Oak Ridge National Laboratory

Neutron Vibrational Spectroscopy

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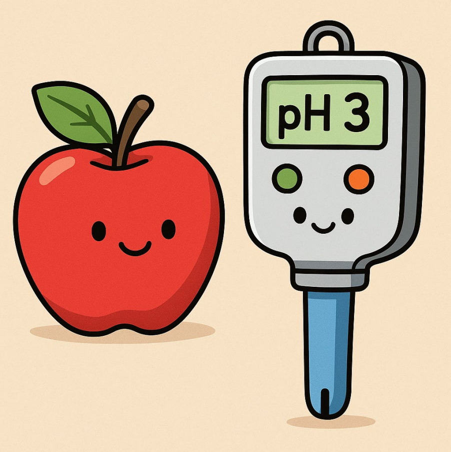
U.S. DEPARTMENT OF ENERGY

2025 National School on
Neutron and X-ray Scattering

What is neutron vibrational spectroscopy (NVS)?

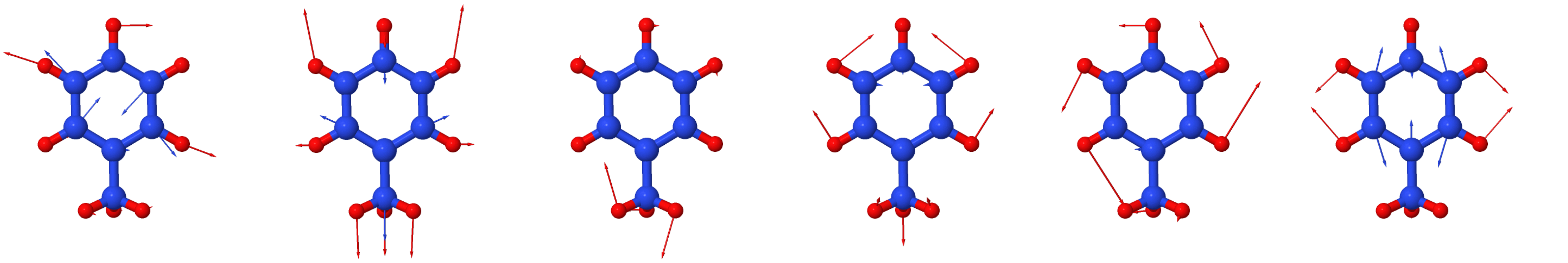
Neutron vibrational spectroscopy (NVS)	Inelastic neutron scattering (INS)
Chemists	Physicists
Molecular systems Organic/inorganic compounds	Condensed matter
Intramolecular modes Intermolecular modes	Phonons Magnons
S(ω) in cm^{-1}	S(Q,E) in meV and $Å^{-1}$
Indirect geometry instrument	Direct geometry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



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

Cartoons generated by ChatGPT

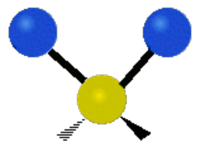
Molecular vibration: the eternal dance of molecules



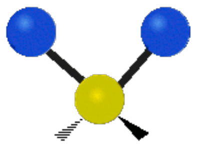
Note: the actual frequency is 40 trillion times faster!

Each molecular vibration has its own “pace” and “motion”.

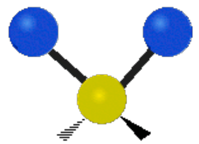
Symmetric stretching



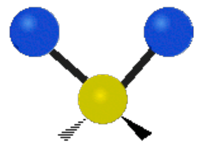
Asymmetric stretching



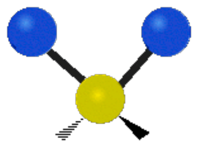
Scissoring (Bending)



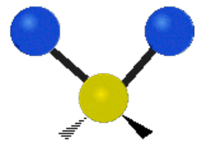
Rocking



Wagging

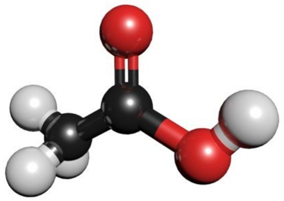


Twisting

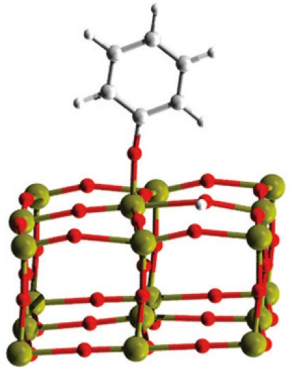


https://en.wikipedia.org/wiki/Molecular_vibration

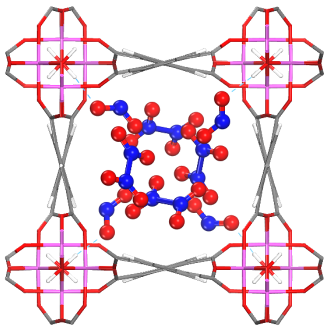
Vibration of molecules in different environment



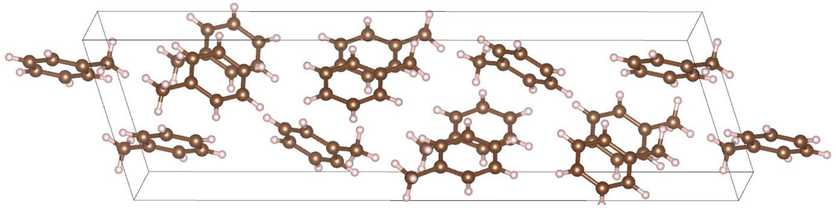
Isolated (gas, non-interacting)



On surface (chemi/physi-adsorbed)



In pores (restricted/confined)



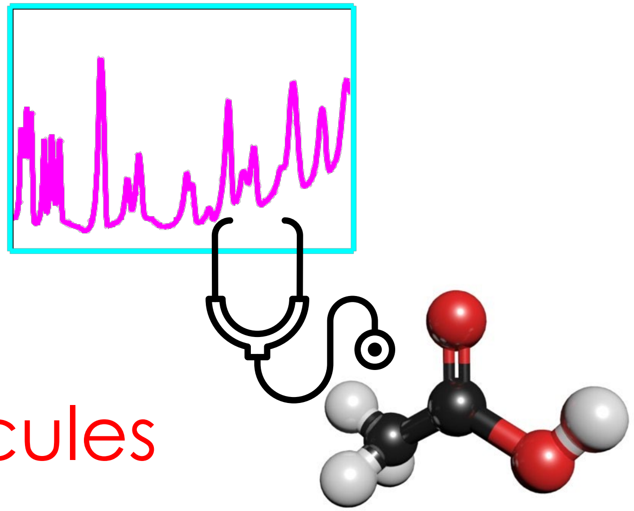
Self-assembled (solid)

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
- 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)
- ……

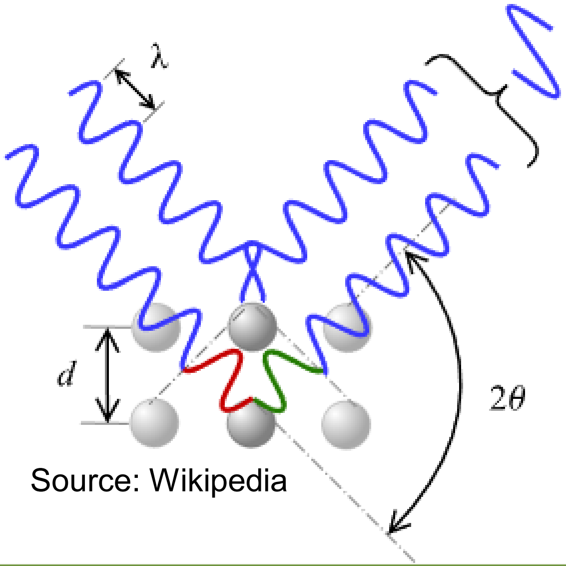


One of the most important vital signs of molecules

How to measure molecular vibration: Vibrational spectroscopy

<u>Crystallographers</u> 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.

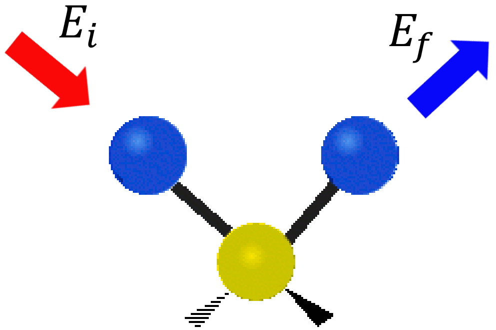
Wavelength
Scattering angle



Source: Wikipedia

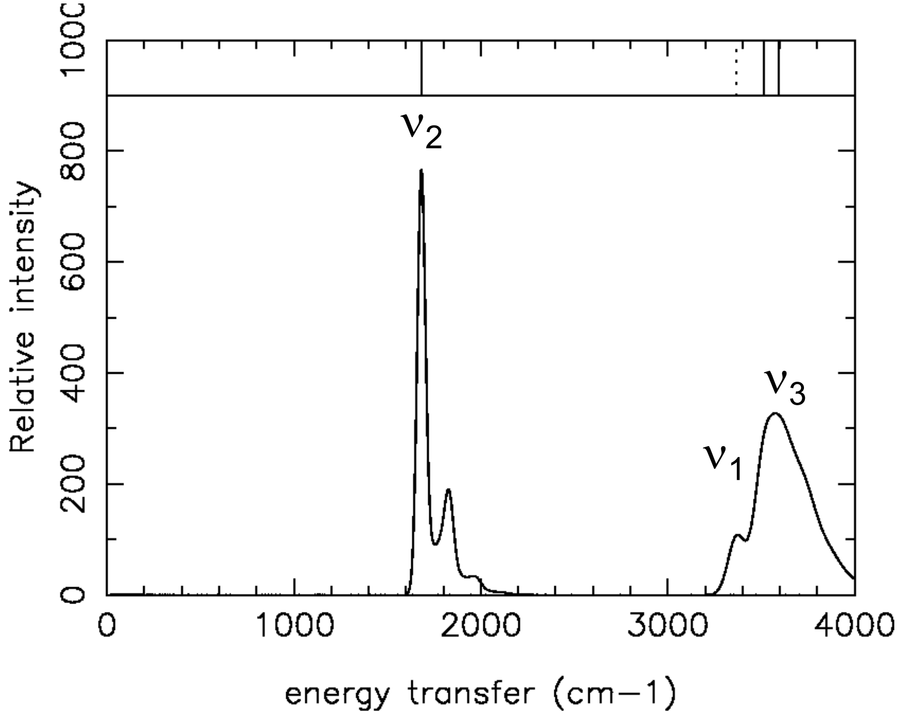
<u>Spectroscopists</u> use (inelastic) scattering of radiation (light, x-ray, neutron,...) to excite vibrational modes. The energy of the radiation is comparable to the energy associated with the vibrational excitations.

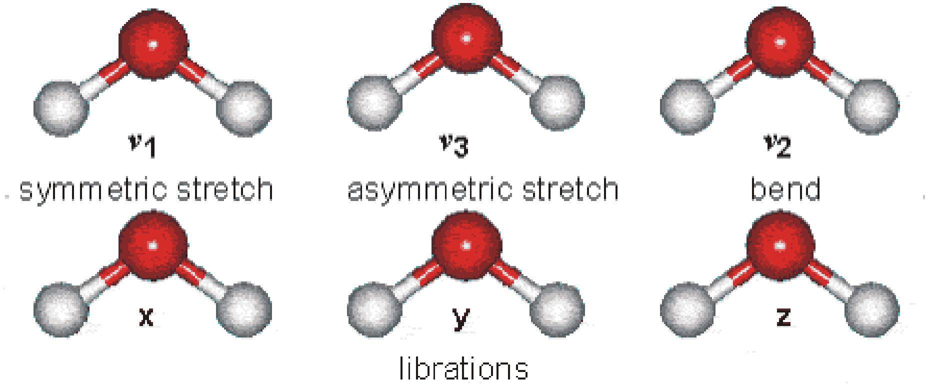
Incident energy
Final energy
(Scattering angle)



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

Interpretation of vibrational spectra: peak assignment





https://www.acamedia.info/sciences/J_G/envrad/microwaves/index.htm

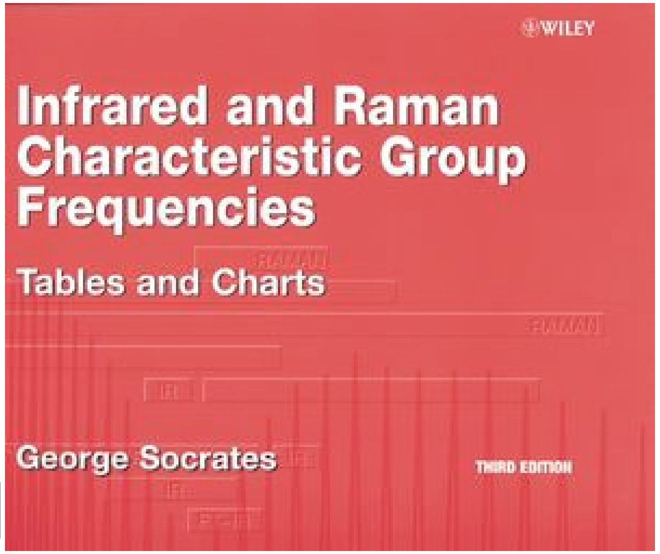


Table 1 Absorption frequencies of some common bonds (shown in bold type)

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

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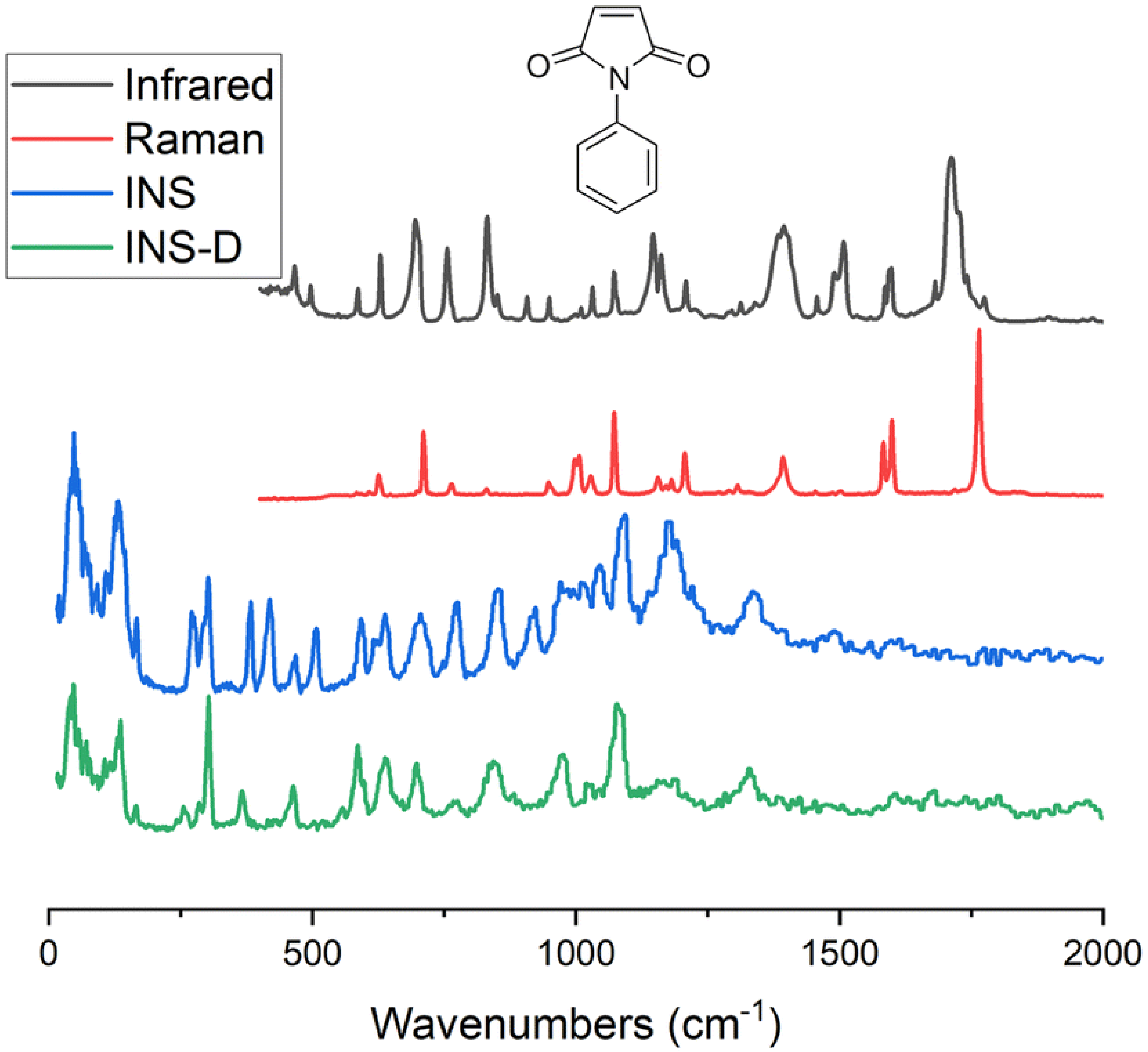
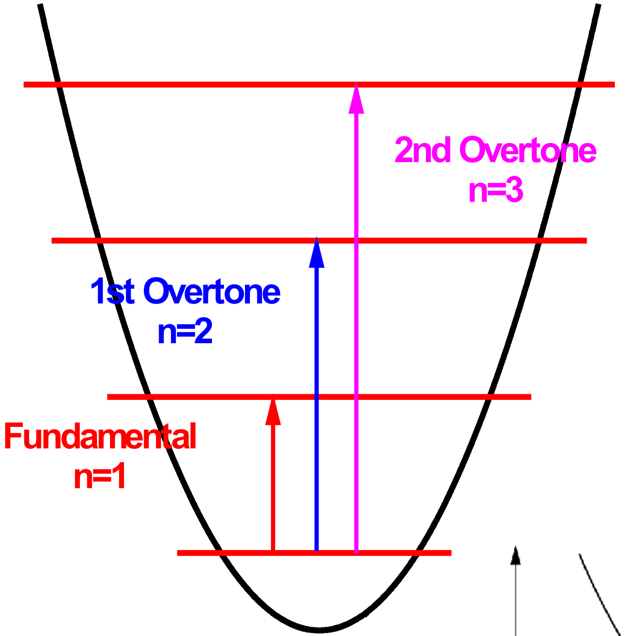
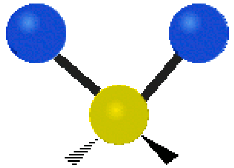


S.F. Parker, *Int.J. Vib. Spect.*, **2**, 1, 6-22 (1998)

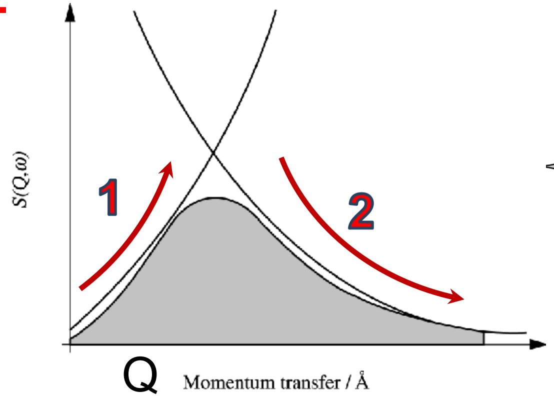
A simple S(Q,ω) map of molecular vibration: key features

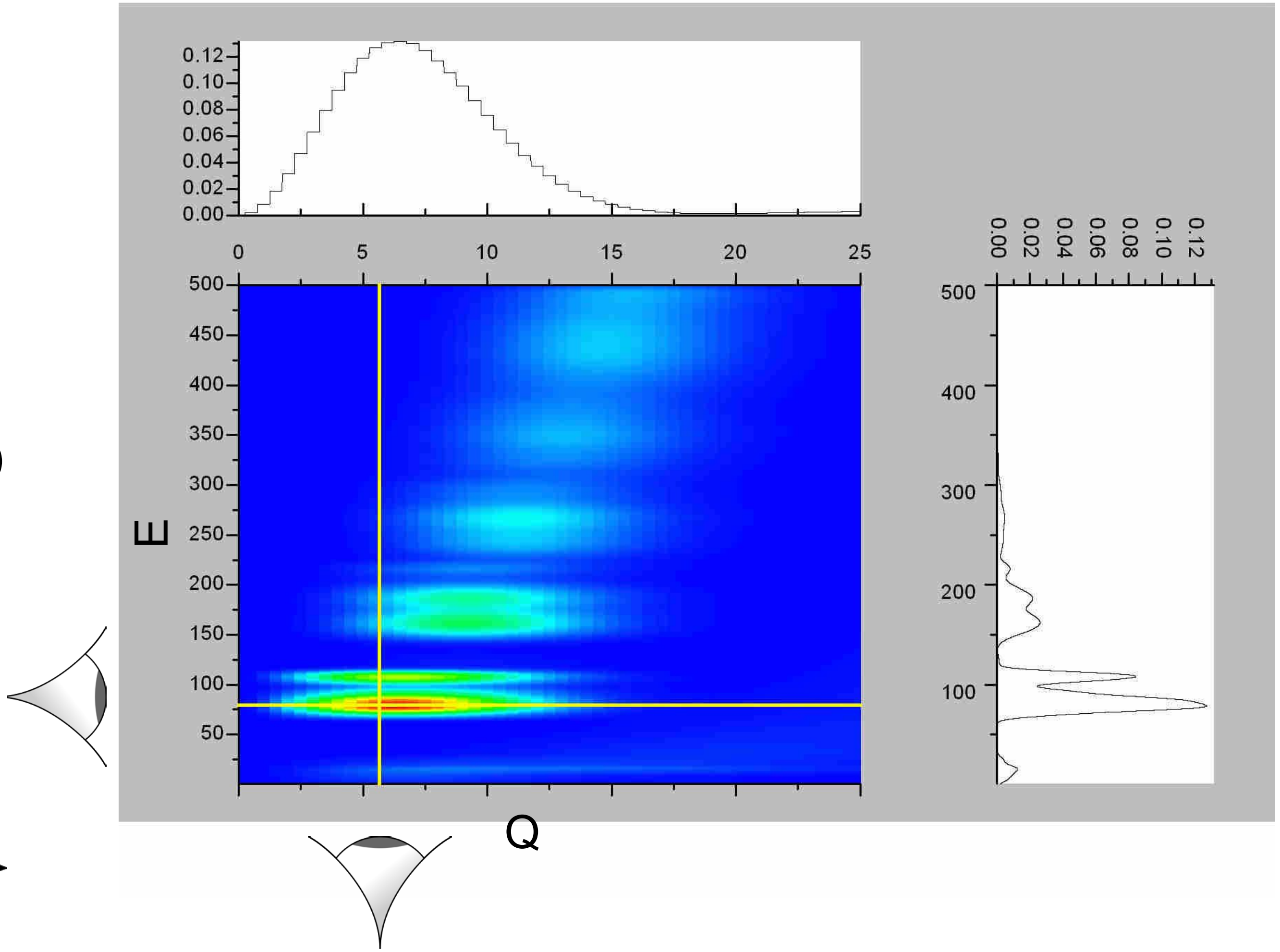


Quantum harmonic oscillator



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

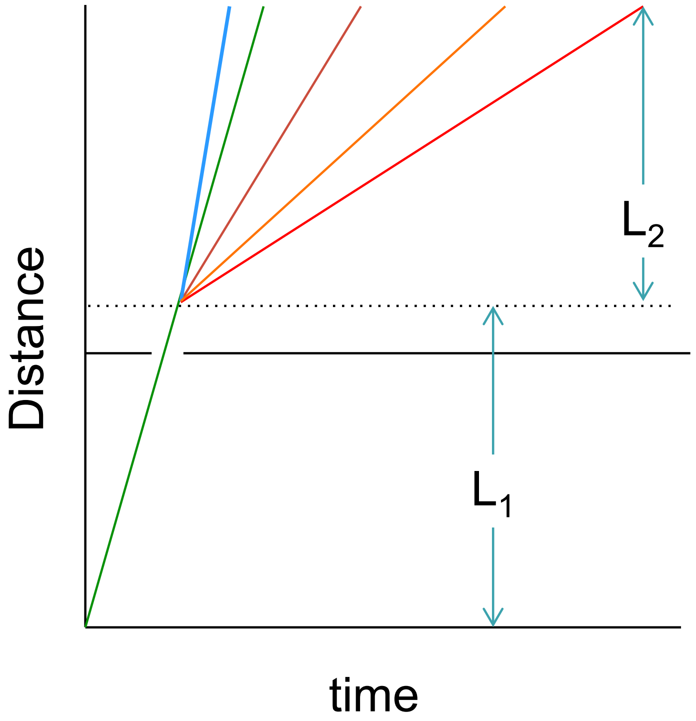




$$S(\boldsymbol{Q}, n\omega_s) = \frac{\overset{1}{\boxed{(\boldsymbol{Q}\cdot\boldsymbol{U}_s)^{2n}}}}{n!}\overset{2}{\boxed{\exp[-(\boldsymbol{Q}\cdot\boldsymbol{U}_{total})^2]}}$$

