

4.3 Chemical Structure, Kinetics and Dynamics

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Abstract

Our informed understanding of the materials world around us is based upon a detailed knowledge of the structure and dynamics of materials on the atomic and molecular level. This contribution reports on molecular and supramolecular structures with sizes from tenths to hundreds of nanometers and dynamic processes studied by inelastic and quasi-elastic spectroscopy in the field of chemistry.

Neutron and X-ray scattering are complementary processes: X-rays scatter from the atomic electrons while the neutrons probe nuclei. This important difference means that neutrons have the ability to accurately locate light elements in the surrounding of heavy atoms. Since the chemistry of a mixed-metal oxide is determined principally by the location of the light oxygen atoms (key examples include high temperature superconductors and colossal magnetoresistance materials), neutron diffraction is the technique of choice for such measurements. Scattering from the nucleus in non-magnetic systems avoids any effect due to charge transfer and thus gives valuable information on the chemical bond. Isotopic effects and contrast between neighbouring elements are also an advantage as compared to X-rays. Neutrons scatter relatively weakly, but the cross-section is well understood and the high penetration depth of neutrons allows measurements under extreme conditions of pressure and temperature, or in-beam chemical reaction measurements on large components. The ESS will give substantial intensity gains over current sources, removing much of the flux-limited problems of current neutron instrumentation. Furthermore, the time-of-flight technique at the ESS, combined with short pulses and long paths, will allow high resolution and high flux to solve more difficult structural problems. The high flux and fixed scattering geometry inherent at ESS will facilitate a new generation of complex sample environments for in-situ experiments.

Chemists respond to the present demands for higher performance materials, cleaner environments and improved efficiency in use of chemicals in a wide variety of ways. These include the use of smart materials that respond to their environment, the use of thin films to build devices and the exploitation of pharmaceuticals and other agents such as catalysts that are active in much smaller quantities than previously used. These developments require the extension of analytical tools to study chemistry and chemicals in small quantities, in complex mixtures and under the conditions of imposed external environments of stress, temperature, chemical environment and other fields or constraints. One of these tools is vibrational spectroscopy, where neutrons have unique properties compared with other techniques. With the larger neutron flux available at the ESS, it will be possible to follow in-situ catalytic reactions. One will be able to record vibrational spectra above room temperature with a spectrometer covering a wide range of energy transfers, at low momentum transfers. The reaction pathways will be tracked down by observing the reaction intermediates. With such an instrument, it will be possible to measure spectra in aqueous solutions, which is the natural medium of biological molecules. Chemistry also involves local and diffusive transport processes which give rise to incoherent (single particle) and coherent (collective) quasielastic scattering. High-resolution neutron spectroscopy yields the microscopic information in space and time. The increased flux at ESS will extend such studies to lower concentrations, to systems with large inherent background, to more complex motions and parameter dependent studies.

I. Introduction

Neutron diffraction gives a unique structural fingerprint of the crystalline state. Light atoms are detected with high precision even in the presence of heavy atoms such as transition metals and actinides. In materials science, archetypal examples include hydrogen storage materials such as metal hydrides [1], and mixed metals oxides such as high temperature superconductors [2] and battery materials [3]. In organic chemistry, the precise location of hydrogen atoms free from charge transfer effects contributes to our detailed understanding of hydrogen bonding from simple model peptide systems to supramolecular chemistry. The possibility of isotopic replacement, and in particular H/D substitution, can be used to great advantage in elucidating specific structural details (Figure 1).

Neutrons probe nuclei and give a better contrast for light elements, isotopic substitutions or neighbour elements in the periodic table.

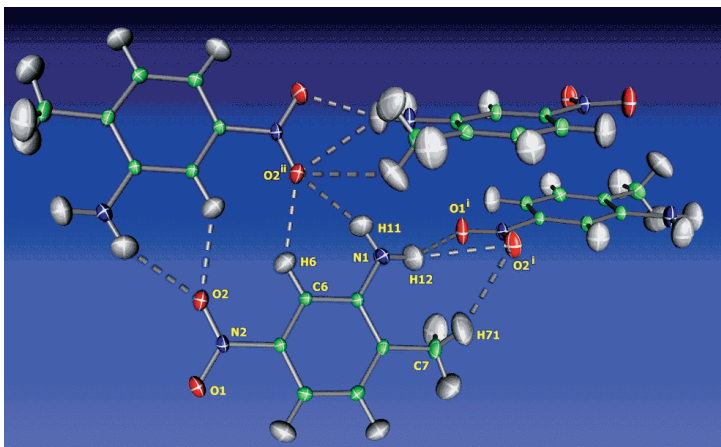


Figure 1: Hydrogen bonding schemes in nitroanilines with non-linear optical activity.

