Revamp of Inelastic Neutron Scattering Instrumentation at Frank Laboratory of Neutron Physics

case for project justification

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Introduction

Atomic motions and NS

- Neutrons can excite atomic vibrations or activate stochastic motions via enegy and momentum exchange during inelastic scattering (and $\downarrow$ of course, too.)
- For inelastic incoherent scattering, the intensity is proportional to the space and time Fourier transforms of the self-correlation function, $G_s\left(\vec{r}, t\right)$, the probability of finding a particle at position $\vec{r}$ at time t when the same particle was at $\vec{r} = 0$ at $t = 0$.

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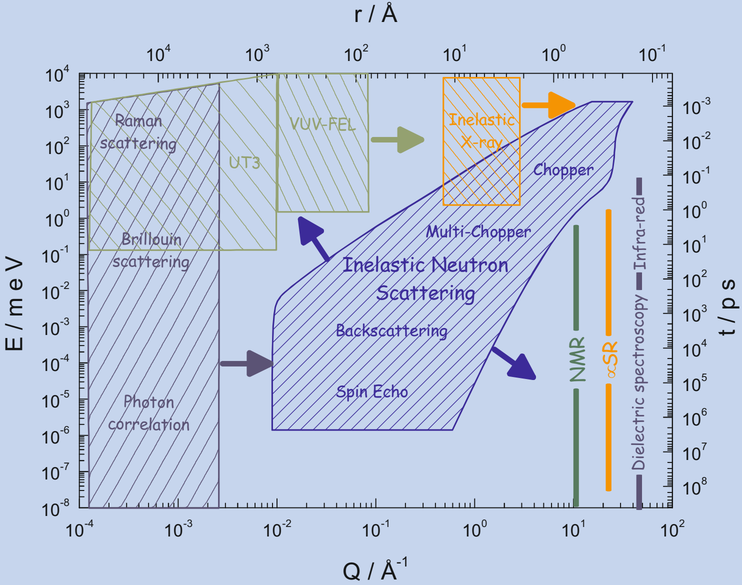
Complementarity

means that advances in the use of one probe, e.g. photons, produce an increased demand for information that can only be provided by another probe, e.g. neutrons.

Complementarity i



Complementarity ii

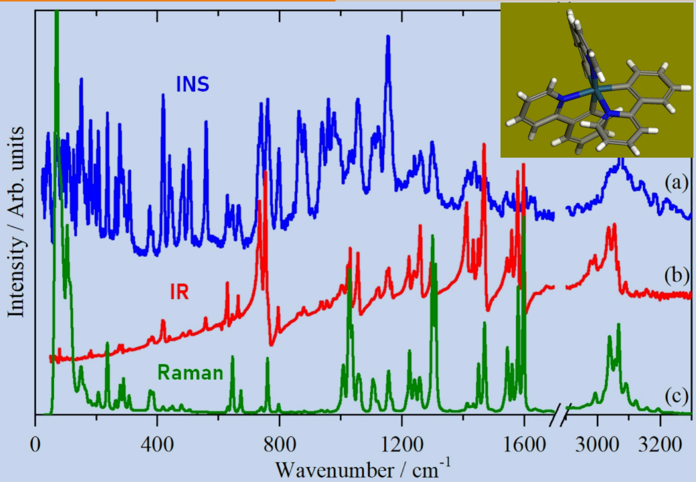
Neutrons:

- “directly” probe atomic (nuclear) vibrations via simple two-body interactions → simple theory
- no selection rules
- neutron has a mass → 2D or 4D spectroscopy: $S(Q,\omega)$ or $S(Q_x,Q_y,Q_z,\omega)$
- INS spectroscopy allows routine access to the terahertz region (<400 cm^{-1})
- large sensitivity to H vibrations (→ H-bonded structures, etc.) $\mathbf{m_n \cong m_H}$
- isotope substitution

IR and Raman:

