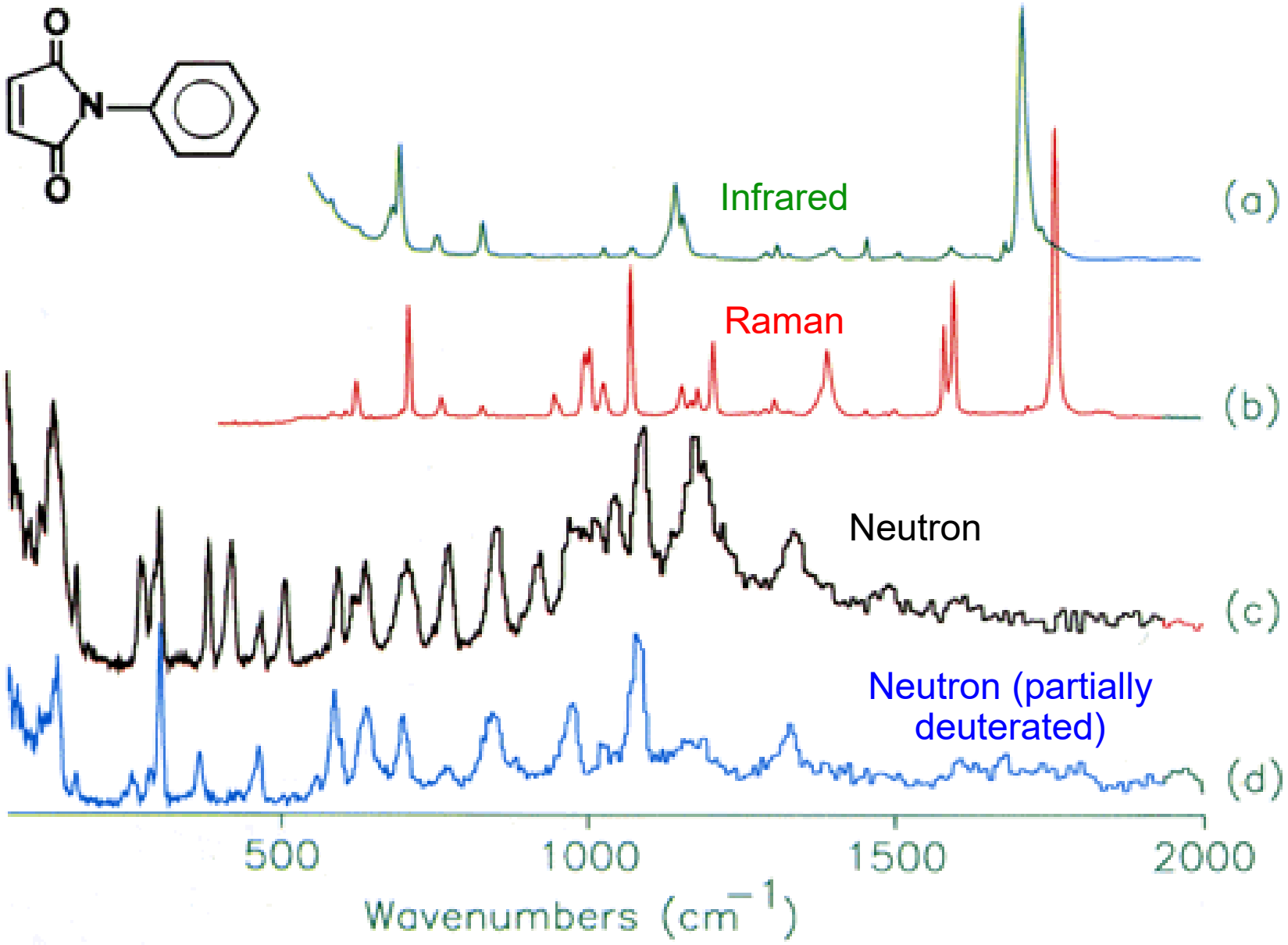
Vibrational spectroscopy with neutrons: pros and cons

VISION (INS/NVS)	Raman/Infrared
Measures dynamics of nuclei (direct)	Measures response of electrons (indirect)
High penetration (bulk probe)	Low penetration (surface probe)
Great sensitivity to H	Cannot always see H
Can see Raman/Infrared-inactive modes	Selection rules apply
Easy access to low energy range (librational and translational modes)	Challenging to see low energy modes (on the order of 100 cm^{-1})
Q trajectories in the (Q,ω) map; averaging over the Brillouin zone	Gamma point only
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

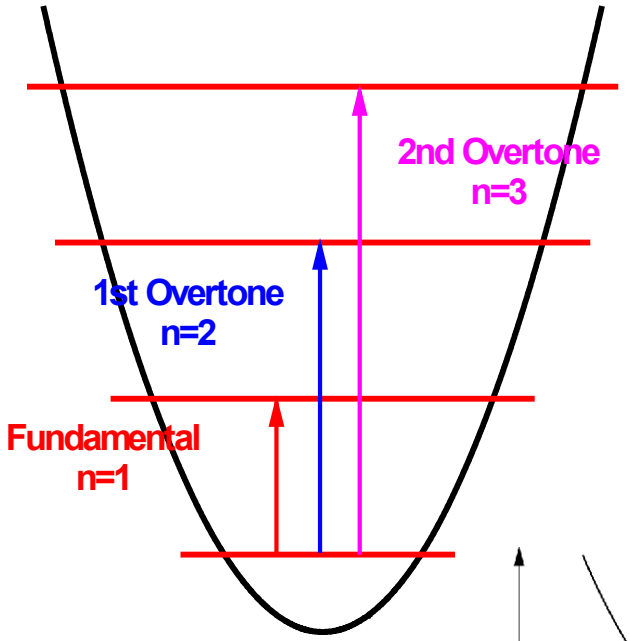
Complementary tools to study molecular vibration

Complementary tools to study molecular vibration

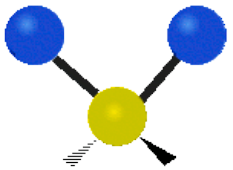


S.F. Parker, *Int.J. Vib. Spect.*, **2**, 1, 6-22 (1998)

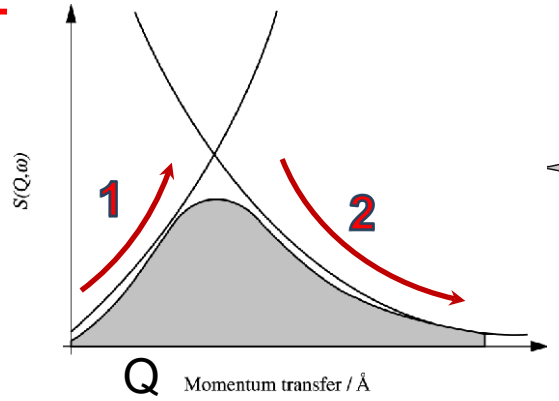
A simple S(Q,ω) map of molecular vibration: key features

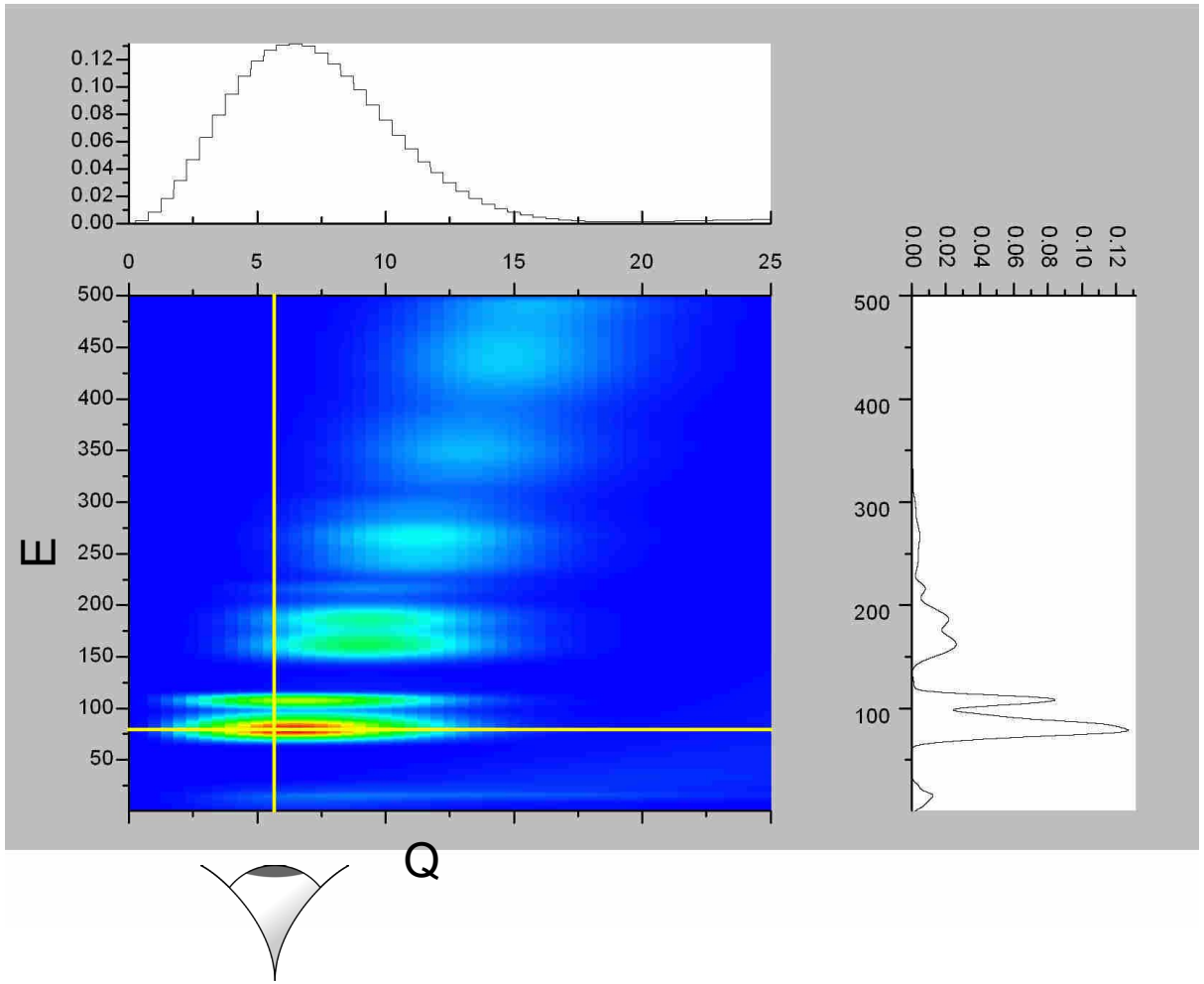


Quantum harmonic oscillator



$$E_n = \hbar\omega_s(n + \frac{1}{2})$$



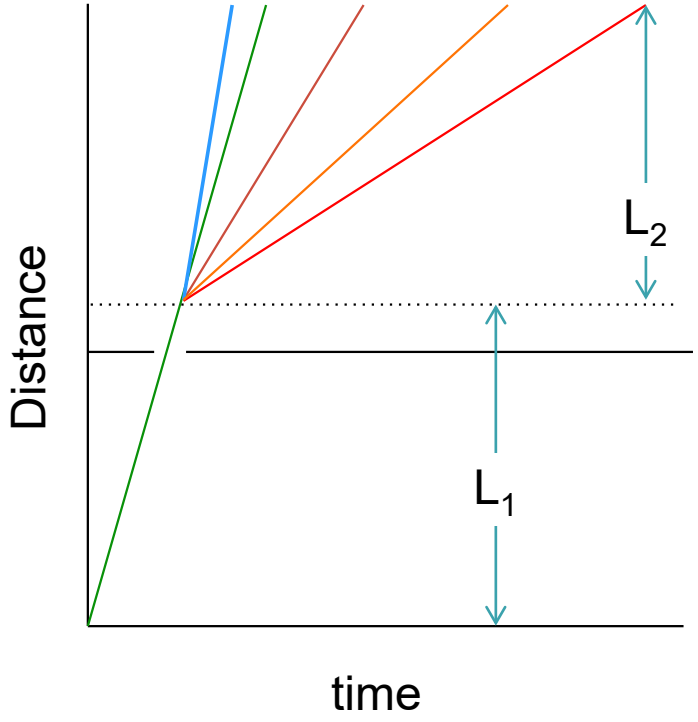


$$S(\boldsymbol{Q}, n\omega_s) = \frac{(\boldsymbol{Q}\cdot\boldsymbol{U}_s)^{2n}}{n!}\exp[-(\boldsymbol{Q}\cdot\boldsymbol{U}_{total})^2]$$

1 2

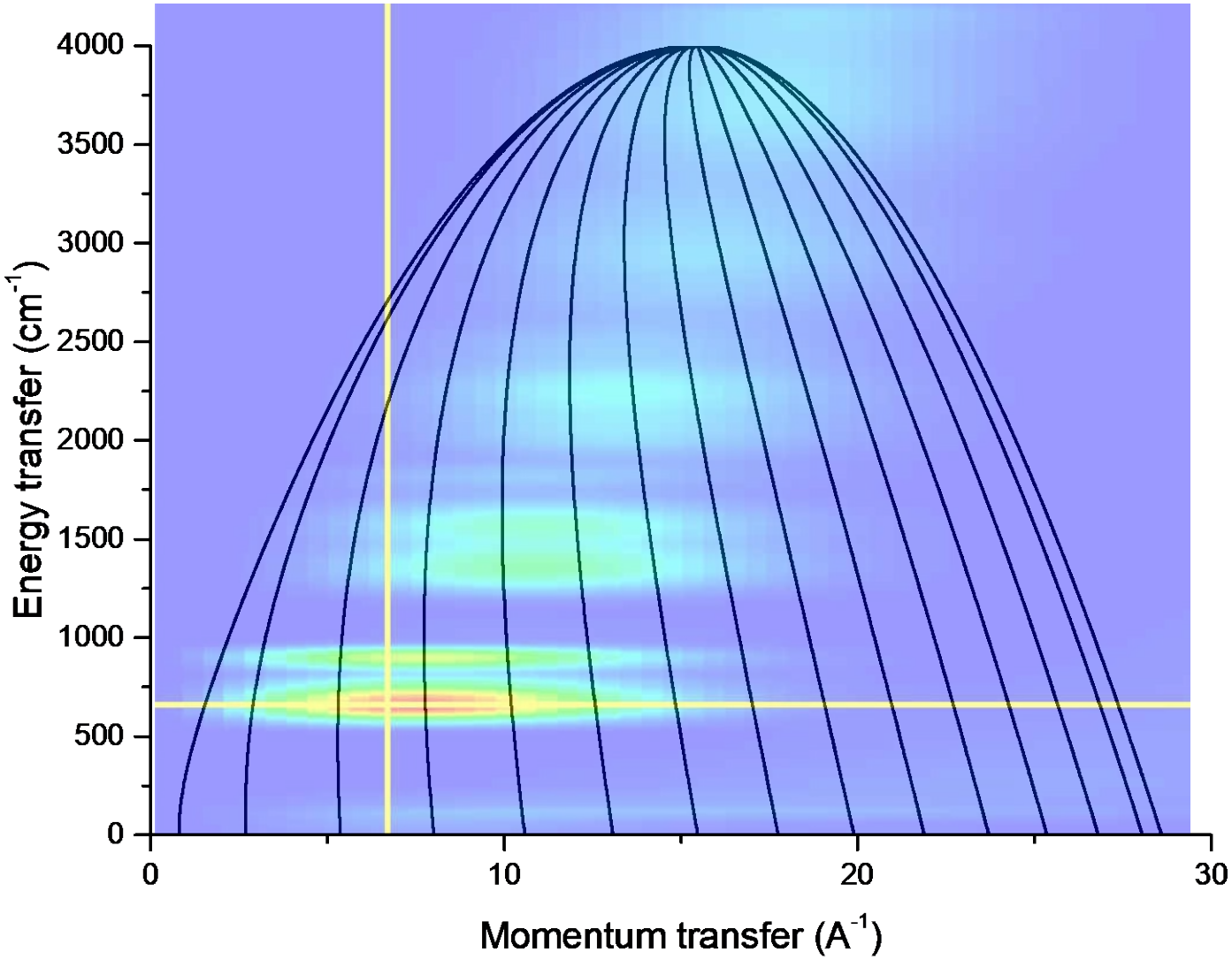
$$\boldsymbol{U}_s = \sqrt{\frac{\hbar}{2m\omega_s}}\boldsymbol{e}_{ds}$$

Choice of instrument for NVS: direct geometry

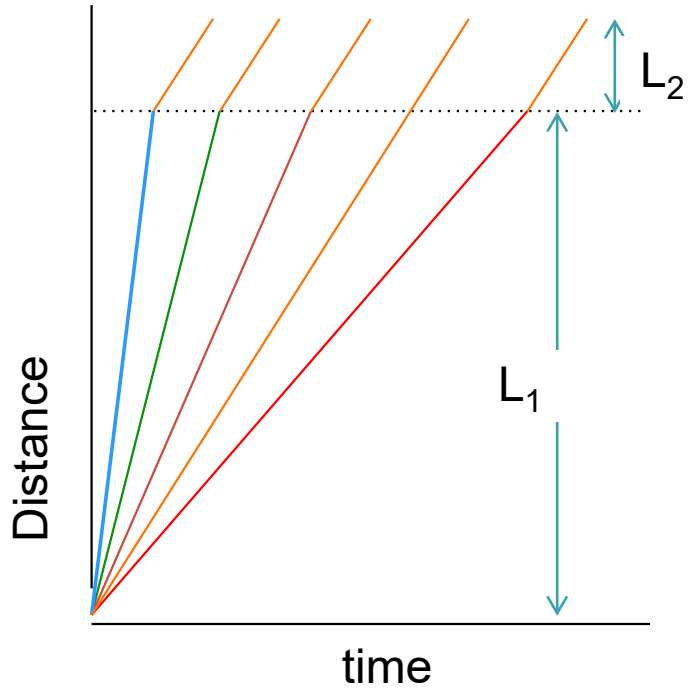


Fixed incident energy, measure final energy and scattering angle.