II. The impact of high flux sources

With increasing neutron fluxes, and particularly with the advent of the ESS, neutron diffraction experiments typically involve the collection of a large series of diffraction profiles. These time-resolved, parametric experiments enable structural trends to be analysed as a function of physical parameters such as temperature [4], pressure [5] and magnetic field. In turn, this leads to a fuller understanding of phase diagrams and structural transitions, and to deeper insights into structure-property relationships. Time-resolved neutron diffraction studies are also a very powerful means of following chemical reactions. Neutron powder diffraction allows bulk analysis of materials in “real-life” industrial configurations yielding important crystallographic, thermodynamic and kinetic information about reaction behaviour. Recent studies include investigations into concrete ageing, silicate compounds, hydrothermal syntheses, self-propagating chemical reactions, amorphisation, hydride formation and decomposition and the charge/discharge behaviour of batteries (Figure 2).

Neutron penetration depth allows in-situ experiments to follow bulk reactions in complex environment.

III. Future opportunities and flagship areas

Energy storage and conversion

Environmental problems, such as the green house effect, lead to research on new solutions for energy management. Fuel cells will probably be the cleanest and most versatile power source of this century. However many scientific problems remain to be solved: efficient catalytic processes at electrode surfaces, ionic diffusion in solid state electrolytes, chemical reaction kinetic optimisation. In all these cases, neutrons will be useful for probing both structural aspects and chemical mechanisms.

Materials for cryo-coolers used in space, tritium storage units, fuel cells and alkaline batteries are now metallic hydrides. From a fundamental point of view, competition between magnetic and hydrogen ordering in rare earth-transition metal

Clean and efficient energy storage and conversion

hydrides has been the subject of much recent research. The recent discovery of switchable mirrors also gives an insight into the physics than can be studied through these compounds. In the surrounding of heavy metals, neutron diffraction is a unique tool for locating the proton in metallic hydrides: during the absorption process, the electron is transferred from the proton to the conduction band and only neutrons, probing the nucleus, can give accurate structural data. Moreover, for forthcoming applications, most of them related to clean energy storage and energy conversion, time resolved experiments would give valuable information on the chemical and kinetic processes involved during charge/discharge cycles, allowing optimisation of these materials.

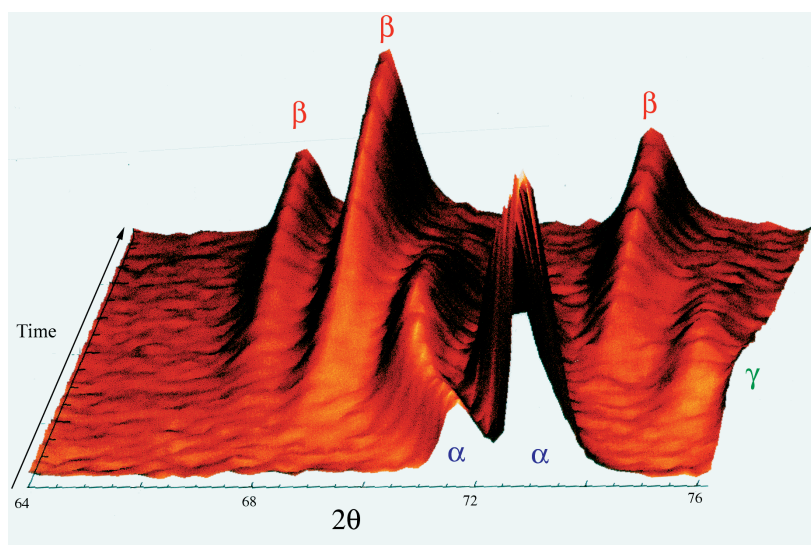


Figure 2: Three dimensional view of the neutron diffraction patterns of a metal hydride electrode during an electrochemical charge in 10 hours. The different phases involved in the reaction are given on the plot [3].

An increase of flux is essential for studying faster processes such as very fast discharge phenomena or short circuit batteries. Materials used in modern batteries often include H and Li as charge carriers. The cations are distributed over various sites in the crystal structure and show high mobility. Their detailed analysis is most important in order to understand the conduction pathway and requires neutron diffraction experiments. In addition, the dynamics can be studied with quasi-elastic neutron scattering. However, the accuracy of crystallographic data is often affected by the complexity of the experimental environments. A better resolution, associated with a larger Q range, will be necessary for solving new problems.

In-situ studies of catalysts

In catalysis, one can study the surface species that result from molecular adsorption, dissociation, or chemical reaction with neutron spectroscopy, even for some systems that

A catalytic cycle involves adsorption, diffusion, and reaction steps. Neutron

cannot be studied by diffraction. The technique is well suited for determining the different adsorption sites for atomic hydrogen on metal or sulfide catalysts [6], for identifying the active species in catalytic reactions, and for understanding deactivation (Figure 3). One limitation is the quantity of catalyst that nowadays has to be prepared (tens of grams). A neutron flux one or two orders of magnitude larger would also allow us to study the adsorption of non-hydrogenous compounds, such as CO, SO₂ and NO_x. Kinetic studies would then also be possible.

scattering techniques can play a major role in all these aspects of catalysis.