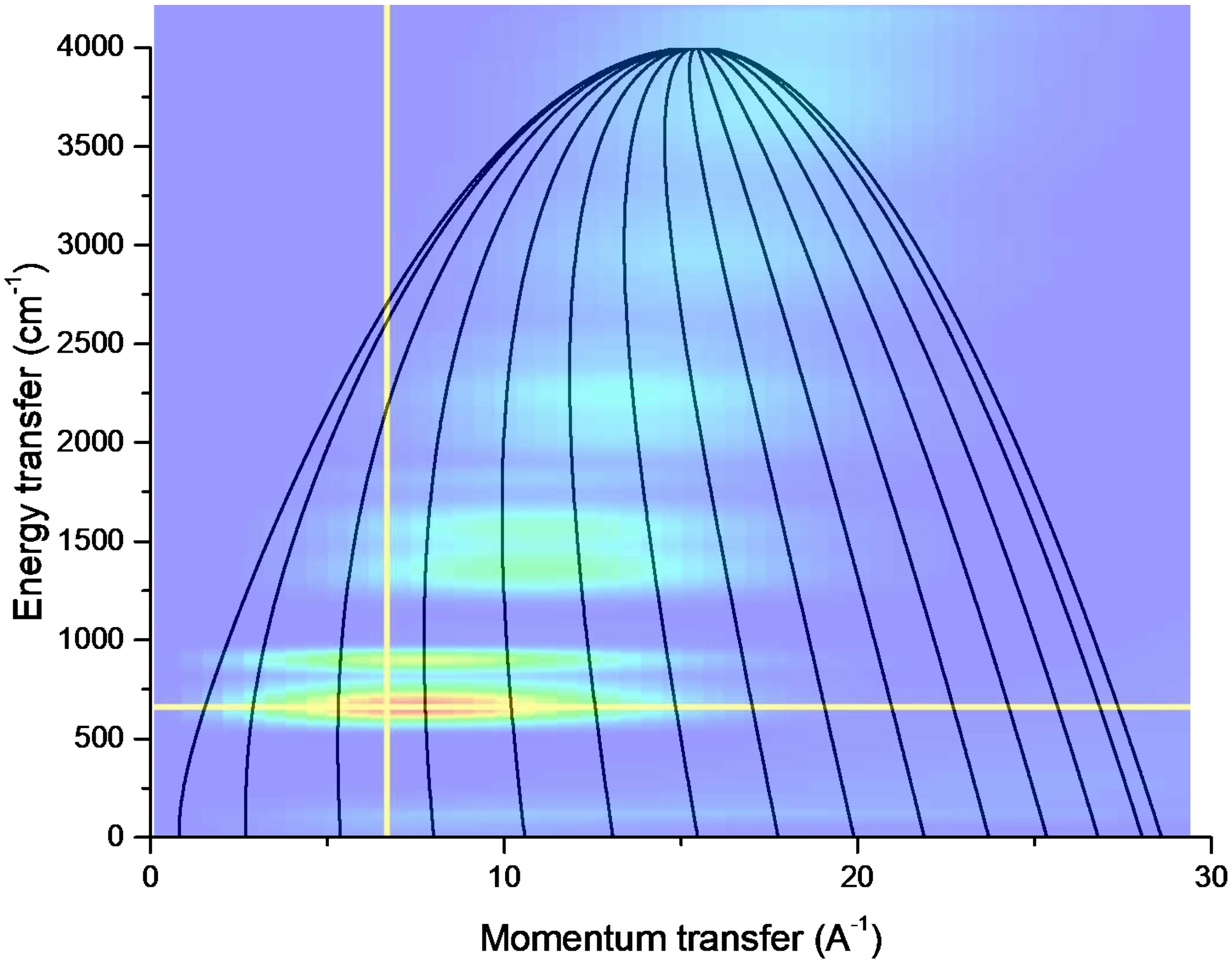
$$\boldsymbol{U}_s = \sqrt{\frac{\hbar}{2m\omega_s}}\boldsymbol{e}_{ds}$$

Choice of instrument for NVS: direct geometry

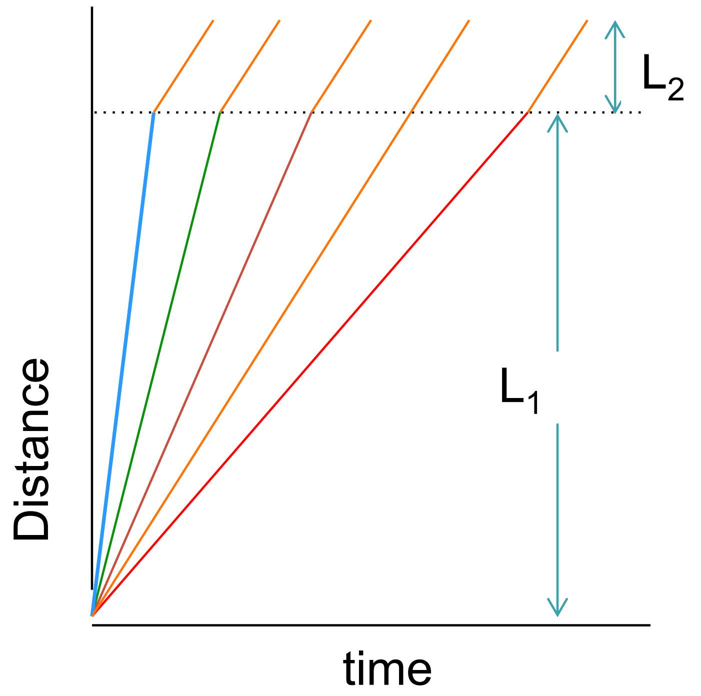


Fixed incident energy, measure final energy and scattering angle.

Examples: ARCS, CNCS, HYSPEC, SEQUIOA, MARI

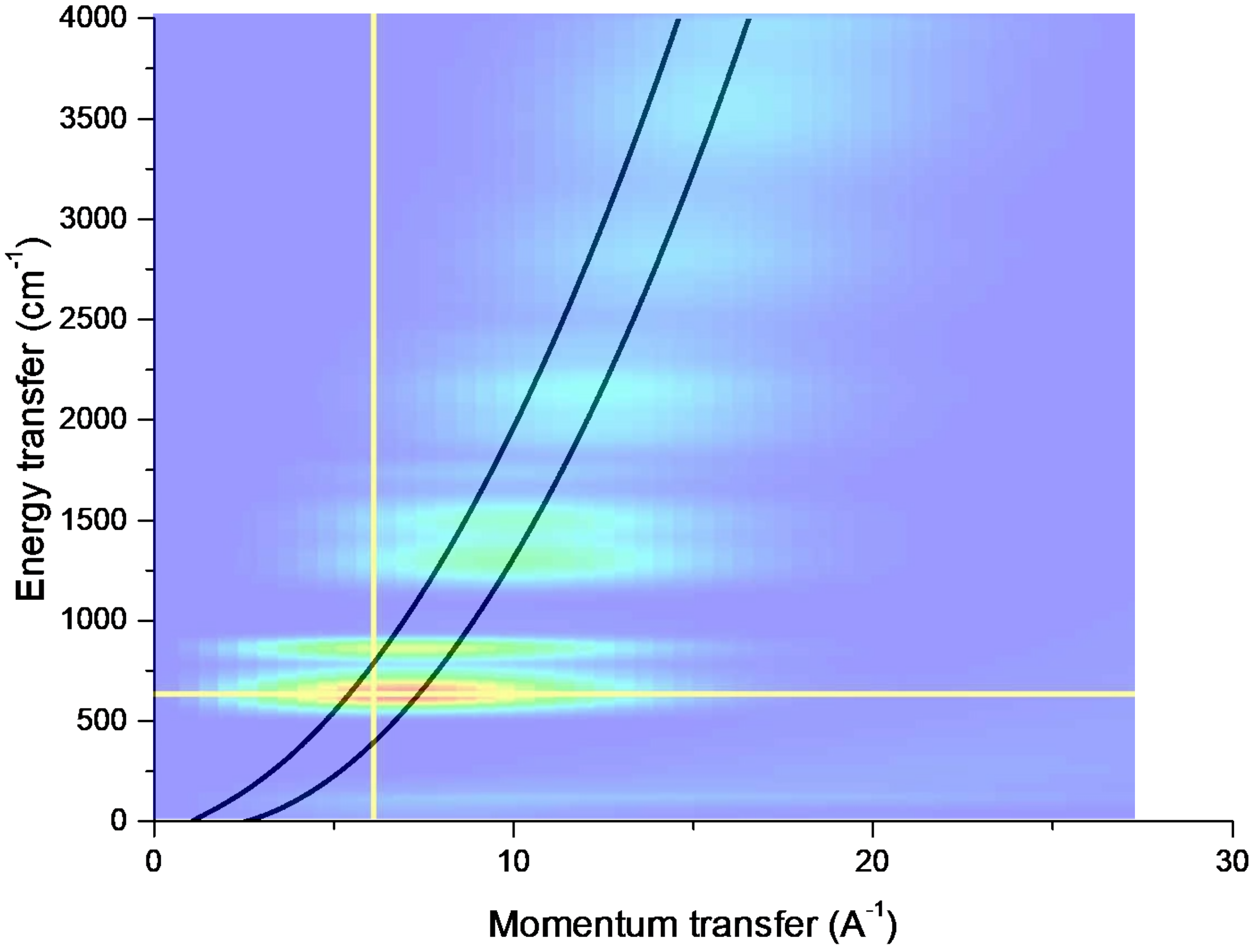


Choice of instrument for NVS: indirect geometry

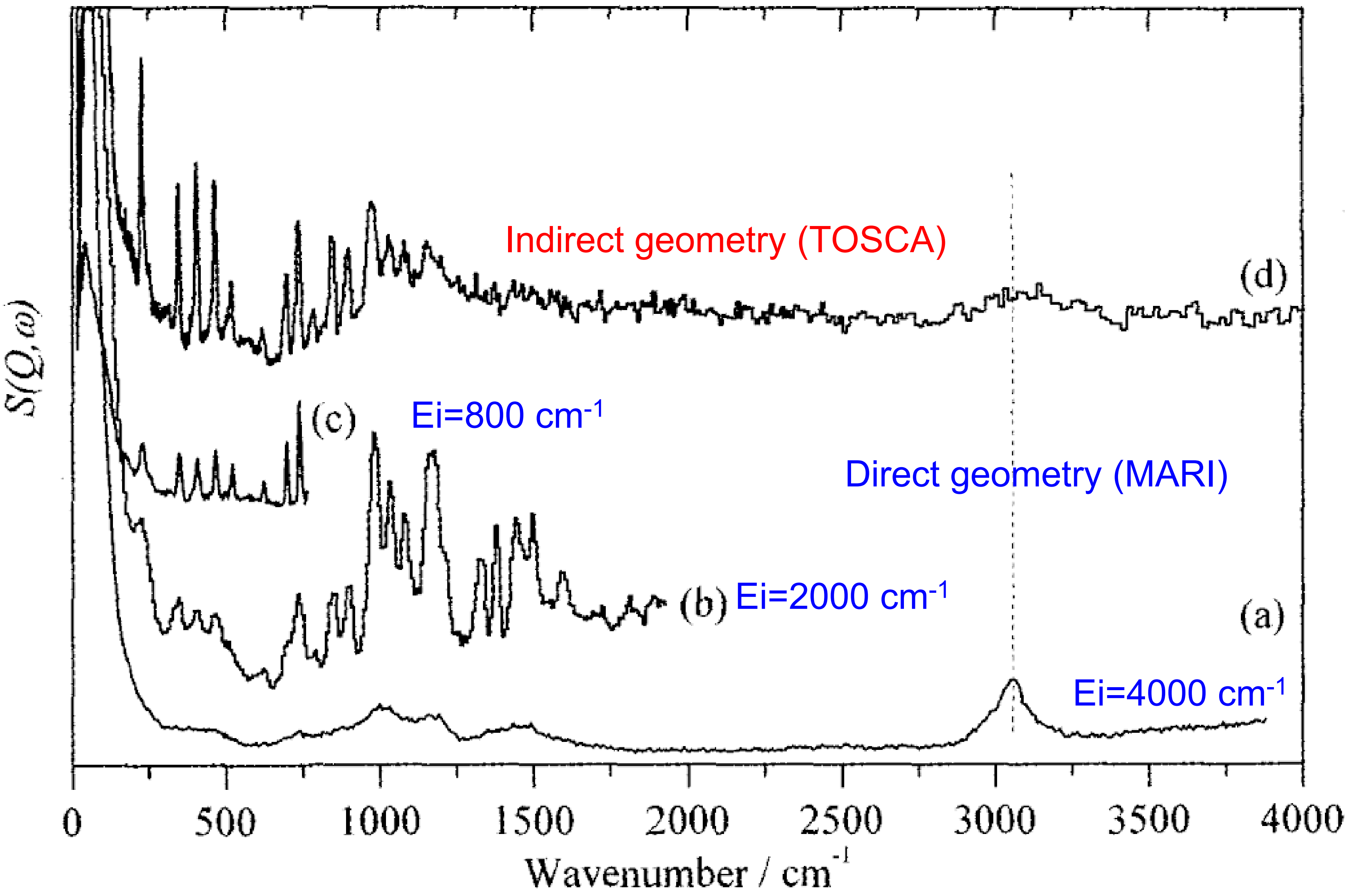


White incident beam,
fixed final energy,
calculate initial energy.

Examples: VISION, TOSCA



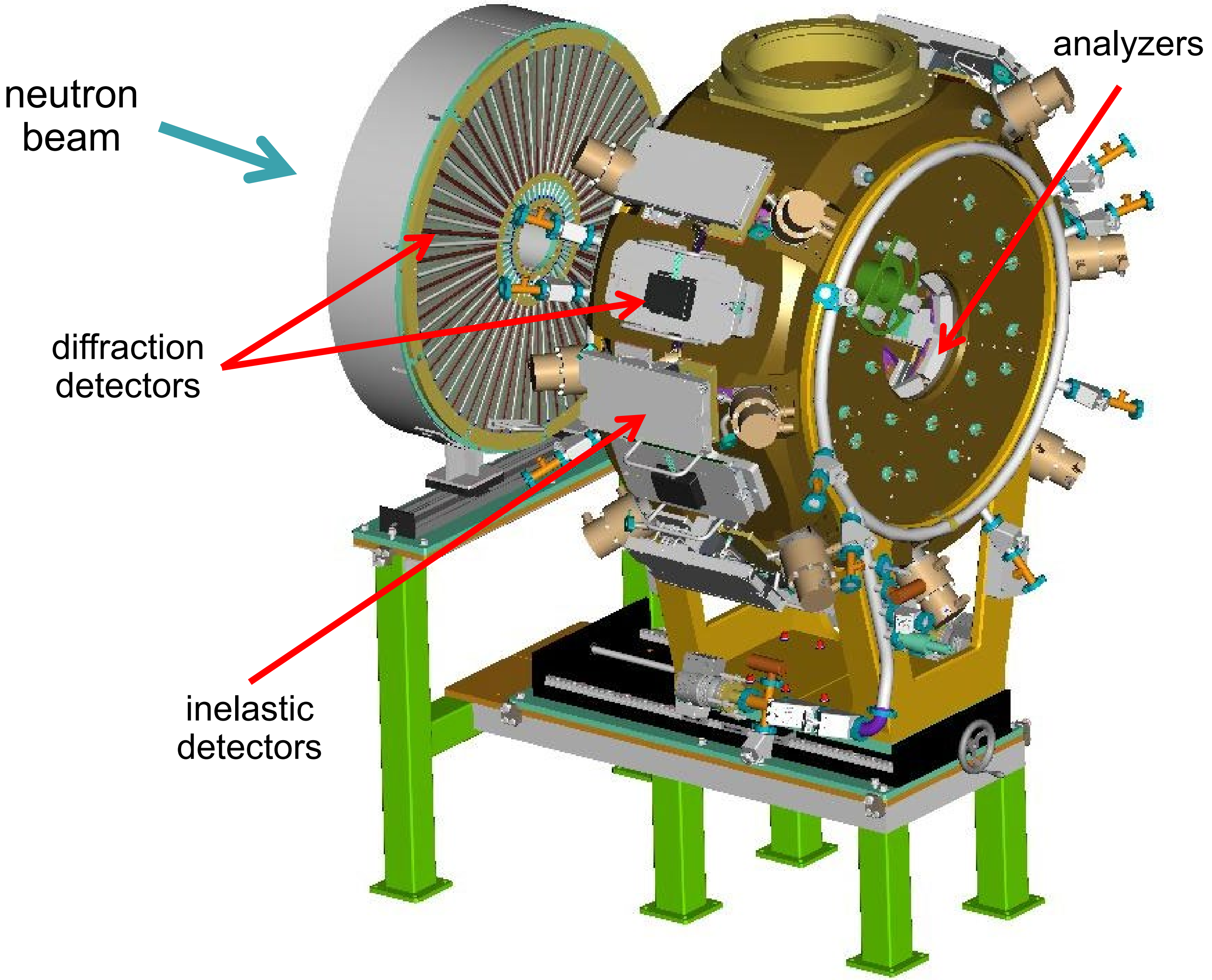
Choice of instrument for NVS: comparison



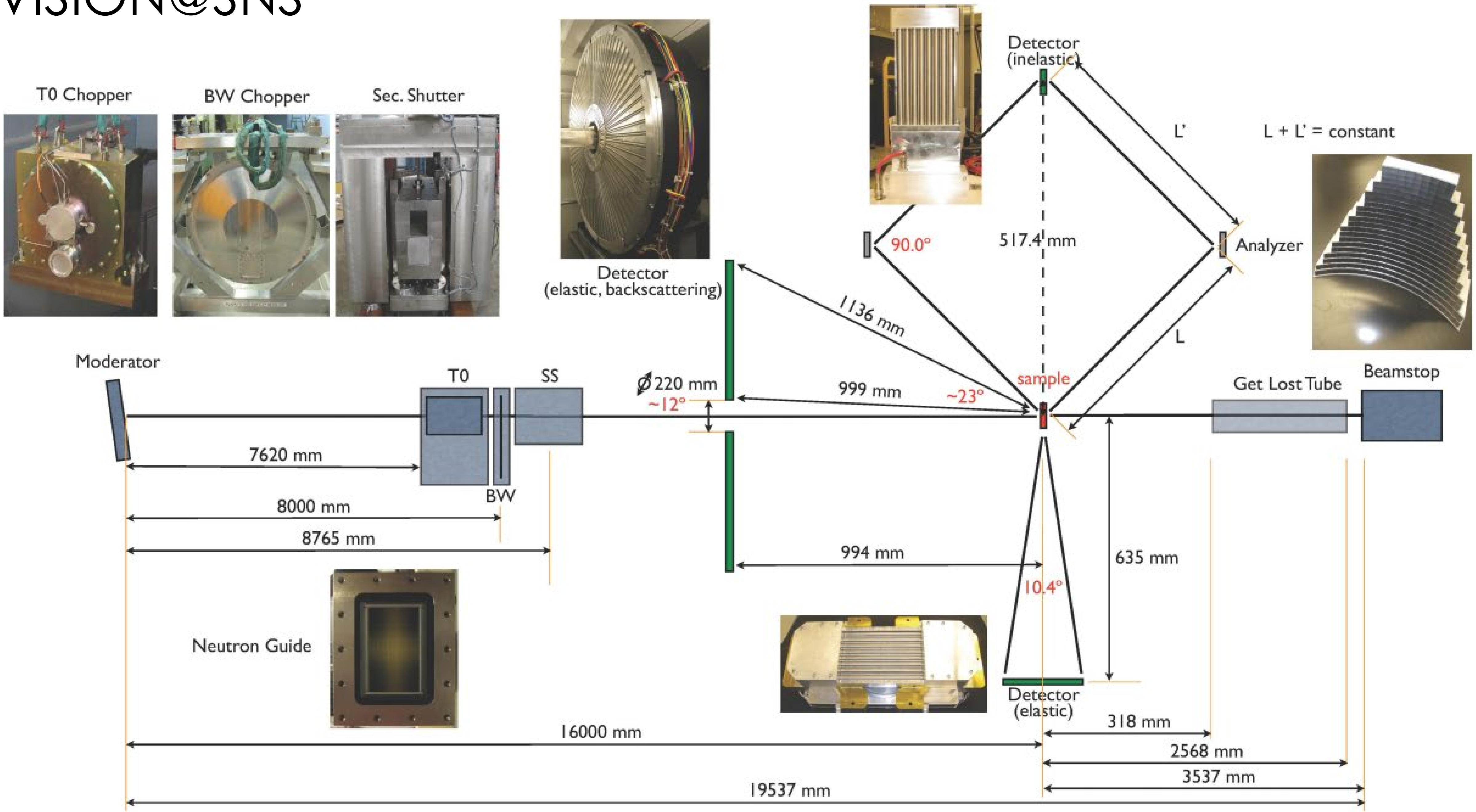
Mitchell et al. Vibration Spectroscopy with Neutrons, World Scientific 2005

