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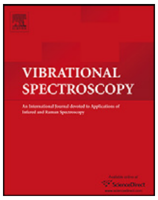

Vibrational spectroscopy with neutrons—Where are we now?

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ABSTRACT

This article reviews recent applications of inelastic neutron-scattering (INS) in the field of vibrational spectroscopy making the link between a broad range of current topics, modelling and instrumentation. We also show how this spectroscopy is positioned with respect the optical techniques, IR and Raman, how this has evolved over time and how it might develop in the future. Principle advantages of INS are described with appropriate examples whilst disadvantages and limitations are described towards the end.

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1. Introduction

There is a small but important overlap between neutron scattering and vibrational spectroscopy that is often referred to as incoherent inelastic scattering (IINS) or more generally INS that has been overviewed in a recent book [1]. There has also been a previous article in this journal [2] that dealt more specifically with molecular systems and readers are referred to these publications for detail on the theory and instrumentation that is normally applied. In the present review we will mainly consider how the advantages of INS have been used to solve specific problems over a much wider variety of scientific areas than considered in the previous review and provide recent examples. We will then examine specific scientific areas that have made greatest use of INS and finally, outline the constraints and limitations of the technique.

Whilst there have been enormous advances in IR and Raman spectroscopies that have allowed much higher spectral and spatial resolution, the corresponding advances in INS have shifted the emphasis from systematic or routine work that compliments optical spectroscopies to a mature technique that excels in selected applications. Neutrons interact almost exclusively with atomic nuclei and all of the advantages and disadvantages of neutron-scattering stem from this interaction. On the one hand, vibrational spectroscopy is mainly concerned with displacements of the atomic nuclei, so probing these directly, rather than probing the response of the electronic structure, has some obvious advantages. On the other hand, the nucleus is considerably smaller than the surrounding electron density and the neutron–nucleus interaction is weaker than the photon–electron interaction so the overall interaction of neutrons with matter is somewhat weak. Neutrons can only be produced in sufficient quantity for spectroscopy by using a research reactor or an accelerator-based neutron-source making INS an expensive technique that is reserved for problems that require the unique properties of this spectroscopy. Inelastic neutron scattering has its roots firmly based in physics and because physical chemists have since become major users these is always some confusion energy-units, which are often expressed as THz, meV or cm^{-1}. In the present review we will restrict ourselves to cm^{-1} and meV, the relation being $8.066\ \mathrm{cm}^{-1} = 1.000$ meV.

2. Advantages of vibrational spectroscopy with neutrons

IINS spectrometers were initially constructed as “add-ons” to the neutron spectrometers of solid-state physicists that might serve a small community of chemists on a very occasional basis. In practice the user-community was much larger than expected and major neutron-scattering centres have purpose-built machines that are regularly over-demanded and have a healthy scientific output. These instruments give a limited but optimised access to a trajectory in Q-ω space and complement time-of-flight (TOF) and triple-axis (TAS) spectrometers, which offer a more comprehensive coverage of Q-ω space. INS is not an exotic technique, the intensities being easily computed from tabulated scattering cross-sections, mean-square amplitudes and instrumental parameters.

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2.1. Isotopic sensitivity

Much of the simplicity arises because neutron-scattering cross-sections for different nuclei are known precisely and are tabulated. Further, these vary almost randomly, not only from element to element, but also from isotope to isotope. For vibrational spectroscopy this means that the intensity changes of the vibrational peaks on isotopic substitution are usually far more pronounced than the more familiar changes in vibrational frequency. The most dramatic, and well known, example of this is hydrogen (^{1}H) that scatters neutrons $\sim$15 times more strongly than any other nucleus, including deuterium (^{2}H). In addition, the larger amplitude of H-atom vibrations further increases the relative INS intensity leading to a pseudo selection rule: *if there is H in the sample, its motions will dominate the spectrum*. In practice, normal modes usually contain such a mixture of internal coordinates that the whole spectrum is reported via the H-atom displacements in INS. It is usual to selectively deuterate samples so that certain H-atoms are "switched-off" providing a considerable aid to detailed assignment. Fig. 1 illustrates the INS spectra of various isotopomers of n-methyl acetamide [3] so that the vibrations of the separate methyl groups and the amide H-atom can easily be distinguished. Subsequently, DFT calculations were used to understand the full vibrational dynamics (see Section 2.5). Similar results have recently been published on small carboxylic acid molecules [4].

