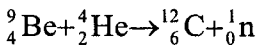


Introduction

Vibrational spectroscopy with neutrons is a spectroscopic technique in which the neutron is used to probe the dynamics of atoms and molecules in solids. In this introductory chapter we provide a descriptive account of the discovery and properties of the neutron, the development of neutron scattering, how inelastic neutron scattering spectroscopy compares with infrared and Raman spectroscopy and the benefits of using the neutron as a spectroscopic probe.

1.1 Historical development of neutron scattering and key concepts

The neutron was discovered by J. Chadwick (1932) who showed that when beryllium was bombarded with α -particles (helium nuclei) neutral particles were emitted having a mass close to the proton mass [1,2]. The particles were called neutrons, designated ${}^1_0\text{n}$.



The neutron is an elementary particle with zero charge, rest mass close to that of the proton, and a magnetic moment (spin $\frac{1}{2}$). Properties of the neutron are listed in Table 1.1. The neutron displays wave-particle duality; whether we treat the neutron as a particle or a wave depends on the phenomenon observed. In incoherent inelastic neutron scattering it is regarded as a particle, although the scattered neutron is treated theoretically as a spherical wave. The wave properties of the neutron are revealed by observing how the phenomena of interference, diffraction, determine the way in which a beam of neutrons propagates and spreads. The de Broglie wavelength of a thermalised neutron (*ca* 1–5 Å) is

comparable to interatomic and intermolecular distances, e.g. C–H, 1.09 Å, and its energy (30–700 cm⁻¹) is comparable to molecular vibrational energies. This is why neutron scattering experiments can yield, simultaneously, both structural and dynamic information on the scattering system.

Table 1.1 Properties of the neutron [3].

Property	Value
Rest mass	
m_n /kg	$1.674\ 928\ 6(10) \times 10^{-27}$
m_n /u (a)	1.008 664 904(14)
$m_n c^2$ /MeV (b)	939.565 63(28)
Spin, I	$\frac{1}{2}$
Charge number, z	0
Mean life /s	889.1(21)

(a) On the unified atomic mass scale, relative to the mass of carbon-12 defined as 12. (b) Energy equivalent.

Early studies (1936–1950) of neutron scattering used radium-beryllium neutron sources but their low neutron flux prevented exploitation of neutron scattering as a spectroscopic technique [4]. Today neutrons are either extracted from a nuclear reactor or generated at a pulsed, accelerator-based spallation source. The exploitation of neutrons from nuclear reactors in structural studies and spectroscopy dates from the 1950s and from pulsed sources from the 1970s. A useful summary of the development of neutron sources is given in [5].

Neutrons are scattered by nuclei whereas photons (X-rays) and electrons are scattered by electrons. There is a certain probability that a neutron passing through a substance will be scattered with no loss of energy; the scattering is *elastic*. The scattered neutron waves may, or may not, undergo interference. *Coherent scattering* arises when the scattered waves from different nuclei of the same type interfere. Coherent elastic scattering is measured in diffraction experiments and tells us the relative positions of atoms, structure. *Incoherent scattering* arises when the natural isotopic and spin mixture of the sample destroys local order and reduces interference between the scattered waves, sometimes completely. (Neutrons are sensitive to the isotopic make-up of

samples, which is exclusively a nuclear property, because they interact with the nucleus.) When the neutron exchanges energy with the sample the scattering is *inelastic*. This is the type of scattering that provides the spectroscopic information that is the subject matter of this book. We have limited our coverage to *inelastic neutron scattering from incoherent systems*, principally hydrogenous molecules, solids and surfaces and use the abbreviation INS for this type of scattering.

The first experiments on neutron diffraction were carried out in 1936. The use of neutron diffraction as a structural technique, in particular for the location of hydrogen atoms, developed from studies of potassium dihydrogenphosphate, KH_2PO_4 , single crystals. The early work on neutron diffraction is described in Bacon's classic text (1962) [6].