Examples: ARCS, CNCS, HYSPEC, SEQUOA, MARI

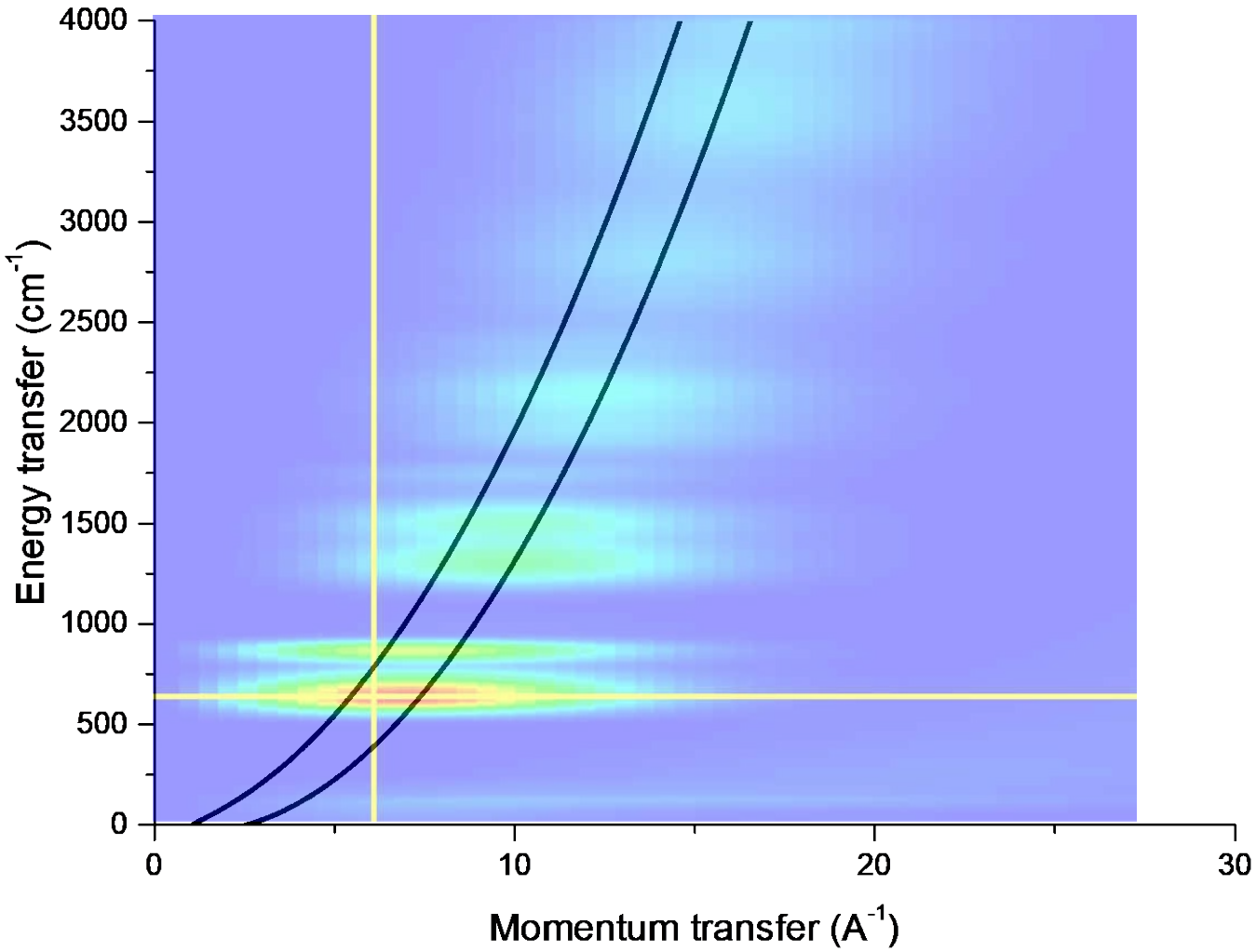


Choice of instrument for NVS: indirect geometry

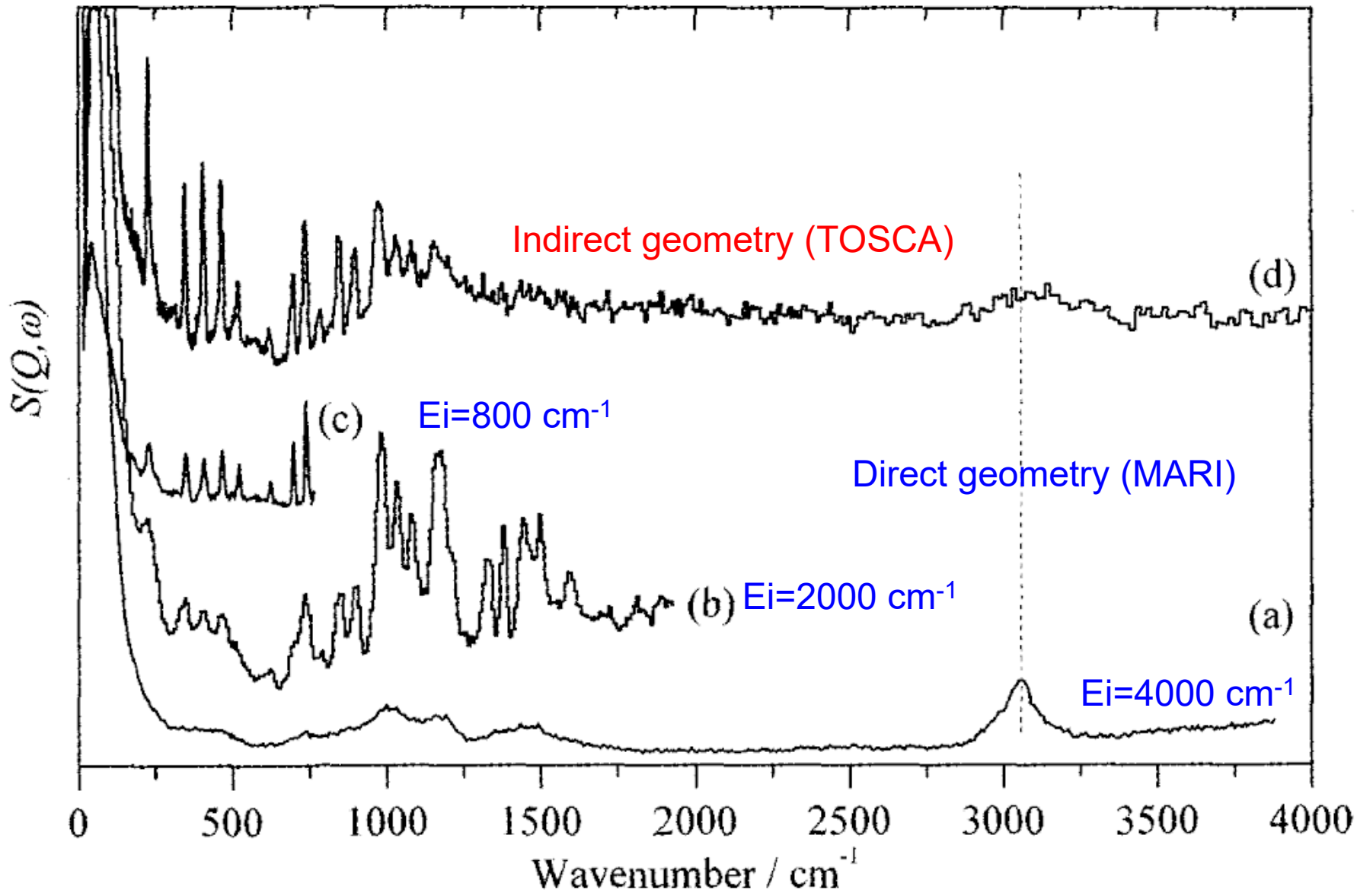


White incident beam,
fixed final energy,
calculate initial energy.

Examples: VISION, TOSCA



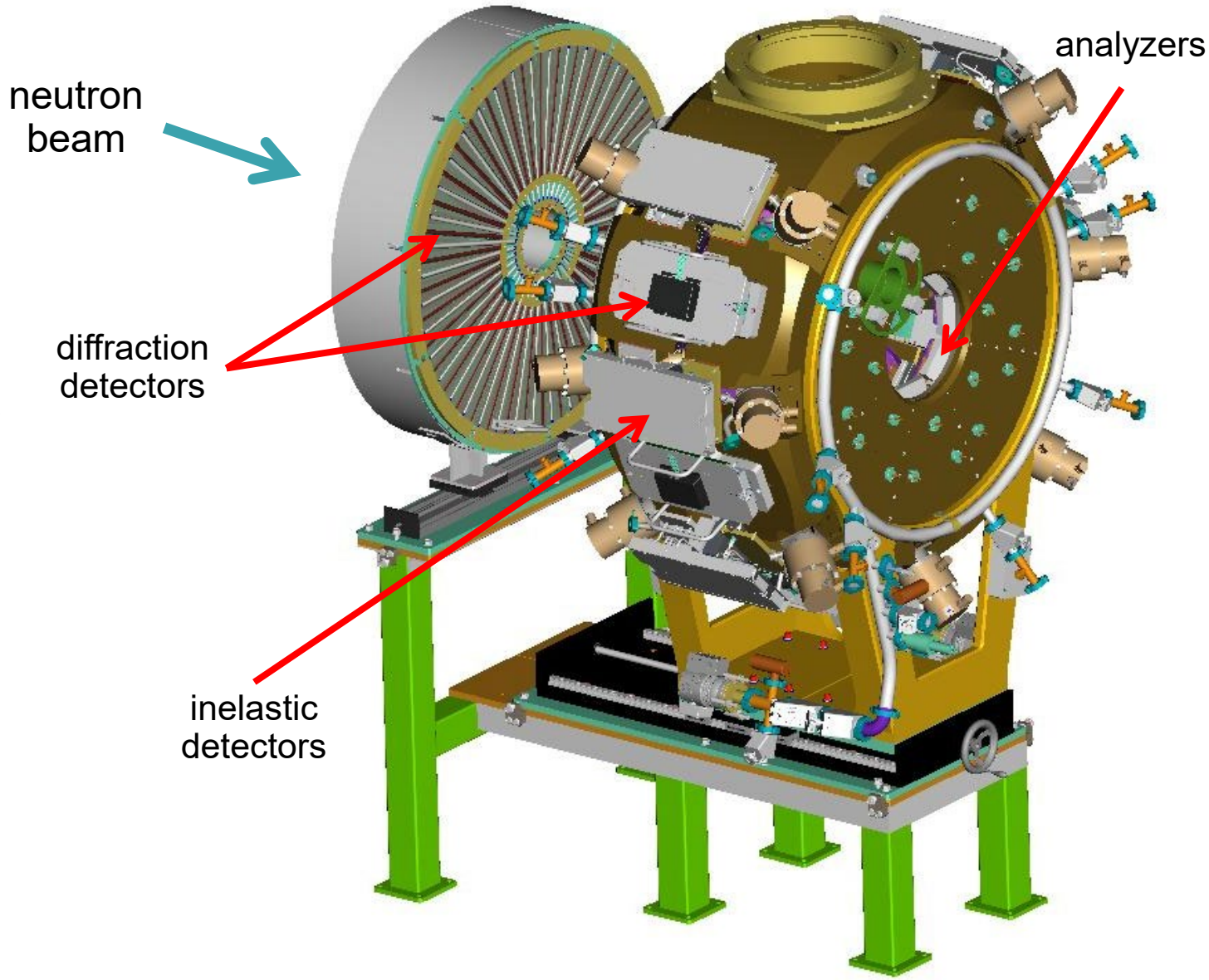
Choice of instrument for NVS: comparison



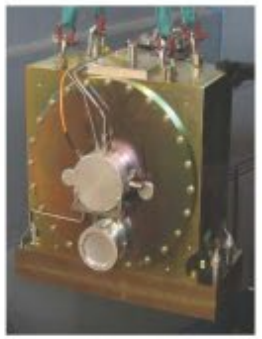
Mitchell et al. Vibration Spectroscopy with Neutrons, World Scientific 2005

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

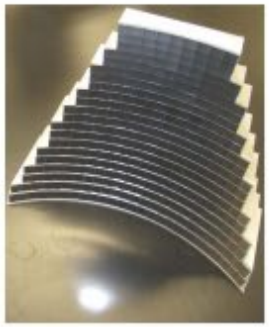

Sec. Shutter


Detector (elastic, backscattering)


Detector (inelastic)

L'

L + L' = constant


Analyzer

90.0°

517.4 mm

L

1136 mm

Moderator

T0

SS

Ø220 mm

~12°

999 mm

~23°

sample

Get Lost Tube

Beamstop

7620 mm

BW

8000 mm

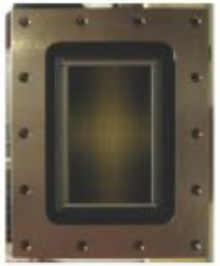
8765 mm

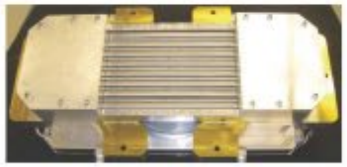
994 mm

635 mm

10.4°

Neutron Guide





Detector (elastic)