VISION@SNS

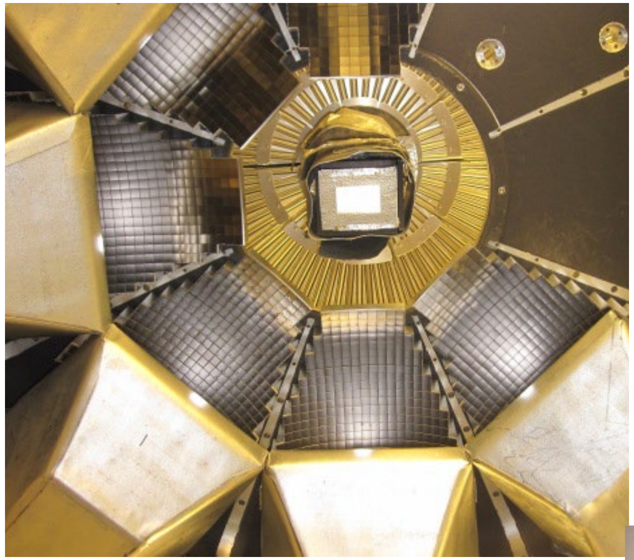
- White incident beam, fixed final energy (indirect geometry)
- High flux and double-focusing
- Broadband (-2 to 1000 meV at 30Hz, 5 to 500 meV at 60 Hz)
- Constant dE/E throughout the spectrum (~1.5%)
- Elastic line HMFW ~150 μeV
- Backward and 90° diffraction banks

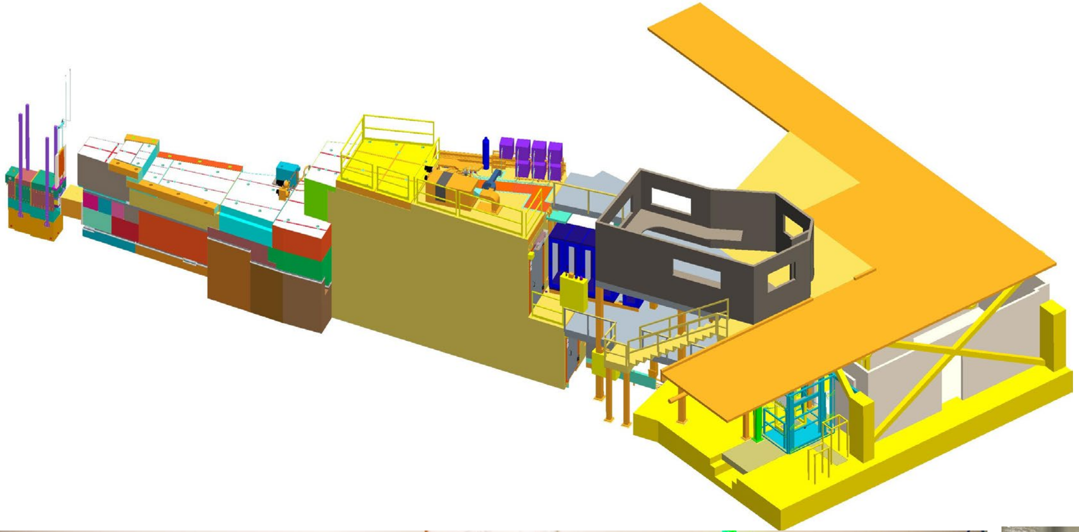


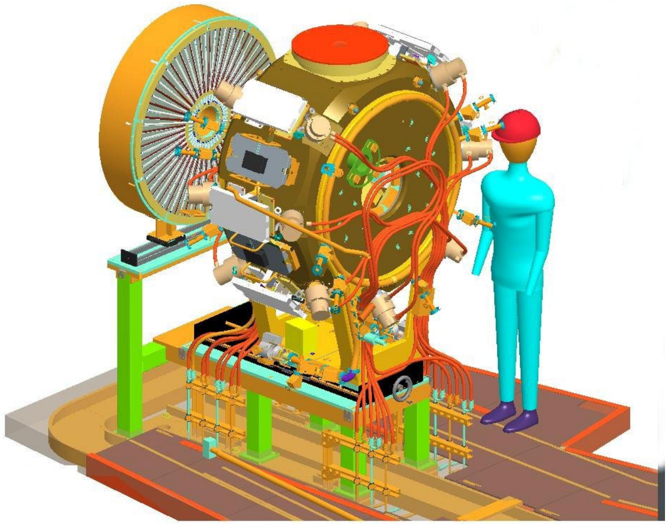
VISION@SNS

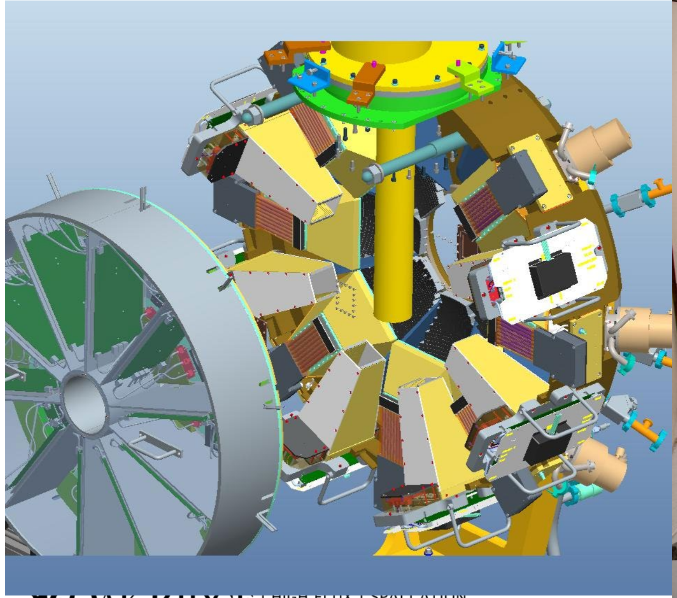

T0 Chopper
BW Chopper
Sec. Shutter
Detector
(elastic, backscattering)
Detector
(inelastic)
L'
L + L' = constant
90.0°
517.4 mm
Analyzer
1136 mm
L
Moderator
T0
SS
Ø220 mm
~12°
999 mm
~23°
sample
Get Lost Tube
Beamstop
7620 mm
BW
8000 mm
8765 mm
994 mm
635 mm
10.4°
Neutron Guide
Detector
(elastic)
318 mm
16000 mm
2568 mm
3537 mm
19537 mm

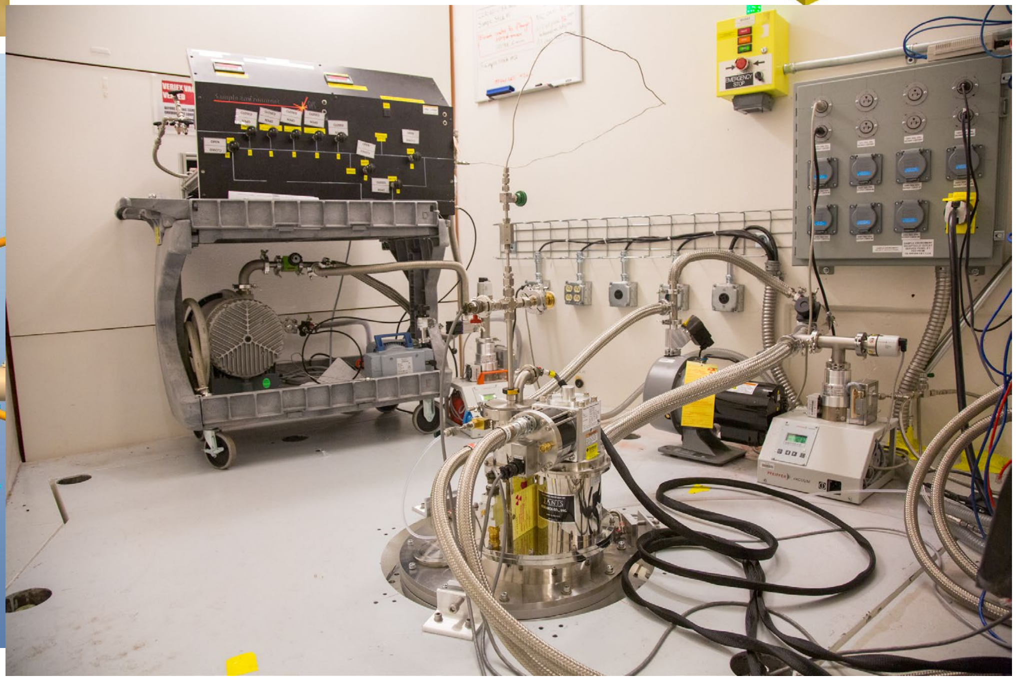
VISION@SNS: a gallery

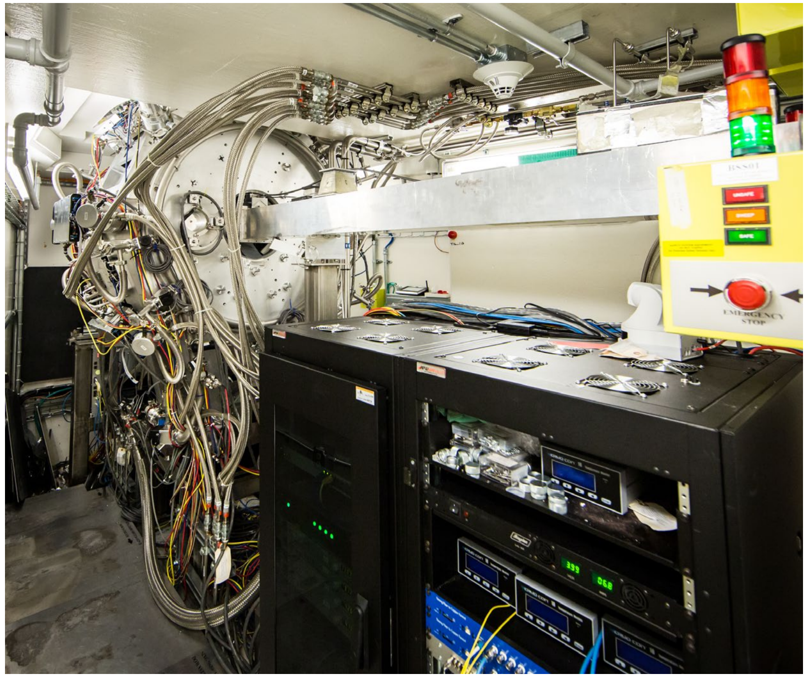




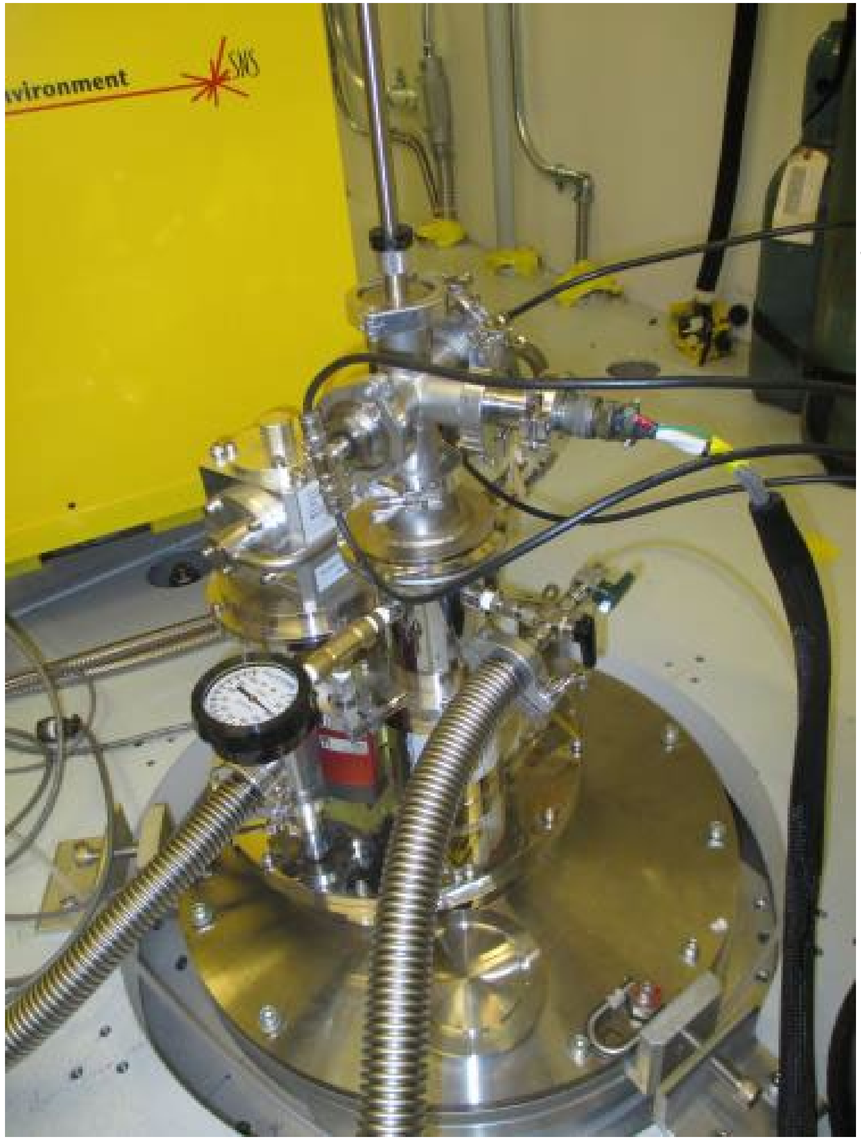




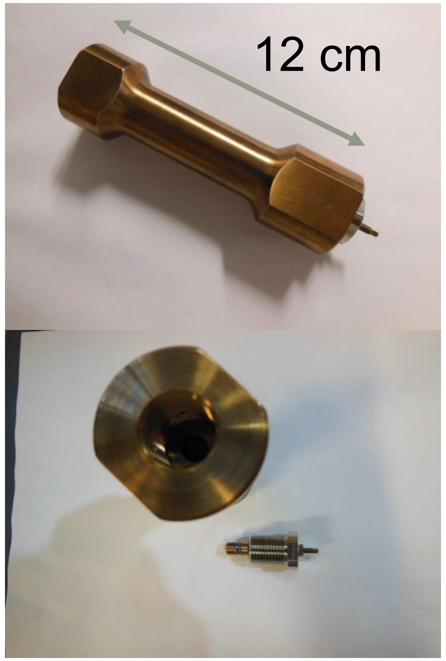


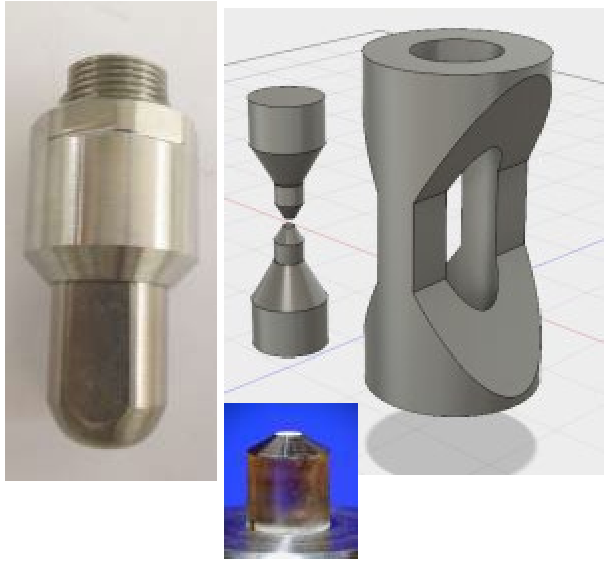


Sample environment at VISION

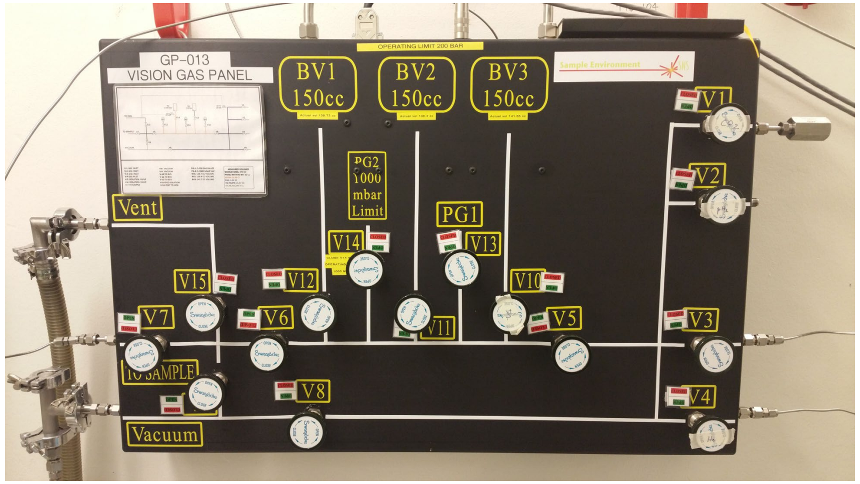


JANIS closed-cycle refrigerator (5-600K)



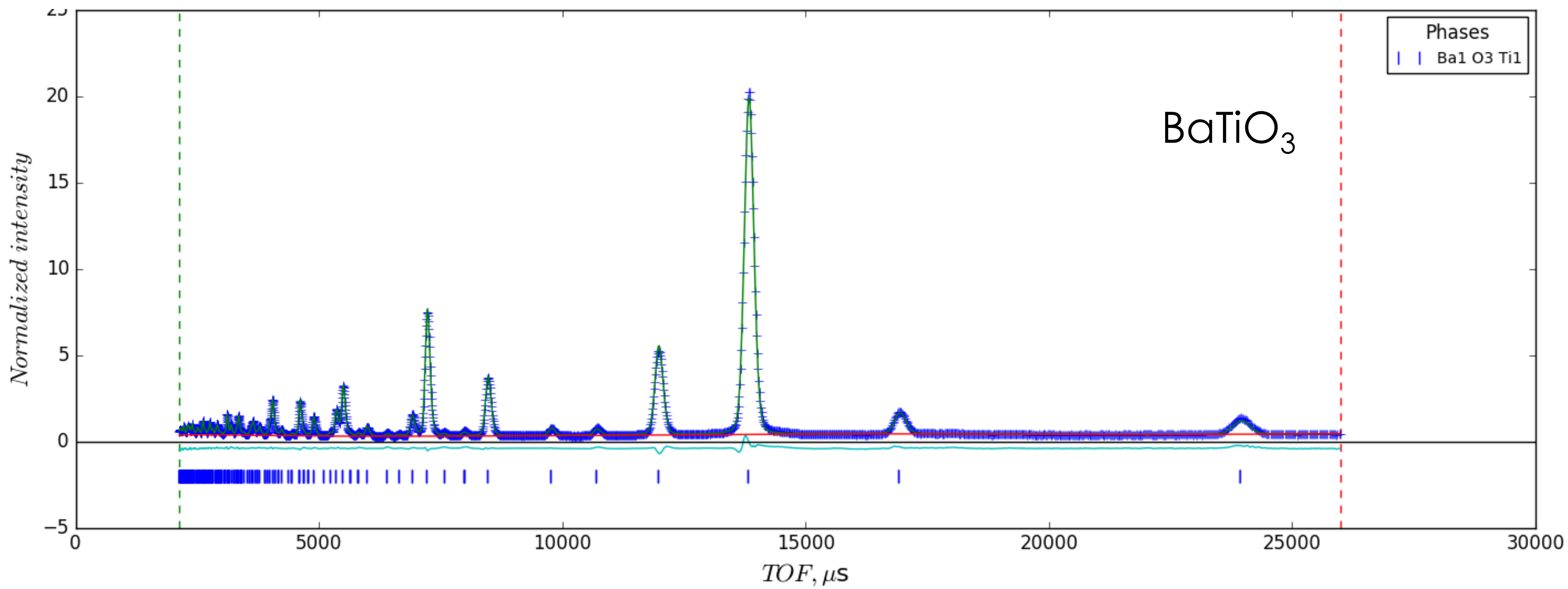


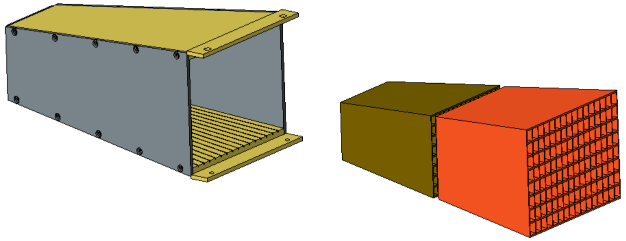
Pressure cells (piston, gas, diamond anvil).