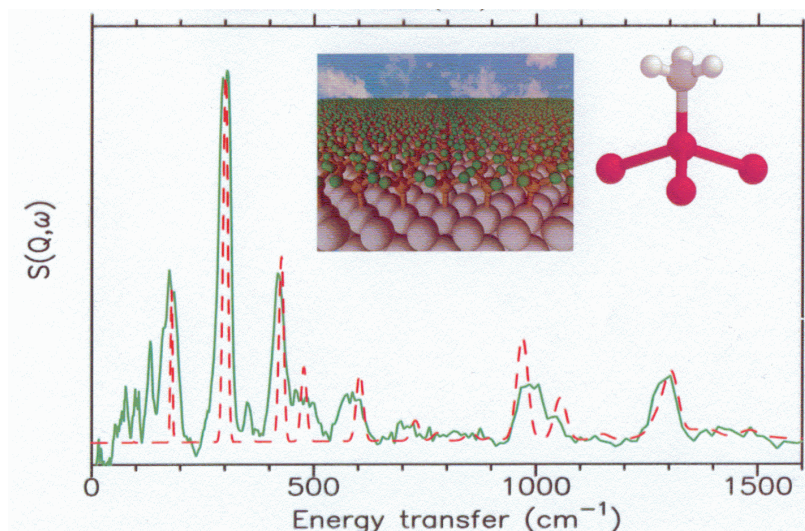


Figure 3: Observed (solid line, recorded at 20 K) and calculated (dashed line) spectra of an industrial palladium catalyst after reaction. The surface is covered with methyl groups, which explains the deactivation [7].

In order to make catalytic processes cleaner and more efficient, one must identify the active species and the reaction intermediates. To follow in-situ catalytic reactions, one needs a spectrometer that can measure the whole vibrational spectrum at small momentum transfer. There are numerous catalytic reactions that would benefit from such an instrument in hydrogenation, oxidation or desulfurisation. For example in the conversion of n-butane to maleic anhydride one could find out if the intermediate is an olefin or an alkoxide. This would permit the building of a kinetic model for the reaction.

Improving catalysts by spectroscopic studies of reagents and intermediates.

Hydrogen bonding and proton dynamics in advanced materials

Analysis of the structure of molecules of biological relevance is important for understanding their different functions. To study the conformational flexibility of these molecules, knowledge of the intra- and inter-molecular forces is required. To achieve this task, vibrational data can be used in combination with quantum mechanical calculations. Hydrogen vibrational dynamics can only be accessed by neutron scattering [8]. A better energy resolution is needed to separate the numerous modes of such complex molecules. So far, measurements have been performed in the solid

Neutron scattering is a powerful means of analysing the proton dynamics of molecules of biological and pharmaceutical interest.

phase; aqueous solutions would be a more natural medium. The analysis of organic molecules interacting with the surface of a substrate, as in biominerals and drug supports, offers new opportunities. The details of the bonding interaction would lead to a basic understanding of the biomimetic processes of formation in biomineralisation.

There has been a recent increase in exciting work in the development of molecular materials with useful and tuneable physical properties such as magnetism, superconductivity, non-linear optical activity, polymorphism, etc. This area is likely to expand dramatically in the next decades. Much of this work is focused on understanding the intermolecular interactions holding 3-D arrays of molecules together, which are often weak hydrogen bonding interactions. The directionality of these interactions is crucial, and the accurate definition of hydrogen atom positions by single crystal neutron diffraction is vital. For example, in pharmaceutical materials the understanding of polymorphism can often rely on small energy differences between molecular configurations, while in supramolecular chemistry accurate quantification of weakly bonded motifs will allow for more rational crystal engineering allowing chemists to tailor properties by designing structures. ESS will advance this expanding area of molecular science by allowing routine characterisation of all atoms in such structures. Specifically, ESS will allow such studies to be carried out on smaller crystals, will offer faster structural characterisation and allow more systematic examinations of the phase space of candidate molecular materials. This maps most appropriately onto the needs of the science.