Energy transfer resulting from inelastic scattering of neutrons by polycrystalline materials was demonstrated by P.A. Egelstaff (1951) [7] and by B.N. Brockhouse and D.G. Hurst (1952) [8]. It was early realised that the study of the vibrations of hydrogen atoms in compounds was particularly well suited to neutron scattering techniques: zirconium hydride was the first hydrogenous substance to be studied [9]. The theory of inelastic neutron scattering and early studies of inorganic and organic hydrogenous compounds are summarised in [10]. For molecules see also [11,12]. Recently the Institut Laue-Langevin (the ILL) has published a pocket-size *Neutron Data Booklet* covering many aspects of neutron production, detection, and scattering [13].

Finally, in this historical introduction, we should recall that neutrons have been the subject of two Nobel Prizes: to J. Chadwick for the discovery of the neutron (1935) and to B.N. Brockhouse and C.G. Shull (1994) for their pioneering contributions to the development of neutron scattering techniques (inelastic scattering and diffraction respectively).

1.2 Inelastic neutron scattering (INS)—a spectroscopic technique

The most common methods for studying molecular vibrations are the well established optical techniques of infrared and Raman spectroscopy. It is through a direct comparison with these techniques that the advantages of INS can be most readily grasped.

INS spectra are readily and accurately modelled.

Measured INS intensities are straightforwardly related to the atomic displacements of the scattering atom, which can often be obtained from simple classical dynamics. Any complications arising from the electro-optic parameters are avoided. Indeed the band positions and intensities of most molecular systems can be accurately calculated using modern *ab initio* computational methods. This is especially valuable since these methods are a well established part of the modern chemist's approach to understanding molecular structure and dynamics. The manipulation of an INS spectrum, e.g. subtracting a background, is straightforward.

INS spectra are sensitive to hydrogen atom vibrations.

Optical (i.e. infrared and Raman) techniques are, generally, most sensitive to vibrations involving the heavier atoms, because of the number of their electrons. The neutron incoherent scattering cross section of hydrogen is uniquely high, and makes it about ten times more visible than any other atom.

INS spectra are not subject to the rules of optical selection.

All vibrations are active in INS and, in principle, measurable. This stems from the mass of the neutron (*ca* 1 unified atomic mass unit). When scattered the neutron transfers momentum to the atom and INS measurements are not limited to observation at the Brillouin zone centre, as are photon techniques. The measured INS intensities are, *inter alia*, proportional to the concentration of the elements in the sample.

Neutrons are penetrating—photons are not.

Neutrons penetrate deeply, of the order of millimetres, into typical samples and pass readily through the walls of containment vessels, generally aluminium or steel. INS results are thus naturally weighted to the measurement of bulk properties.

Wide spectral range

INS spectrometers cover the whole molecular vibrational range of interest (16–4000 cm^{-1} , see Fig. 1.1). The lower energy range (below 400 cm^{-1}) is readily accessible, a region that is more difficult experimentally for infrared and Raman spectroscopies. With modern instrumentation, the quality of INS spectra approaches that of infrared and Raman spectra obtained from the same system under the same conditions.

1.3 INS spectra

In an INS experiment we observe how the strength of neutron scattering varies with the energy transfer and momentum transfer. The spectrum is typically in neutron energy loss, where energy is transferred from the incident neutrons to the scattering atoms.