318 mm

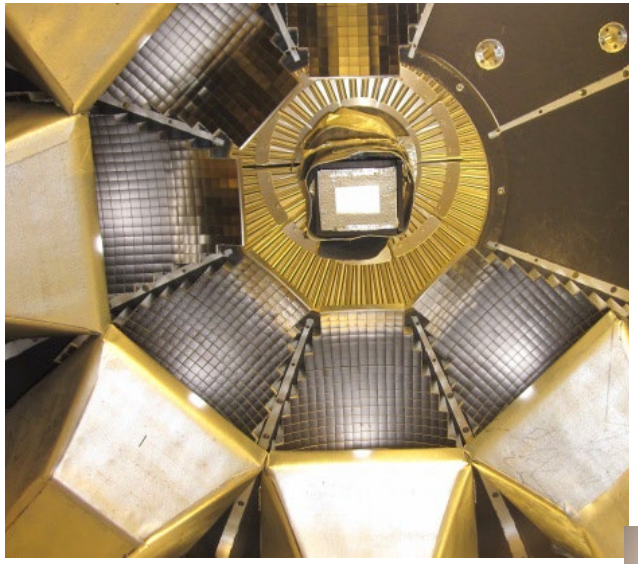
16000 mm

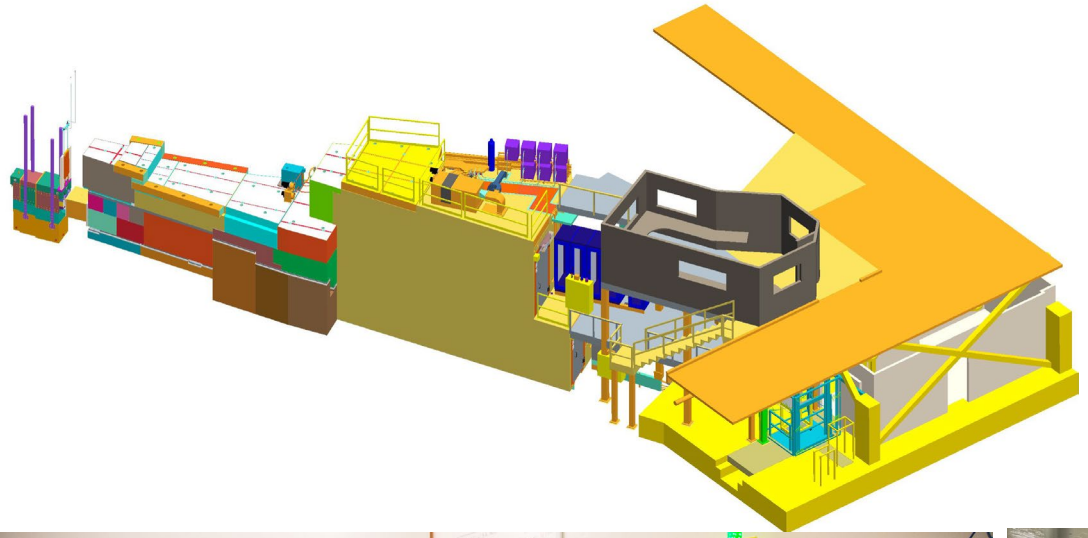
2568 mm

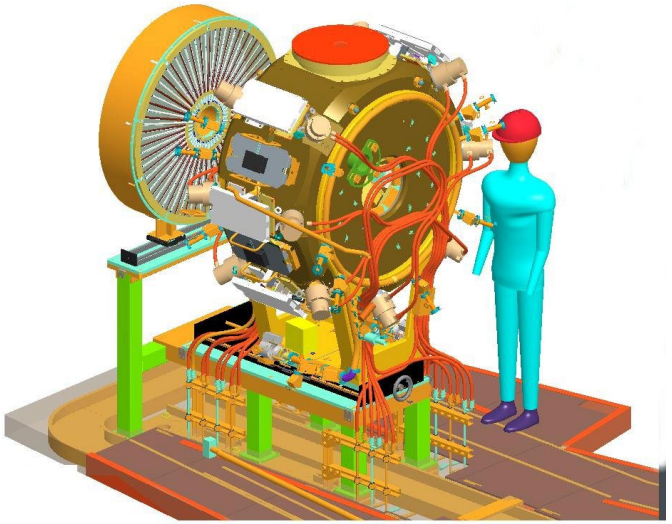
3537 mm

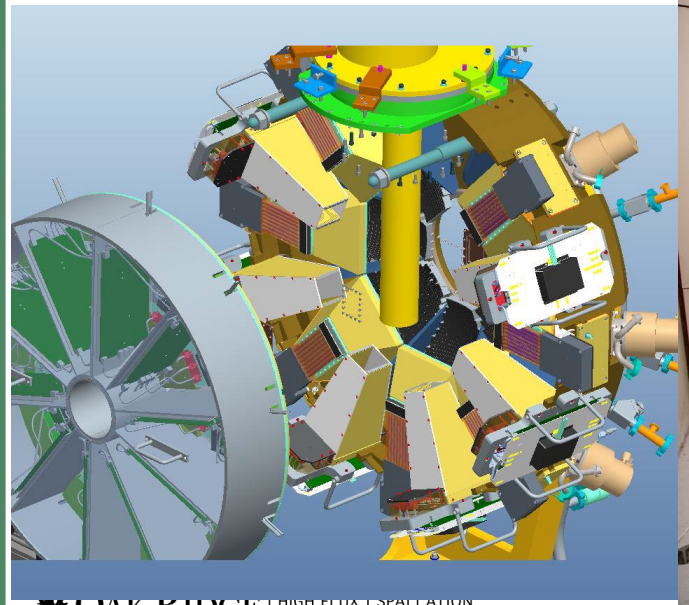
19537 mm

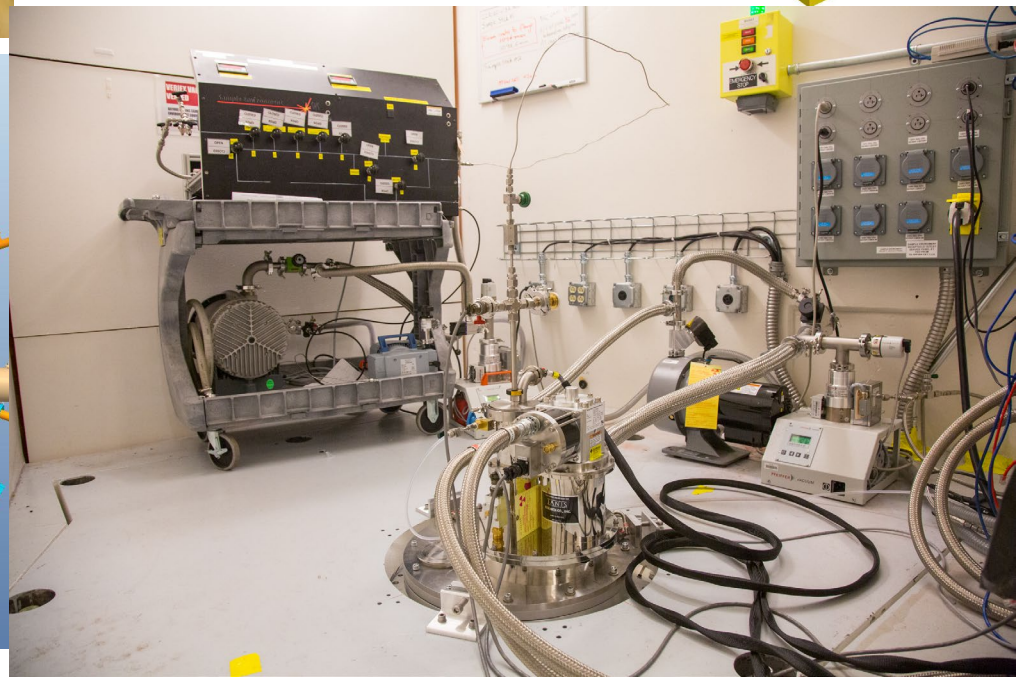
VISION@SNS: a gallery

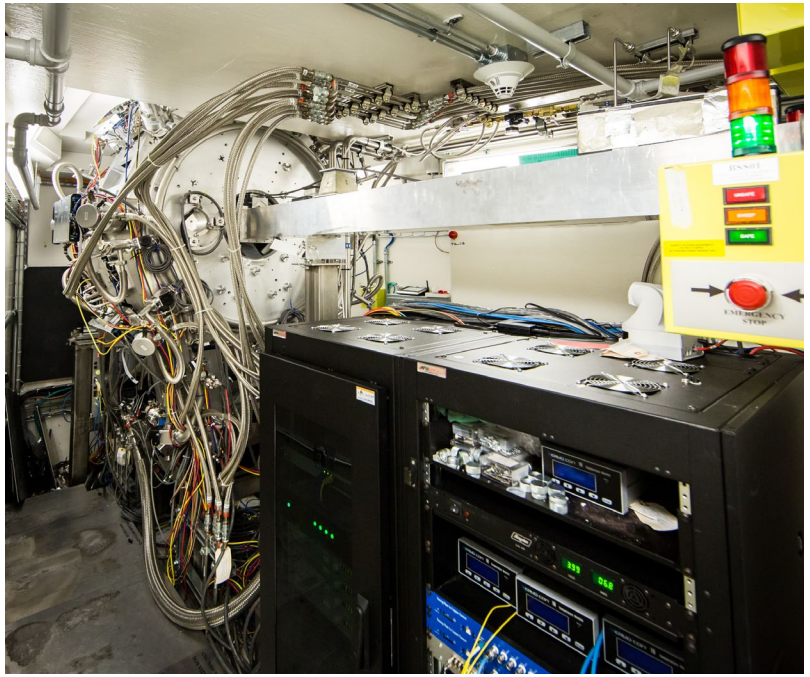




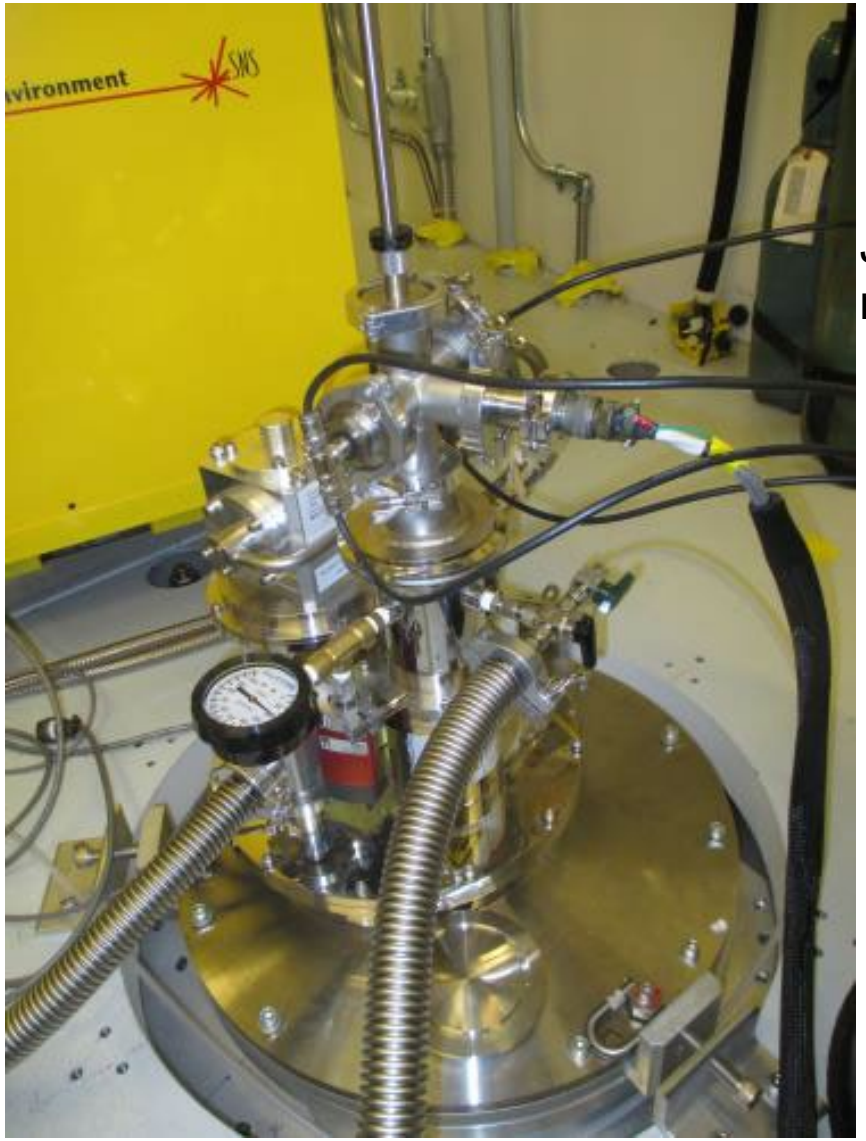




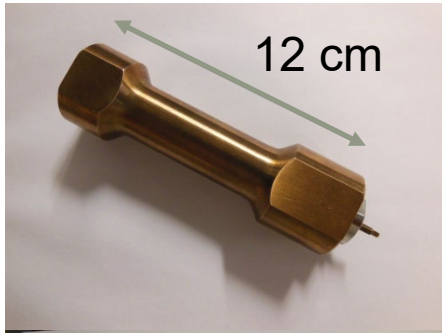


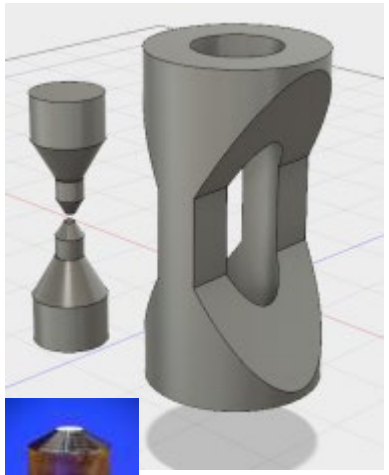


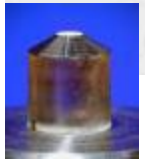
Sample environment at VISION



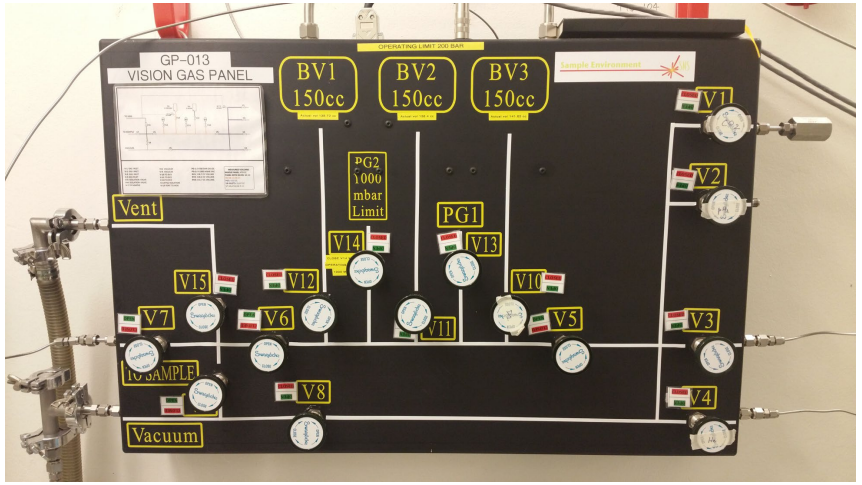
JANIS closed-cycle refrigerator (5-600K)





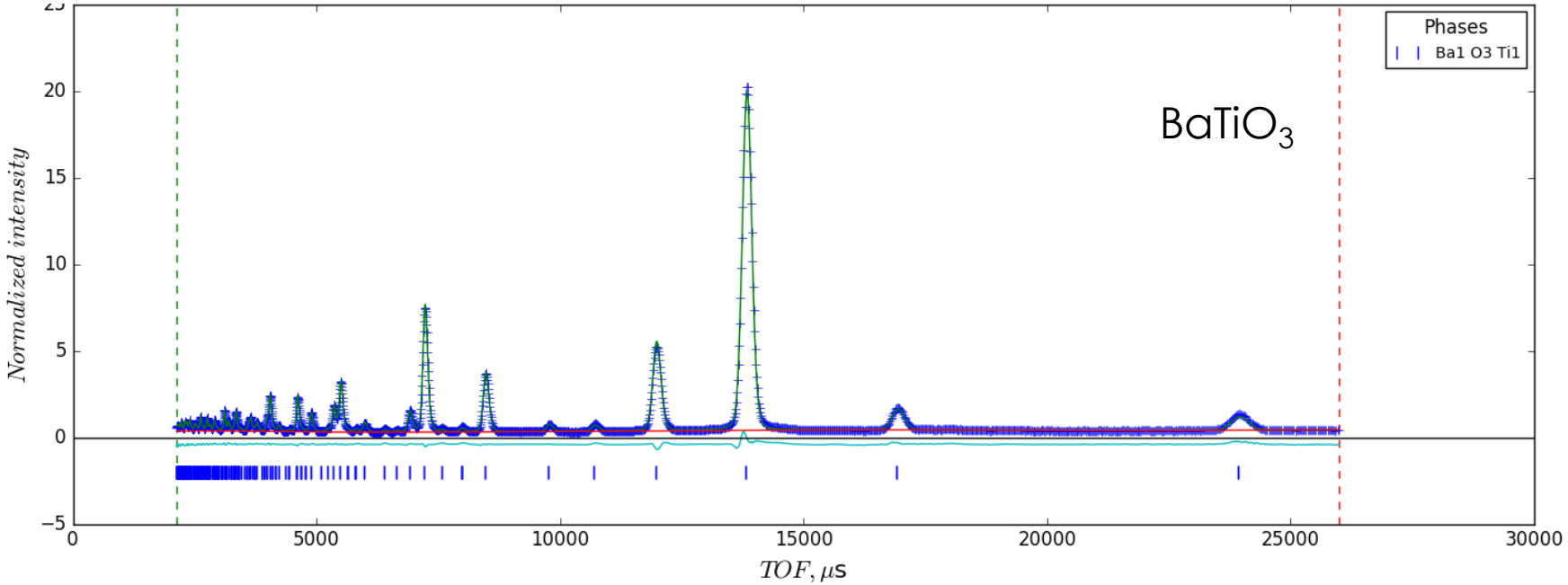


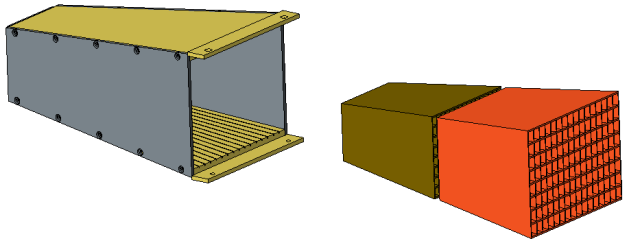
Pressure cells (piston, gas, diamond anvil).

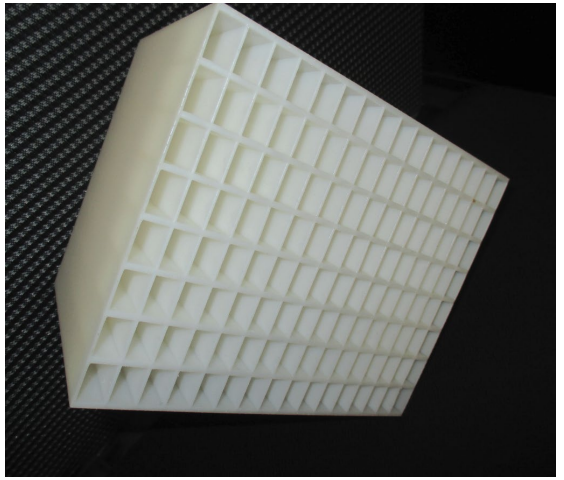


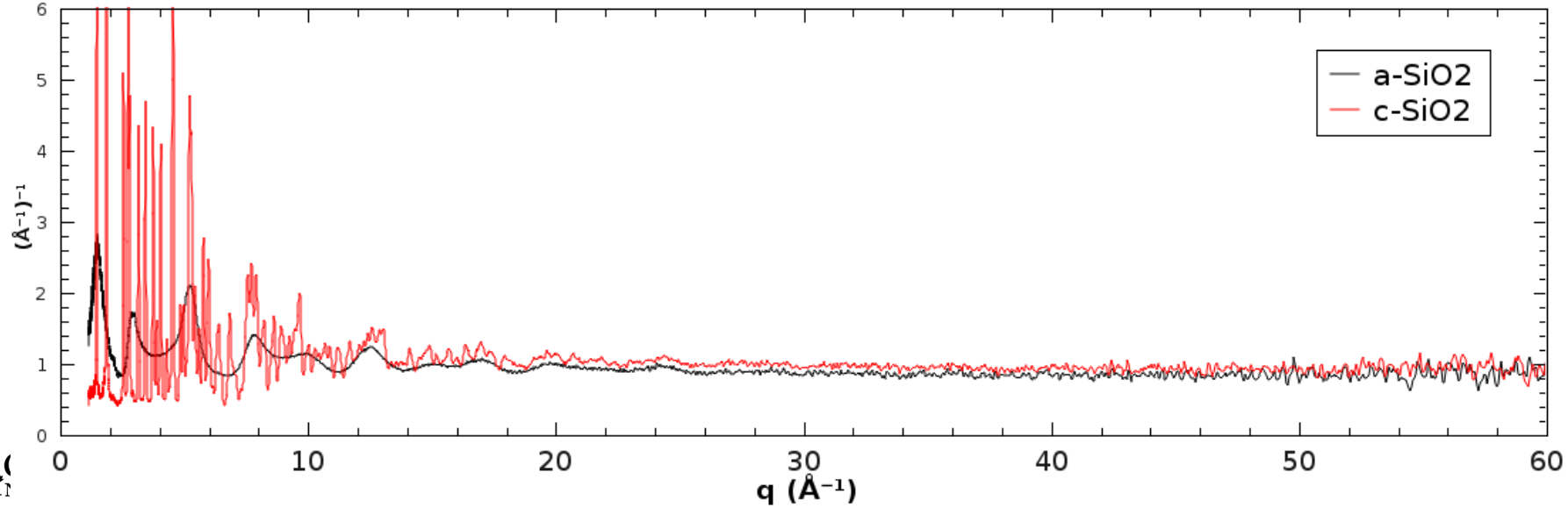
Gas handling panel for gas dosing, mixing, flow, adsorption (vacuum to 200 bar)

VISION diffraction banks

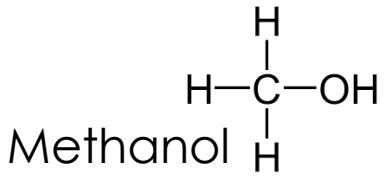




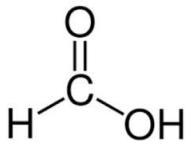




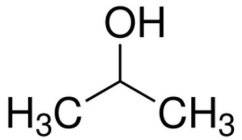
Can you match the molecules with the spectra?