- probe vibrations “indirectly” through associated variation of electronic properties, such as EDM or polarizability → theoretical description difficult.
- operate at Γ point only
- high sensitivity
- high spectral resolution
- speed
- μ-spectroscopy gaining popularity
- availability of instrumentation

Complementarity put into practice i

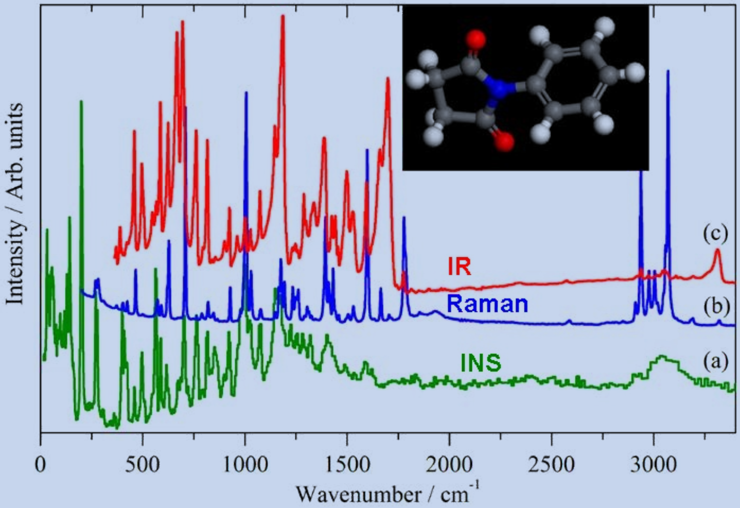


Vibrational spectra of *fac*-tris[2-phenylpyridinato-C^2, N]iridium(III), Ir(ppy)$_3$. (S.F. Parker, J. Phys. Commun. **3** (2019) 065010)

The resolution of state-of-the-art INS spectrometers is effectively comparable to that of most IR and Raman spectrometers because bandwidths in the solid state are dominated by intermolecular interactions that are typically 10 cm^{-1} or more, and high resolution is unnecessary.

For a complete vibrational characterisation, INS spectra are essential, particularly to understand the low energy metal-to-ligand modes that are important in energy dissipation.

Complementarity put into practice ii



Out-of-phase carbonyl stretch at 1700 cm^{-1} is very strong in the IR, weak in the Raman and absent in the INS. Conversely, the out-of-plane carbonyl bend at 407 cm^{-1} is strong in the INS, weak in Raman and absent in the IR.

N-phenylsuccinimide – an important compound in thermosetting resin industry.

S.F. Parker et al, Journal of Physics: Conference Series **554** (2014) 012004

Case for special attention to low wavenumber region

- In the previous slide we saw low wavenumber cutoffs: for Raman at ca. 200 cm^{-1}, and for IR at ca 400 cm^{-1}.

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- In the previous slide we saw low wavenumber cutoffs:
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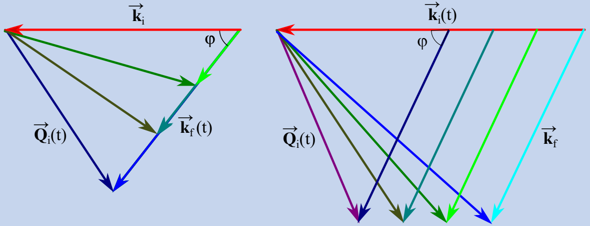
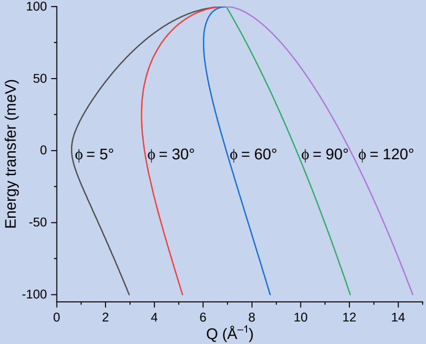
- Often IR can be extended towards 0 cm^{-1}, i.e. into the far IR region, however at a considerable cost.
- "Often" does not mean "always".
  E.g. in studies of supported metal catalysts where the absorption of light by the support results in a spectral cut-off that can be as high as 1400 cm^{-1}.
  For INS spectroscopy, this is irrelevant, and most support materials e.g. alumina, silica, carbon, are transparent and the entire spectral range is accessible.
- An INS spectrometer can cover a broad spectral range, routinely reaching down to nearly 0 cm^{-1}.