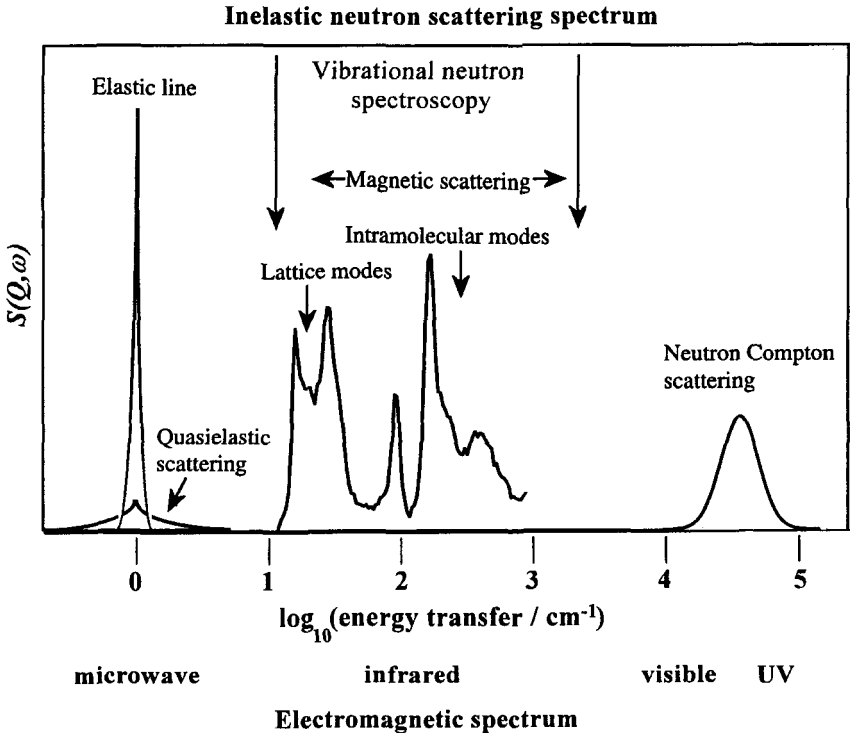


Fig. 1.1 INS spectroscopy in relation to optical (photon) spectroscopies. INS spectra are within the wavenumber range $16\text{--}4000\text{ cm}^{-1}$, the same as the mid-infrared range. The vertical axis is the neutron scattering intensity expressed as the scattering law (or function), see text.

The atoms are embedded in the molecule and can only gain energy in the vibrational quanta characterised by the molecular structure. As an example we show in Fig. 1.2 the INS spectrum of a solid molecular system, Zeise's salt, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, and make comparison with its infrared and Raman spectrum.. Several points are apparent: the most

basic is that when the same mode is observed by different types of spectroscopy it occurs at the same energy. This must be the case since the vibrational energies are determined by the molecule not the technique. It is also apparent that to obtain a complete description of the spectrum all three forms of vibrational spectroscopy are needed.

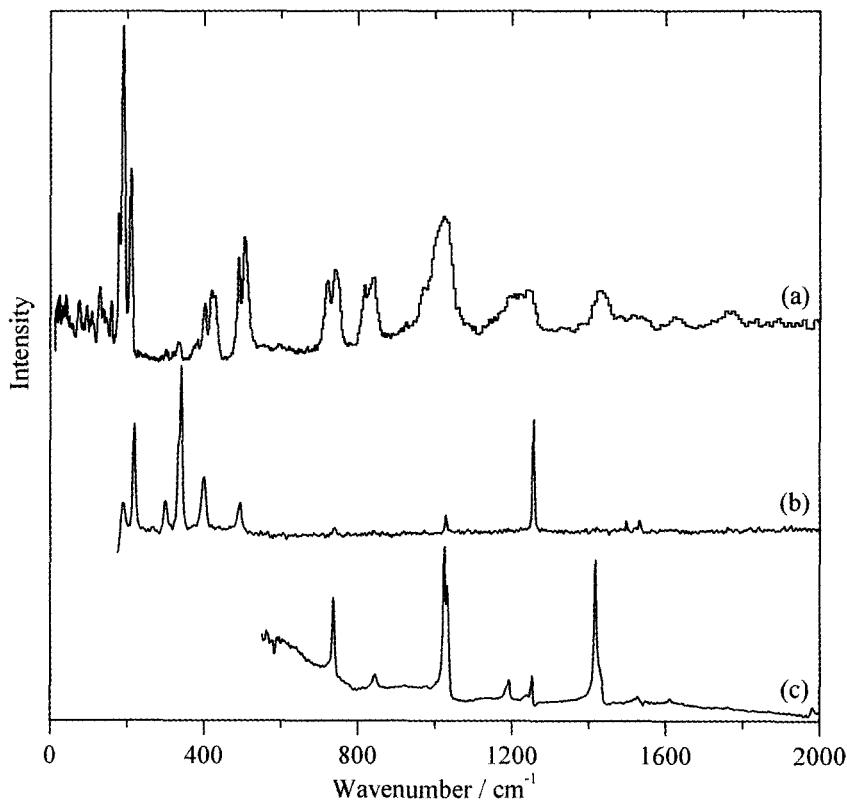


Fig. 1.2 (a) INS (ISIS, TOSCA spectrometer), (b) Raman, (c) infrared spectra of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$. Relative intensities are not to scale. See also Fig. 7.18.