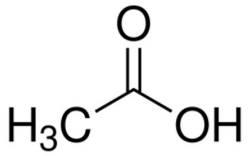
Methanol



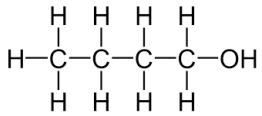
Formic acid



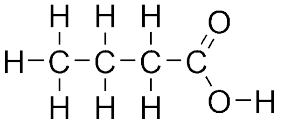
Ethanol



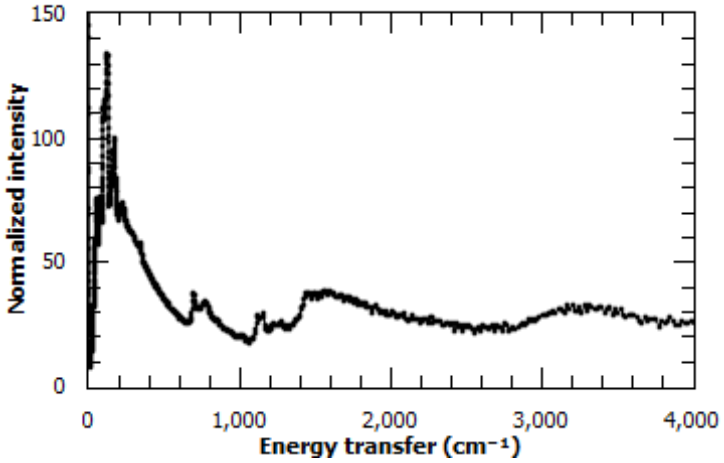
Acetic acid

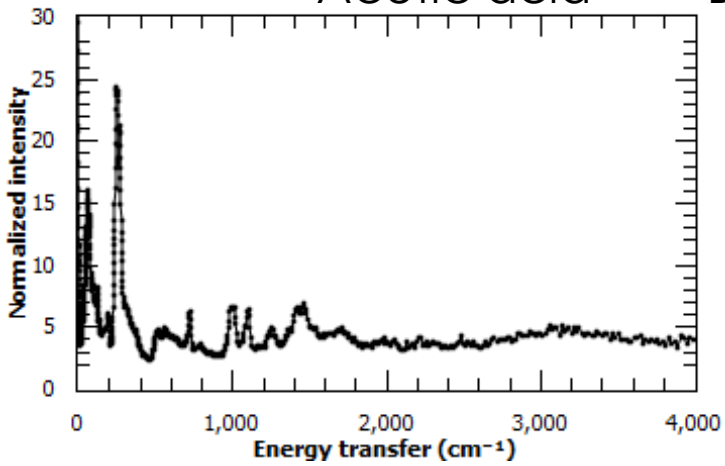


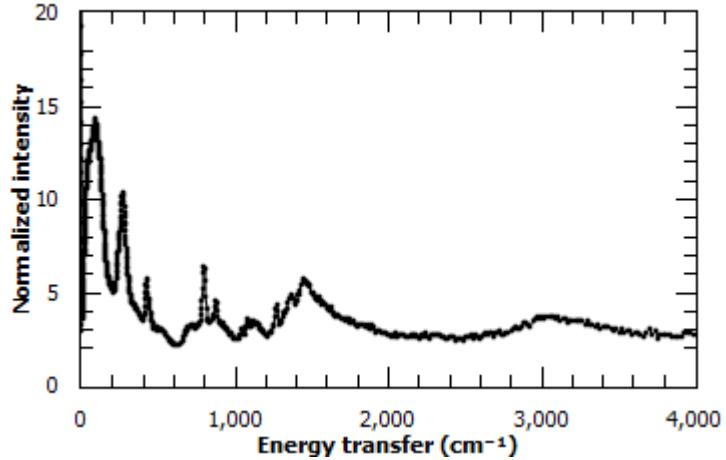
Butanol

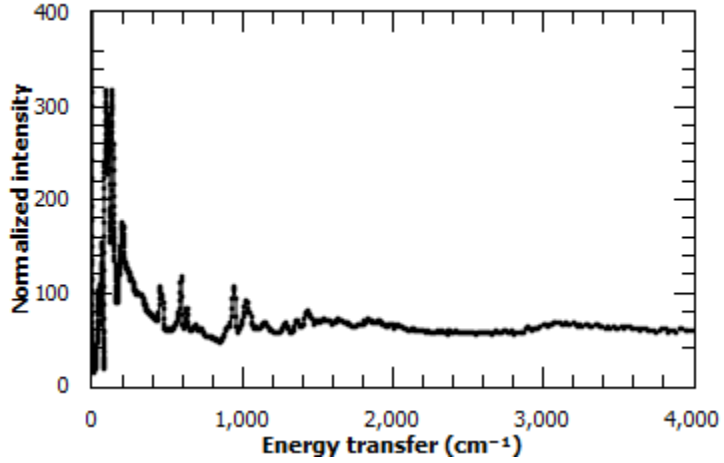


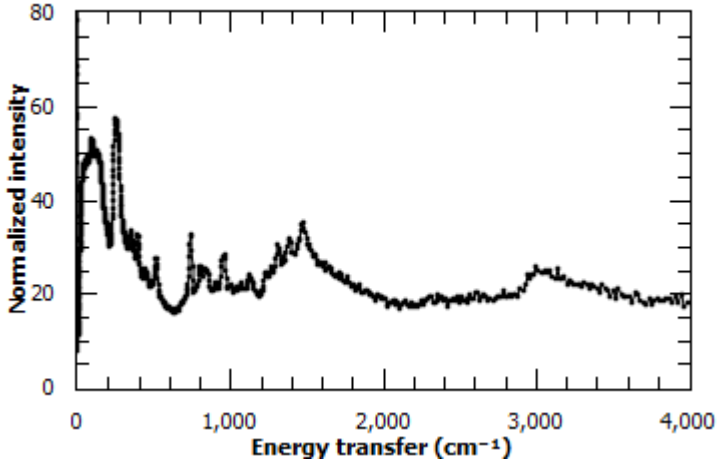
Butyric acid

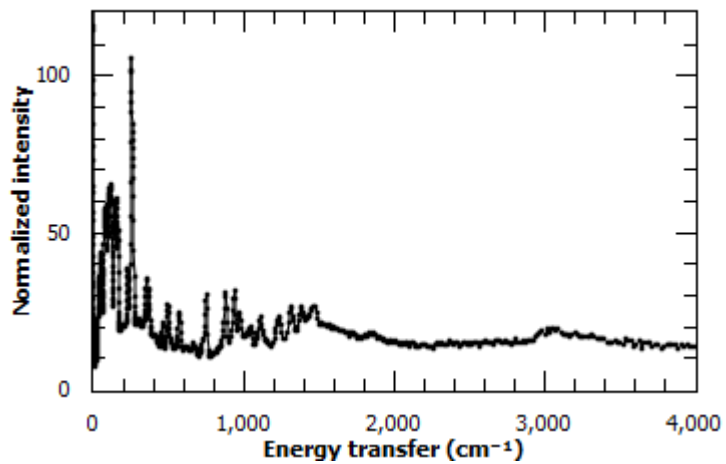




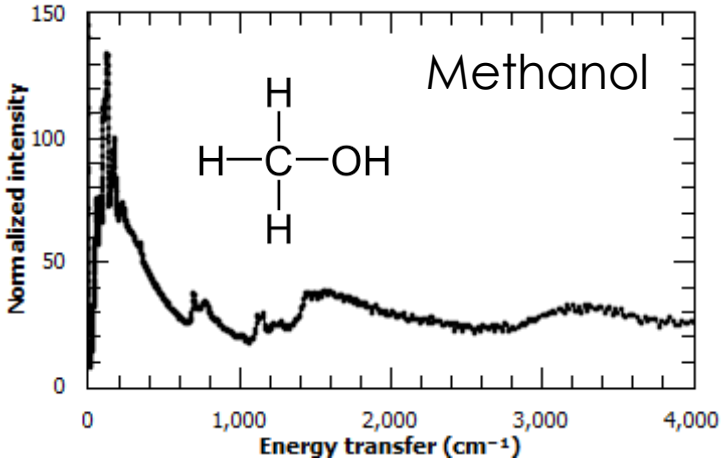


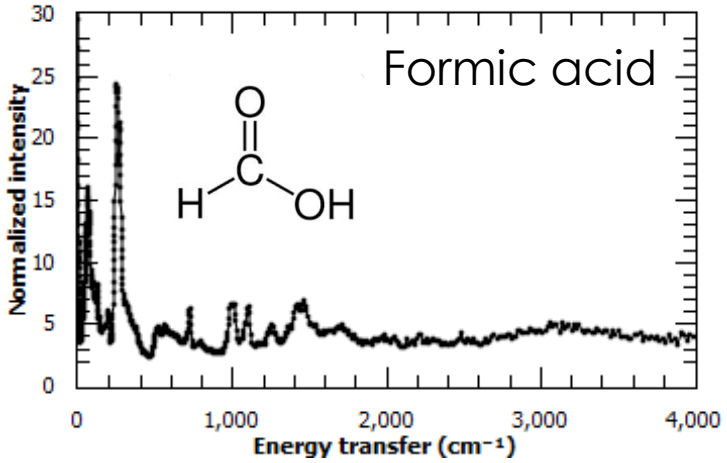


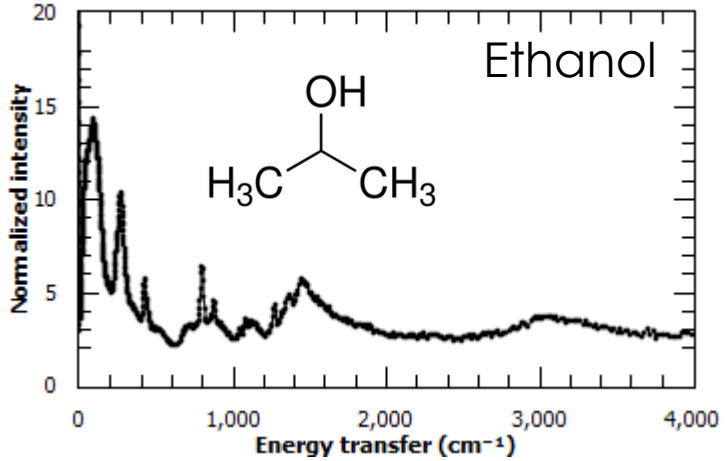


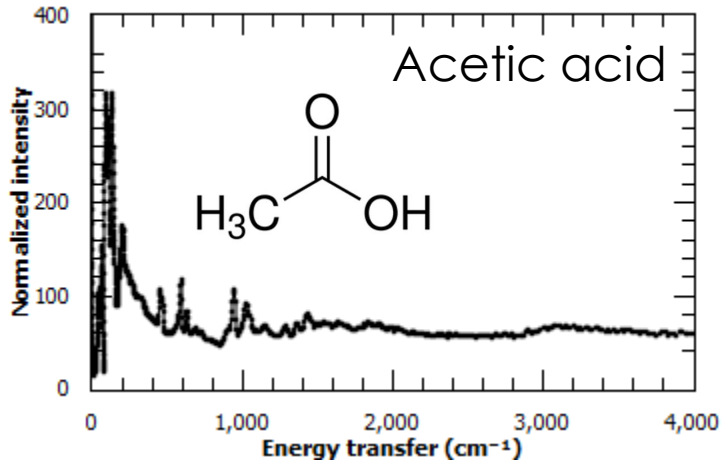


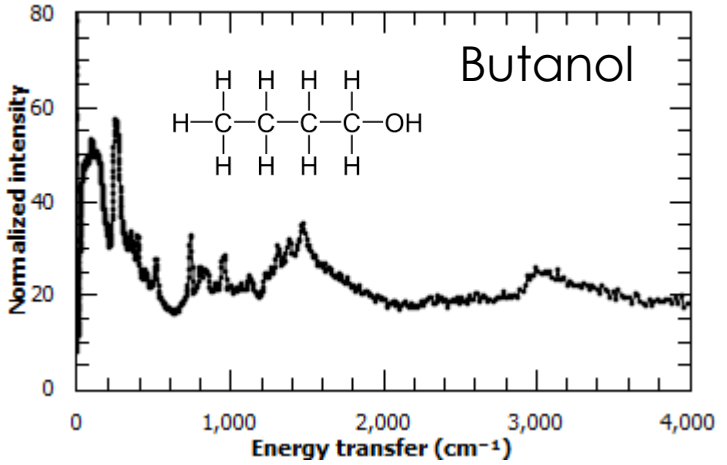
Can you match the molecules with the spectra?

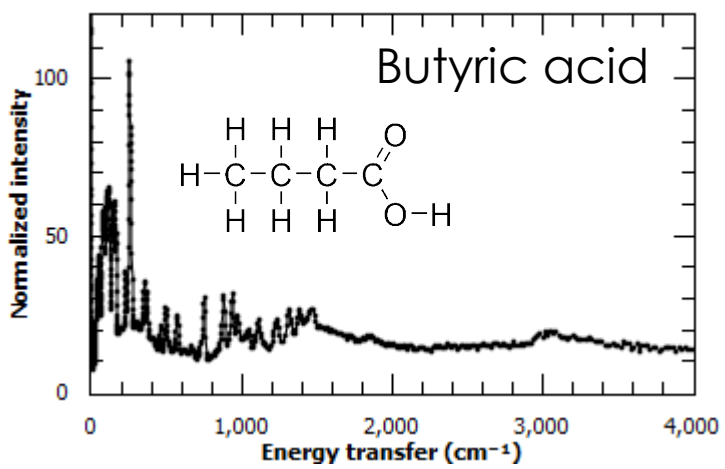




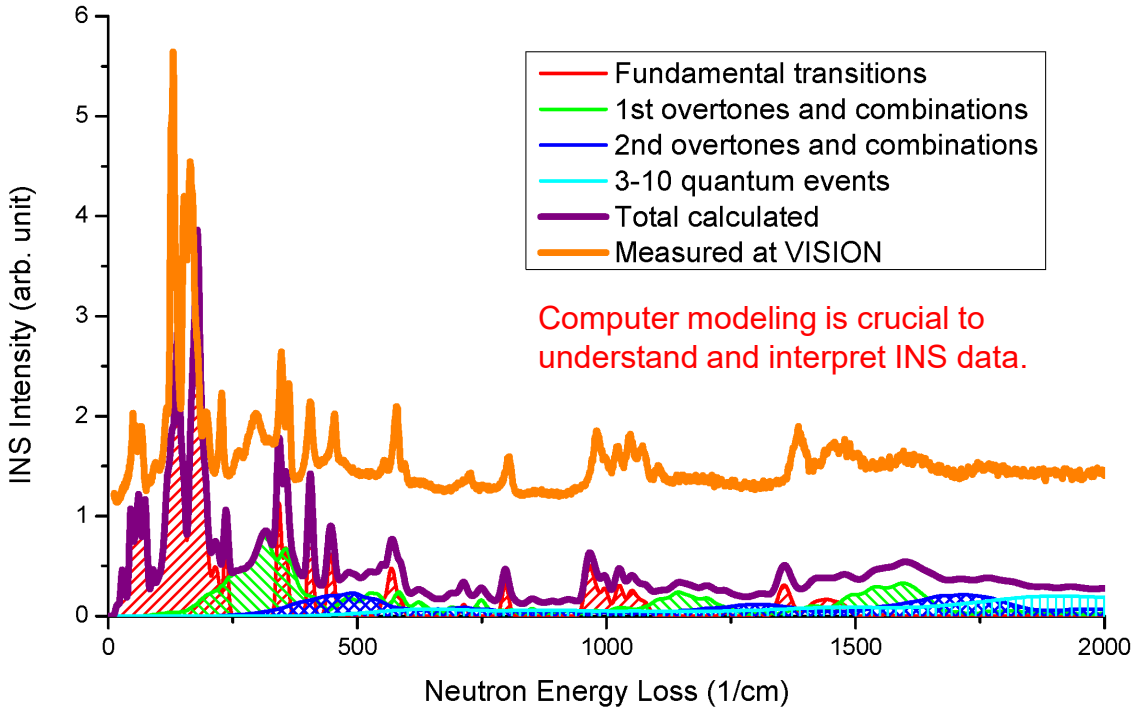




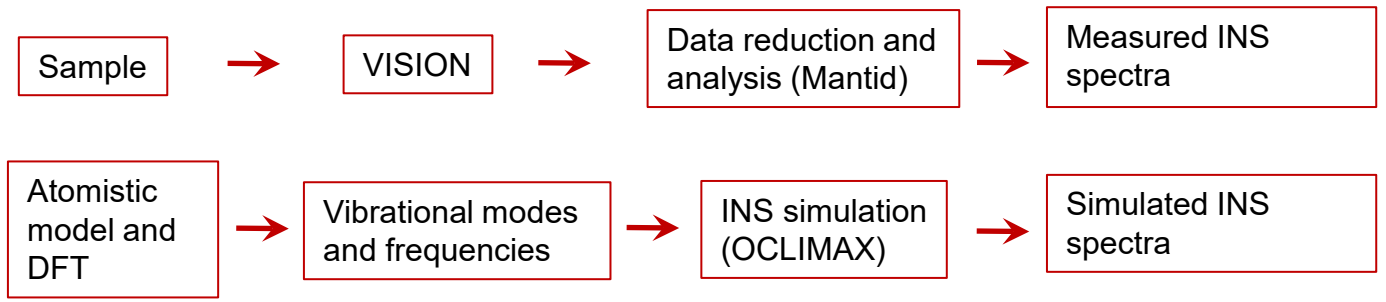




Integrated modeling for data interpretation



- 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 10Gb and Infiniband networking for connectivity.
- Installed as part of the ORNL Compute and Data Environment for Science (CADES)



The "digital twin" at VISION

VirtuES cluster

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

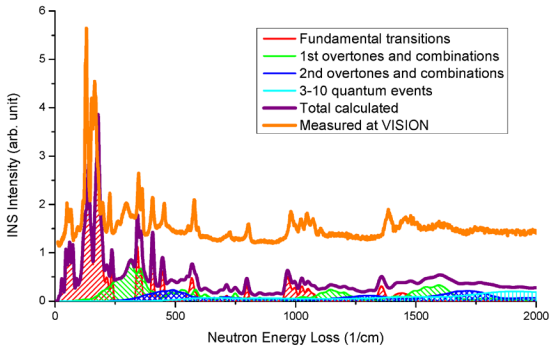
ORCA

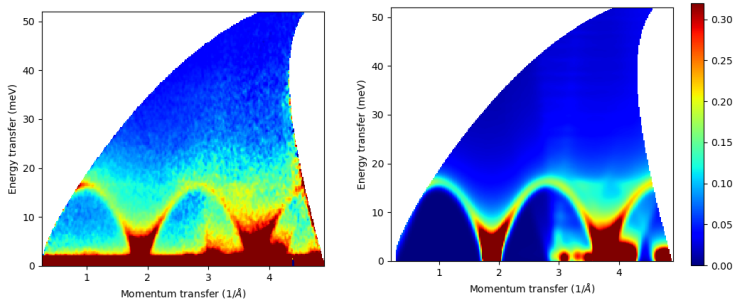
NWCHEM HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

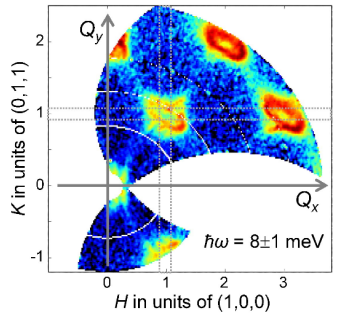
RMG

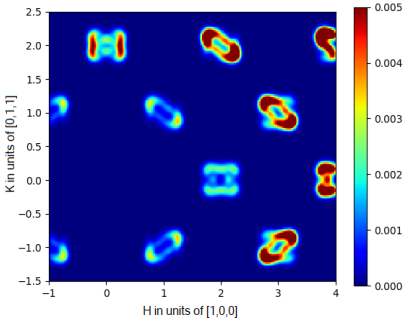
pymatgen 2.0.0

OCLIMAX



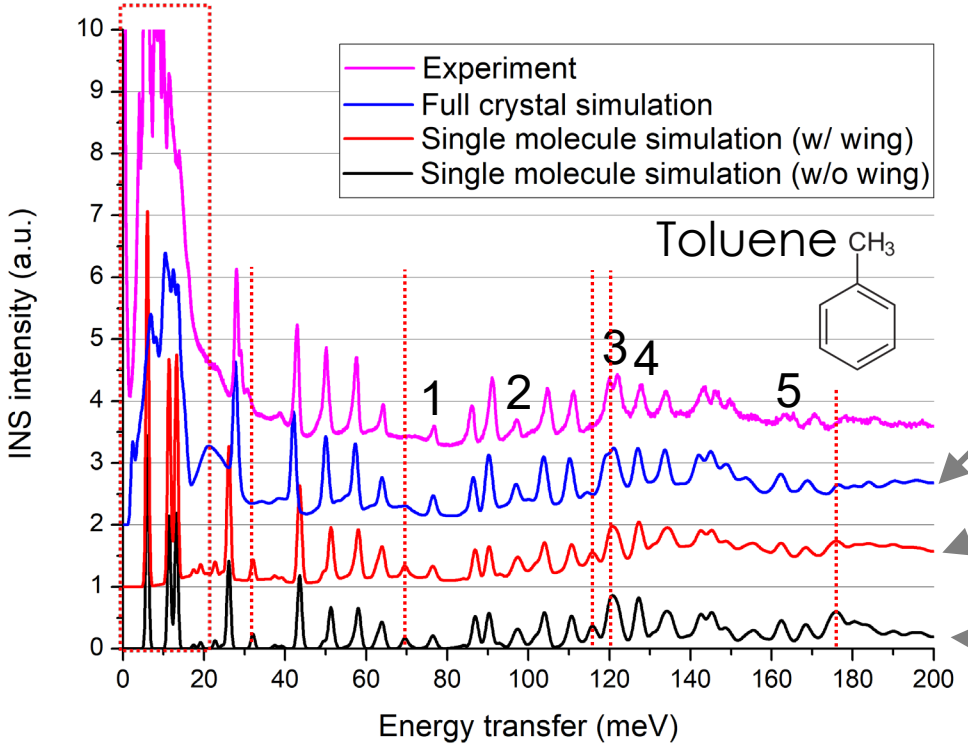


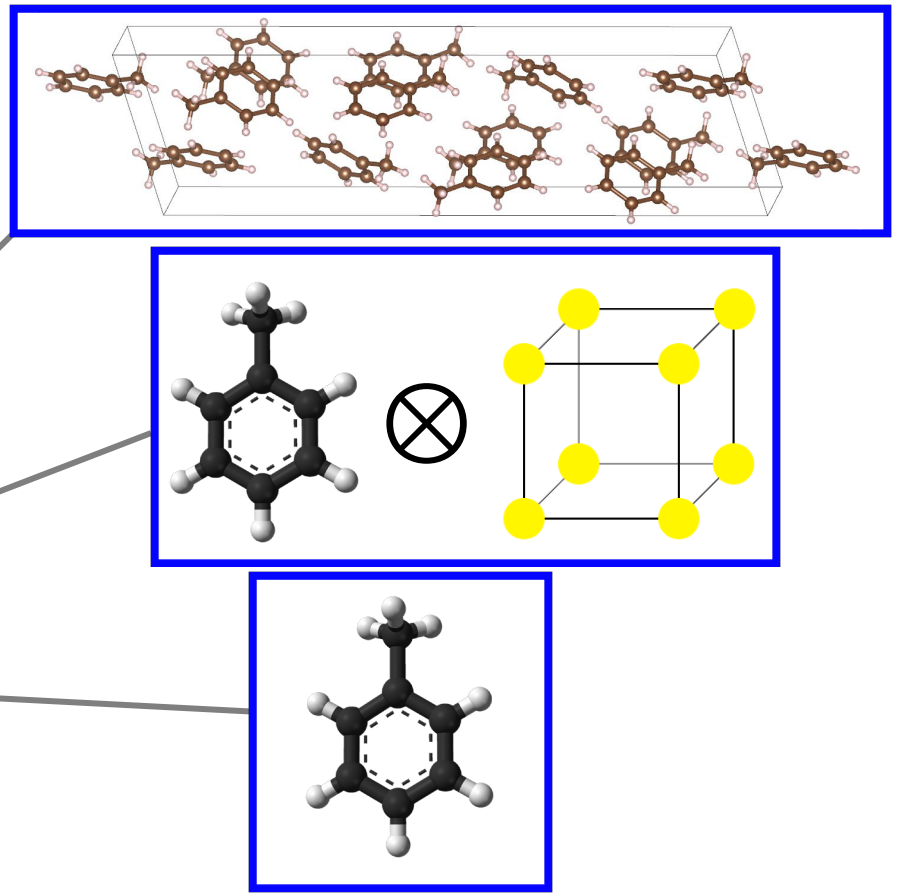


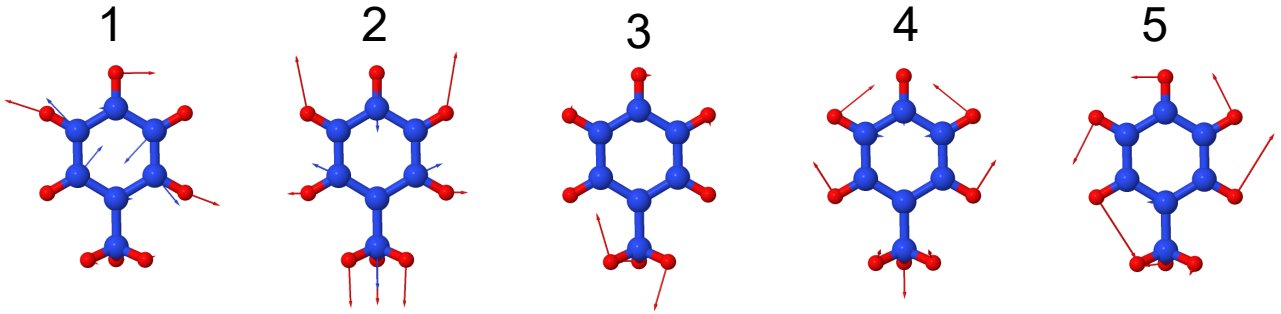


VISION, CNCS, HYSPEC, SEQUOIA, ARCS and many other neutron spectrometers.