Advanced molecular materials

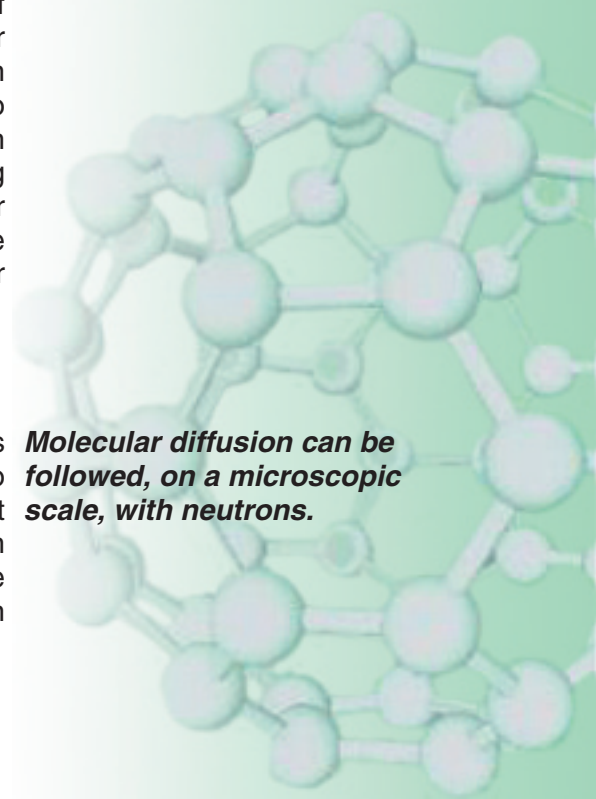
Proton transfer along a hydrogen bond is the simplest example of a chemical reaction, a covalent bond is broken and the hybridisation of the acceptor and donor atoms is exchanged. The potential energy barrier to proton transfer, separating the two wells which correspond to the stable positions of the hydrogen atom, is therefore high and the mechanism for transfer entails tunnelling through the barrier. However, because of the modulation of the electronic state of the molecular skeleton during proton transfer, molecular vibrations also participate, thus promoting or hindering proton transfer. New theoretical methods are being developed to handle coupled tunnelling and vibrational dynamics. Neutron scattering is a uniquely powerful tool for precisely locating hydrogen atoms in these systems and then measuring their dynamics. The tunnelling dynamics in hydrogen bonds can be probed directly by quasi-elastic scattering and molecular vibrations are measured by inelastic scattering.

Hydrogen bonds play a fundamental role in the structure and reactivity of chemical and biological systems.

Diffusion in porous materials

Molecular diffusion in porous materials, such as zeolites, is important in catalysis or separation processes. In addition to their fundamental character in elucidating confinement effects, the aim of these studies is to create new diffusion models valid for complex systems. When the size of the molecule is comparable to the pore size this leads to diffusion

Molecular diffusion can be followed, on a microscopic scale, with neutrons.



limitations, and diffusion coefficients are 3 to 12 orders of magnitude lower than in the gas phase. Various experimental and theoretical techniques (Figure 4) are used to determine diffusion coefficients. In several cases, it has been found that quasi-elastic neutron scattering is the only technique which is able to derive reliable intracrystalline diffusivities [10]. The neutron spin echo technique allows us to probe much longer time scales, this has been demonstrated for the diffusion of deuterated molecules in zeolites.

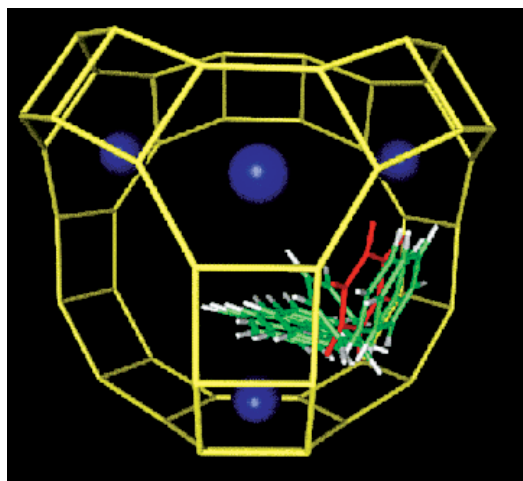
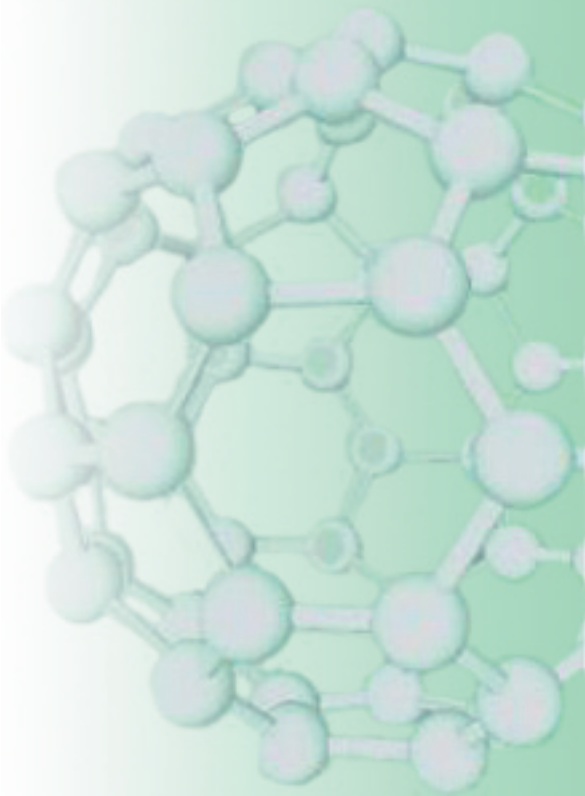


Figure 4: Minimum energy path for benzene in NaY zeolite, between a cation site (Na in blue) and a window site (the molecule at the transition state is in red) [9].

