Neutron Vibrational Spectroscopy

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Outline

• Background and instrumentation
• Data analysis and modeling
• Applications
• Q&A
**What is neutron vibrational spectroscopy (NVS)?**

<table>
<thead>
<tr>
<th>Neutron vibrational spectroscopy (NVS)</th>
<th>Inelastic neutron scattering (INS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemists</td>
<td>Physicists</td>
</tr>
<tr>
<td>Molecular systems</td>
<td>Condensed matter</td>
</tr>
<tr>
<td>Organic/inorganic compounds</td>
<td></td>
</tr>
<tr>
<td>Intramolecular modes</td>
<td>Phonons</td>
</tr>
<tr>
<td>Intermolecular modes</td>
<td>Magnons</td>
</tr>
<tr>
<td>$S(\omega)$ in cm$^{-1}$</td>
<td>$S(Q,E)$ in meV</td>
</tr>
<tr>
<td>Indirect geometry instrument</td>
<td>Direct geometry instrument</td>
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</table>

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

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

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

![Graph showing energy transfer vs. relative intensity with peaks labeled $\nu_1$, $\nu_2$, and $\nu_3$.]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Type of Compound</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\text{C}-\text{H}$ (stretch)</td>
<td>alkanes</td>
<td>2800–3000 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}-\text{H}$ (stretch)</td>
<td>alkenes, aromatics</td>
<td>3000–3100 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}-\text{H}$ (stretch)</td>
<td>alkynes</td>
<td>3300 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{O}-\text{H}$ (stretch)</td>
<td>alcohols, phenols</td>
<td>3600–3650 (free) cm$^{-1}$; 3200–3500 (H-bonded) (broad)</td>
</tr>
<tr>
<td>$=\text{O}-\text{H}$ (stretch)</td>
<td>carboxylic acids</td>
<td>2500–3300 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{N}-\text{H}$ (stretch)</td>
<td>amines</td>
<td>3300–3500 cm$^{-1}$ (doublet for $\text{NH}_2$)</td>
</tr>
<tr>
<td>$=\text{C}=\text{O}$ (stretch)</td>
<td>aldehydes</td>
<td>2720 and 2820 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}=\text{C}$ (stretch)</td>
<td>alkenes</td>
<td>1600–1680 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}=\text{C}$ (stretch)</td>
<td>aromatics</td>
<td>1500–1600 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}=\text{C}-\text{H}$ (stretch)</td>
<td>alkynes</td>
<td>2100–2270 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}=$ (stretch)</td>
<td>aldehyde, ketones, carboxylic acids</td>
<td>1680–1740 cm$^{-1}$</td>
</tr>
<tr>
<td>$=\text{C}=$ (stretch)</td>
<td>nitriles</td>
<td>2220–2260 cm$^{-1}$</td>
</tr>
<tr>
<td>$\text{C}=$ (stretch)</td>
<td>amines</td>
<td>1180–1350 cm$^{-1}$</td>
</tr>
<tr>
<td>$\text{C}=\text{H}$ (bending)</td>
<td>alkanes</td>
<td>1375 (methyl)</td>
</tr>
<tr>
<td>$\text{C}=\text{H}$ (bending)</td>
<td>alkanes</td>
<td>1460 (methyl and methylene)</td>
</tr>
<tr>
<td>$\text{C}=\text{H}$ (bending)</td>
<td>alkanes</td>
<td>1370 and 1385 (isopropyl split)</td>
</tr>
<tr>
<td>$\text{C}=\text{H}$ (bending)</td>
<td>alkynes</td>
<td>2100–2270 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Infrared and Raman Characteristic Group Frequencies

Table of absorption frequencies of some common bonds (shown in bold type).
## Vibrational spectroscopy with neutrons: pros and cons

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

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

Complementary tools to study molecular vibration
Complementary tools to study molecular vibration

A simple $S(Q, \omega)$ map of molecular vibration: key features

$$S(Q, n\omega_s) = \frac{(Q \cdot U_s)^{2n}}{n!} \exp[-(Q \cdot U_{total})^2]$$

$$U_s = \sqrt{\frac{\hbar}{2m\omega_s}} e_{ds}$$
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

Indirect geometry (TOSCA)

Direct geometry (MARI)

E_i = 800 cm^{-1}

E_i = 2000 cm^{-1}

E_i = 4000 cm^{-1}
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: a gallery
Sample environment at VISION

JANIS closed-cycle refrigerator (5-600K)

12 cm

Pressure cells (piston, gas, diamond anvil).

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

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

Sample → VISION → Data reduction and analysis (Mantid) → Measured INS spectra → Numerical code tools for INS analysis:
- CASTEP
- VASP
- QE
- CP2K
- Gaussian

INS simulation (OClimax) → Simulated INS spectra → Measured INS spectra → Measured diffraction

Peak assignment → (An)harmonicity → Phase transition → Understanding mechanisms and properties at atomic level

Structure-dynamics correlation

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

• Interpret neutron data
  – assigning peaks to vibrational modes

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

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

We can measure it. We do understand it.
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
OCLIMAX bridges theory and INS experiments

Common atomistic modeling tools

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

Virtual experiment for doping effects and isotope labeling

Breaking down the total intensity into partial contributions from individual species or atoms
Single crystal RuCl₃

Using experiment to correct theory

Coherent effects in powder spectra: aluminum

MARI (10K)

ARCS (RT)

OCLIMAX (10K)

OCLIMAX (RT)


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?
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.

**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.
Metal hydrides: why putting hydrogen in metals?

- **Hydrogen storage**
  - Mg$_2$NiH$_4$, LaNi$_5$H$_5$, 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$^3$

The mysterious peak at high H concentration

Possible H sites in ZrV2Hx:
- 32e sites, 3V+1Zr ($^1$H)
- 96g sites, 2V+2Zr ($^0$H)
- 8a sites, 4V (unstable)

Possible H-H distances in ZrV2Hx:
- $^1$H-$^1$H > 2.1Å
- $^0$H-$^0$H/TH ~ 1.6Å

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

H-M vibration

Translational modes

Borgschulte et al., PNAS 117, 4021 (2020)
Violation of Switendick criterion under ambient pressure

• Origin of the unexpected peak

Pair distribution function of ZrV$_2$TH$_{4-x}$OH$_x$ 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


https://neutrons.ornl.gov/vision
Questions?

Neutron Vibrational Spectroscopy - Yongqiang Cheng

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

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