Because of the strong scattering by the H-nucleus the majority of INS experiments are made on samples containing H-atoms, which are fairly ubiquitous in chemistry, physics, materials science and biology. However, in the context of this article, there is some overlap between traditional fields in chemistry and physics, particularly with respect to computational lattice dynamics (see later), and INS is widely used on TOF instruments to study phonons in coherently scattering materials (formally, INS includes both coherent and incoherent scattering whilst IINS is strictly incoherent). For example, "rattling modes" have recently been studied in $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ in which encaged atoms are supposed to be decoupled from the lattice phonons [5]. Given the more powerful neutron sources and instrumentation currently being commissioned in the US and Japan and upgrades to existing instruments, such studies on coherently scattering materials will be less time-consuming in the future.

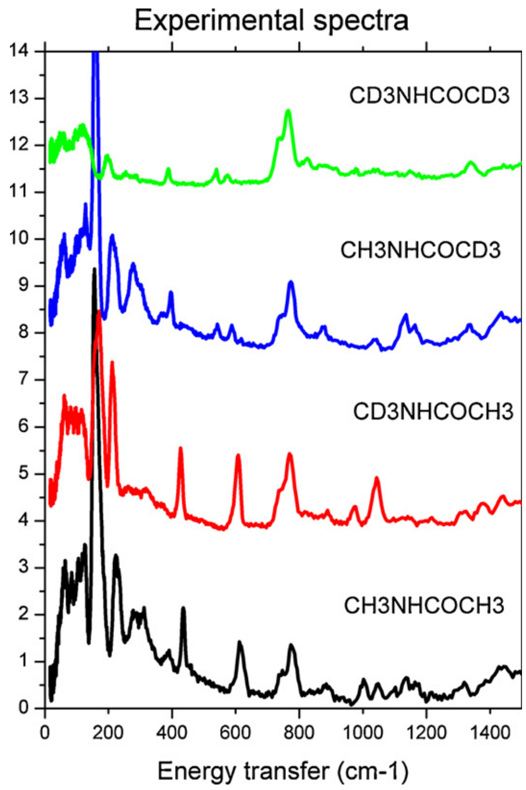

Fig. 1. Measured INS spectra of N-methyl acetamide with different parts of the molecule having been selectively deuterated [3]. Note that in the top spectrum only the amide H-atom remains and that the spectrum is then only from this atom.

2.2. "No" selection rules

Within the normal concept that modes are either IR or Raman active, INS has no selection rules, simply because scattering is from the nucleus. Much of the early work with INS took advantage of the H-atom sensitivity and lack of selection rules to measure torsions of groups such as CH_3 and NH_3 that are forbidden in both optical spectroscopies. Similarly, higher harmonics (overtones and combinations) are also active in INS, their spectral intensities being simply related to the amplitudes of displacement [6] (see Section 2.5). Currently, this means that the whole vibrational spectrum is obtained directly and assignments can normally be made without matching of IR and Raman, or recourse to low-intensity overtones and combinations in these spectroscopies. Several examples are given in Ref. [2].

2.3. Momentum transfer, measurement away from $k = 0$

Due to the neutron mass (1 amu) there can be significant momentum transfer associated with the inelastic scattering event. This means that we are not confined to measurements at the long-wavelength limit where all motions within the periodic system are in phase. Consequently, INS contains a wealth of information arising from interatomic (or molecular) interactions between fundamental repeat units, and how this changes as a function of the phase-relation of vibrators over many unit-cells. Whilst this is normally the domain of phonon spectroscopy in solid-state physics, as spectral resolution increases, it is becoming increasingly common the see these dispersion effects in molecular solids, particularly at lower energy-transfers and where there is long-range hydrogen bonding. For protonated, polycrystalline samples the IINS spectrum is effectively the hydrogen vibrational density of states. This is particularly useful, especially when comparing measured INS spectra with calculations that include dispersion (see Section 2.5). A careful study of phonons and their possible softening on cooling in negative thermal expansion (NTE) framework compounds illustrates the importance of full-phonon treatments [7]. In some instances such as the rattling modes of encaged atoms in skutterudites [5], it would be the absence of dispersion that indicates the decoupling of the encaged atoms from the lattice modes.

2.4. Penetration

Neutrons will penetrate several millimetres into most materials which makes INS a true bulk technique. Further, sample environments are particularly simple because no special window-materials are required, making in-situ, pressure, gas-loading, etc., straightforward. There has long been interest in hydrogen in metals, in the lattice-gas context, for embrittlement of steels [8], and more recently for hydrogen storage in which the interaction between hydrogen and the substrate can be extracted in some detail [9]. In the simplest case INS gives the site-symmetry of the interstitial H-atom [10] where this was impossible to determine by other spectroscopies or crystallographic techniques.

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