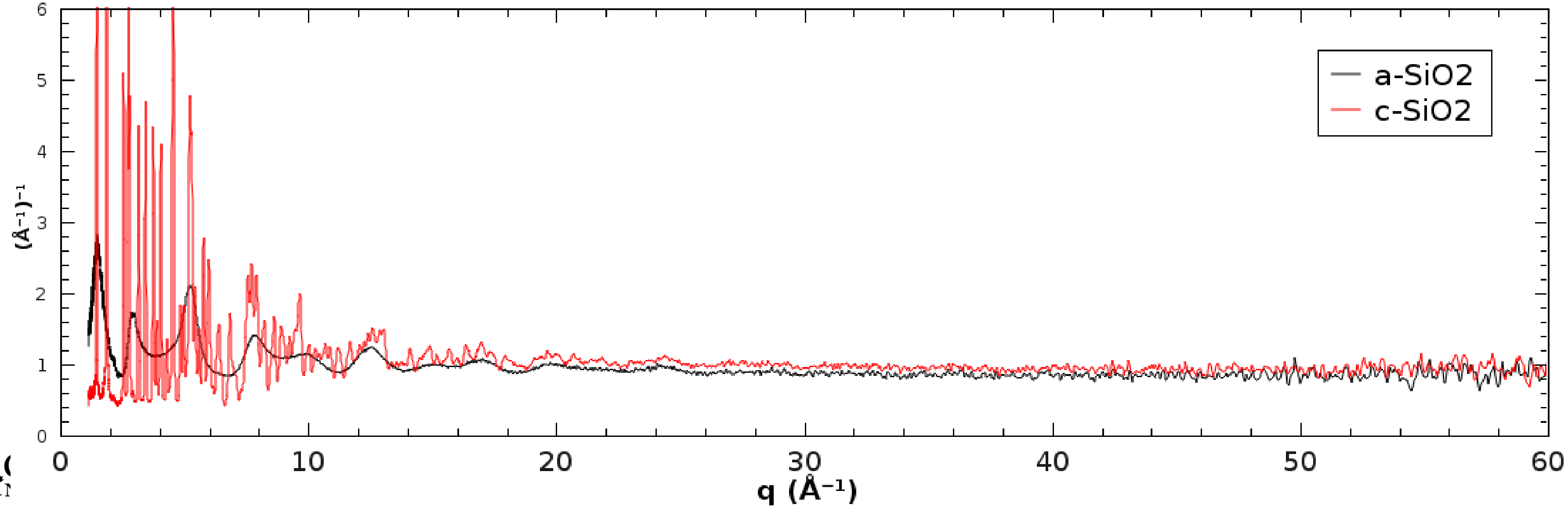


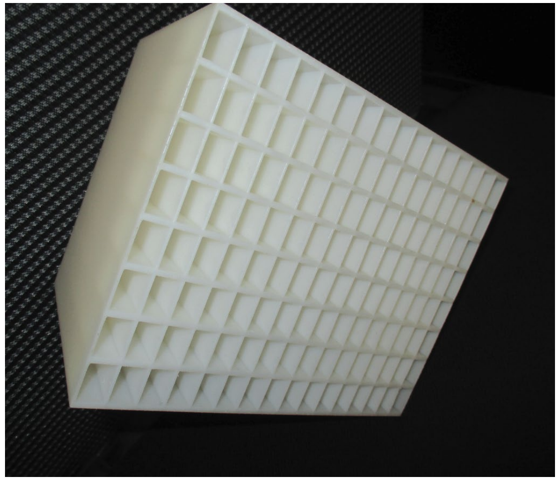
Gas handling panel for gas dosing, mixing, flow, adsorption (vacuum to 200 bar)

VISION diffraction banks

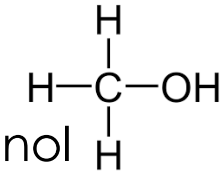




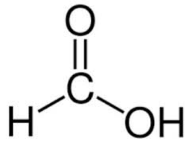




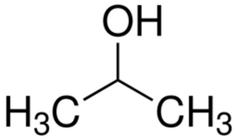
Can you match the molecules with the spectra?



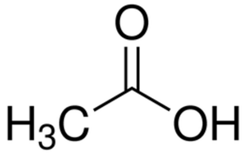
Methanol



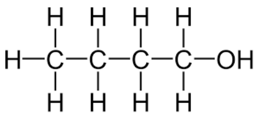
Formic acid



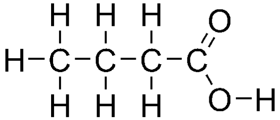
Ethanol



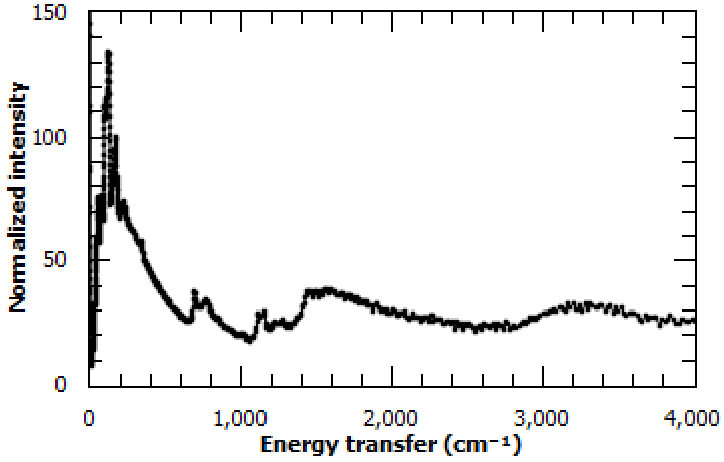
Acetic acid

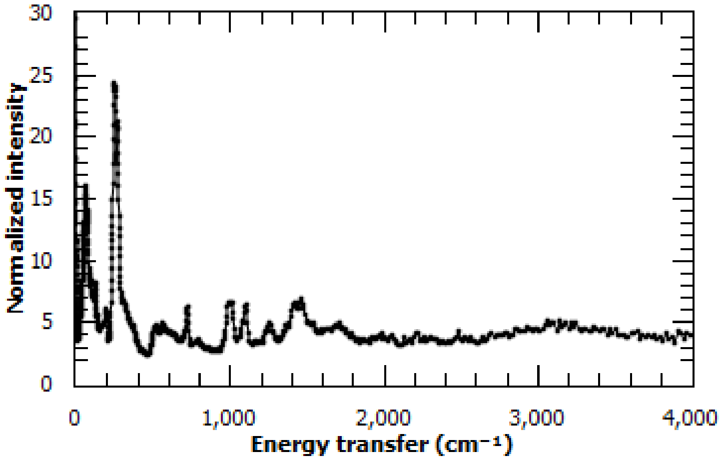


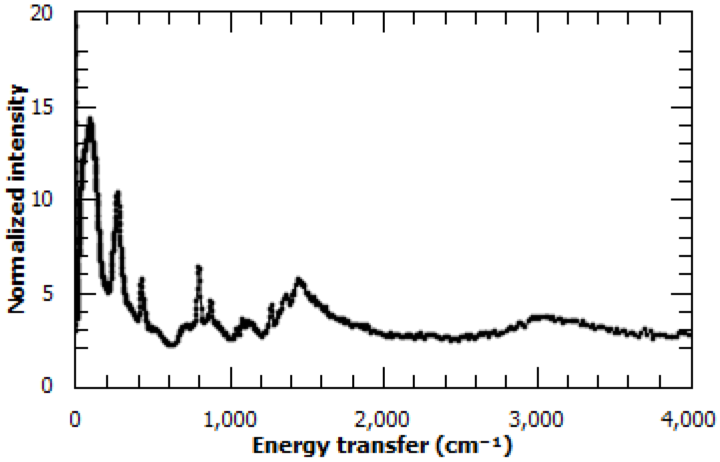
Butanol

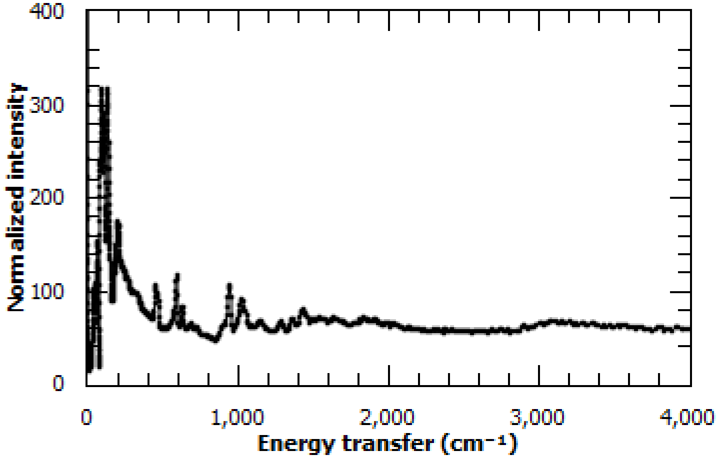


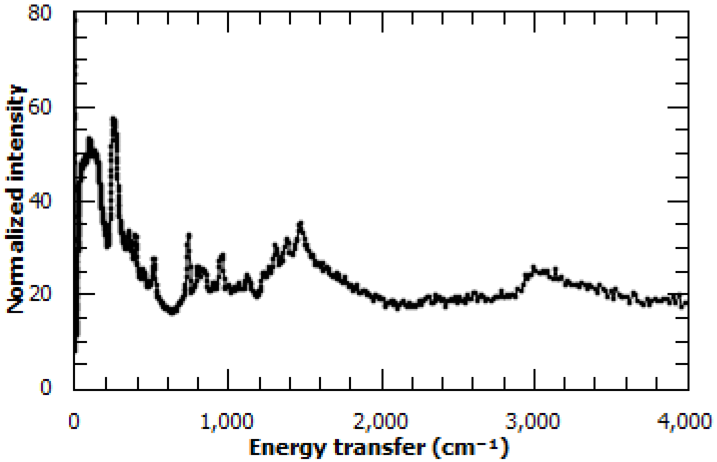
Butyric acid

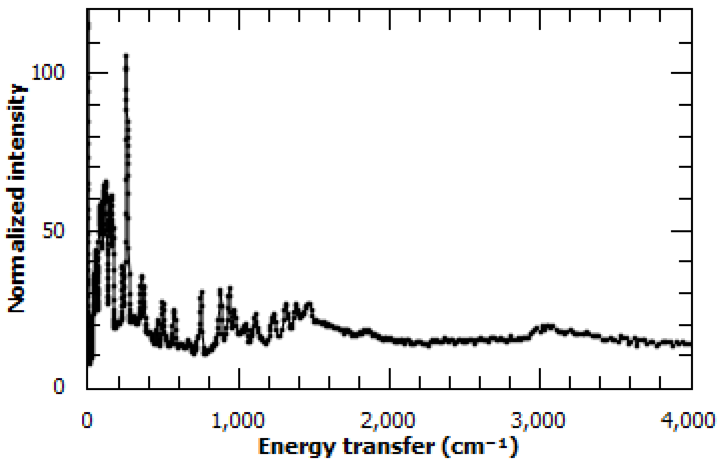












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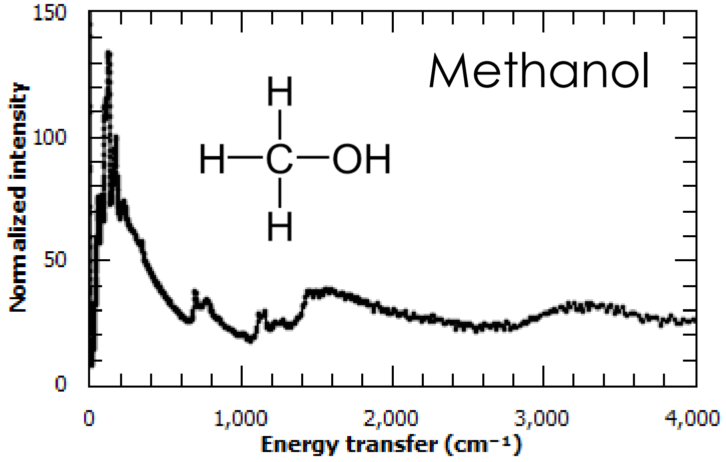
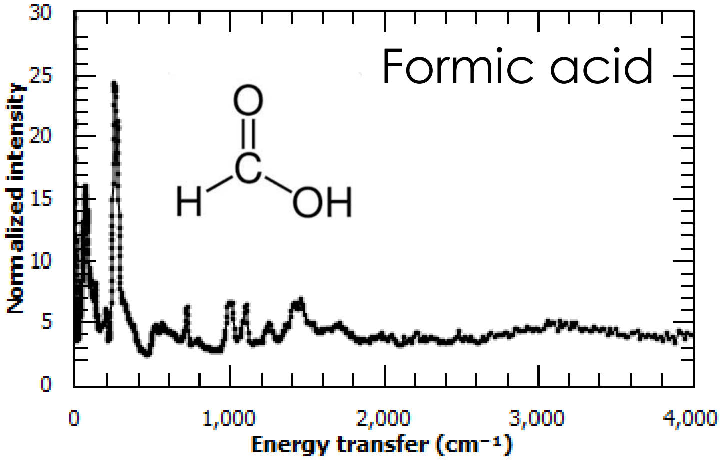
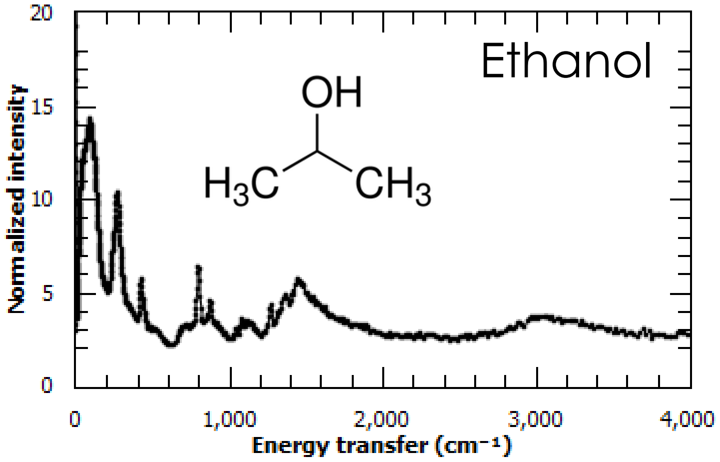
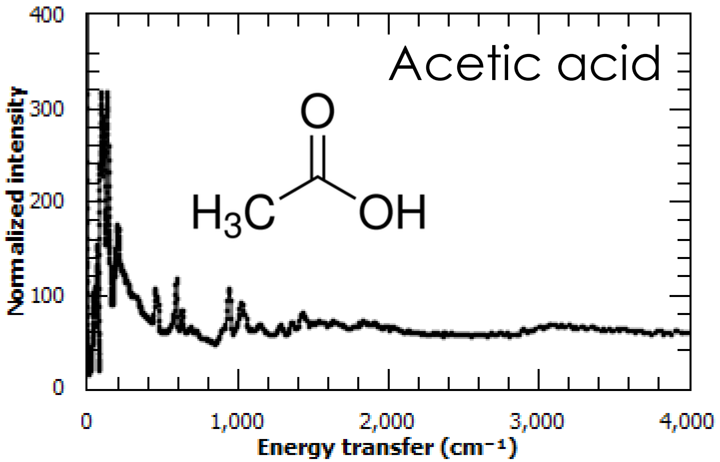
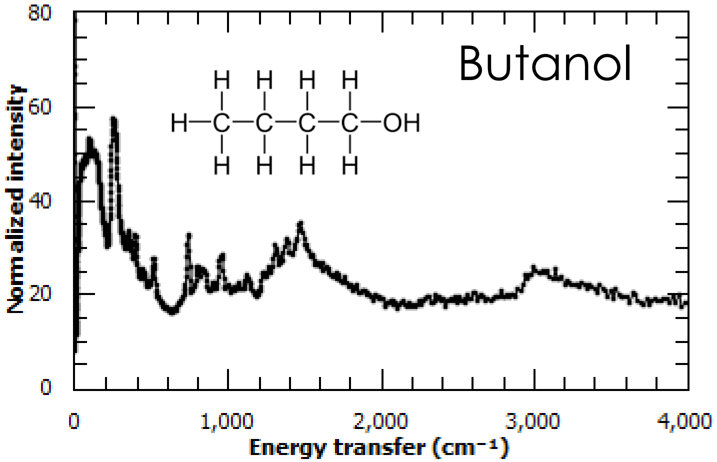
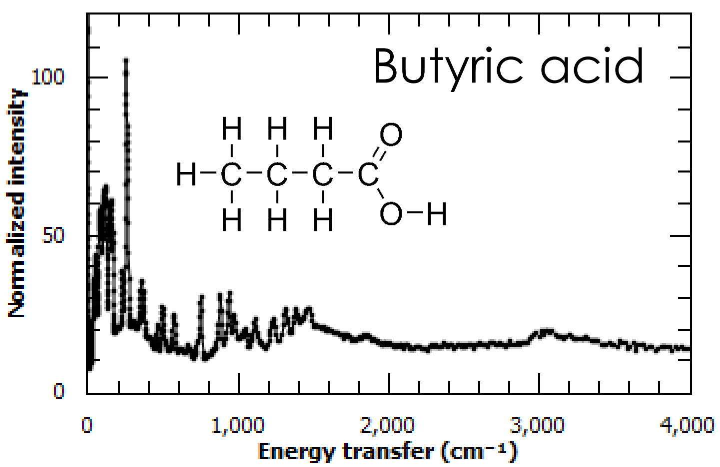




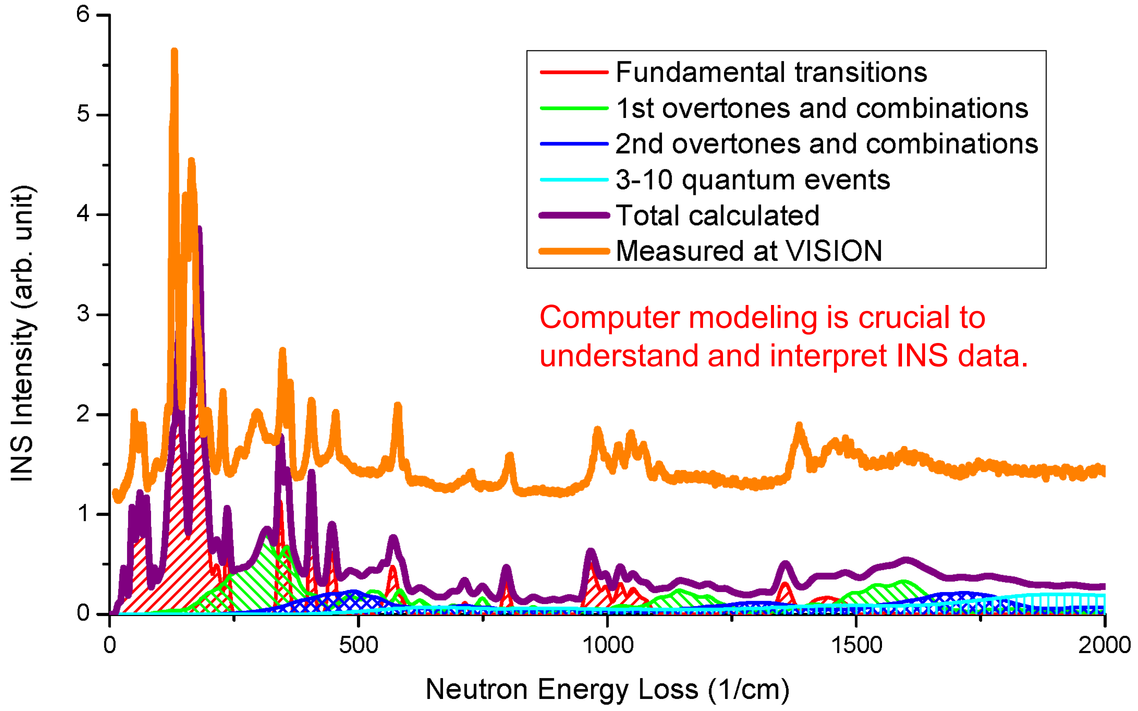








Integrated modeling for data interpretation



- 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)

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

Atomistic model and DFT → Vibrational modes and frequencies → INS simulation (OCLIMAX) → Simulated INS spectra

The "digital twin" at VISION

VirtuES cluster

OCLIMAX bridges theory and INS experiments

Common atomistic modeling tools

QUANTUMESPRESSO

Vienna Ab-initio Simulation Package

CASTEP

CP2K

CRYSTAL a computational tool for solid state chemistry and physics

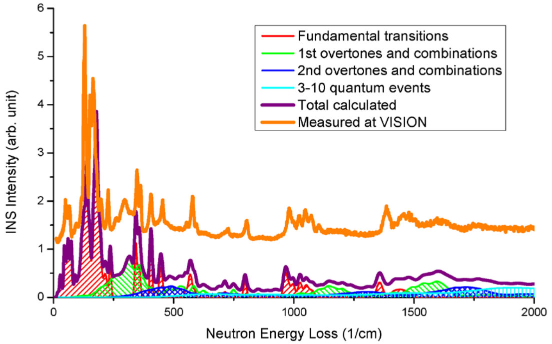
ORCA

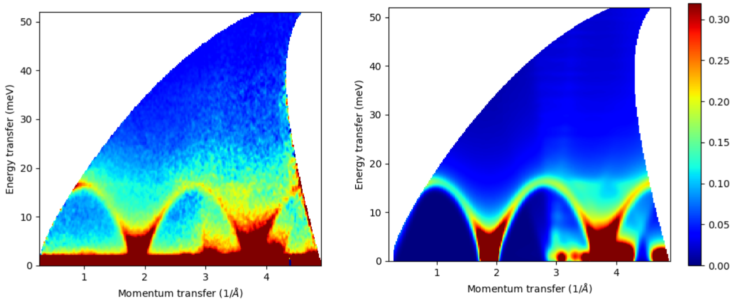
NWCHEM HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