OCLIMAX example: From single molecule to solid

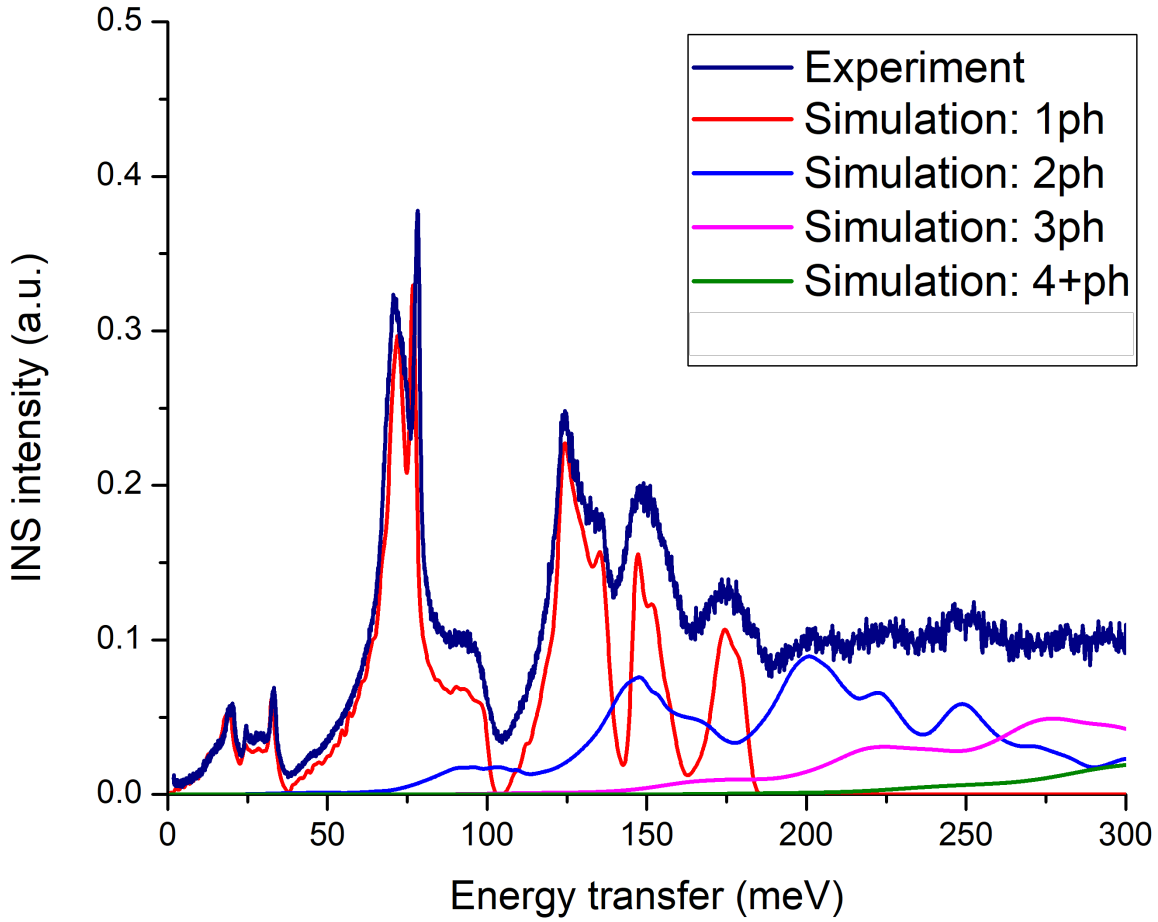


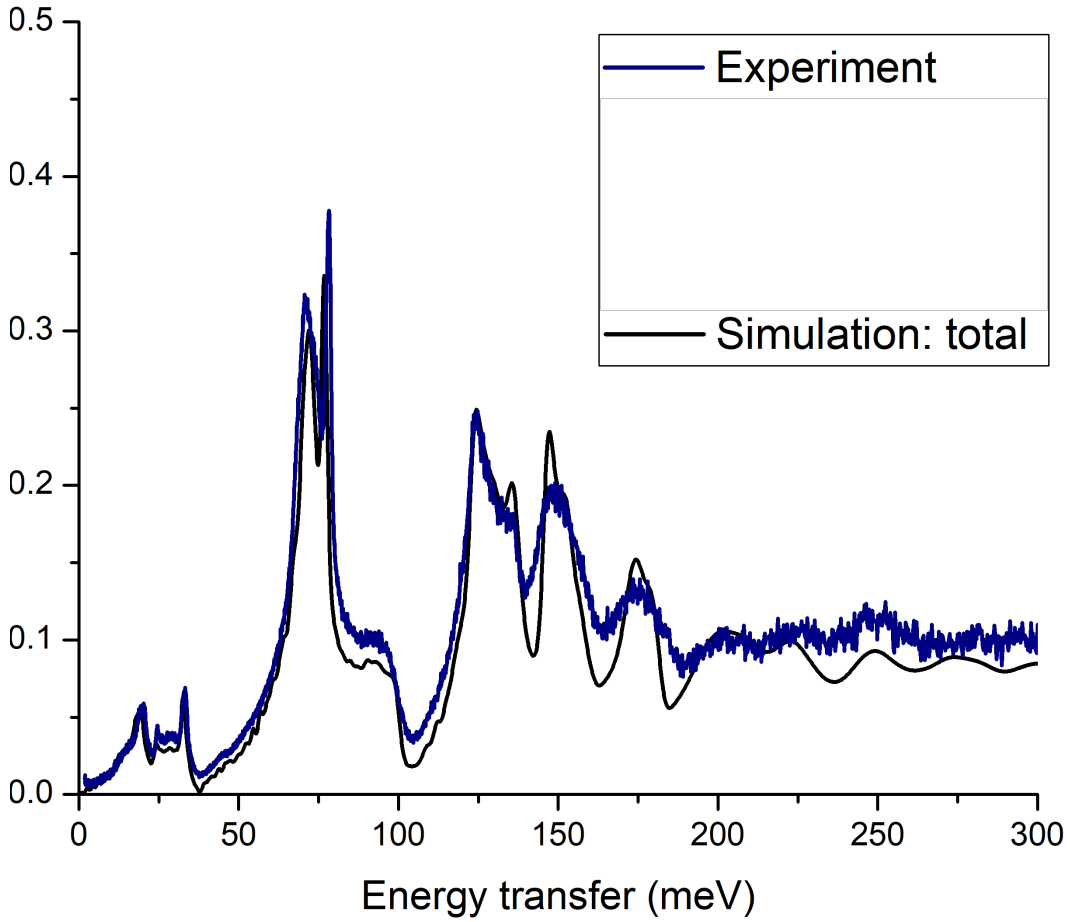




- ✓ Understanding intermolecular interactions (van der Waals forces, hydrogen bonding, charge transfer)

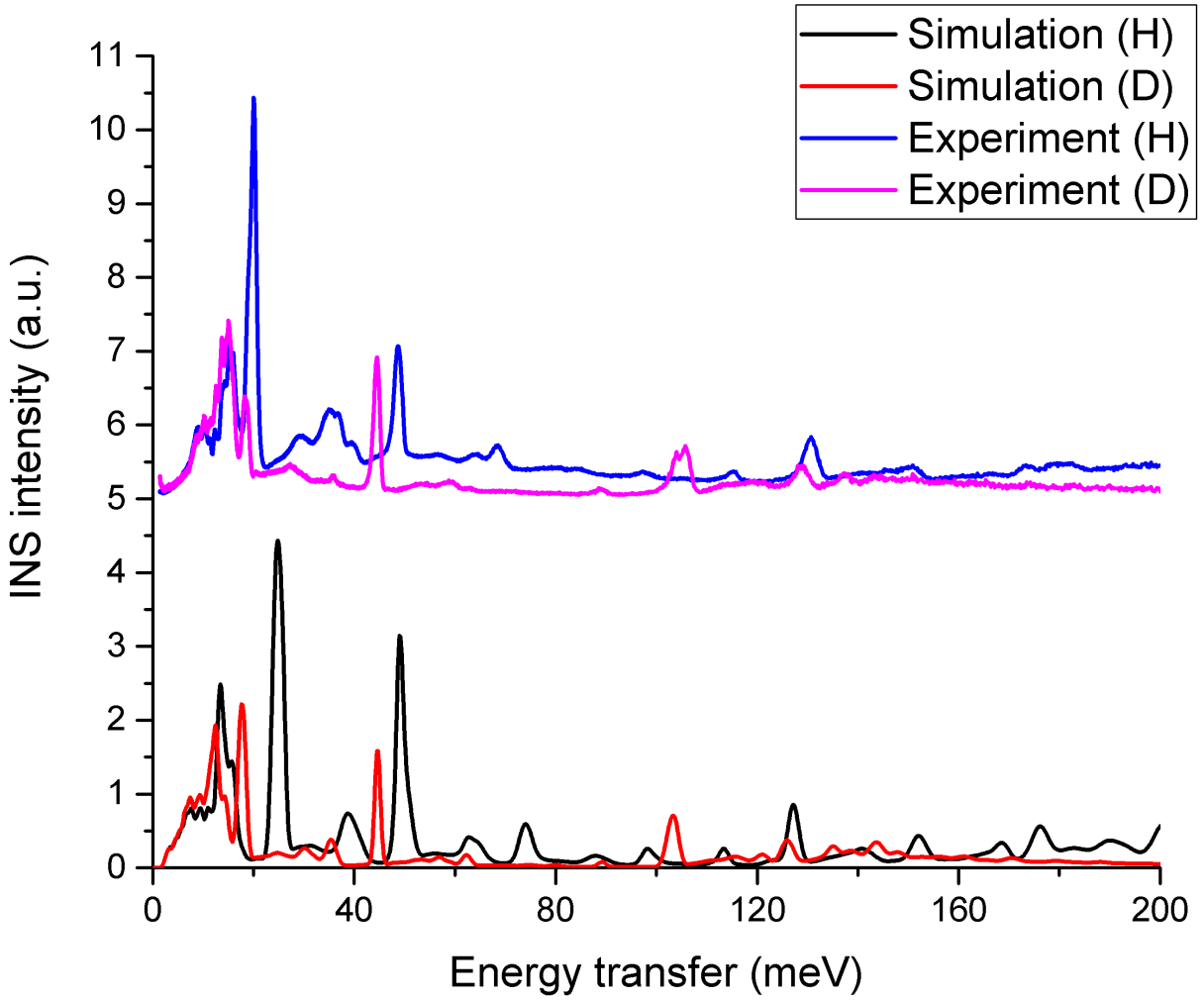
OCLIMAX example: Multiphonon excitations

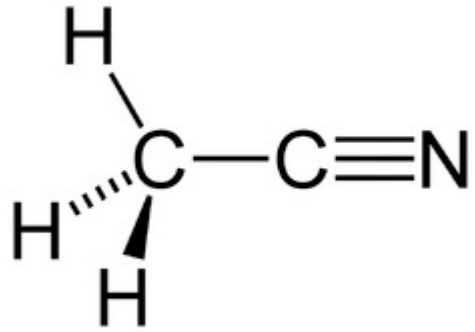




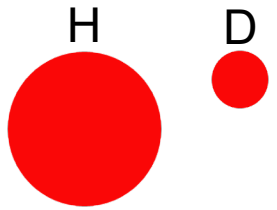
- ✓ Solving phonon density of states
- ✓ Understanding anharmonicity and potential energy landscape

Isotope substitution: acetonitrile





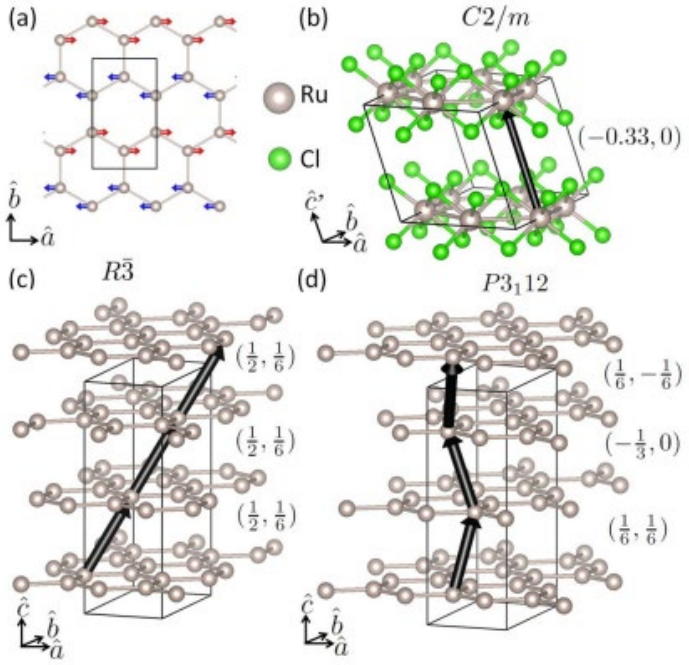
$$\omega = \sqrt{\frac{k}{m}}$$



- ✓ 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



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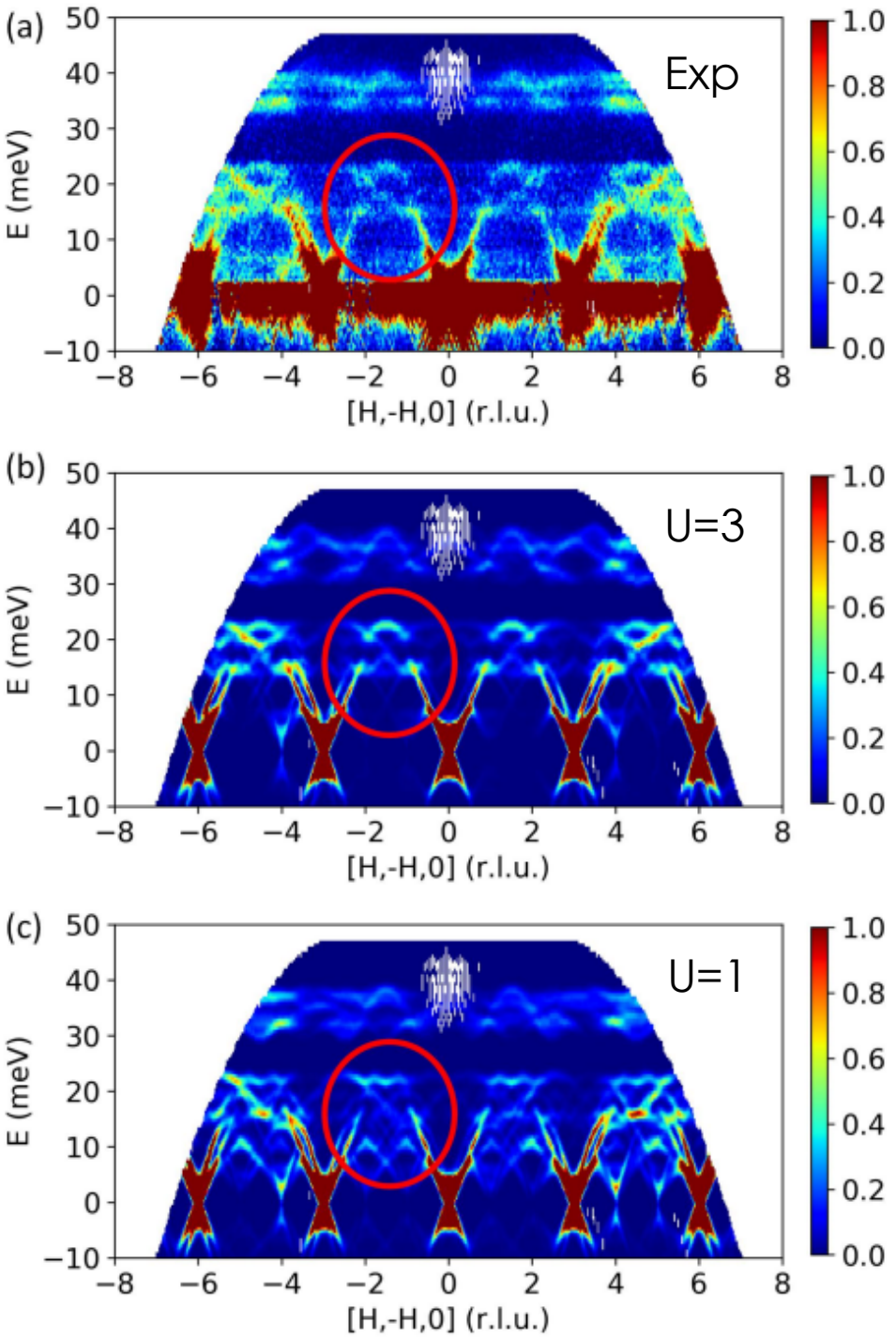
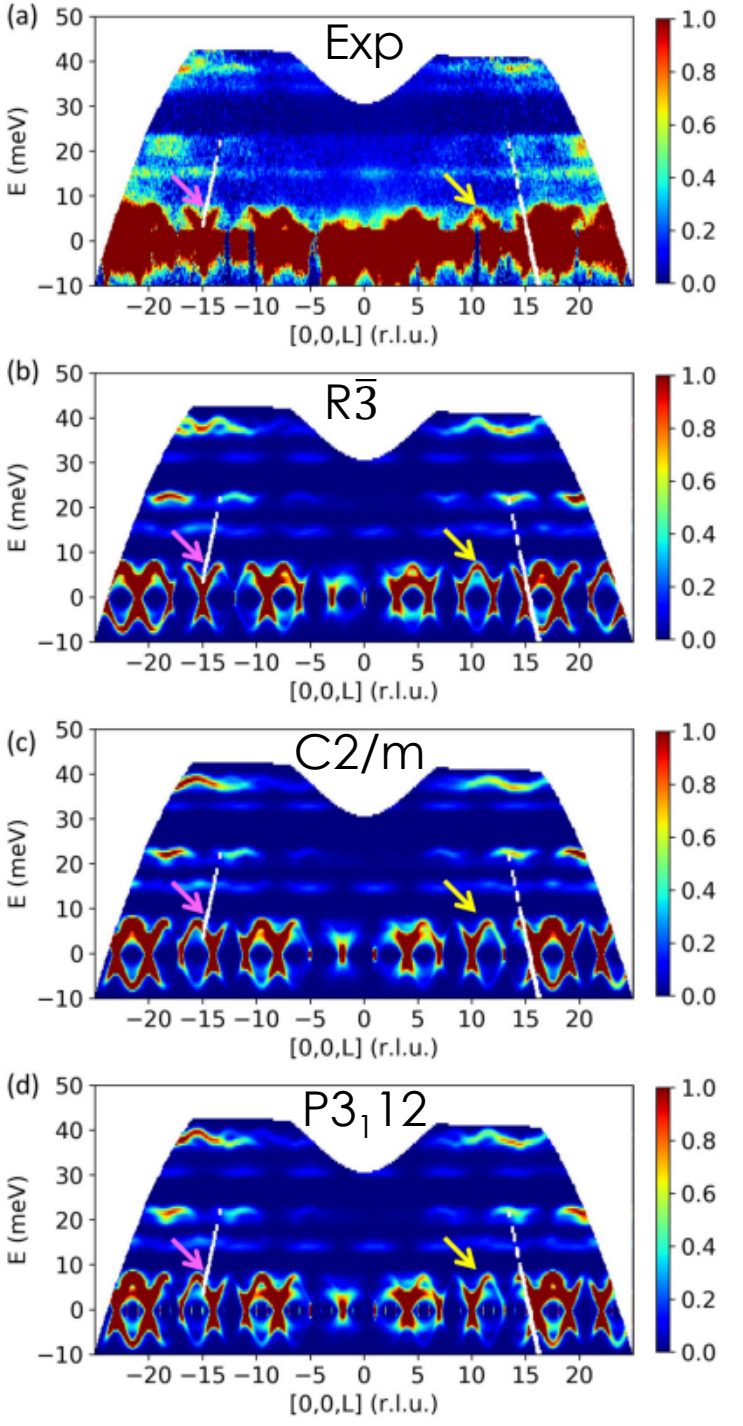
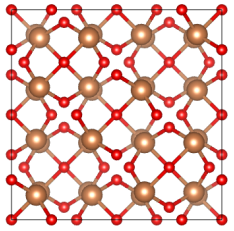


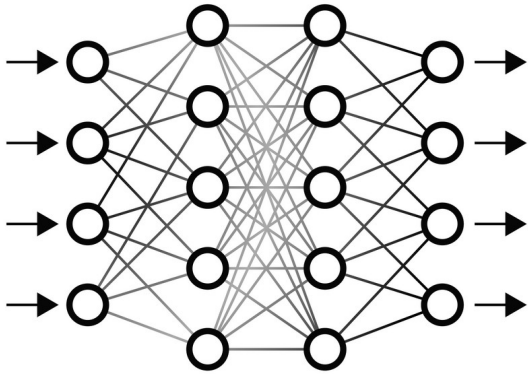


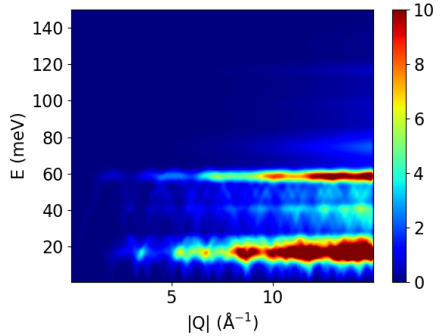
What can we do in the age of AI/ML?