Rotational tunnelling

Rotational tunnelling is one of the simplest quantum dynamical processes. High resolution neutron spectroscopy has significantly promoted our understanding of the properties and importance of quantum motion in solids. This is largely due to the extreme (exponential) sensitivity of tunnelling to the intermolecular potentials in combination with the fact that it can be unambiguously identified. Rotational tunnelling, combined with theoretical chemistry programs, is especially suited to obtaining precise rotational potentials. They allow the determination of the intermolecular interaction potentials [11] via the use of pressure, of disorder in molecular alloys and glassy systems, of the influence of time dependent perturbation of the environment (coupling with phonons) and of deviations from single particle dynamics by coupling to other degrees of freedom. This last field, multidimensional tunnelling processes, will be one of the most exciting in the future. Rotation-translation coupling is already established [12]. The coherent counterclockwise rotation of a methyl group and its centre of mass in a four-fold environment imposes a surprising fourfold proton density distribution of a three-fold rotor (Figure 5) confirmed by neutron diffraction.

Rotational tunnelling is a uniquely sensitive probe of fundamental and system properties. Neutrons yield complete microscopic information.



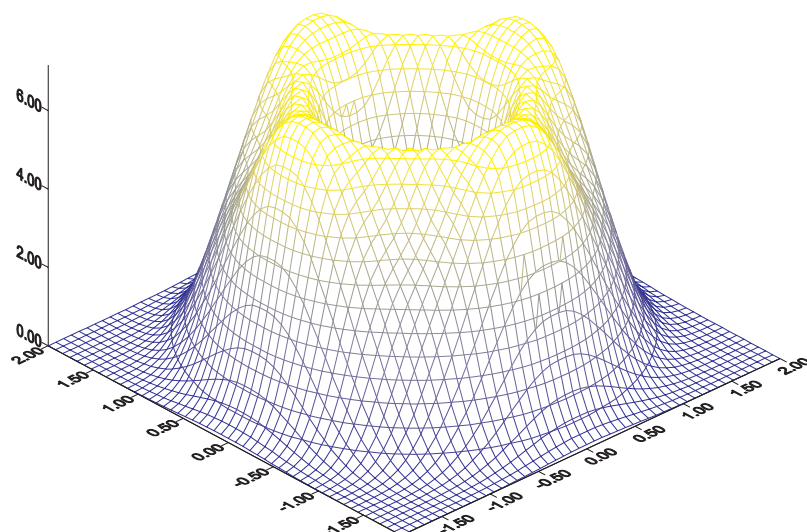


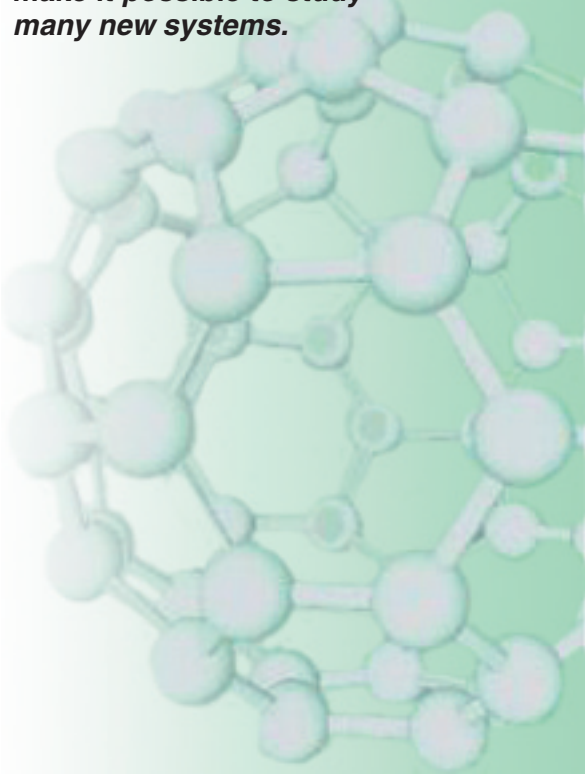
Figure 5: Four-fold proton density distribution of a three-fold rotor due to rotation-translation coupling in a four-fold environment [12].

Tunnel splittings of excited rotational states, well dispersed molecules isolated in a matrix, extended coherent surfaces, single crystals, disordered materials, time-dependent effects such as spin conversion, new forms of multidimensional tunnelling and new non-hydrogenous rotors will become routinely accessible to rotational tunnelling spectroscopy with ESS.

Electrochemistry at surfaces

Neutron reflection experiments are relatively new, but are now being applied to a wide range of chemical studies. A good example is the application of this technique to electrochemistry. The interesting chemistry happens at interfaces (electrodes) and a wide-range of different chemical species are present. Neutron reflection is an excellent tool for the determination of the distribution of various ions and molecules near an interface and for the determination of the composition and structure of deposited layers. The underlying scientific problems arise from important technologies such as those of energy storage, analytical and microanalytical devices and biological sensors. At present relatively few experiments have been conducted [13,14] but considerable progress can be foreseen. The uniform surface areas of samples that are available for study is often very limited and a few mm² is more common than the few cm² usual for reflection experiments with current instrumentation and sources. Higher flux instrumentation will allow experiments on such, more realistic, samples. The changes that occur in electrochemical devices will also be followed in real time, or by application of cyclic data acquisition phased with external potentials or currents.