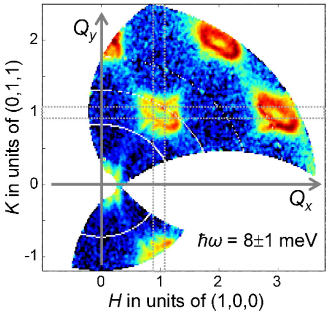
RMG

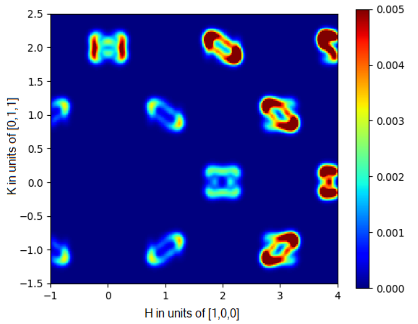
phonopy 2.0.0

OCLIMAX



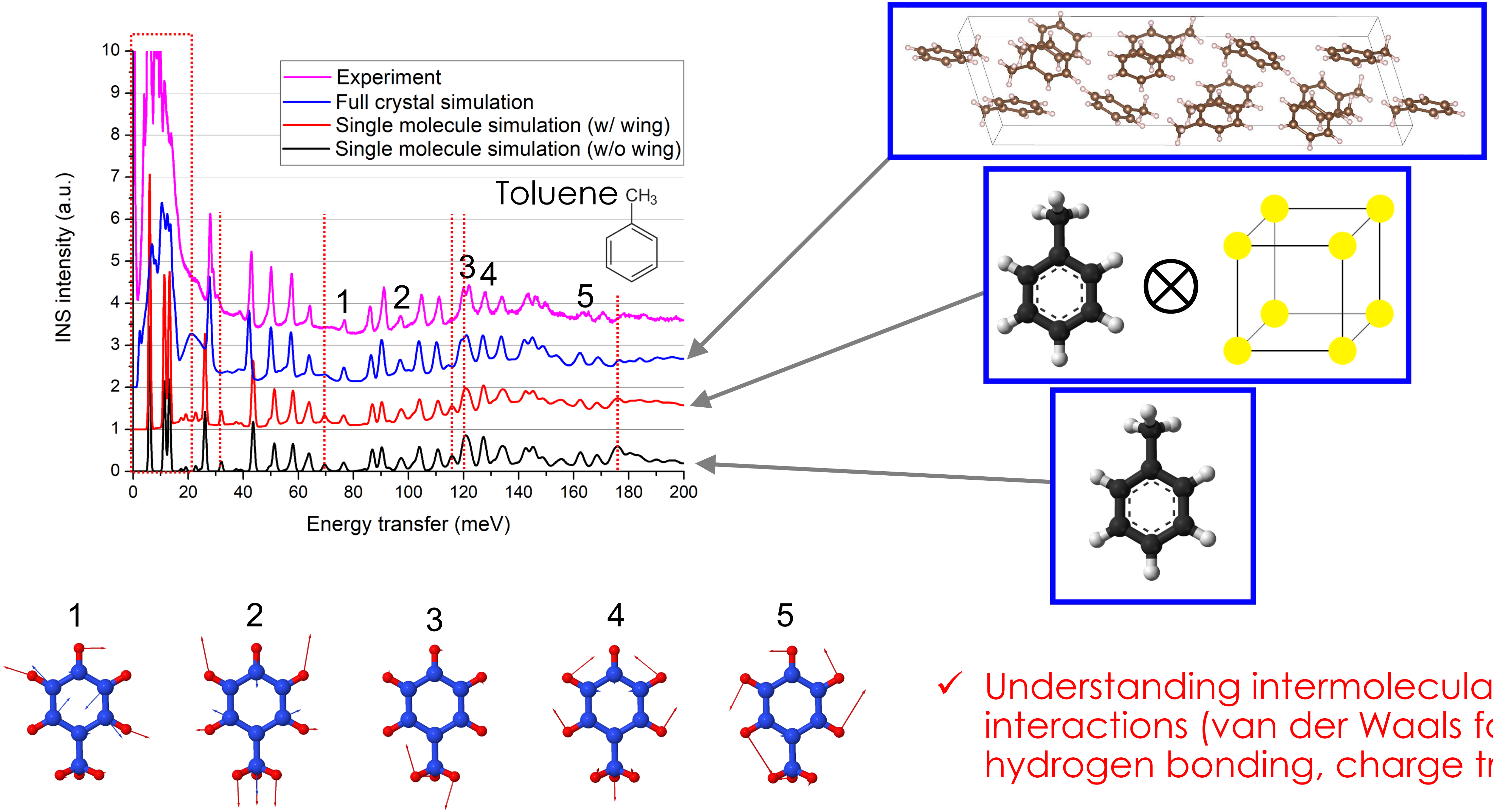






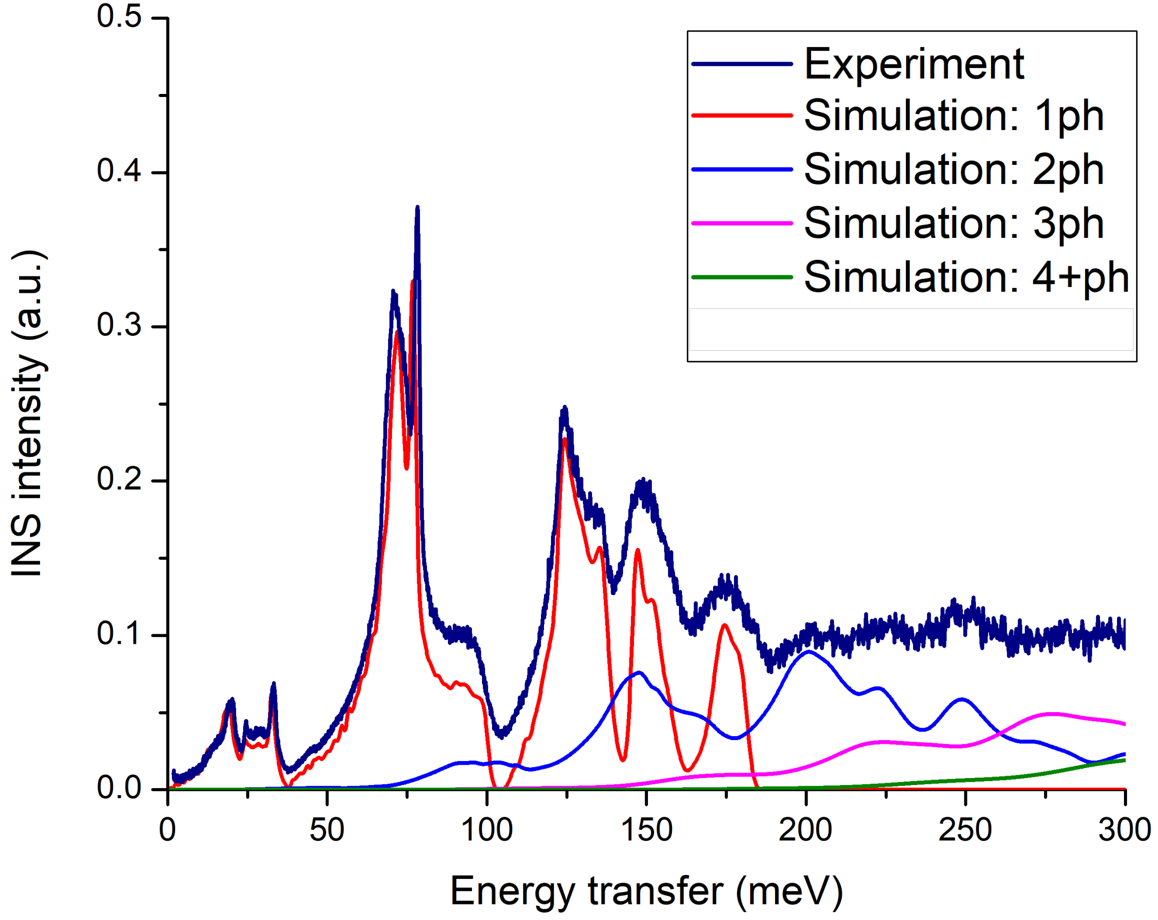
VISION, CNCS, HYSPEC, SEQUOIA, ARCS and many other neutron spectrometers.

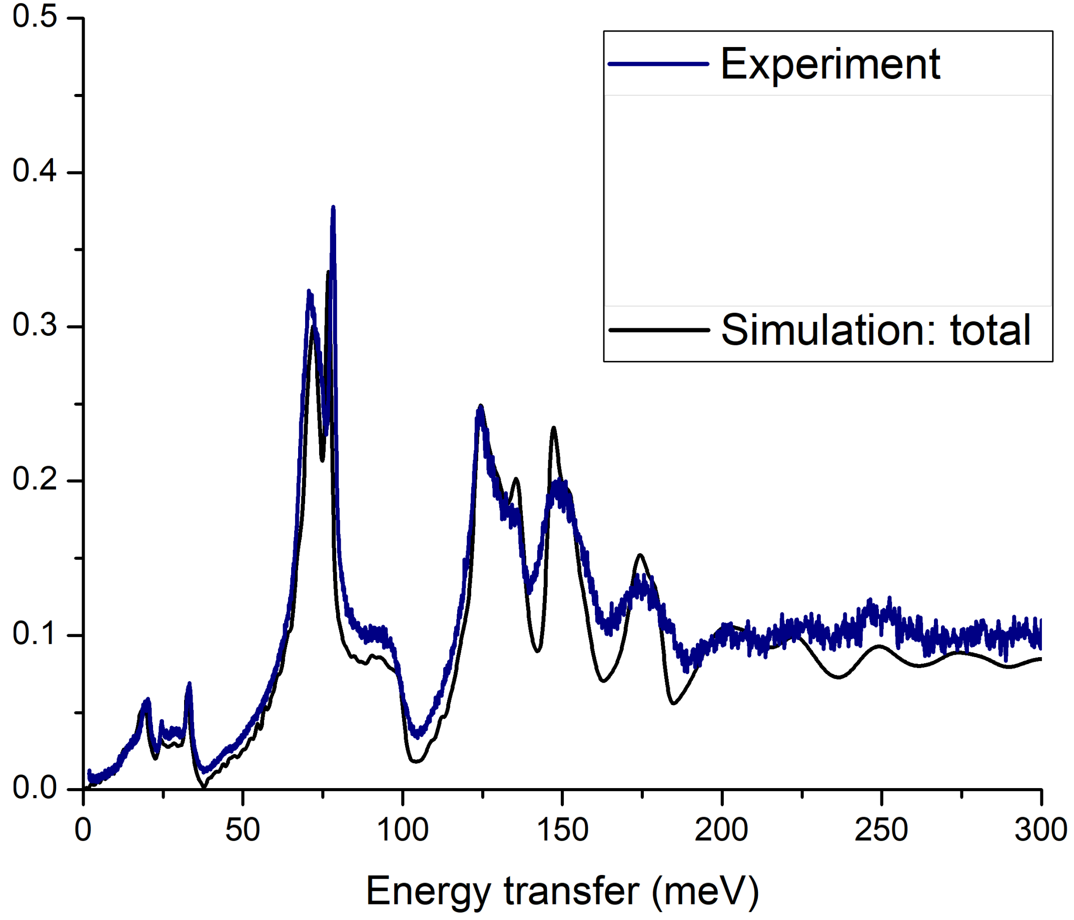
OCLIMAX example: From single molecule to solid



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

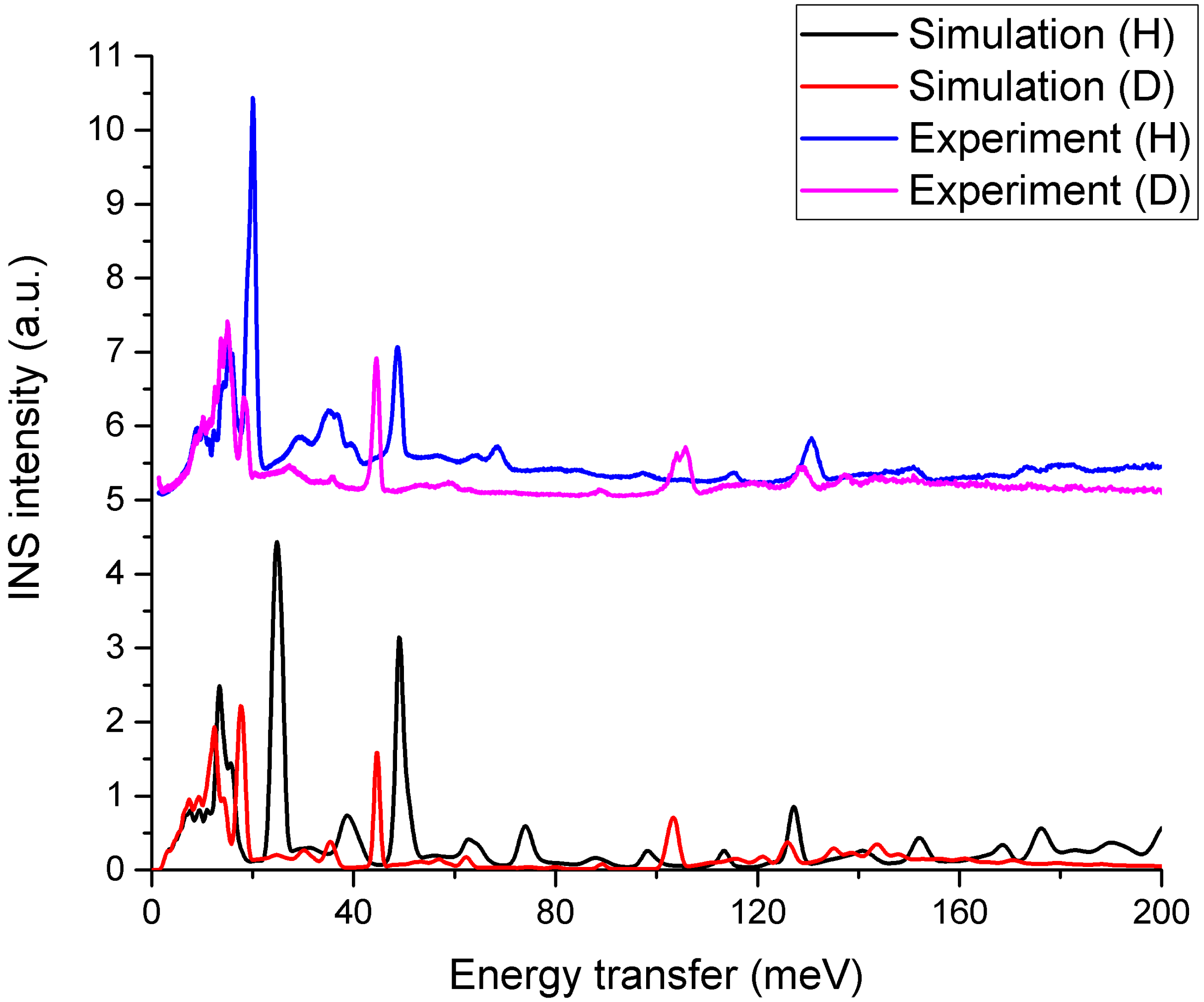
OCLIMAX example: Multiphonon excitations

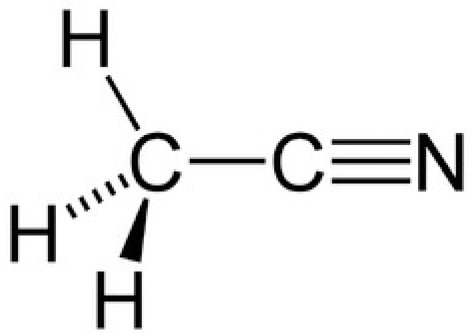




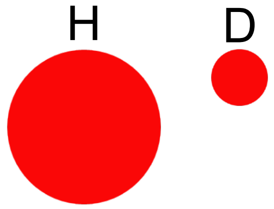
- ✓ Solving phonon density of states
- ✓ Understanding anharmonicity and potential energy landscape

Isotope substitution: acetonitrile





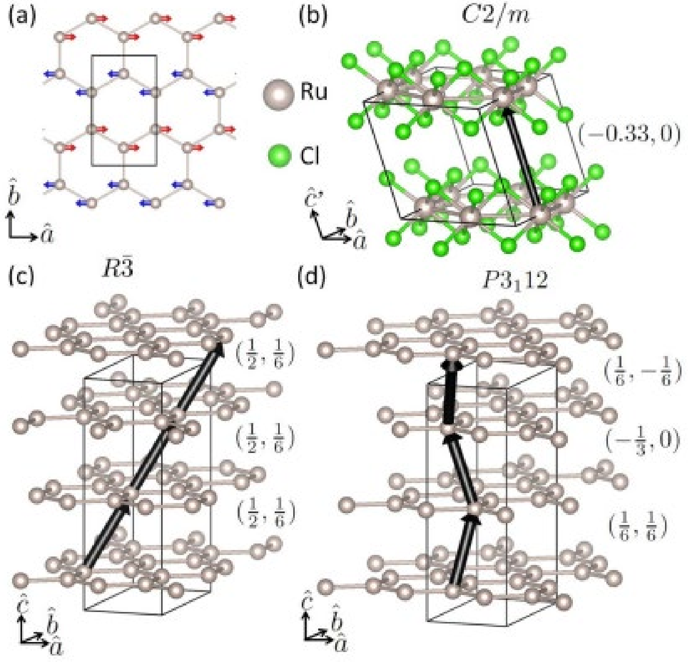
$$\omega = \sqrt{\frac{k}{m}}$$

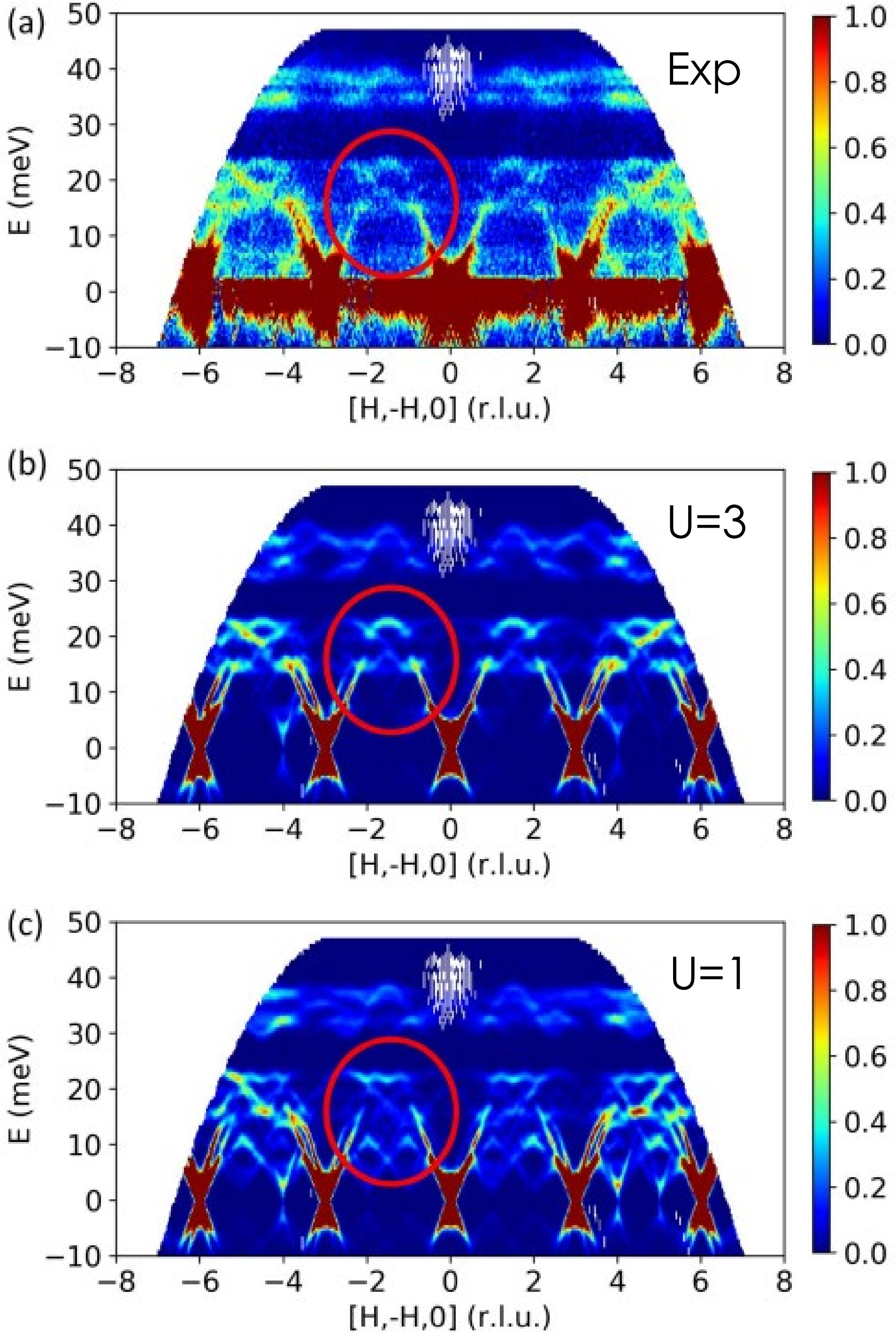


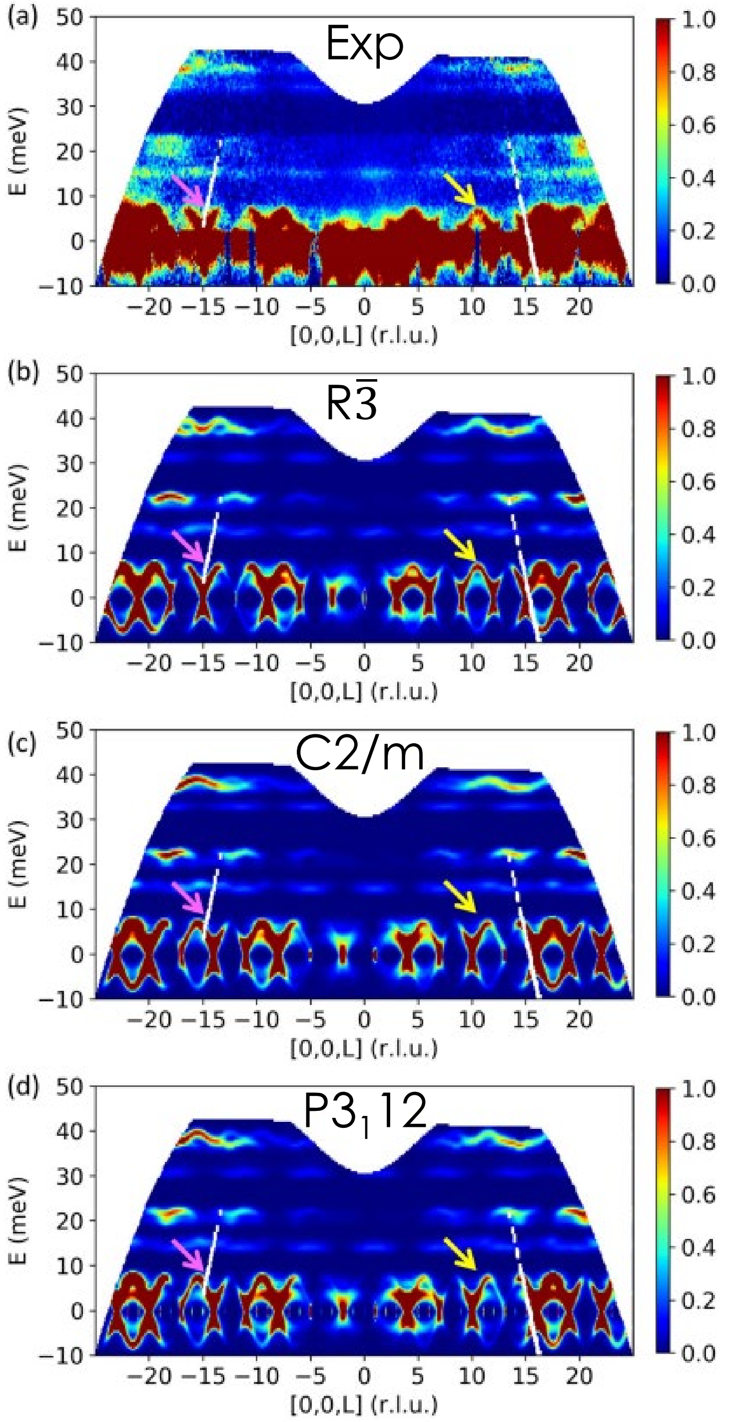
- ✓ Virtual experiment for doping effects and isotope labeling
- ✓ Breaking down the total intensity into partial contributions from individual species or atoms

Single crystal $RuCl_3$

Using experiment to correct theory



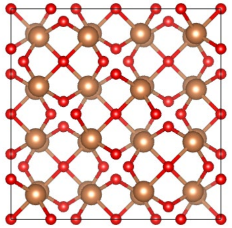




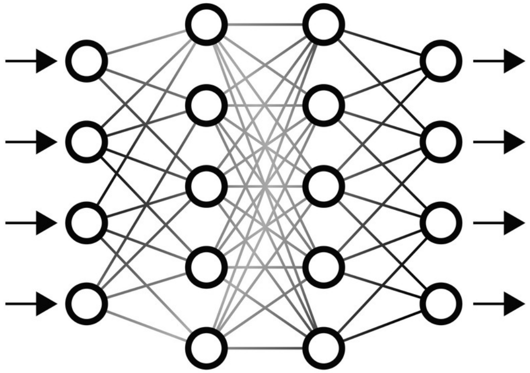
S. Mu et al. Phys. Rev. Res., **4**, 013067 (2022)

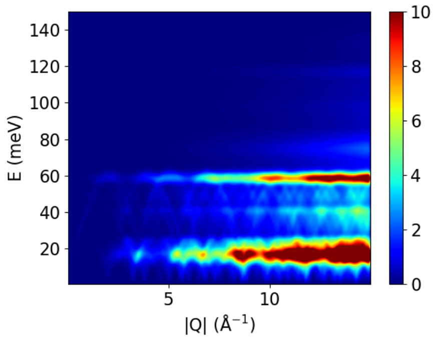
What can we do in the age of AI/ML?