- Can we develop new approaches that will
  - Benefit most users, even those with little/no modeling expertise
  - Not require significant computing resources
  - Produce simulated spectra in real-time



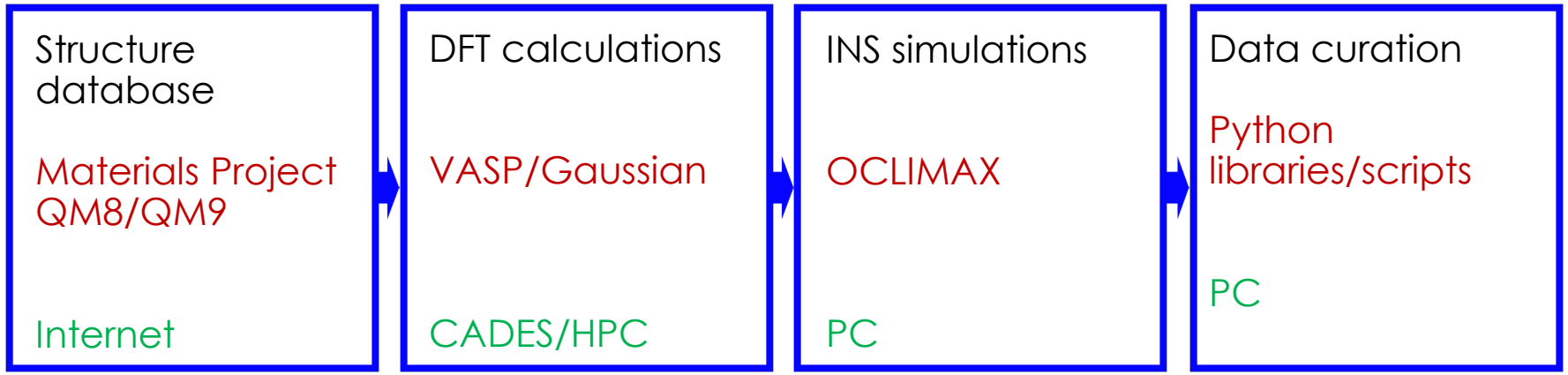
Atomic structure





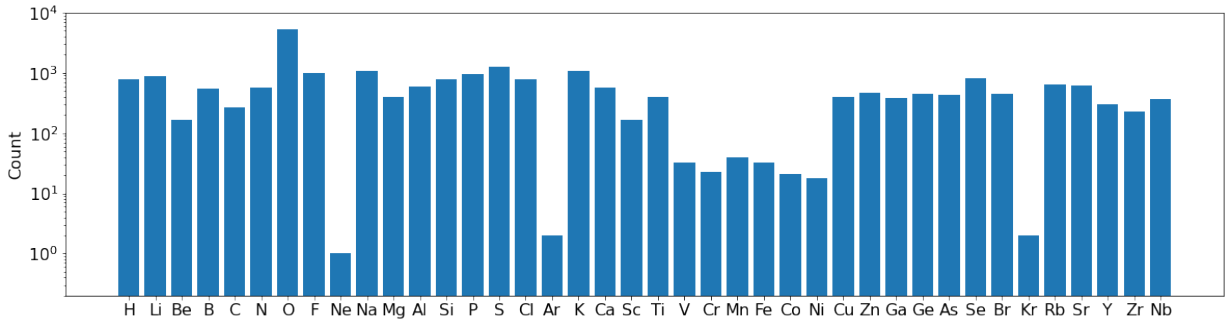
INS spectra

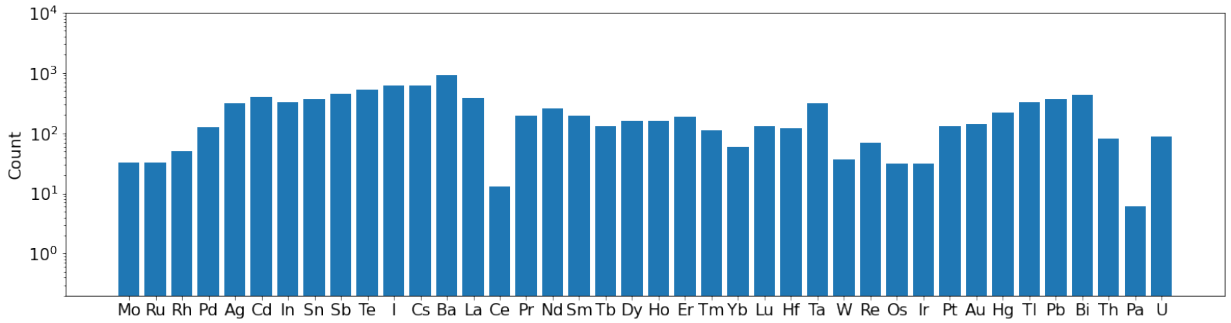
Generation of largescale synthetic INS database



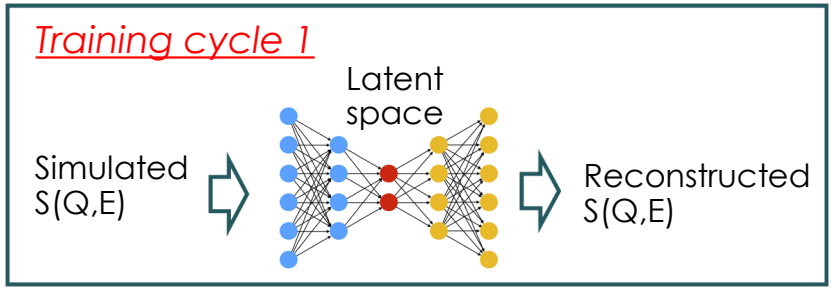
Products generated from this workflow:

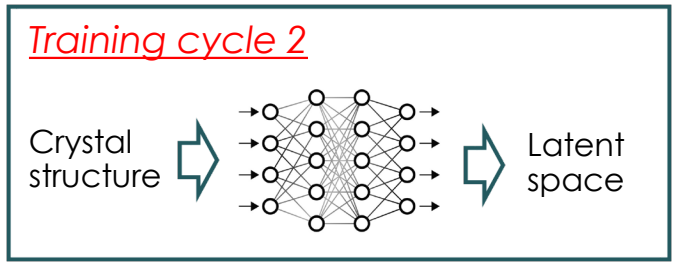
1. 1D S(E) (VISION) spectra for 20,000+ small organic molecules (QM8, with 8 or less nonhydrogen atoms)
2. 1D S(E) (VISION) spectra for 133,000+ organic molecules (QM9, HPC access provided by Max)
3. 1D S(E) (VISION) spectra for 10,000+ inorganic crystals (phonondb@kyoto-u)
4. 2D S(Q,E) for 10,000+ inorganic crystals (powder)
5. 2D S(Q,E) for 10,000+ inorganic crystals (single crystal along high symmetry directions and full 4D data)

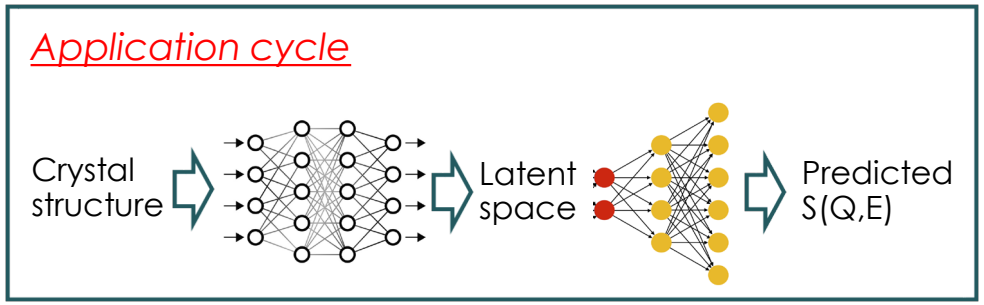


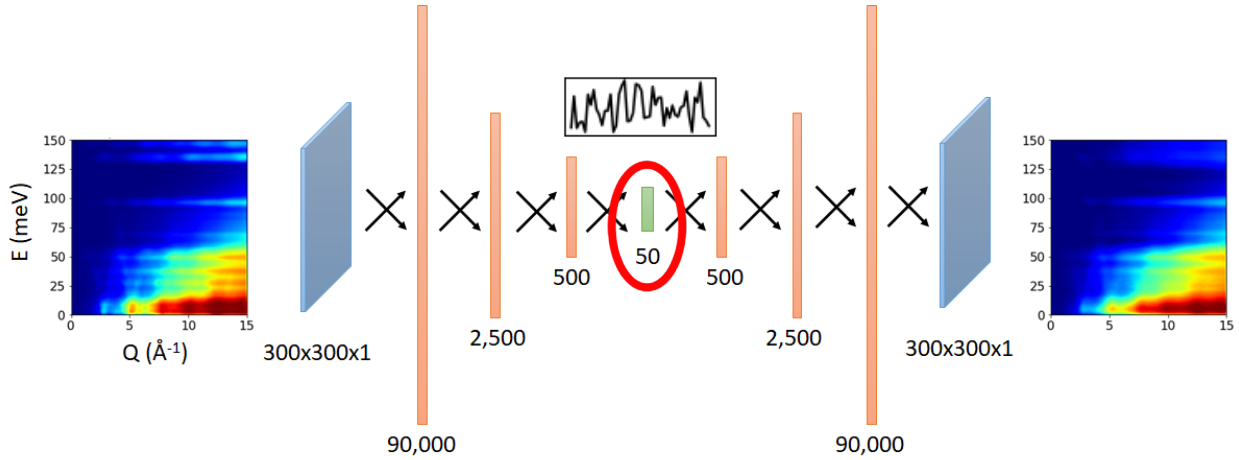


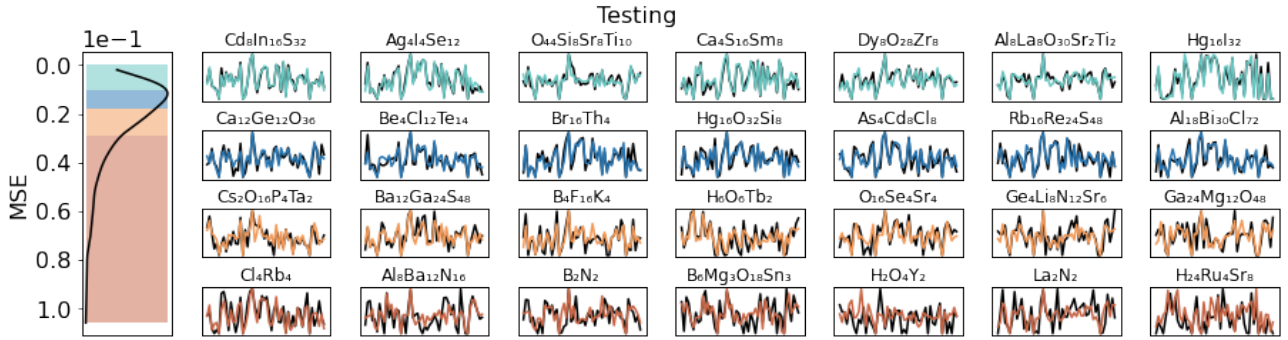
Direct prediction of powder S(Q,E)

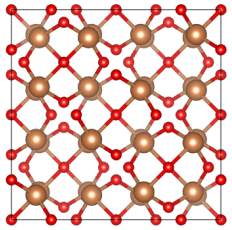


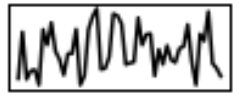


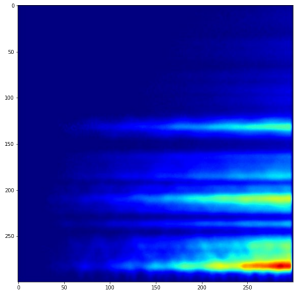




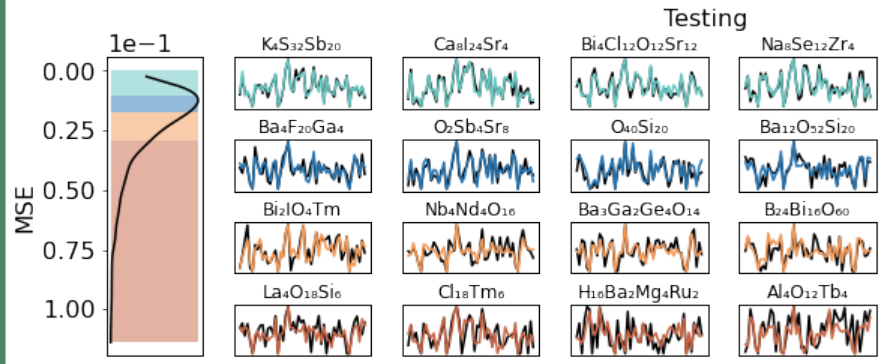


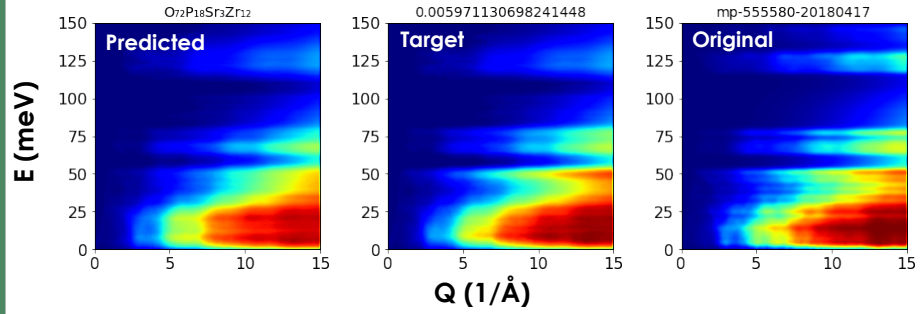




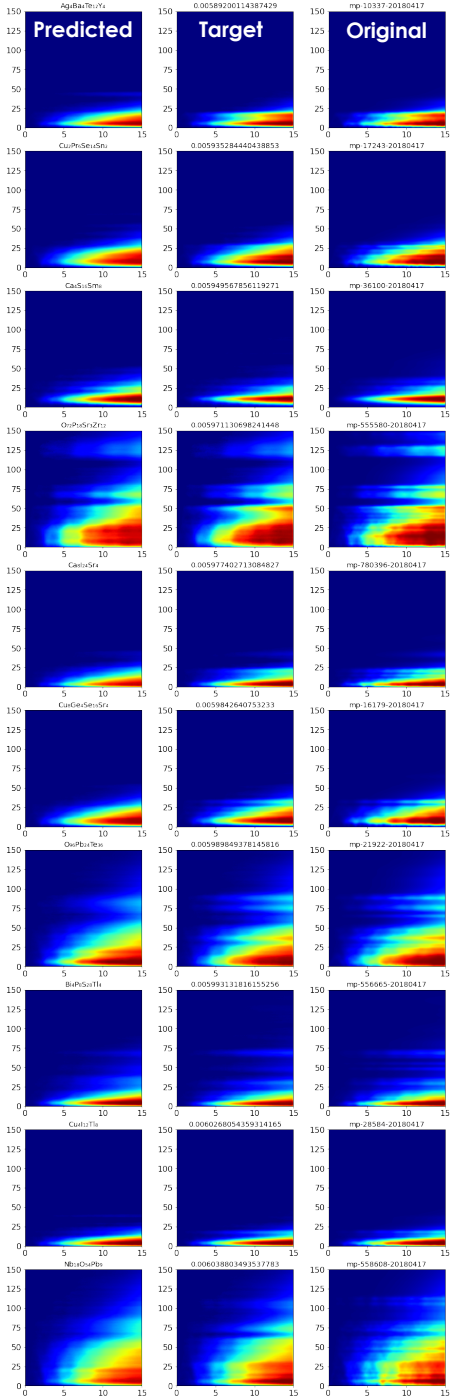


Direct prediction of powder S(Q,E)

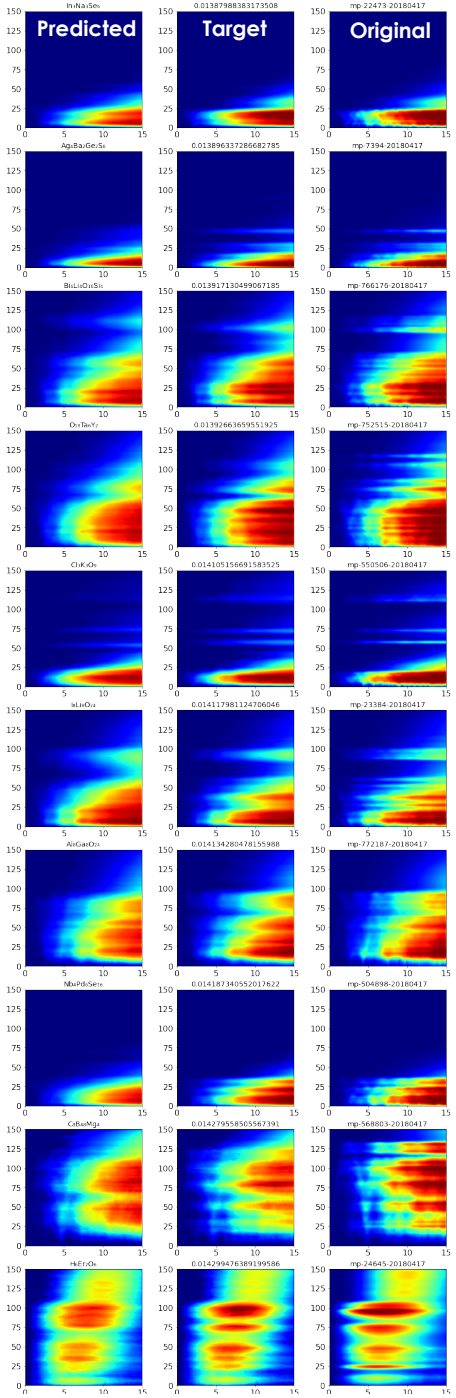




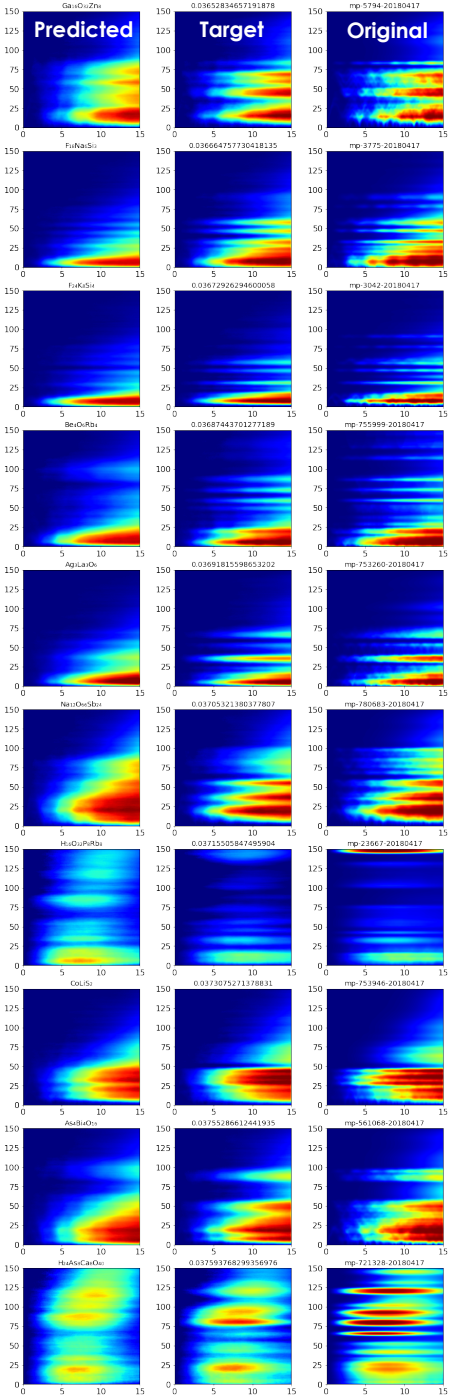
Best



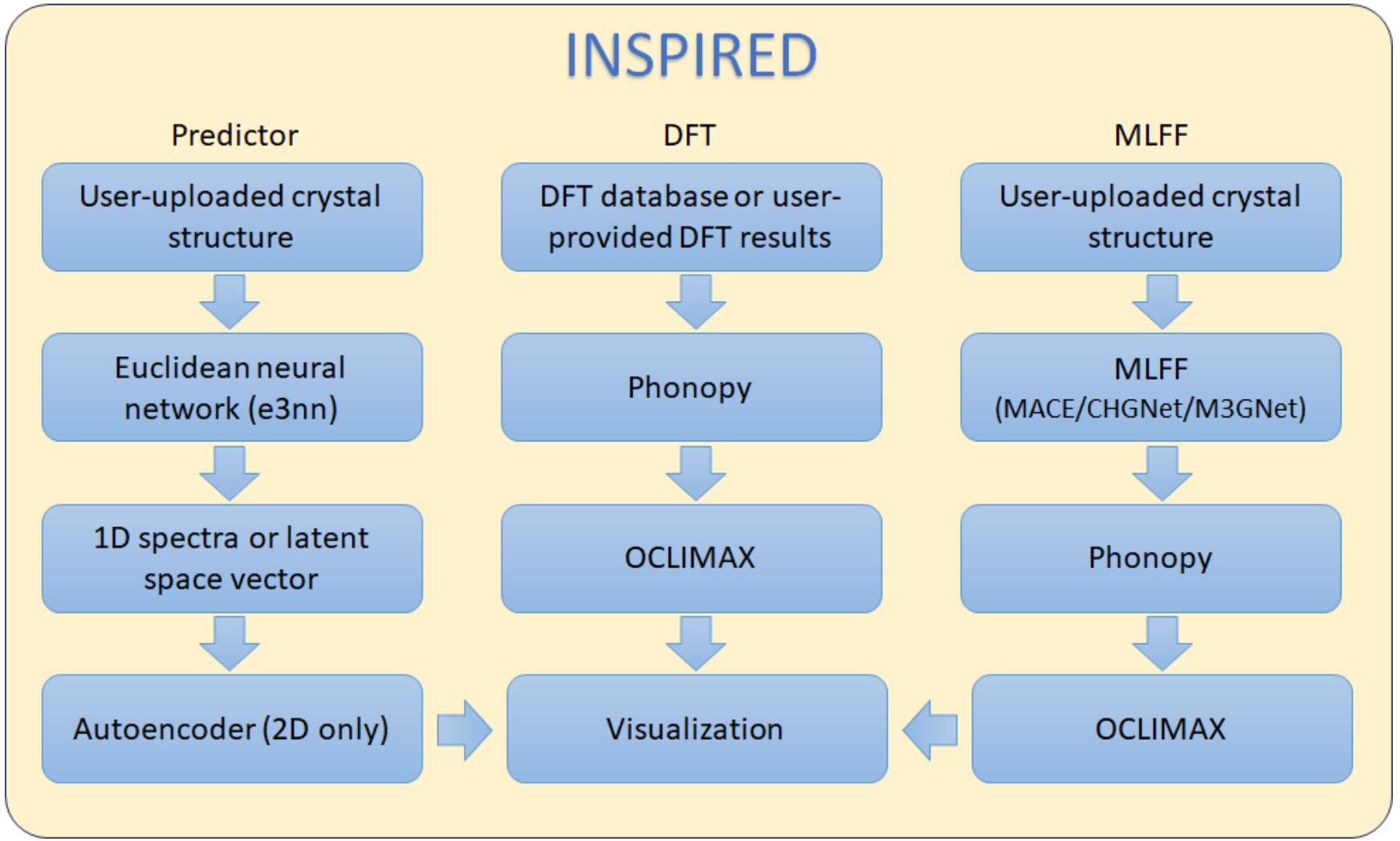
Average



Worst

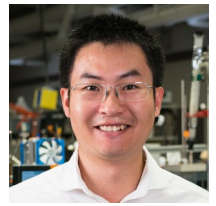


INSPIRED: Inelastic Neutron Scattering Prediction for Instantaneous Results and Experimental Design