Neutron reflection is a powerful tool for the study of interfaces, such as those in electrochemical systems. The high flux at ESS will reduce the required sample area and make it possible to study many new systems.



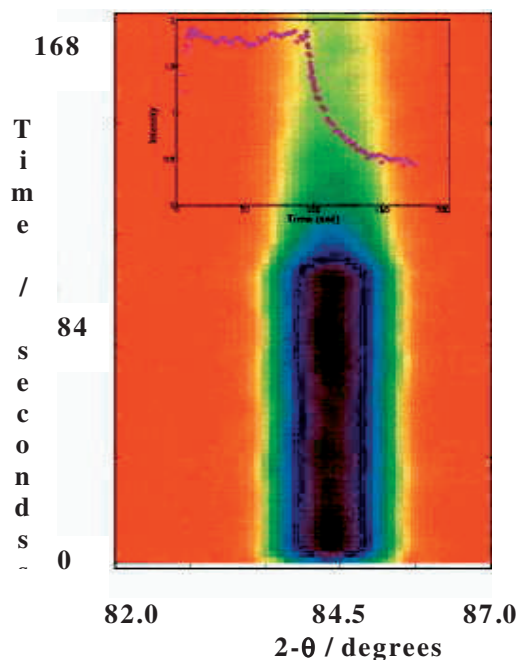


Figure 6: Diffraction from a dispersion of $\text{Ni}(\text{OH})_2$ particles in D_2O showing the change in intensity of the 004 peak in one direction when flow starts. Each time slice is two seconds [16].

An example of an experiment that is of interest to the chemical industry is one in which the alignment of plate-like particles under flow is studied [15]. This is shown in the Figure 6. Particles with ~ 90 nm diameter and approximate aspect ratio of 5:1 were prepared as model experimental systems. Each particle is a single crystal. The alignment can be followed by diffraction of neutrons from the particles in the dispersion. This can be followed dynamically by use of a cyclic data acquisition procedure. Experiments are limited by the small signal in relation to the background. At present only relatively large volumes can be studied. This type of data, in conjunction with small-angle neutron scattering, has already been used to identify phase changes under shear. This type of experiment, including magnetic and electric orientation, could become common if higher flux were available to study small samples that could be subject to more uniform fields.

Polymer synthesis

Small-angle neutron scattering has become a pre-eminent tool for the characterisation of polymers, colloidal particles and a variety of mesophases. Work to follow the synthesis of these materials in-situ will become more common [17]. This has been difficult up to now because of the poor time resolution available and the need to study samples which are dilute in the component of interest, and which contain many other different molecules. It is to be expected that investigations aimed at deepening the understanding of polymerisation mechanisms will develop. For example, these could study the location of initiator in emulsion polymerisation reactions or the conformation of the polymer molecules as they form. SANS has been widely used to look at the

Stroboscopic data acquisition offers many possibilities for the study of dynamic processes under the influences of external fields such as flow, stress, electrical and magnetic forces.

SANS can be used to follow polymerisation reactions in real time; to determine reaction mechanisms and the influences of synthesis conditions on the structure of materials.

morphology of the resulting latex particles [18] but only a little work has been viable with present flux [19].

Chemical kinetics

ESS, with a high flux and instruments optimised for resolution for particular experiments, will allow a much wider range of kinetic experiments. Cyclic data acquisition permits a time resolution of 1 ms. At present, experiments have been performed on pulsed flow and ultrasonic excitation of a crystal. For example, studies of reorientation dynamics in concentrated colloids have already been made. Future applications would include cyclic electrochemical processes. This would give information about the distribution of ions in both solid and liquid phases: this would be studied by neutron reflection, SANS and neutron diffraction.

Time resolved studies of chemical kinetics with stroboscopic data acquisition.

IV. Instrumentation requirements

Chemistry has wide-ranging requirements for neutron instrumentation. These include elastic scattering, quasi-elastic scattering and inelastic scattering.

Relation to ESS-instrumentation

In determining more complex structures, or looking at more subtle microstructure, high resolution powder diffraction is crucial to provide a sufficiently large number of well-defined Bragg peaks. With ESS fluxes, a high-resolution machine will be able to study small samples, such as isotopically enriched materials or compounds synthesised in small quantities by novel synthetic routes.