- 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



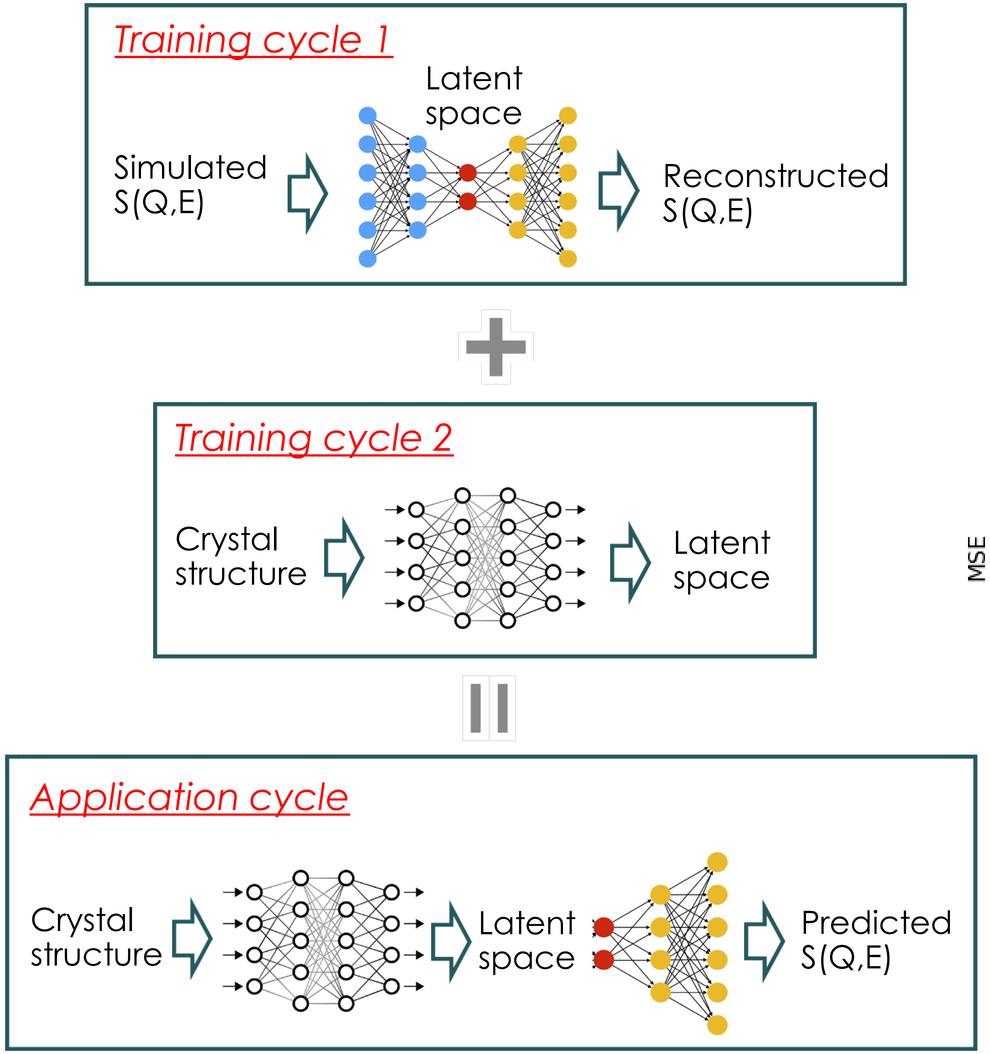
Atomic structure

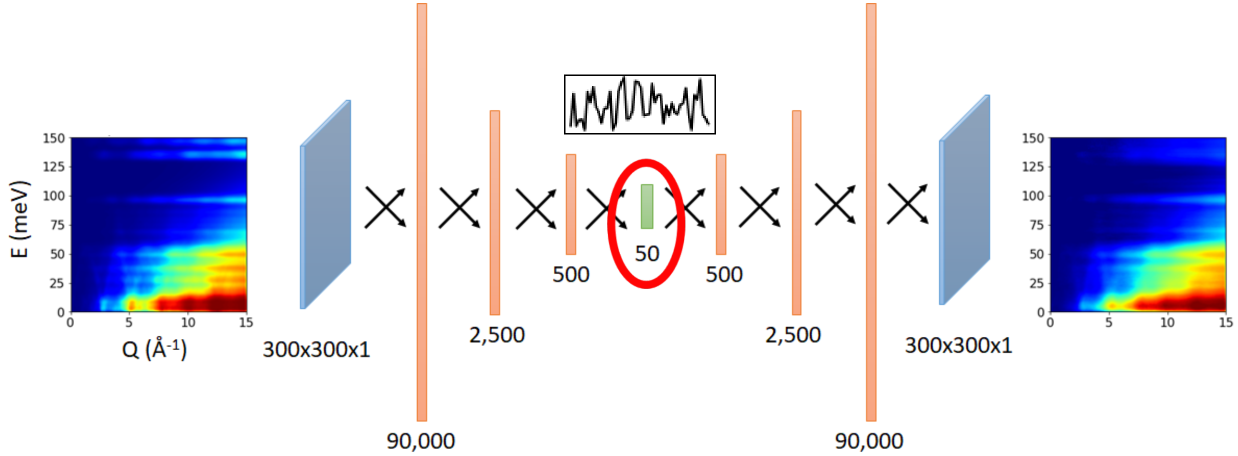


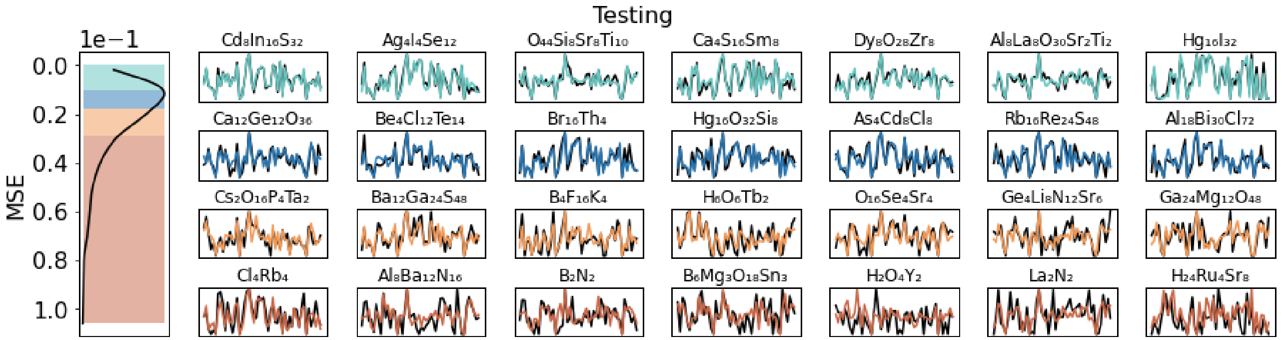


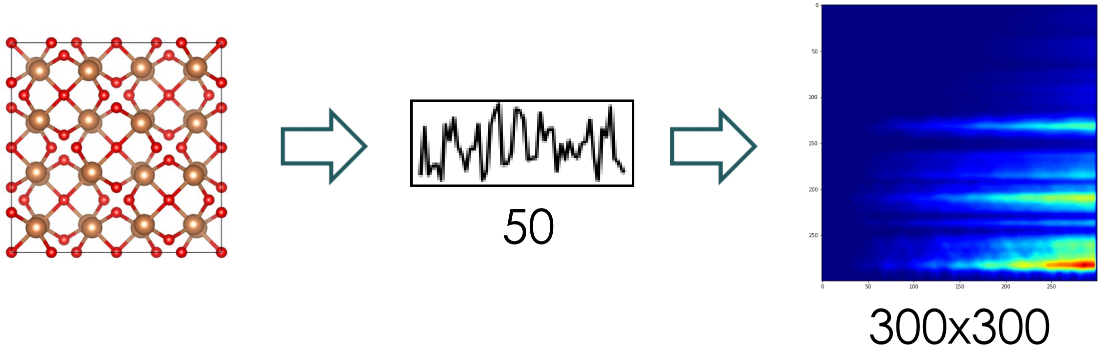
INS spectra

Direct prediction of powder S(Q,E)

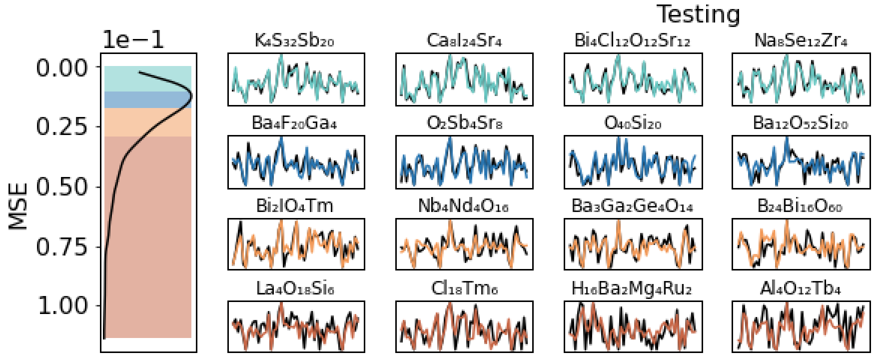


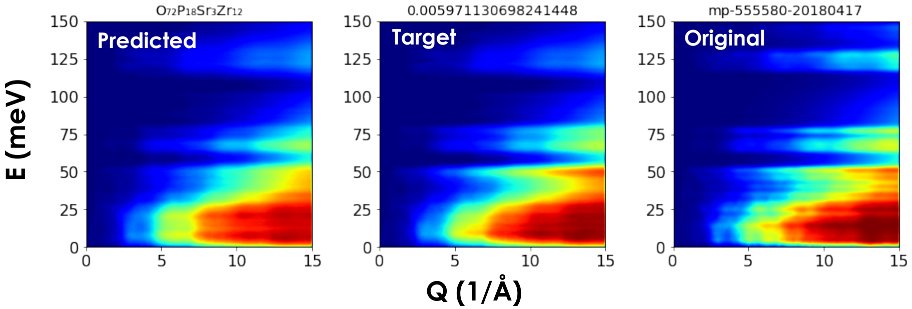


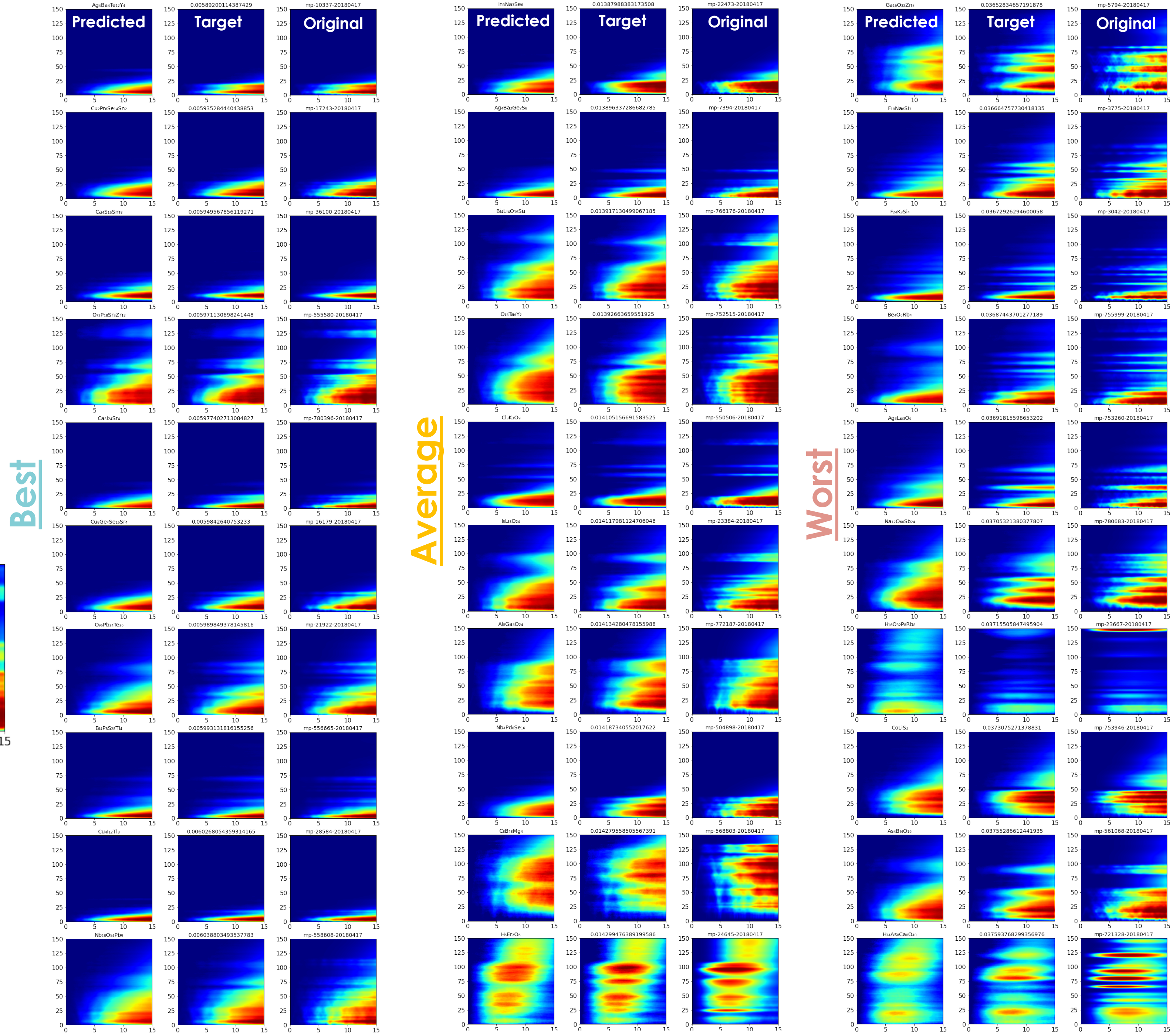




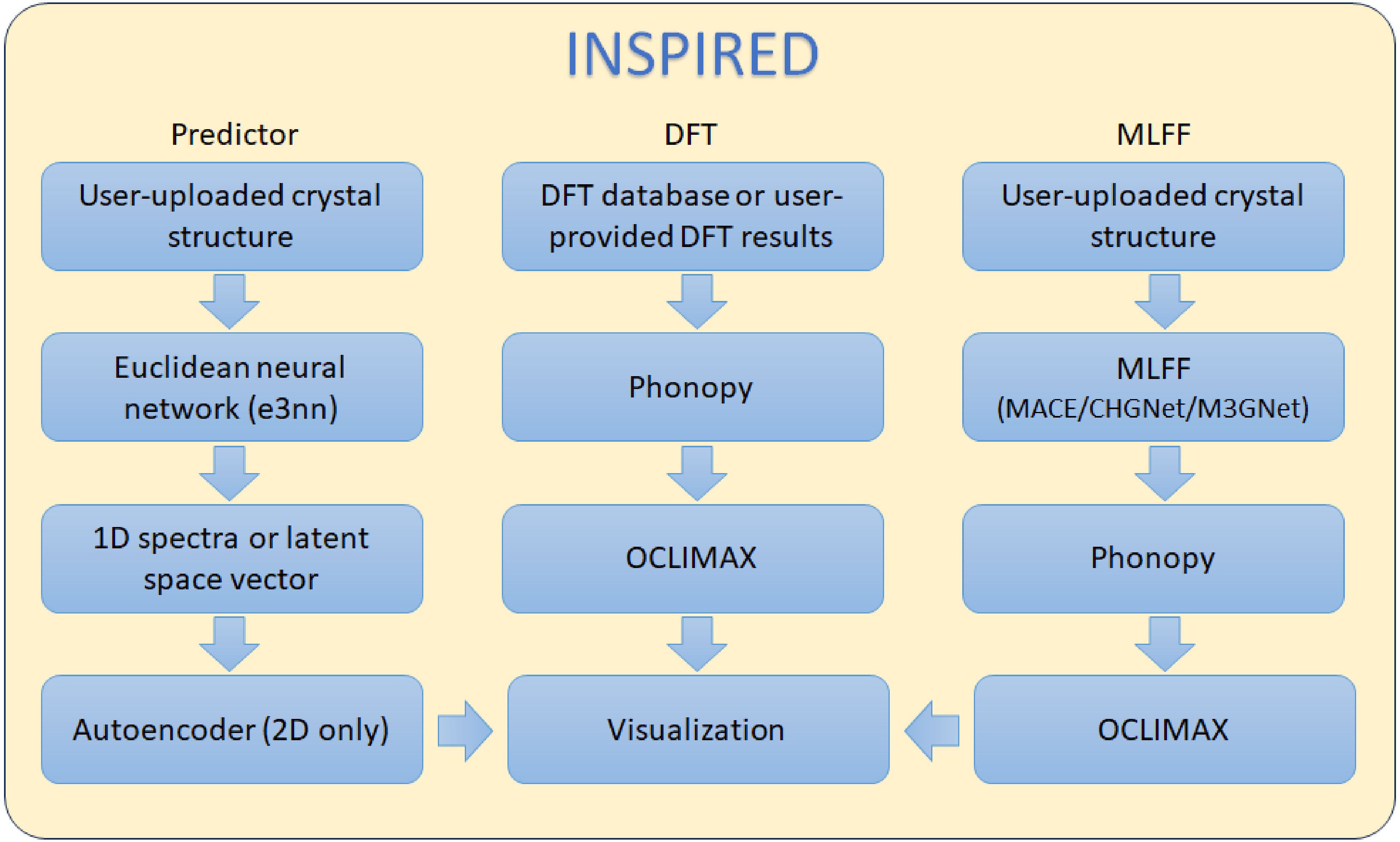
Direct prediction of powder S(Q,E)





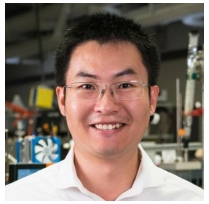


INSPIRED: Inelastic Neutron Scattering Prediction for Instantaneous Results and Experimental Design