Bowen Han

Andrei Savici

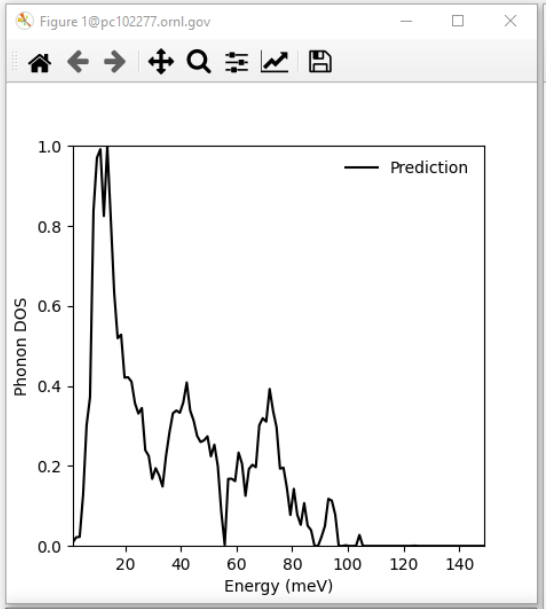


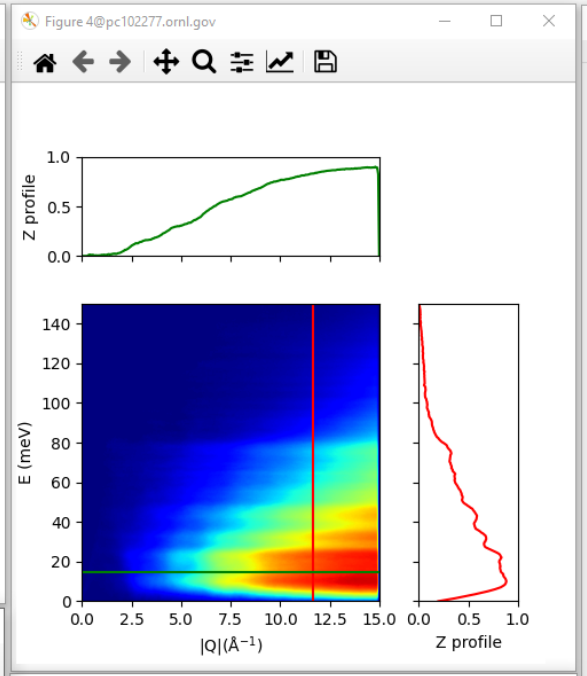
Mingda Li

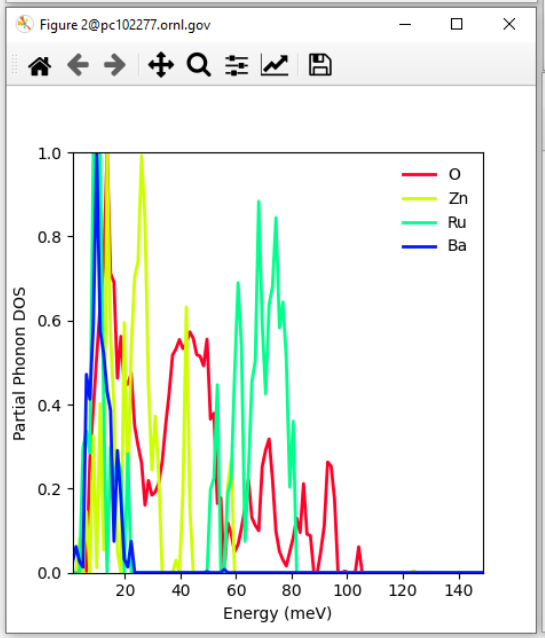
https://github.com/cyqjh/inspired
https://zenodo.org/records/10723108

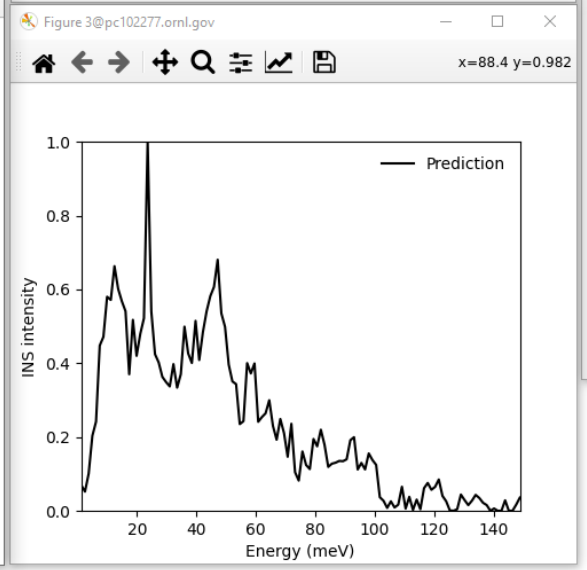
Computer Physics Communications 304 (2024) 109288

INSPIRED: Predictor



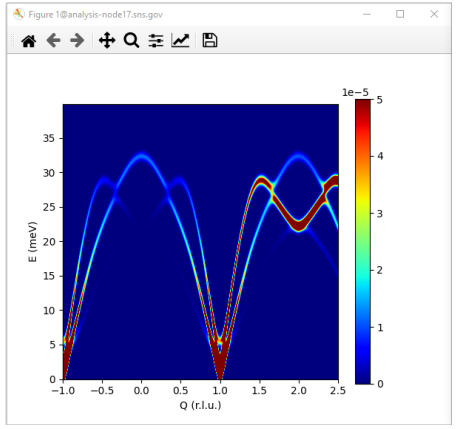


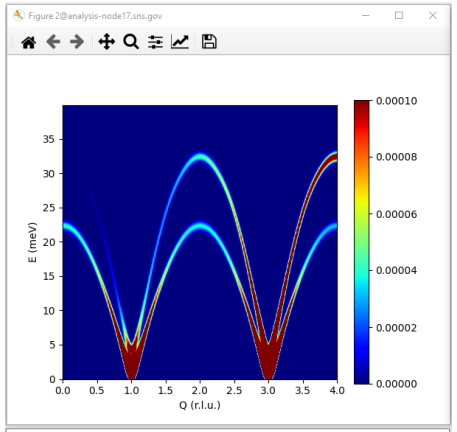


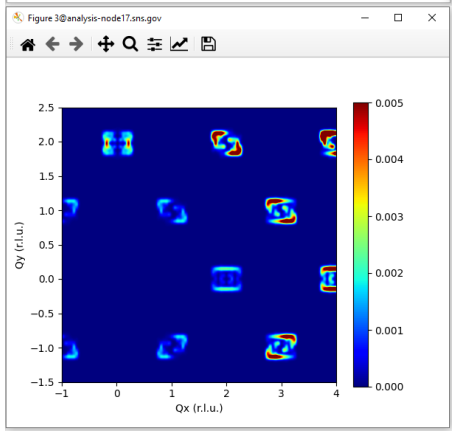


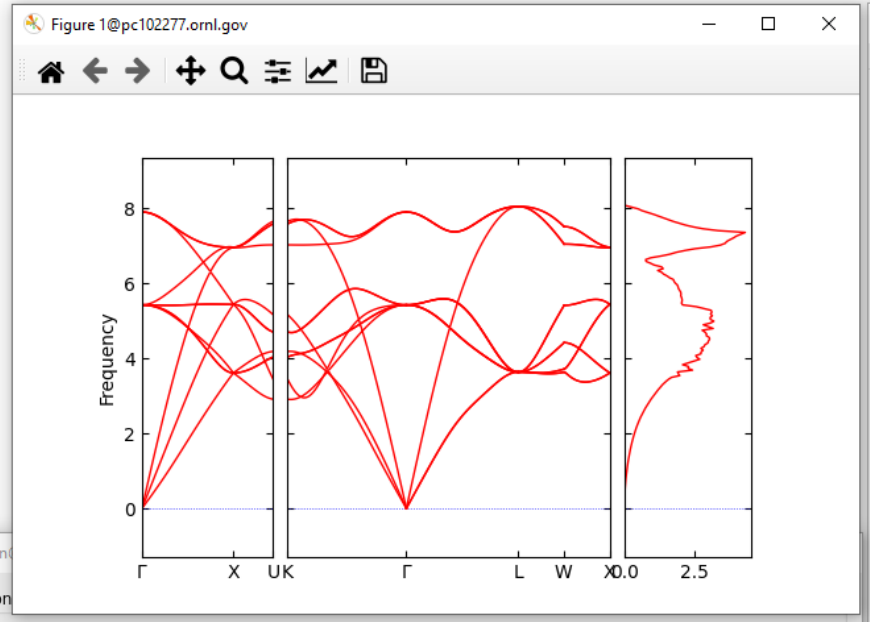

```
INFO: Crystal structure loaded successfully
INFO: Cell lengths:  [ 5.7749  5.7749 14.1823]
INFO: Cell angles:  [ 90.  90. 120.]
INFO: Cell volume:  409.6059305442873
INFO: Number of atoms in cell:  30
INFO: Chemical formula:  Ba3O9Ru2Zn
INFO: Space group:  176 P 63/m
```

INSPIRED: DFT database









Set up simulation

Phonon calculation

Q mesh 12 12 12 Default Save mesh

BAND_POINTS scaling factor 1.0

OCLIMAX parameters

Task	2D S(Q,Q) single crystal	Output	0	Q1	1 0 0
Temperature	300	MAXO	1	Q2	0 1 1
Mask	0	Theta	0.0 60.0	Q3	0 1 -1
E Unit	meV	Norm	0	Q1_bin	-1 0.05 4.0
Ei	40	Ecut	0.01	Q2_bin	-1.5 0.05 2.5
Emin	0.1	Qmin	0.10	Q3_bin	-0.05 0.05 0.05
Emax	40.0	Qmax	10.00	E_bin	6 1 8
dE	0.1	dQ	0.10	x-axis	Q1
ERES	0.4	QRES	-1	y-axis	Q2

Single crystal parameters

Load parameters | Use default | Save/Use current parameters

Help

Inspired@pc102277.ornl.gov

Menu

Predictor | DFT database | MLFF | About

Search DFT Database [4]

Use My DFT Data Browse DFT folder:

Step 1

Type: By composition

RegEx Value: Cu

Example: (Na)(Cl) will return entries containing Na and Cl. With "Exact match" checked, it will return entries containing Na and Cl only. Click "Help" for more info.

Exact match

Search

Load selected model

MP ID	Formula	Space group (
mp-30-Cheng23	Cu	Fm-3m(225)

Step 2 (Optional)

View structure | Plot phonon dispersion and DOS

Step 3

Set up INS simulation

Parameter file:

Step 4

Run INS simulation

Step 5

Energy unit in plot: meV

Customize range | Interactive 2D cross-sectional S(Q,E) plot

Xmin Xmax Ymin Ymax Zmin Zmax

Plot INS spectrum

Help

Current Working Directory: /home/yyc/proj/inspired/tests

Universal MLFFs (pre-trained foundation models)

nature computational science

Article

https://doi.org/10.1038/s43588-022-00349-3

A universal graph deep learning interatomic potential for the periodic table

Received: 18 March 2022

Accepted: 5 October 2022

Chi Chen & Shyue Ping Ong

nature machine intelligence

Article

https://doi.org/10.1038/s42256-023-00716-3

CHGNet as a pretrained universal neural network potential for charge-informed atomistic modelling

Received: 2 March 2023

Accepted: 4 August 2023

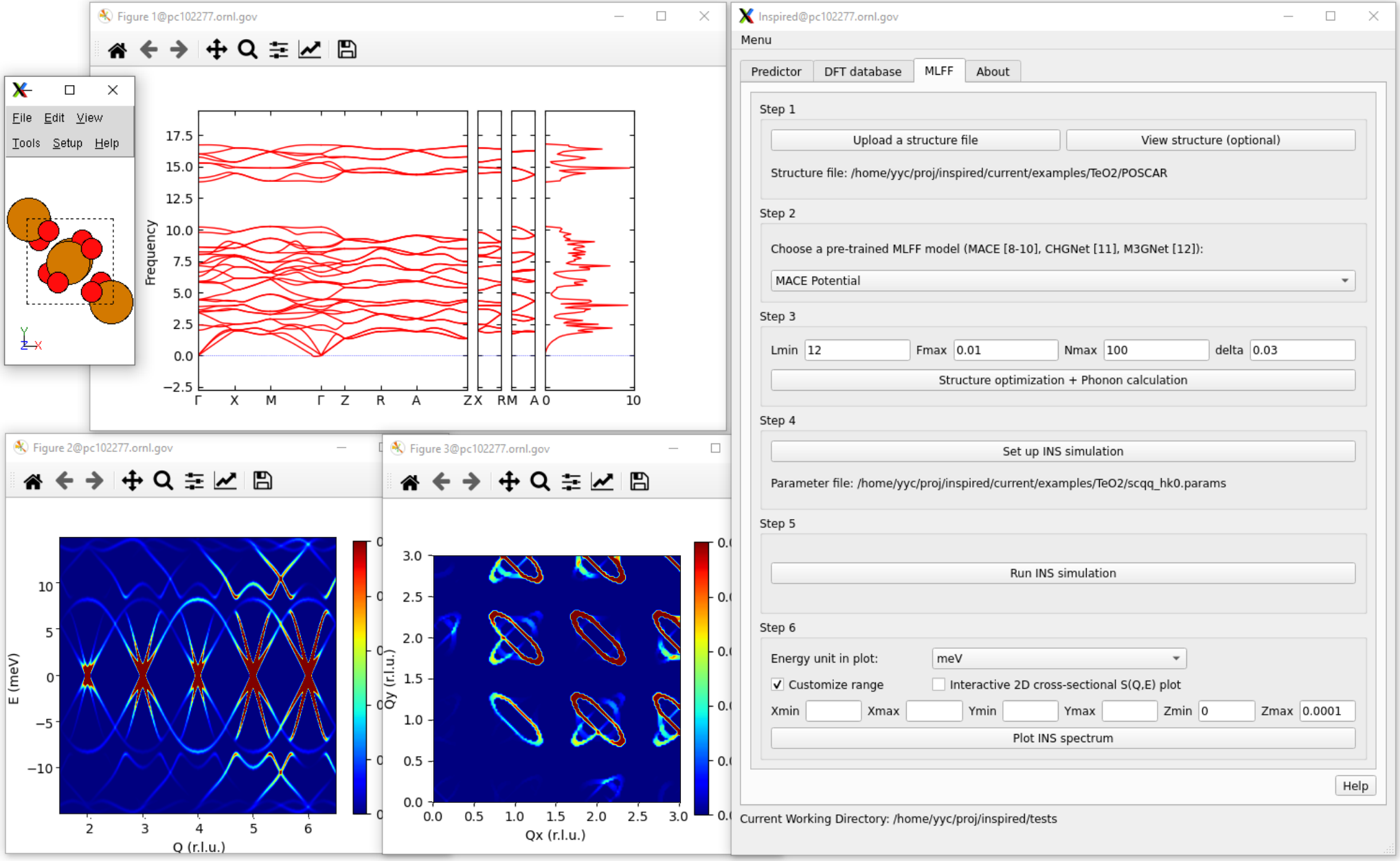
Bowen Deng[1,2], Peichen Zhong[1,2], KyuJung Jun[1,2], Janosh Riebesell[2,3], Kevin Han[2], Christopher J. Bartel[1,4] & Gerbrand Ceder[1,2]

[Submitted on 29 Dec 2023 (v1), last revised 1 Mar 2024 (this version, v2)]

A foundation model for atomistic materials chemistry

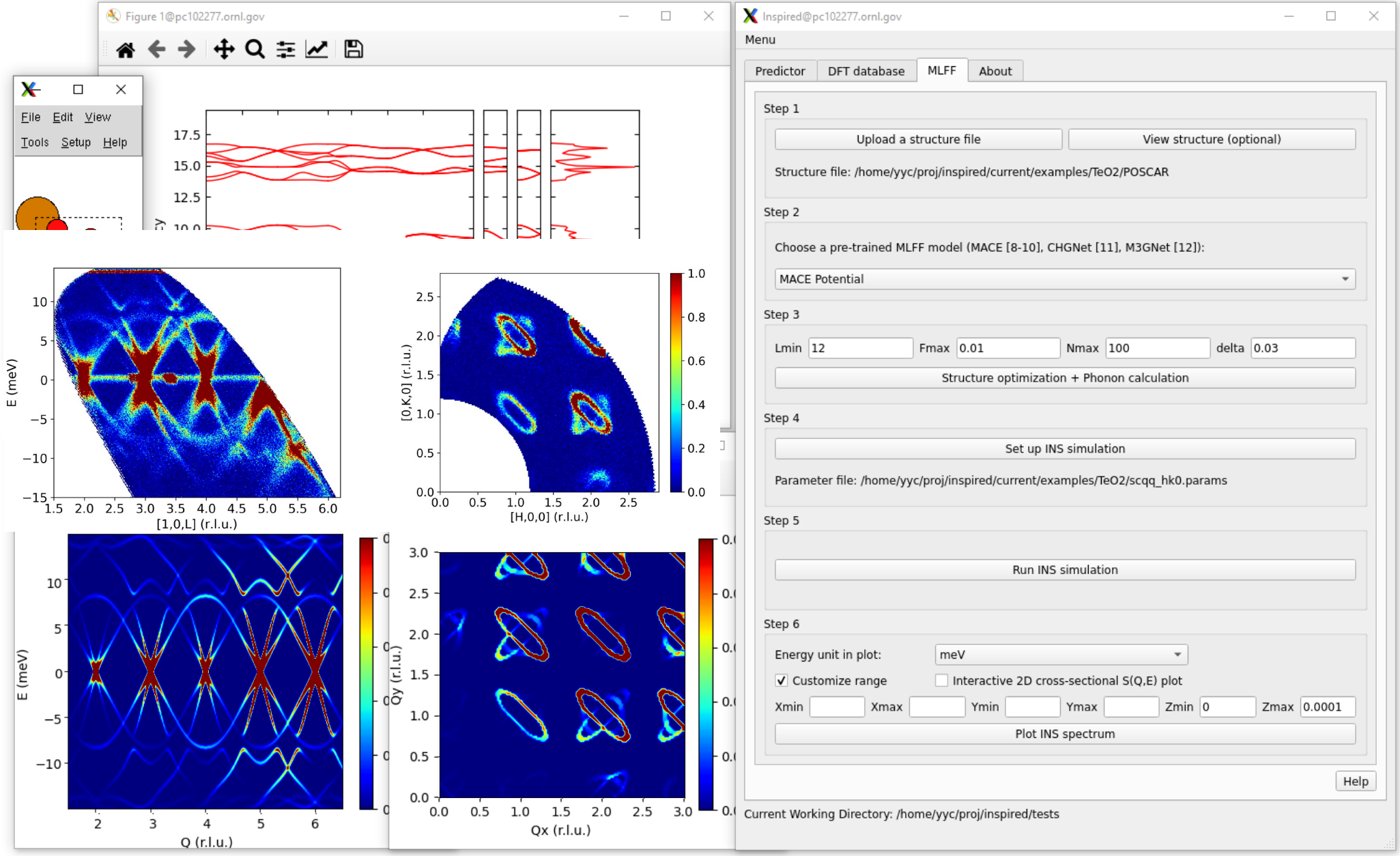
Ilyes Batatia, Philipp Benner, Yuan Chiang, Alin M. Elena, Dávid P. Kovács, Janosh Riebesell, Xavier R. Advincula, Mark Asta, Matthew Avaylon, William J. Baldwin, Fabian Berger, Noam Bernstein, Arghya Bhowmik, Samuel M. Blau, Vlad Cărare, James P. Darby, Sandip De, Flaviano Della Pia, Volker L. Deringer, Rokas Elijošius, Zakariya El-Machachi, Fabio Falcioni, Edvin Fako, Andrea C. Ferrari, Annalena Genreith-Schriever, Janine George, Rhys E. A. Goodall, Clare P. Grey, Petr Grigorev, Shuang Han, Will Handley, Hendrik H. Heenen, Kersti Hermansson, Christian Holm, Jad Jaafar, Stephan Hofmann, Konstantin S. Jakob, Hyunwook Jung, Venkat Kapil, Aaron D. Kaplan, Nima Karimitari, James R. Kermode, Namu Kroupa, Jolla Kullgren, Matthew C. Kuner, Domantas Kuryla, Guoda Liepuoniute, Johannes T. Margraf, Ioan-Bogdan Magdău, Angelos Michaelides, J. Harry Moore, Aakash A. Naik, Samuel P. Niblett, Sam Walton Norwood, Niamh O'Neill, Christoph Ortner, Kristin A. Persson, Karsten Reuter, Andrew S. Rosen, Lars L. Schaaf, Christoph Schran, Benjamin X. Shi, Eric Sivonxay, Tamás K. Stenczel, Viktor Svahn, Christopher Sutton, Thomas D. Swinburne, Jules Tilly, Cas van der Oord, Eszter Varga-Umbrich, Tejs Vegge, Martin Vondrák, Yangshuai Wang, William C. Witt, Fabian Zills, Gábor Csányi