In the INS spectrum of Zeise's salt vibrations involving hydrogen atom displacements have high intensity, for example the torsion of the ethene ligand at 190 cm^{-1} is particularly strong, although all the modes above 100 cm^{-1} involve ethene. The scattering from other atoms, chlorine

in this case, appears weakly. This is exemplified by the Pt–Cl stretch at 336 cm^{-1} that gives a very intense Raman band but only a weak INS feature.

Some peaks in the INS spectrum are not seen in the infrared or Raman spectra: for example the factor group splitting of all the modes in the INS is readily apparent because of the absence of selection rules. In the infrared and Raman spectra, some of the factor group components are either forbidden or have zero intensity.

Access to the low energy region ($<300\text{ cm}^{-1}$) is the usual situation in INS spectroscopy. For infrared and, to a lesser extent, Raman spectroscopy, this is not the case and for instrumental reasons, $200\text{--}400\text{ cm}^{-1}$ is the usual cut-off. Even when the region can be observed, it is often found that at least some of the librational and translational modes are very weak in an infrared or Raman spectrum.

1.4 Information content of an INS spectrum

To make the most of the INS technique and to avoid pitfalls some knowledge of the physics of neutron scattering is desirable. The theory of neutron scattering can be presented at various levels of sophistication. In the classic texts [14, 15] the formalism and the accompanying symbolism can look formidable indeed. In this book, while the presentation of the necessary theory is accurate and rigorous, our concern is the information content of the equations rather than their derivation. Our aim is to acquaint the reader with the basic concepts of neutron scattering, to make the connection between theory and experiment and to show how useful information can be extracted from the experimental data.

The INS technique can be simply summarised. The observed positions of the transitions (the eigenvalues) are a function of the molecule's structure and the intramolecular forces, as in optical spectroscopy, and correspond to the energies lost by the neutron. The strength of the observed transition is a function of the atomic displacement occurring during that vibration (the eigenvector) and the momentum lost by the neutron. The atomic displacements are again determined by the molecule's structure and the intramolecular forces but

the momentum transferred is determined by the neutron spectrometer. INS spectroscopy gives direct access to both the vibrational eigenvalues and eigenvectors and no other technique gives it so straightforwardly.

1.5 When to use neutrons

Neutron scattering as a spectroscopic technique is demanding of time, effort and commitment. To use the technique the experimentalist has to travel to a neutron facility with their sample and, sometimes, with their equipment. So, knowing when to use neutrons, is important.

We might first remind ourselves of when the use of a spectroscopic technique is indicated. Most molecular properties are rationalised through an appeal to an equilibrium molecular structure. Detailed understanding of a molecular structure is the objective of much of the published chemical literature and is best achieved by the use of diffraction techniques. These offer a direct approach to molecular structure. However, many systems of interest and importance to the chemical and materials science communities do not appear as single crystals. Wherever long range order is absent, or seriously confused, diffraction techniques falter and recourse must be had to alternative approaches. All spectroscopies offer an indirect method of obtaining structural information. In molecular vibrational spectroscopy the vibrational resonances that are characteristic of the molecular structure are studied. The spectra are measured and compared with the calculated responses of putative molecular structures. Neutron vibrational spectroscopy is simply another variant on this theme but one that is uniquely advantaged by our ability to calculate the spectral band positions and intensities simply and with confidence.

No one could hope to prescribe which systems should, or should not, be studied by INS; therefore, in this book we offer a review of all the fields of research that have profitably exploited the INS technique. We have been particularly careful to make the results accessible to the broader chemical and materials science community by simplifying, where desirable, the theoretical approaches, in using generally available

ab initio methods, accepting the conventions of optical spectroscopy and retaining the wavenumber as our energy unit.