Bowen Han

Andrei Savici



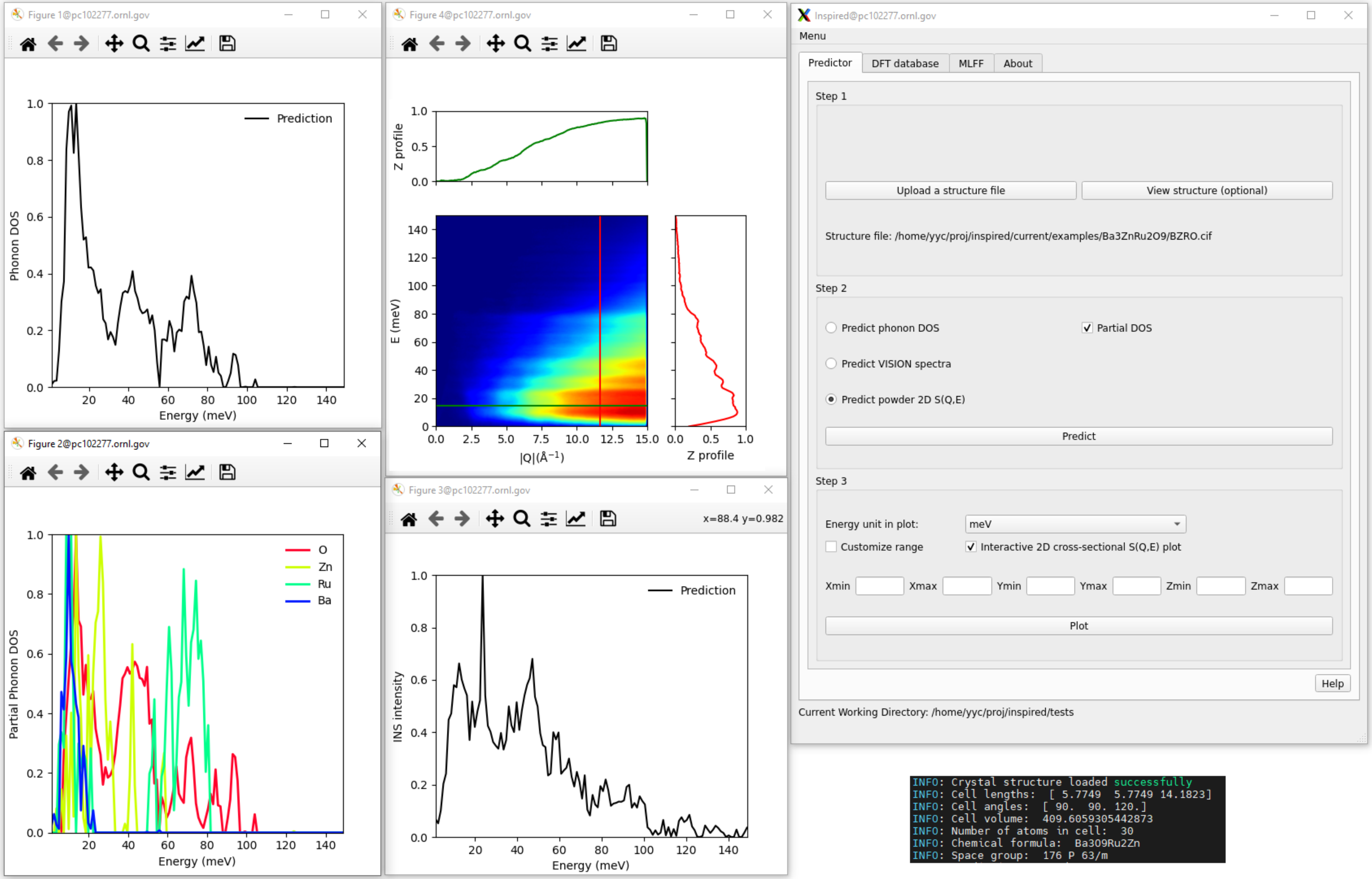
Mingda Li

https://github.com/cyqjh/inspired

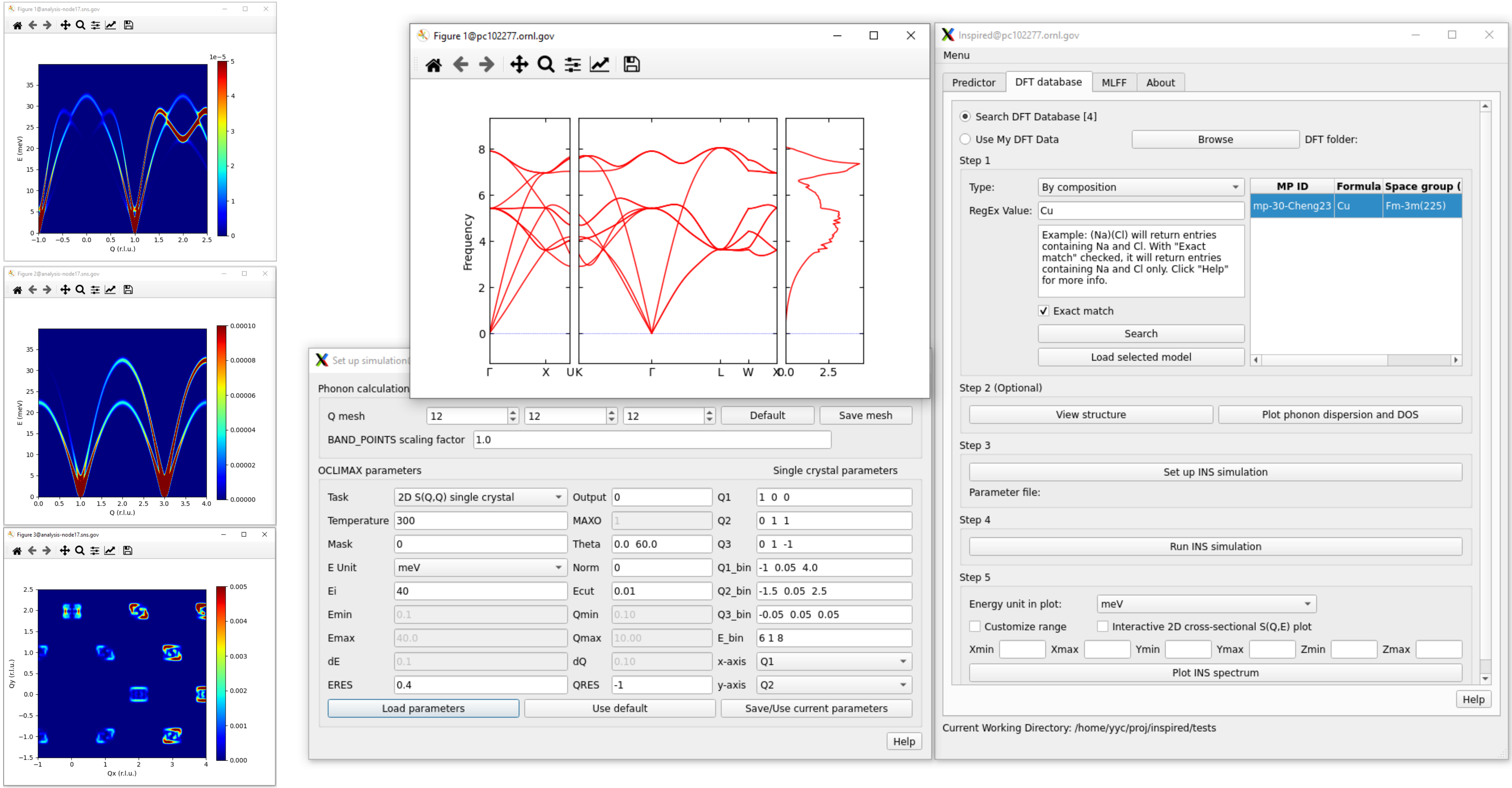
https://zenodo.org/records/10723108

Computer Physics Communications 304 (2024) 109288

INSPIRED: Predictor



INSPIRED: DFT database

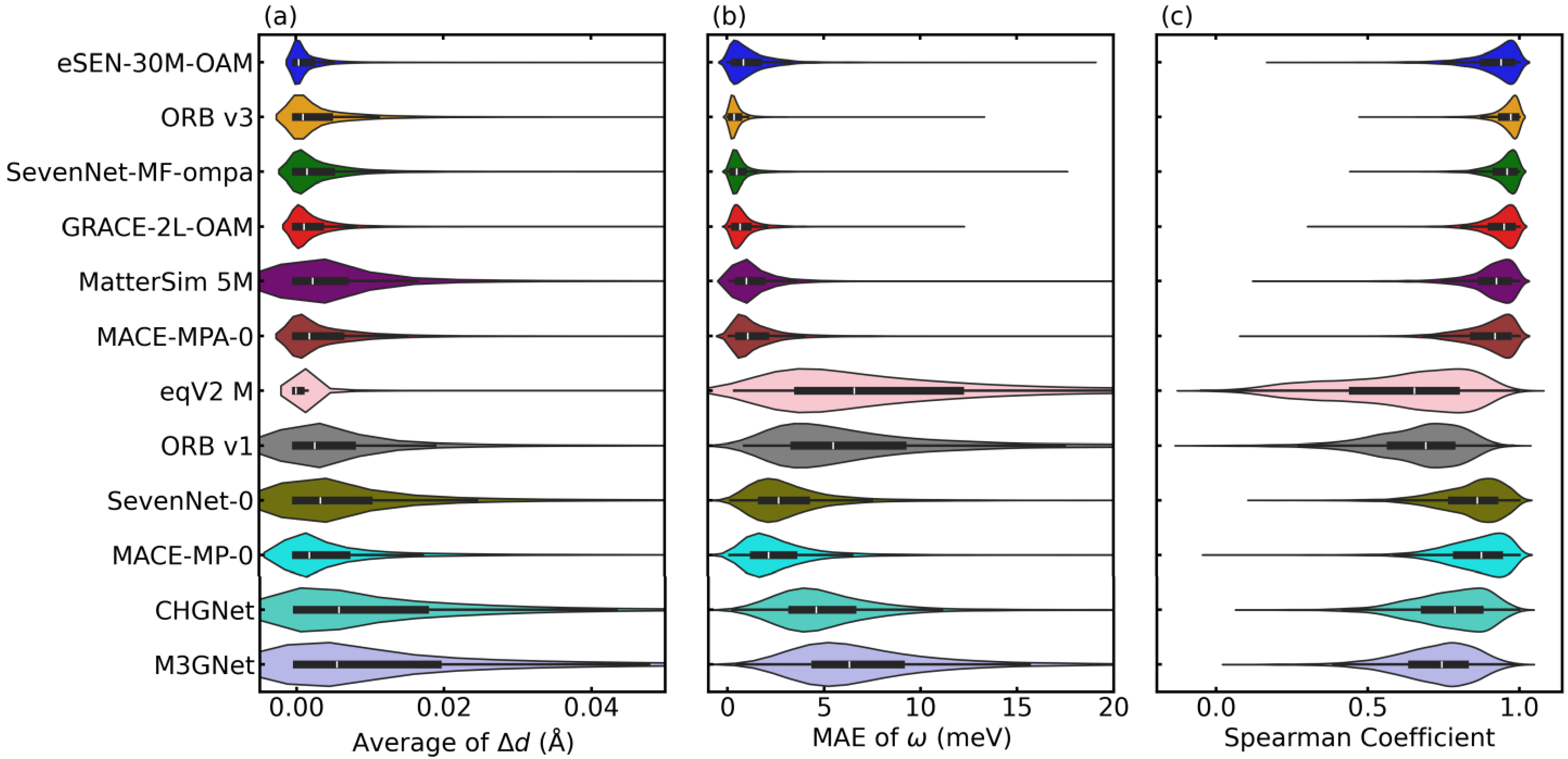


Benchmarking machine-learning interatomic potentials (MLIPs) for phonons and vibrational spectroscopy

Model	CPS ↑	Acc ↑	F1 ↑	DAF ↑	Prec ↑	MAE ↓	R^2 ↑	κ_{SRME} ↓	RMSD ↓	Training Set	Params	Targets	Date Added	r_{cut}
eSEN-30M-OAM	0.888	0.977	0.925	6.069	0.928	0.018	0.866	0.170	0.061	6.6M (113M) OMat24+MPtrj+sAlex	30.2M	EFSG	2025-03-17	6 Å
ORB v3	0.861	0.971	0.905	5.912	0.904	0.024	0.821	0.210	0.075	6.47M (133M) MPtrj+Alex+OMat24	25.5M	EFSG	2025-04-05	6 Å
SevenNet-MF-ompa	0.845	0.969	0.901	5.825	0.890	0.021	0.867	0.317	0.064	6.6M (113M) OMat24+sAlex+MPtrj	25.7M	EFSG	2025-03-13	6 Å
GRACE-2L-OAM	0.837	0.963	0.880	5.774	0.883	0.023	0.862	0.294	0.067	6.6M (113M) OMat24+sAlex+MPtrj	12.6M	EFSG	2025-02-06	6 Å
DPA-3.1-3M-FT	0.802	0.963	0.884	5.667	0.866	0.023	0.869	0.469	0.069	163M OpenLAM	3.27M	EFSG	2025-06-05	6 Å
eSEN-30M-MP	0.797	0.946	0.831	5.260	0.804	0.033	0.822	0.340	0.075	146k (1.58M) MPtrj	30.1M	EFSG	2025-03-17	6 Å
MACE-MPA-0	0.795	0.954	0.852	5.582	0.853	0.028	0.842	0.412	0.073	3.37M (12M) MPtrj+sAlex	9.06M	EFSG	2024-12-09	6 Å
AlphaNet-v1-OMA	0.769	0.968	0.901	5.747	0.879	0.024	0.831	0.644	0.079	6.6M (113M) OMat24+sAlex+MPtrj	4.65M	EFSG	2025-05-12	5 Å
MatterSim v1 5M	0.767	0.959	0.862	5.852	0.895	0.024	0.863	0.574	0.073	17M MatterSim	4.55M	EFSG	2024-12-16	5 Å
GRACE-1L-OAM	0.761	0.944	0.824	5.255	0.803	0.031	0.842	0.516	0.072	6.6M (113M) OMat24+sAlex+MPtrj	3.45M	EFSG	2025-02-06	6 Å
Eqnorm MPtrj	0.756	0.929	0.786	4.844	0.741	0.040	0.799	0.408	0.084	146k (1.58M) MPtrj	1.31M	EFSG	2025-05-26	6 Å
DPA-3.1-MPtrj	0.718	0.936	0.803	5.024	0.768	0.037	0.812	0.650	0.080	146k (1.58M) MPtrj	4.81M	EFSG	2025-06-05	6 Å
SevenNet-l3i5	0.714	0.920	0.760	4.629	0.708	0.044	0.776	0.550	0.085	146k (1.58M) MPtrj	1.17M	EFSG	2024-12-10	5 Å
HIENet	0.707	0.929	0.777	4.932	0.754	0.041	0.793	0.642	0.080	146k (1.58M) MPtrj	7.51M	EFSG	2025-07-01	5 Å
MatRIS v0.5.0 MPtrj	0.681	0.938	0.809	5.049	0.772	0.037	0.803	0.861	0.077	146k (1.58M) MPtrj	5.83M	EFSGM	2025-03-13	6 Å
GRACE-2L-MPtrj	0.681	0.896	0.691	4.163	0.636	0.052	0.741	0.525	0.090	146k (1.58M) MPtrj	15.3M	EFSG	2024-11-21	6 Å
MACE-MP-0	0.644	0.878	0.669	3.777	0.577	0.057	0.697	0.647	0.091	146k (1.58M) MPtrj	4.69M	EFSG	2023-07-14	6 Å
eqV2 M	0.558	0.975	0.917	6.047	0.924	0.020	0.848	1.771	0.069	3.37M (102M) OMat24+MPtrj	86.6M	EFSD	2024-10-18	12 Å
ORB v2	0.529	0.965	0.880	6.041	0.924	0.028	0.824	1.732	0.097	3.25M (32.1M) MPtrj+Alex	25.2M	EFSD	2024-10-11	10 Å
eqV2 S DeNS	0.522	0.941	0.815	5.042	0.771	0.036	0.788	1.676	0.076	146k (1.58M) MPtrj	31.2M	EFSD	2024-10-18	12 Å
ORB v2 MPtrj	0.470	0.922	0.765	4.702	0.719	0.045	0.756	1.725	0.101	146k (1.58M) MPtrj	25.2M	EFSD	2024-10-14	10 Å
M3GNet	0.428	0.813	0.569	2.882	0.441	0.075	0.585	1.412	0.112	62.8k (188k) MPF	228k	EFSG	2022-09-20	5 Å
CHGNet	0.400	0.851	0.613	3.361	0.514	0.063	0.689	1.717	0.095	146k (1.58M) MPtrj	413k	EFSGM	2023-03-03	5 Å
GNoME	NaN	0.955	0.829	5.523	0.844	0.035	0.785	n/a	n/a	6M (89M) GNoME	16.2M	EFG	2024-02-03	5 Å

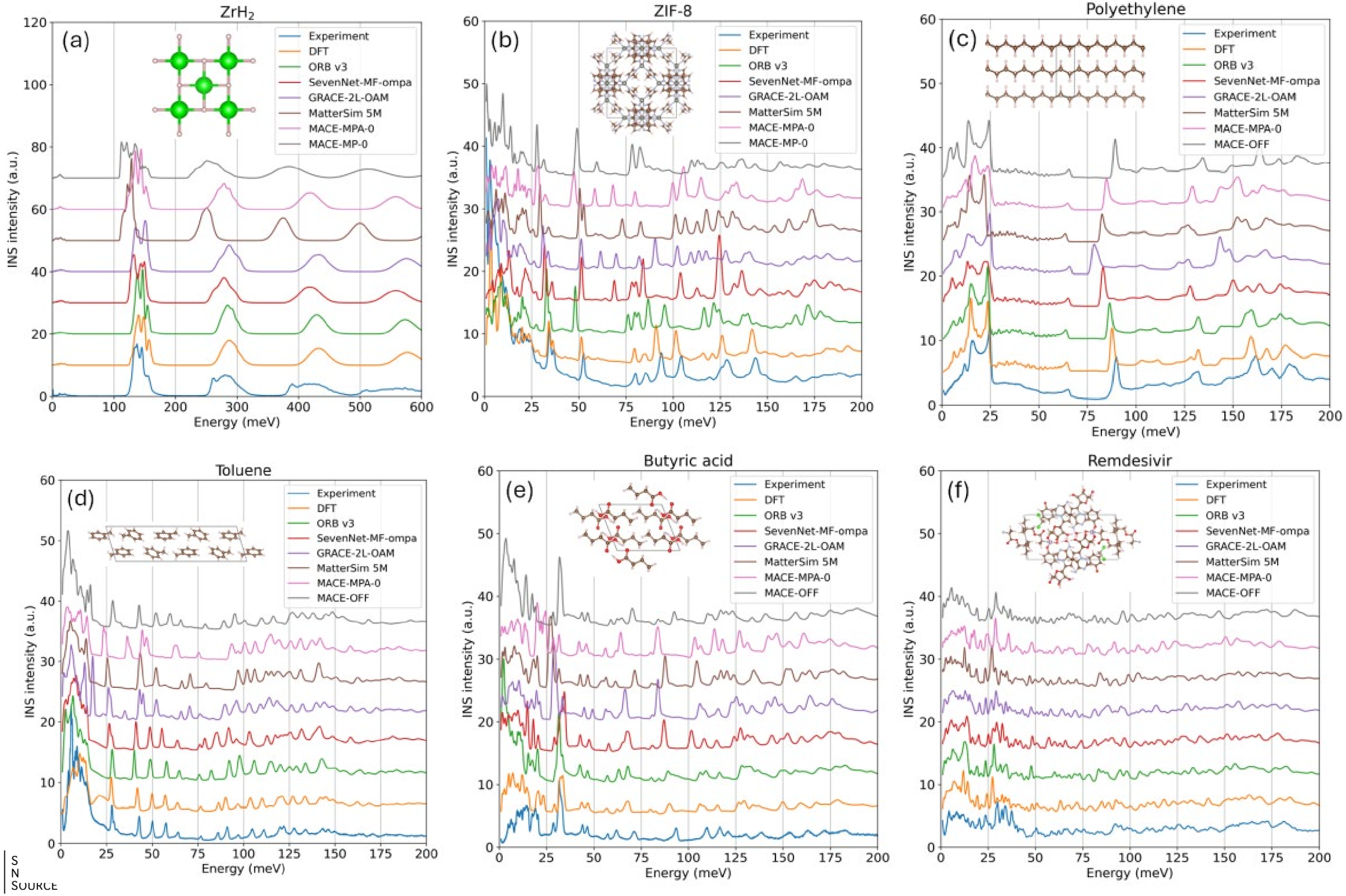
https://matbench-discovery.materialsproject.org/

Benchmarking machine-learning interatomic potentials (MLIPs) for phonons and vibrational spectroscopy

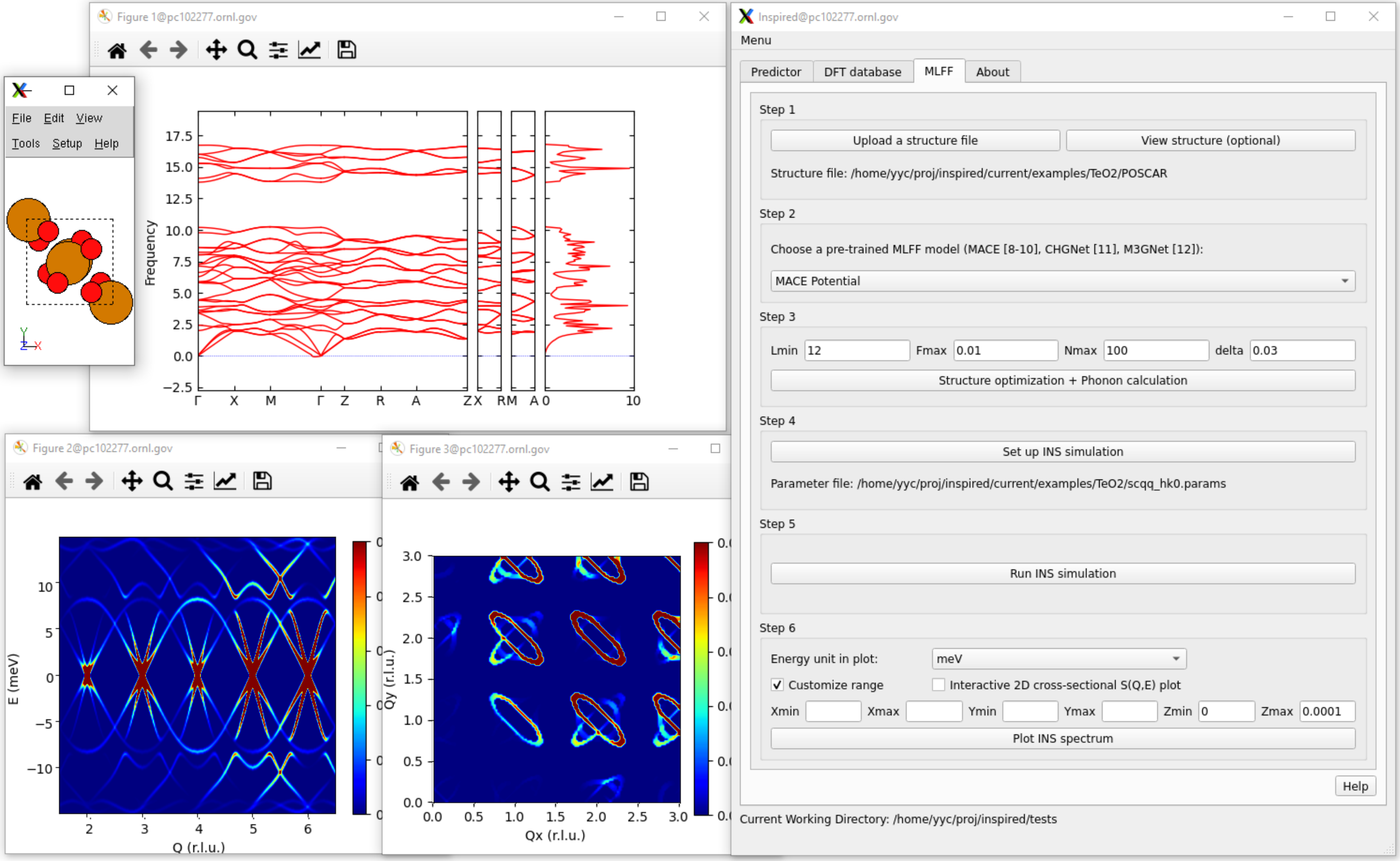


Bowen Han and Yongqiang Cheng 2025 Mach. Learn.: Sci. Technol. 6 030504

Benchmarking machine-learning interatomic potentials (MLIPs) for phonons and vibrational spectroscopy