INSPIRED: MLFF



INSPIRED: MLFF

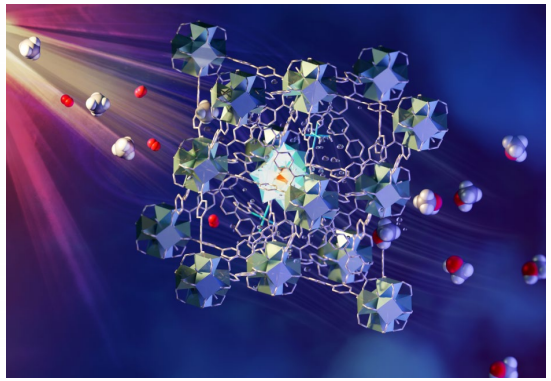
Juneja et al. Quasiparticle twist dynamics in non-symmorphic materials, Materials Today Physics 21 (2021) 100548



Applications

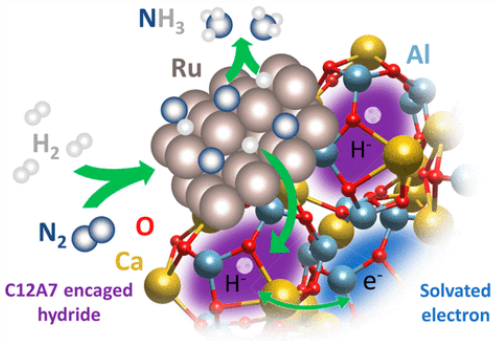
Metal-organic framework

- 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)



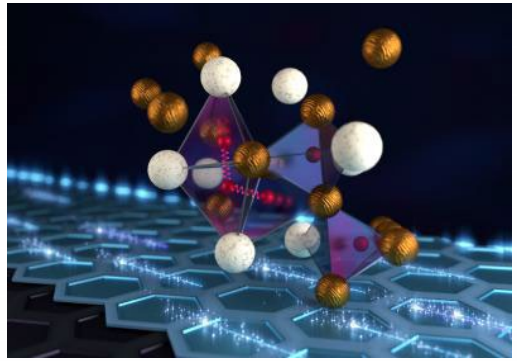
Nano-catalyst

- 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)



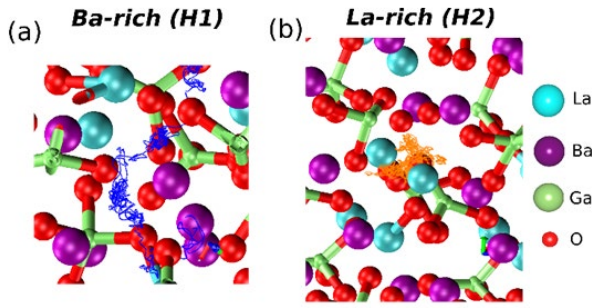
Complex hydride

- 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)



Energy materials

- 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)

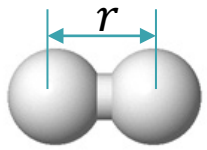


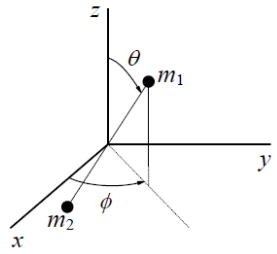
NVS for molecular hydrogen

Quantum diatomic rotor

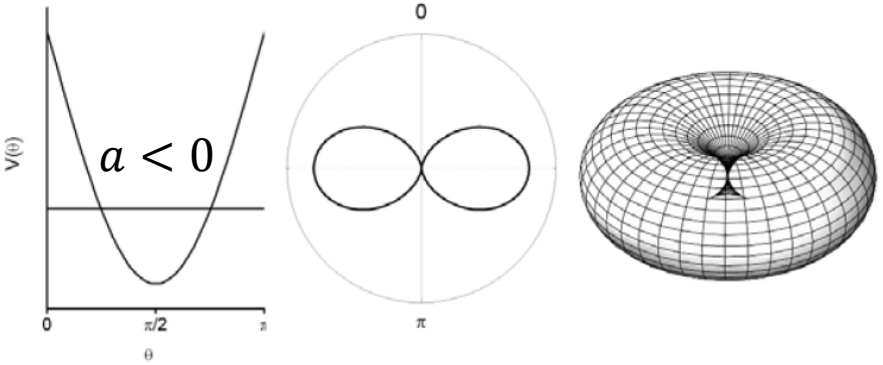
$$E_{rot} = J(J+1)B_{rot}$$

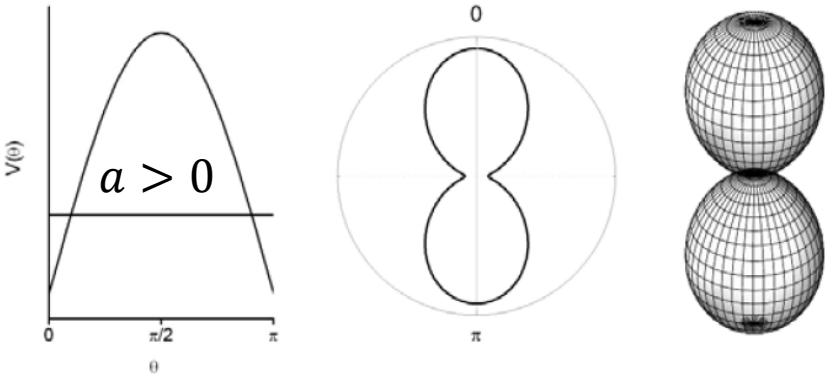
$$B_{rot} = \frac{\hbar^2}{2I} = \frac{\hbar^2}{mr^2}$$



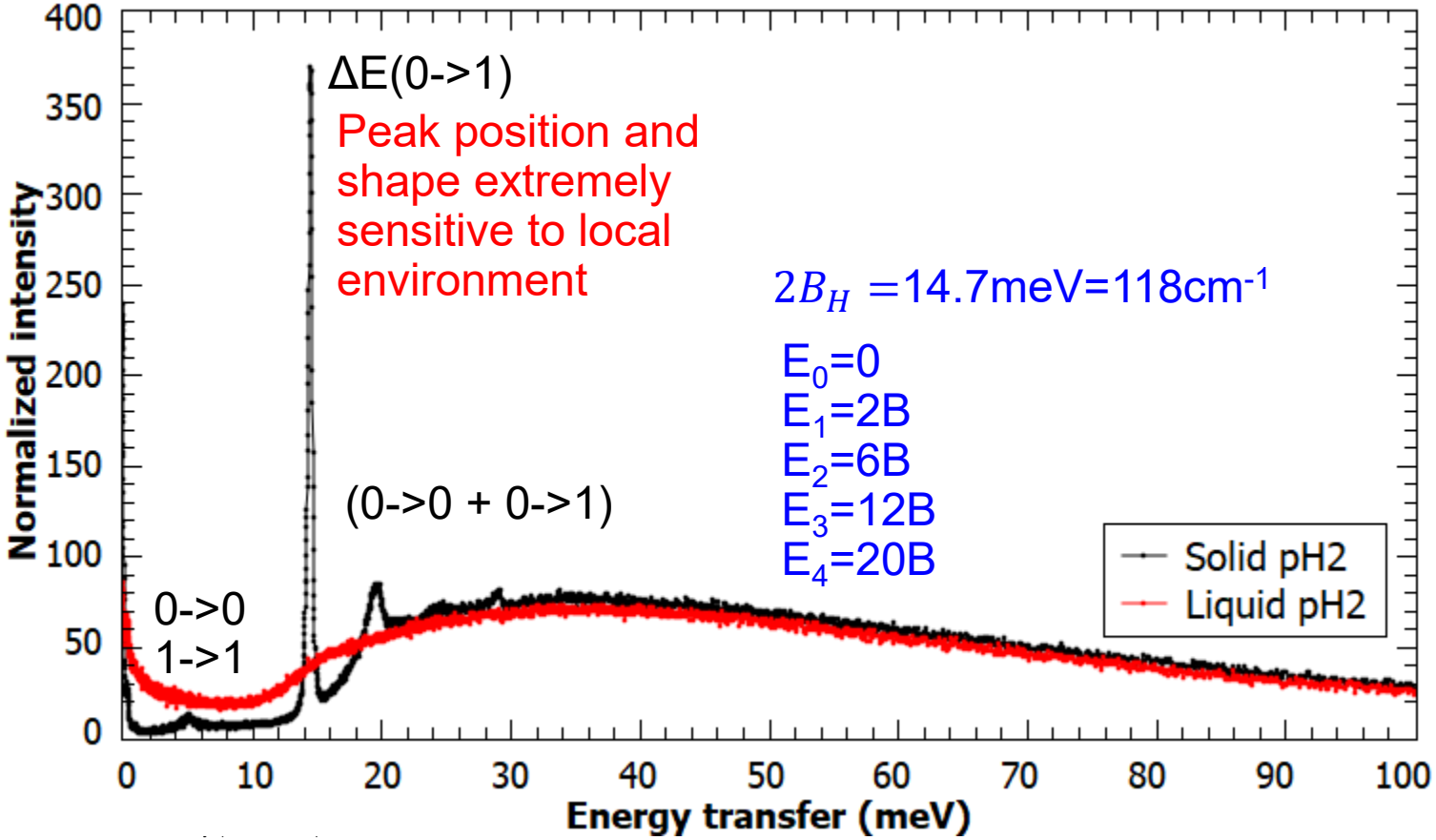


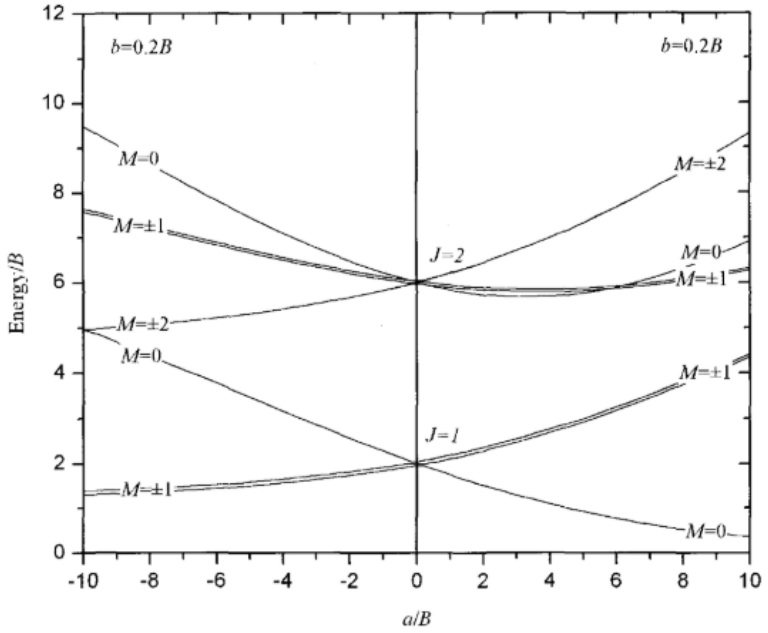
$$V(\theta,\phi) = \left[a + \frac{b}{2}\cos 2\phi\right]\sin^2\theta$$



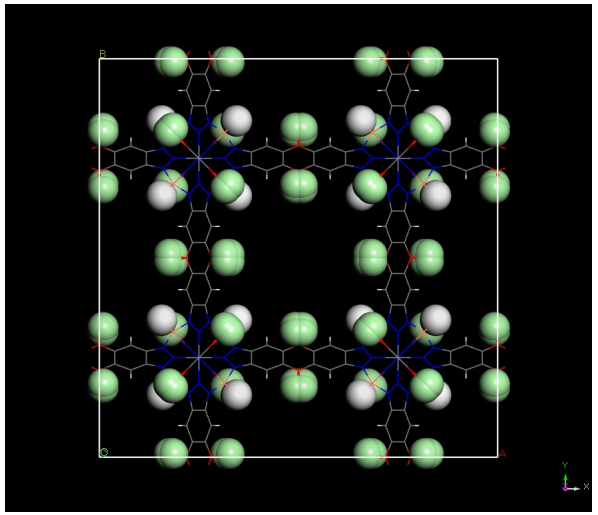


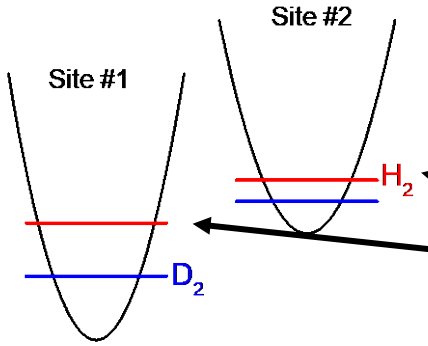
Mitchell et al. Vibrational Spectroscopy with Neutrons 2004

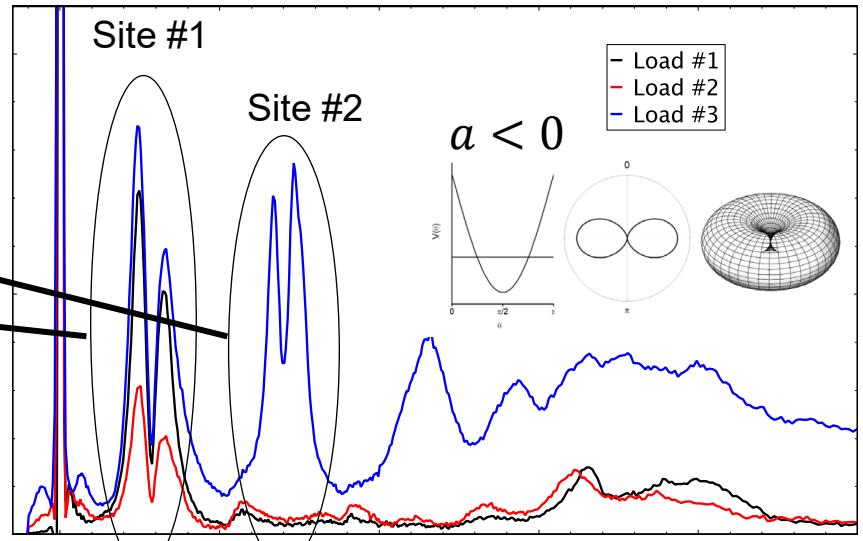




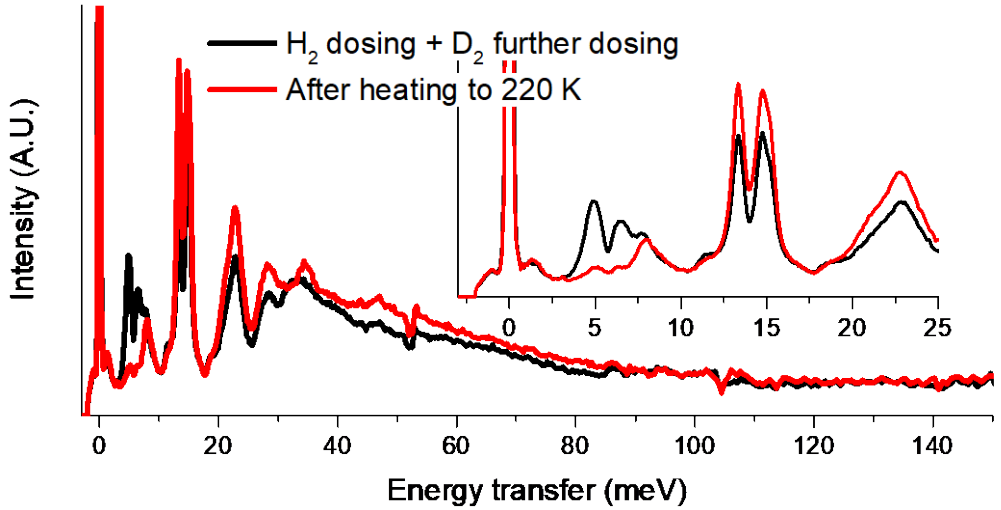
Quantum Sieving Hydrogen in a metal-organic framework

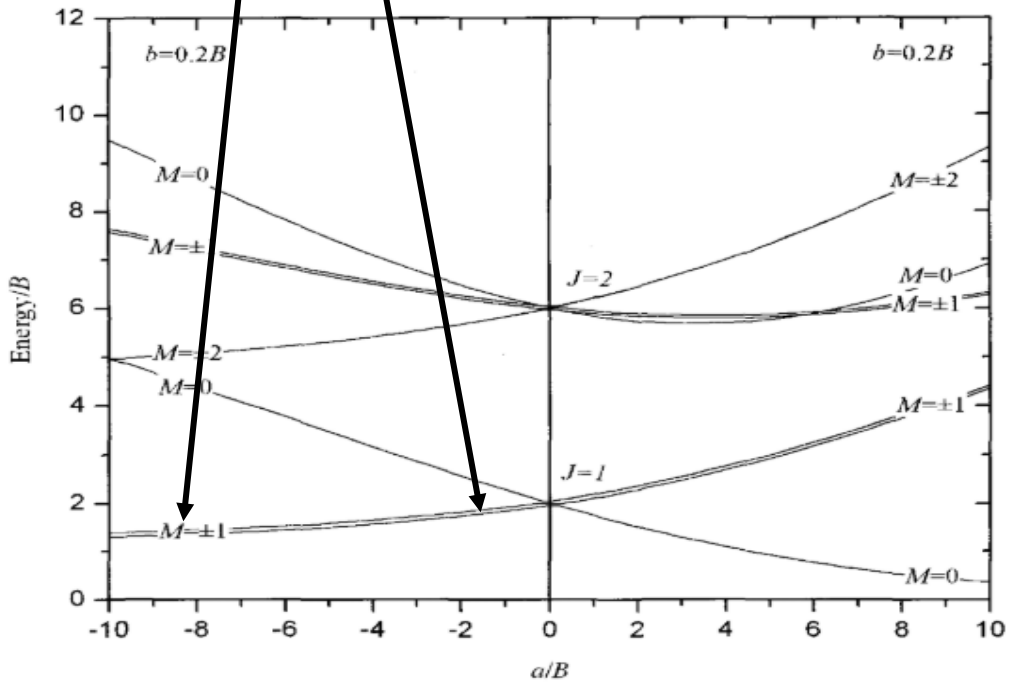






Quantum sieving is a technique for isotope separations; heavier isotopes induce favorable adsorption in nanoscale pores due to the difference in zero-point energy of isotopes.

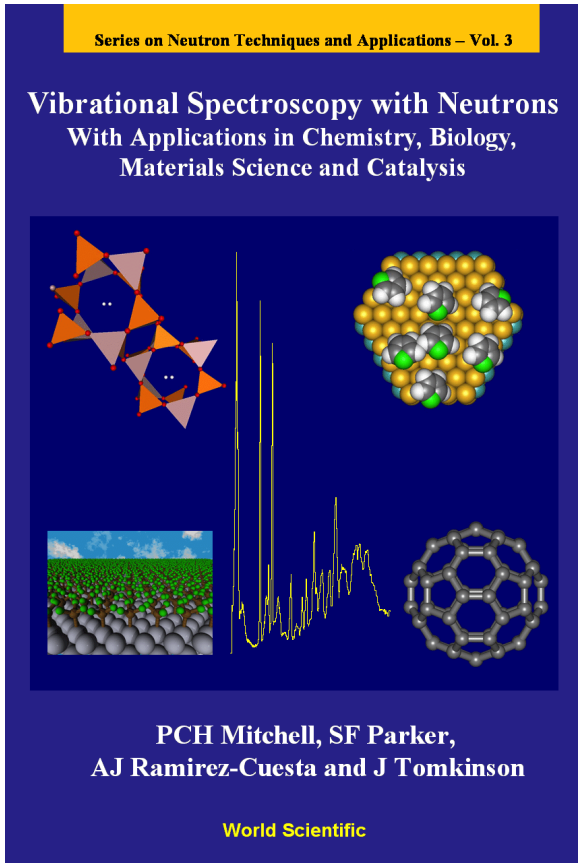




Weinrauch, I. et al. Nature Communications, 8, 14496 (2017).

Take-home messages:

- NVS focuses on applications of INS in chemistry.
- NVS and Raman/IR are complementary tools to provide a complete picture of molecular vibration.
- VISION is the instrument at SNS optimized for NVS.
- Modeling plays a critical role in NVS data interpretation.
- VISION has a digital twin powered by the VirtuES cluster and high throughput workflow/software.
- AI/ML has potential to accelerate NVS experiment design and data analysis.



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- 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

Han, B; Savici, A. T.; Li, M.; Cheng, Y. Q. INSPIRED: Inelastic neutron scattering prediction for instantaneous results and experimental design. Computer Physics Communications, 304, 109288, 2024

https://neutrons.ornl.gov/vision

Questions?

chengy@ornl.gov