INS instrument geometries

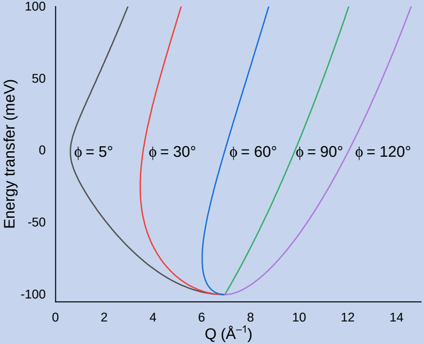
Direct vs. Indirect geometry



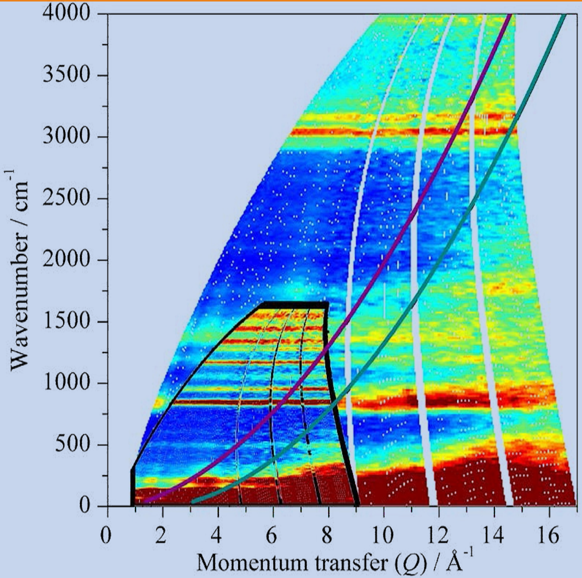
Direct geometry



Indirect geometry



Direct vs. Indirect geometry ii



(Q, ω) plot of iodomethane recorded on MAPS at 20 K with incident energies of 4840 and 2017 cm^{-1}.
The solid lines are the trajectories of an indirect geometry instrument with a final energy of 40 cm^{-1} for scattering angles of 45° (purple trace) and 135° (olive trace).

Direct vs. Indirect geometry iii

In favour of direct geometry:

- Can access a much larger range in Q and, can *always* access smaller Q
- Traditionally considered better suited for magnetism
- The existing machines have up to ten-fold larger detector area
- Resolution is a fraction of the incident energy.

In favour of indirect geometry:

- Simple operation
- If Q irrelevant, large acceptance instrument designs also possible
- Generally considered more versatile
- Resolution is a fraction of the energy transfer.

Challenges to INS

Some challenges to Inelastic Spectrpscopy

- Study of small samples
  - pharmaceuticals
  - matter under spatial confinement
- In highly correlated systems we need a 4D $S(Q, \omega)$. Example: topological Hall effect
- Access range of timescales as large as possible
- Study magnetic multilayers
- Study samples under extreme environments
- Study high absorption isotopes (as e.g. the performance of Li-ion batteries)
- Provide flexible resolution