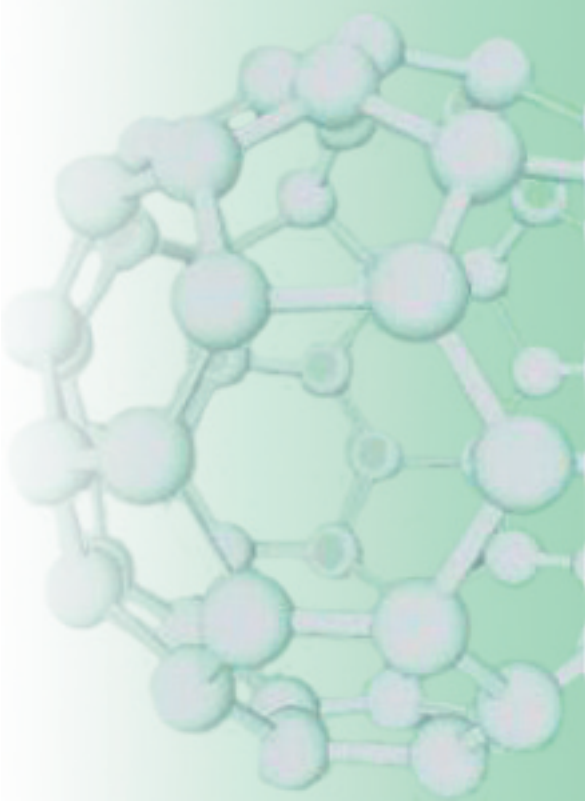
Powder and single crystal diffractions, small angle scattering and reflectometry.

Parametric studies provide a wealth of information on structure-property relationships. A powder diffractometer for rapid time-resolved experiments should have good detector stability, short acquisition time, large Q range, best achievable resolution and a versatile sample environment. Data accumulation times should be of the order of 10 ms.

To increase pressure beyond the present limit (about 50 GPa) it is necessary to reduce sample sizes to about 0.01 mm^3 . This type of study obviously needs a powder diffractometer optimised for extreme environments with high flux and large beam time to get valuable results. The possibility of combining HP ($> 50 \text{ GPa}$) and HT ($> 2000 \text{ K}$) is a challenging goal.

A high throughput small-molecule single crystal diffractometer will offer high quality data from sub-mm^3 samples of both organic and inorganic materials in around 1 hour. With sufficiently large crystals, parametric studies as a function of temperature and/or pressure should be routine. The capability for single crystal experiments on larger molecules will also provide detailed insights into the behaviour of complex supramolecular assemblies and large inorganic systems.

Small-angle scattering will be important, with a wide range of momentum transfer in a single configuration to follow dynamic



processes. An ability to choose the resolution appropriate to the problem is desirable. A Q range of at least 0.001 to 0.5 \AA^{-1} should be accessible.

Neutron reflection, for studying interfaces, will need a high flux and a wide dynamic range to cover reflectivities as small as 10^{-8} . A range of $Q_{\text{max}}/Q_{\text{min}}$ of 30 in a single configuration is required. ***Inelastic and quasi-elastic scattering.***

Vibrational spectroscopy for in-situ catalysis or biological molecules in aqueous solutions requires measurements of spectra at low momentum transfer values, $Q < 2 \text{ \AA}^{-1}$, up to 400 meV, at intermediate resolution. A high resolution instrument, $\Delta E/E \approx 1\%$, is also required.

Transport processes, intramolecular vibrations, hydrogen bond dynamics and rotational tunnelling are all influenced or perturbed or coupled to lattice vibrations. A direct geometry high performance time-of-flight instrument, for the energy regime up to 100 meV, is necessary for controlling and exploiting the phonon density of states.

In the quasi-elastic domain, spectrometers with well-defined line shapes are needed. Only an instrument able to access large Q values at intermediate resolution will allow us to differentiate between different models of motion. Polarisation analysis would be useful to separate coherent and incoherent scattering, e.g. to eliminate Bragg peaks or to study collective phenomena.

Backscattering spectrometers should be available with the best possible energy resolution for very slow motions or strong potentials, and with large momentum transfers.

A neutron spin echo spectrometer with a Fourier time limit of $1 \mu\text{s}$ is required for following slow diffusion.

Apart from the general requirements for improvement in flux, and in resolution in energy and momentum transfer, that will benefit most experiments, there are some interesting possibilities for a new, pulsed neutron source. Instruments could be built that have some of the available configurations optimised for cyclic data acquisition with appropriate short sample to detector distances and high spatial resolution on the detector.