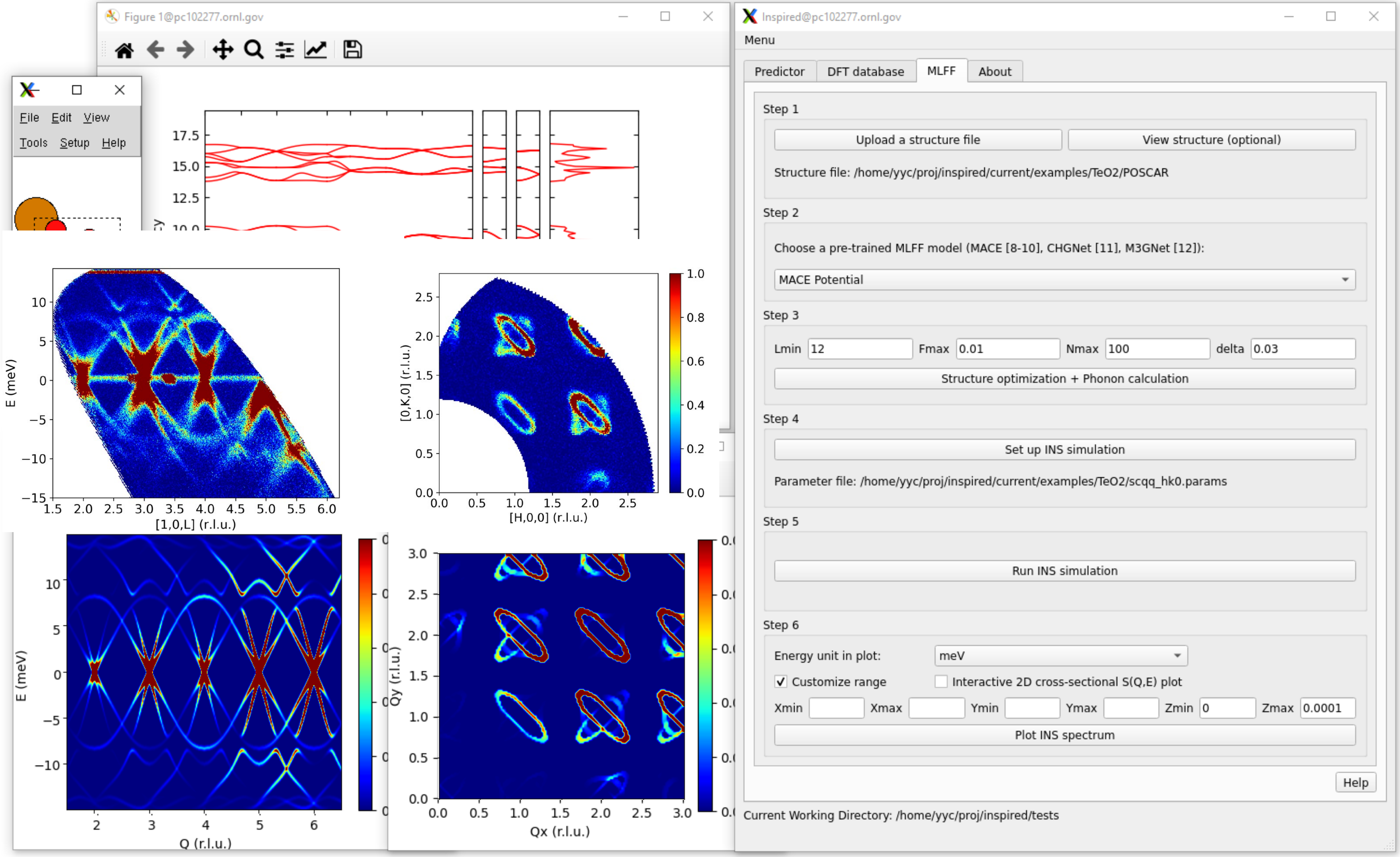


INSPIRED: MLFF



INSPIRED: MLFF

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

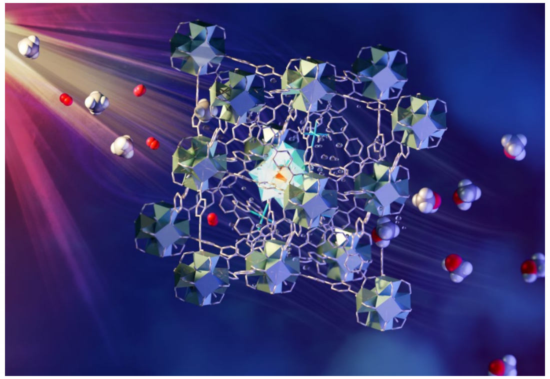


Oak Ridge National Laboratory

Applications

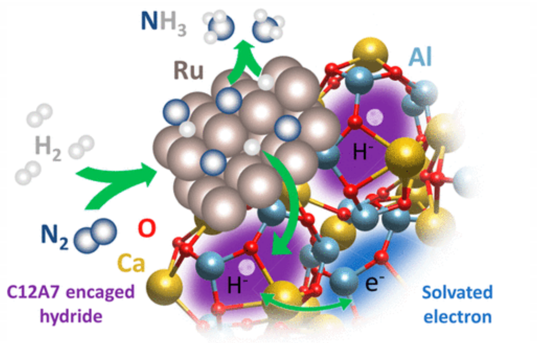
Metal-organic framework

- 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)



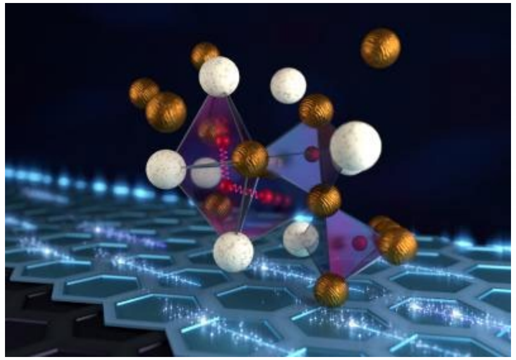
Nano-catalyst

- 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)



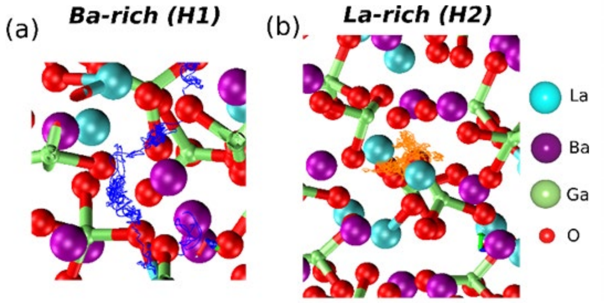
Complex hydride

- 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)

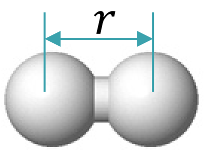


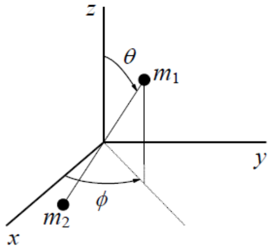
NVS for molecular hydrogen

Quantum diatomic rotor

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

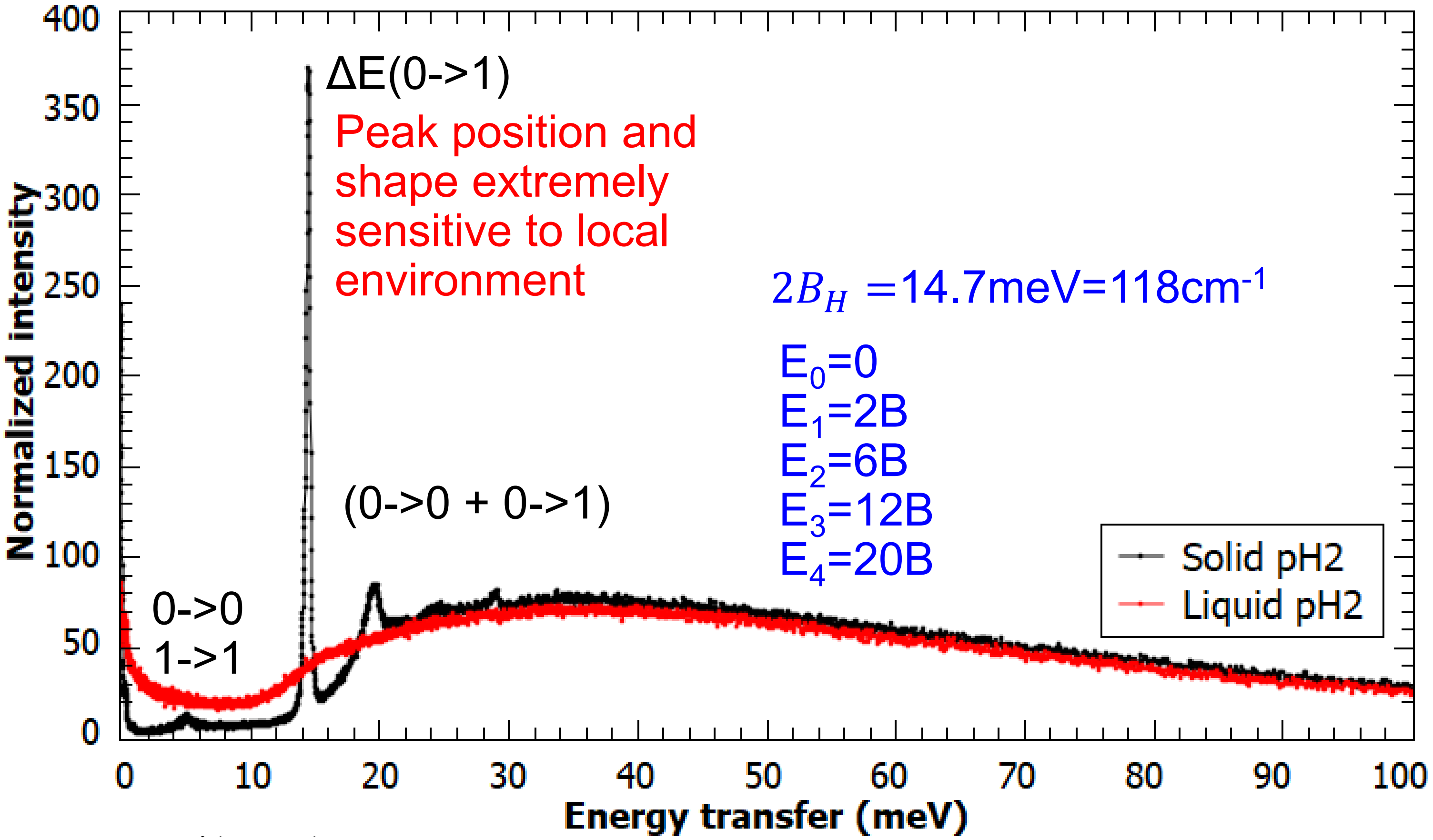
$$B_{rot} = \frac{\hbar^2}{2I} = \frac{\hbar^2}{mr^2}$$

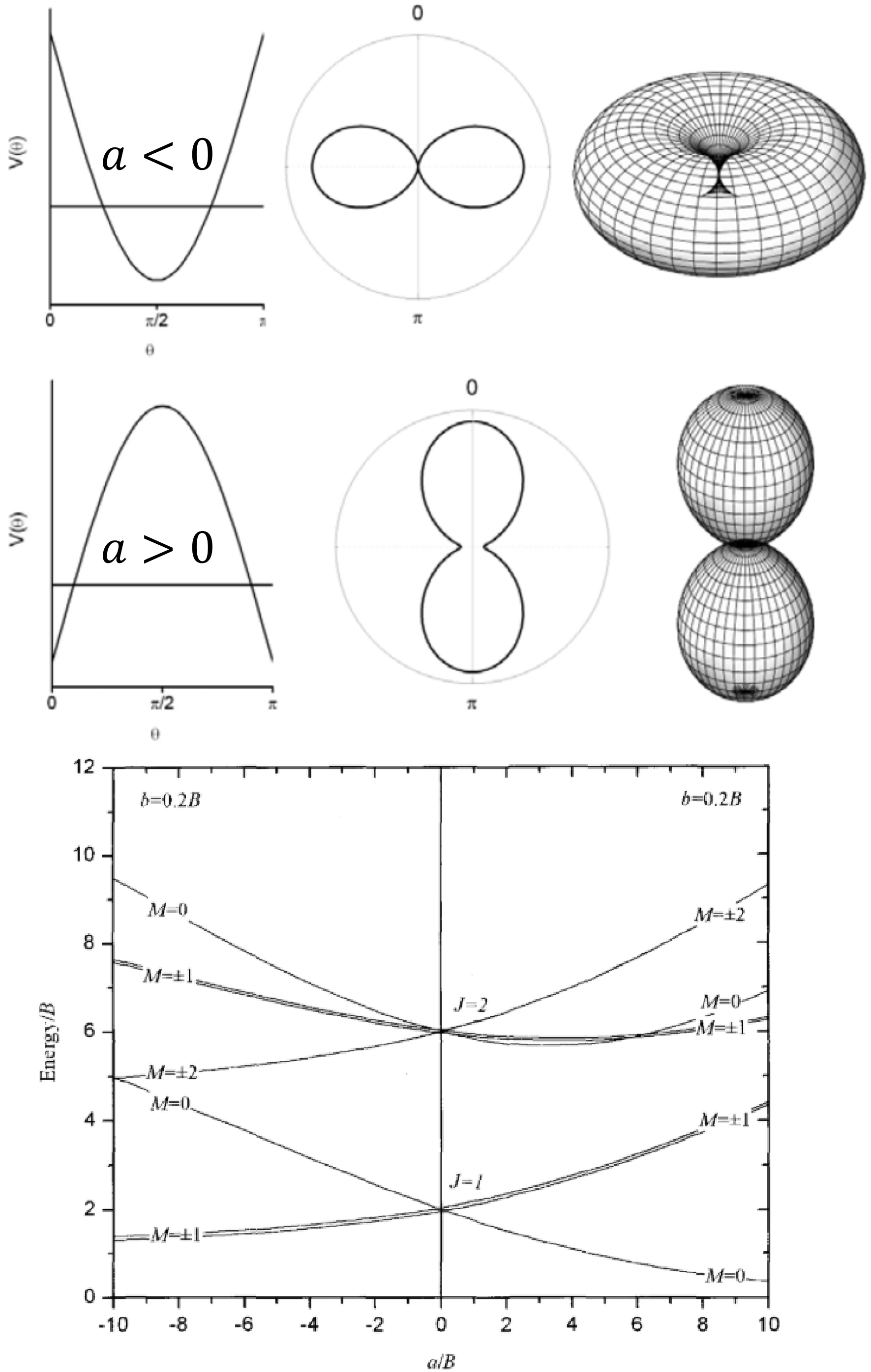




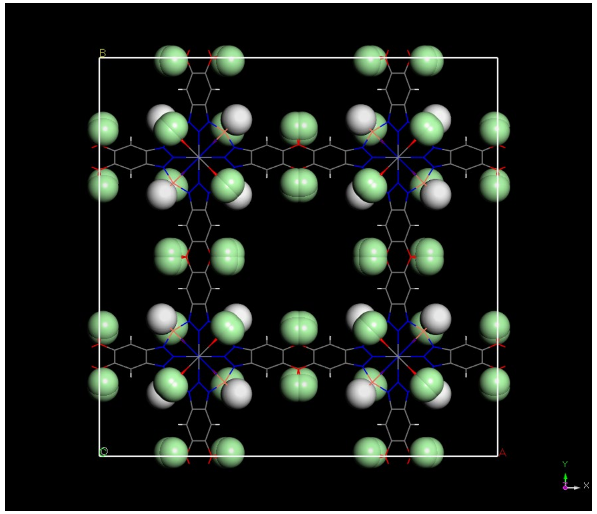
$$V(\theta,\phi) = \left[a + \frac{b}{2}\cos 2\phi\right]\sin^2\theta$$

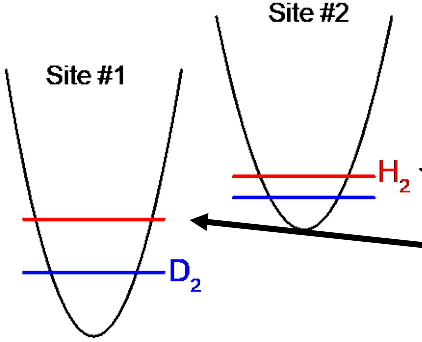
Mitchell et al. Vibrational Spectroscopy with Neutrons 2004

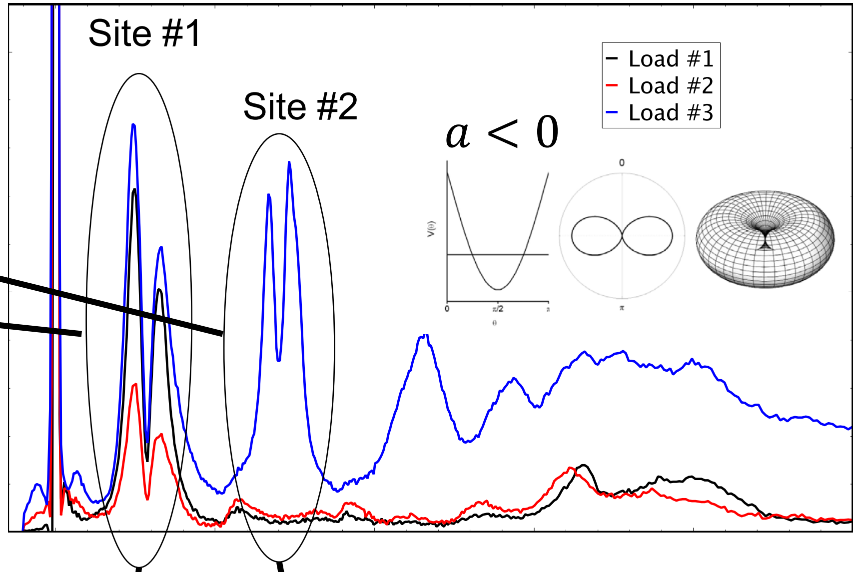




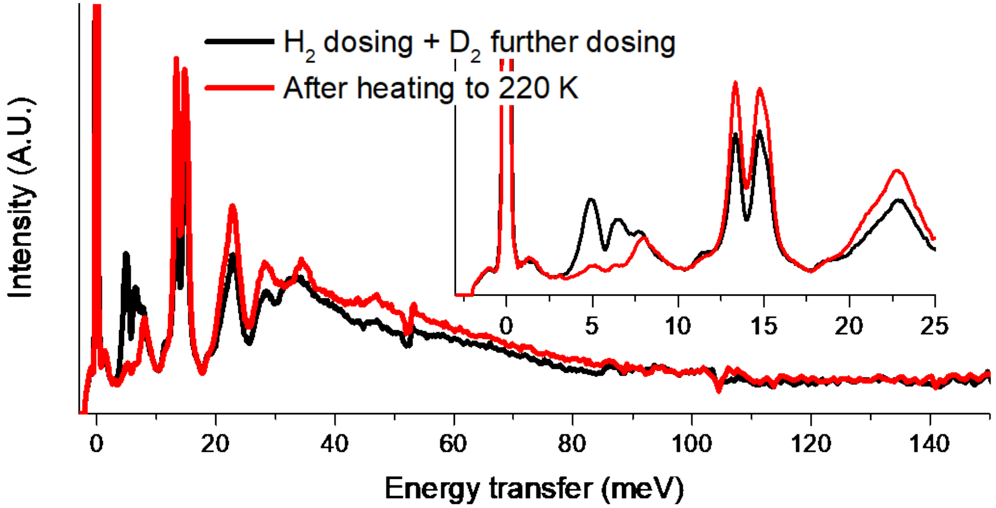
Quantum Sieving Hydrogen in a metal-organic framework

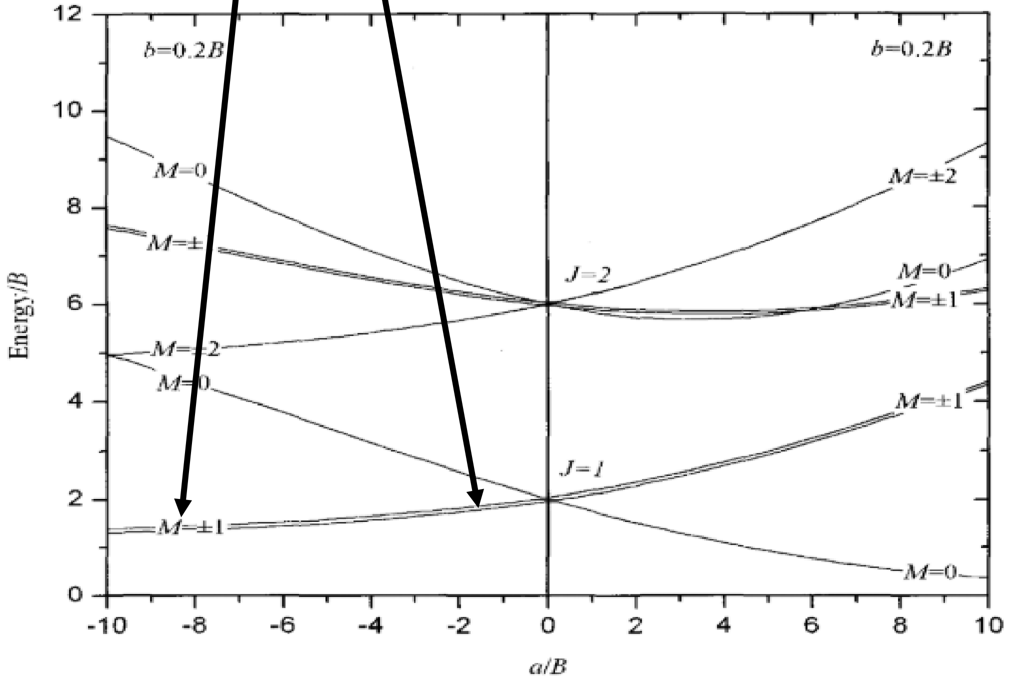






Quantum sieving is a technique for isotope separations; heavier isotopes induce favorable adsorption in nanoscale pores due to the difference in zero-point energy of isotopes.





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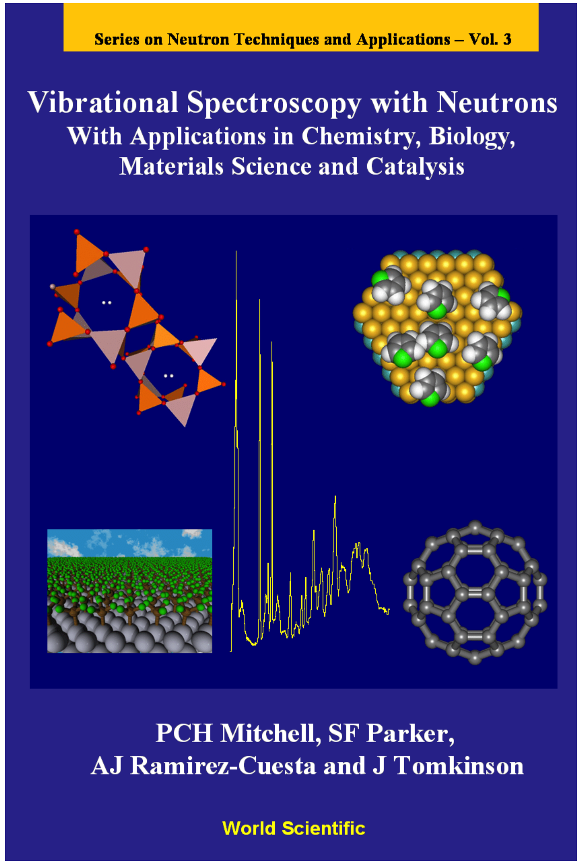
Take-home messages:

- 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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https://neutrons.ornl.gov/vision

Questions?

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