A few hot topics currently under the interest of the INS community at FLNP

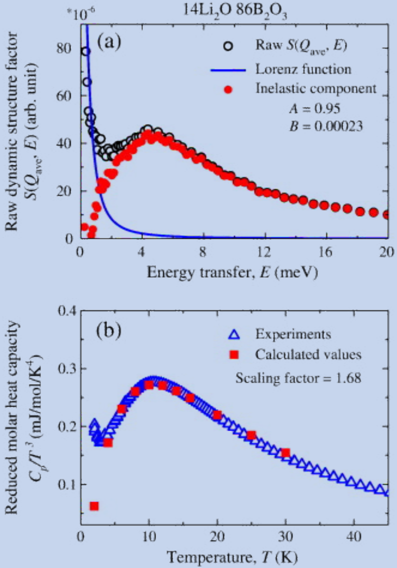
A few topics now under the interest of INS community @ FLNP

- Molecular crystals and glass-formers at low temperatures in connection with complementary studies and *ab initio* quantum chemical calculations.
  - Debye (‘cystal-like’) vs. non-Debye (‘glassy’) $G(\omega)$ at low ω and l-He temperatures
  - dynamics in glasses of ODIC, CONDIS and like phases
- Pharmaceuticals in bulk (native) state and as “micronized” or amorphized powders
- Matter under spatial confinement
  - “hard” nanomatrices (e.g. membranes)
  - “soft” confinement (e.g. microfibres)
- Materials for energy storage, e.g. plasticizer-SPE systems for Li batteries
- Catalysts
- Photonic materials of industrial applications

— non-Debye $G(\omega)$ in lithium borate glasses $x\mathrm{Li_2O}\cdot(100-x)\,\mathrm{B_2O_3}$

- The so-called Boson peak (INS) scales all excess heat capacities
  - Excess heat capacity at liq. He temperatures — the domain of adiabatic calorimetry → Japan, soon Inst. Nucl. Phys, Kraków.
  - The experimental non-Debye heat capacities are successfully reproduced using the excess vibrational density of states measured INS.

Yu Matsuda, H. Kawaji, et al., J.Non-Cryst. Sol. **357** (2011) 534–537



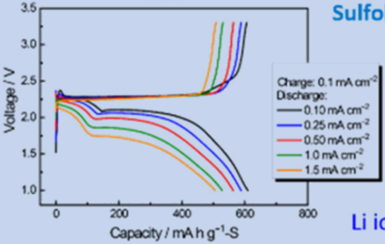
— Electrolyte solvents to optimize Li-ion batteries.

Science driver / objective:

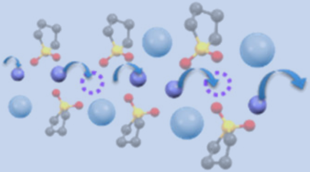
- Low ionic conductivity of solvent-free SPEs
- PEO-miscible electrolyte solvent has been used as the plasticizer to promote the segmental motion of PEO chains.
- When the amount of the liquid plasticizer reaches a level where the ionic conduction is dominated by the liquid-in-polymer instead of the segmental motion of polymer chains, the SPE becomes a GPE.
- The GPE combines the advantages of the polymer electrolyte (high viscoelasticity) and liquid electrolyte (high ionic conductivity), and is of great significance in the Li-ion batteries.

— Electrolytes to optimize Li-ion batteries. Li coordination

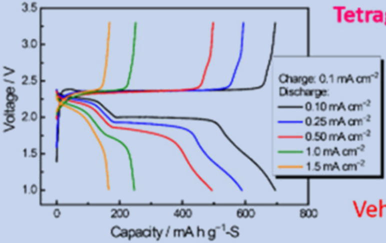
Li-S battery performance



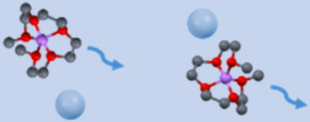
Sulfolane-based concentrated electrolytes



Li ion hopping/exchange mechanism is dominant.



Tetraglyme-based concentrated electrolytes



Vehicular mechanism of Li ion is dominant.

A. Nakanishi, K. Ueno, et al., J. Phys.Chem.C 2019, **123**, 23, 14229–14238

— GP membranes for safety of Li-ion batteries.