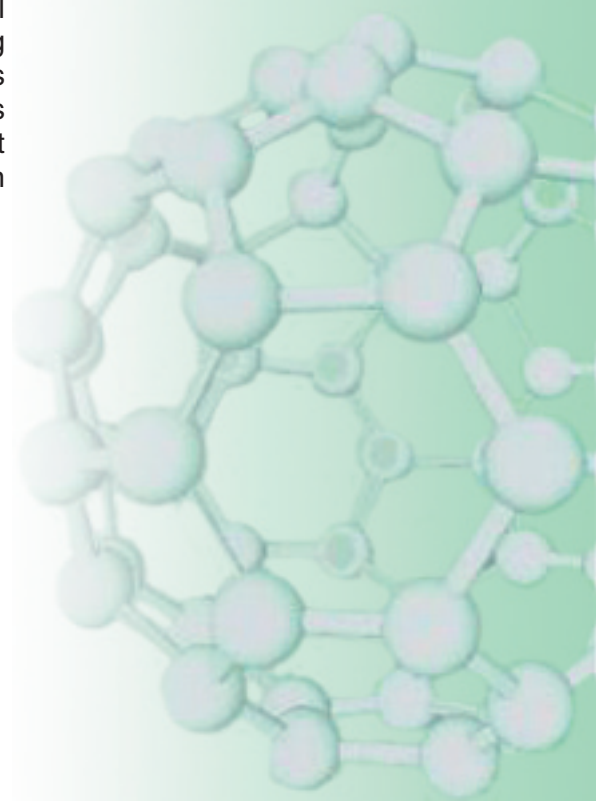
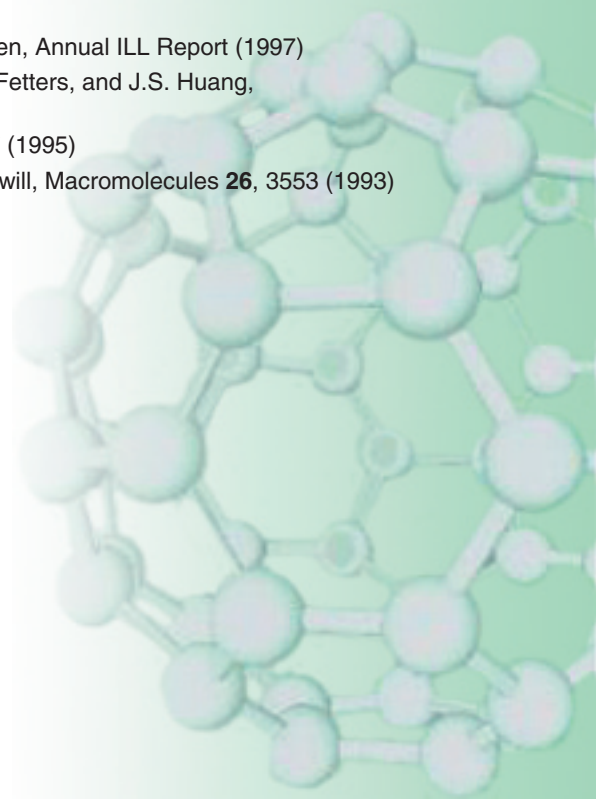


Table with instrument priorities

50 Hz short pulse target station	16 ² / ₃ Hz long pulse target station
High resolution powder	High intensity SANS
Thermal chopper	Variable cold chopper
Cold chopper	High intensity reflectometer
High energy chopper	High resolution neutron spin echo
Chemical single crystal	Focusing low Q SANS
High resolution reflectometer	
Magnetic powder	
High resolution backscattering	
Single pulse diffractometer	

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Achievements of neutrons in chemistry

- In molecular compounds, neutron diffraction has provided the most definitive answers to structural problems, especially (i) accurate positional parameters of all atoms; (ii) accurate determination of thermal motion; (iii) structures in which hydrogen bonding plays a major role (e.g. ferroelectrics, hydrides, and hydrates, including the role of water in biomolecular systems).
- Neutron powder diffraction, through the Rietveld technique, has produced the most accurate, reliable, and complete refined structures from powder data. In combination with X-ray powder diffraction, complex superconductors and host-guest interactions in zeolites have been studied.
- The simultaneous determination of the structure and dynamics of a chemical species under synthesis has enabled unstable reaction trajectories to be characterised in great detail.
- Neutron spectroscopy has assisted crystallography in locating hydrogens away from the points of high symmetry where they had been previously determined by X-ray crystallography.
- Neutron spectroscopy has been key to an understanding of the nature of hydrogen in materials. For example, the state of the majority of adsorbed hydrogen on the hydrodesulphurisation catalyst MoS_2 was determined to be molecular. On the other hand, atomic hydrogen was observed by neutron spectroscopy on RuS_2 . This different behaviour towards a hydrogen atmosphere revealed that RuS_2 has a pseudometallic compartment whereas for MoS_2 redox or acid base properties are involved.
- Neutron spectroscopy has contributed to our understanding of industrial processes. Deactivation of an industrial Pd catalyst has been explained by the presence of a layer of methyl groups on the surface, which prevents the interaction of larger organic molecules with the metal.
- The local diffusion of molecules through porous solids, such as zeolites, can be followed by neutrons where other methods either fail or are inappropriate. Only with quasi-elastic neutron scattering has it been possible to measure simultaneously self and transport diffusivities.
- High intensity neutron powder diffraction has enabled in-situ diffraction measurements to be performed on real systems. Nickel-Metal hydrides batteries have been studied and the results have helped to overcome cycle life problem by showing how the appearance of an intermediate phase reduces the constraints during the cycling process. The rate-limiting factor for high charge-discharge rates of secondary batteries was shown to be the kinetics of the metal to hydride phase transition rather than the diffusion of hydrogen.
- In combination with X-rays, neutron diffraction has probed charge distributions that are essential for understanding some of the most profound details of a crystal structure, for example the effects of charge transfer, magnetostriction, and the onset of superconductivity.
- Neutron diffraction has been used to study not just crystal structure but also disorder and phase transition behaviour in molecular systems and, in particular, in the fullerenes and their derivatives.