The reader is invited to study the contents pages to appreciate the broad range of subjects that have been successfully tackled by INS. Then having read through those sections of relevance to their own speciality decide for themselves when, and how, to apply the INS technique to best effect.

1.6 A note on units, symbols and chemical names

Throughout this book, we have, as far as possible, used SI units or derived units, and the symbols for physical quantities and the printing conventions recommended by the International Union of Pure and Applied Chemistry (IUPAC) [3]. The single significant deviation from this approach is the use of the (Å) as the unit of length.

The reciprocal Ångstrom unit is also conventionally used for momentum (Å⁻¹) throughout the neutron scattering literature. There was neither a common optical spectroscopic alternative (as there was to justify the adoption of the wavenumber, cm⁻¹, for the unit of energy) nor chemical reason (as there was to justify the adoption of the atomic mass unit, u or amu, for the unit of mass). For quantities not defined by IUPAC we have mostly used symbols consistent with the neutron scattering literature [14,15] but have, on rare occasions, been forced to invent our own symbol for the sake of clarity. We provide a table of symbols and units (p. xix).

In handling physical quantities and their units we have used the method of quantity calculus [3] (also called dimensional analysis). The value of a physical quantity is expressed as the product of a numerical value and a unit

$$\text{physical quantity} = \text{numerical value} \times \text{unit} \quad (1.4)$$

In tabulating numerical values of physical quantities and labelling the axes of graphs, we use the quotient of a physical quantity and a unit in such a form that the values are pure numbers, for example

$$\omega / \text{cm}^{-1} = 500 \quad (1.5)$$

Finally, the reader should be beware that the neutron scattering literature, certainly the older literature, often fails to use systematic chemical names. While not wishing to be accused of pedantry, we have chosen to use the systematic name where to do so would be unlikely to cause a problem of understanding (e.g. ethene for ethylene, ethyne for acetylene), and, otherwise, the common name with, at first use, the correct name in parenthesis (e.g. the $[\text{HF}_2]^-$ or $[\text{HFH}]^-$ ion, commonly bifluoride in the neutron scattering literature but, correctly, hydrogendifluoride or even difluorohydrogenate(1-) [16]. We write the systematic names and formulae of coordination compounds and organometallics following the latest (provisional) IUPAC convention: listing the ligands in alphabetical order 17.

1.6.1 Spectrometers—accuracy and precision of reported results

Vibrational spectroscopy with neutrons has been dominated by one particular type of instrument, which combined a broad energy range and good spectral resolution. The principal technique used to obtain these advantages was to restrict the final neutron energy to low values ($< 40 \text{ cm}^{-1}$). This opened the spectral range to the full energy range available from the neutron source. Historically, the initial emphasis was to increase the spectral range available (reactor with thermal source \rightarrow reactor with hot source \rightarrow spallation source). More recently the emphasis has shifted to spectrometers with improved resolution, whilst retaining the broad range (beryllium filter \rightarrow beryllium-graphite filter \rightarrow crystal analyser). Throughout the book we use the term *low-bandpass spectrometer* to mean an indirect geometry spectrometer with low final energy, broad spectral range and good spectral resolution. Such spectrometers are described in §3.4.2. Direct geometry chopper instruments have been much less used in this field and this is reflected in the number of results obtained by this technique.

We report the published values of the spectral transitions uncritically as given by the original authors, except for any necessary change to wavenumber units. Generally no more than three significant figures is justified but we confess to not having been consistent in rounding published values. The accuracy of these values will have suffered more or

less from several sources of experimental error but especially instrumental calibration errors. Their precision is strongly dependent on the instrumental resolution and appropriateness of subsequent fitting procedures, if any, that were used. Generally the spectral accuracy will not be better than the instrumental resolution (§3.4.2.3.1, §3.4.3.1).

In the figure captions we follow the convention of attributing the spectra to an identified instrument at its Institution. If no such attribution is given, the reader should assume that the spectrum was recorded using TOSCA (or its predecessor TFXA) at ISIS.

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