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## HERBI – SCIENCE CASE

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### ***The Present***

Since its realisation in the late 1980's, the high-resolution backscattering spectrometer IRIS has maintained a position amongst the world's premier backscattering spectrometers in the field of quasi-elastic (QENS) and low energy inelastic (INS) neutron spectroscopy. Not only does the instrument regularly demonstrate both a high over subscription and publication rate but it also supports a thriving and highly respected user community. All UK based scientific institutions applying for beam time on IRIS over the past five years have attained a rating of at least 4 in the last two Research Assessment Exercises, with over 80% being awarded a 5 or better.

Optimised for operation at 50Hz on Target Station I, and hence collecting data within a 20ms time window, IRIS views the broad cold neutron wavelength profile afforded by the 25K hydrogen moderator. Over the past decade, the spectrometer has proved most beneficial in providing further understanding, both theoretical and experimental, of topics as diverse as macromolecules (polymers and biomaterials), glass transitions, low energy magnetic phenomena, ionic conductors, quantum fluids and dynamics in confined geometries. As an example, two macromolecular topics of current interest are the enhancement of energy storage media and further development of biomaterials.

- *Energy Storage Media*

The development of batteries, electrolytes (ionic conductors), hydrogen storage material and metal hydride battery components requires information concerning the mobility and transport properties of ions. QENS has proved paramount in providing the information necessary for a clearer understanding of the underlying diffusion mechanisms.

Research continues apace to aid development of clean replenishable fuels for future generations. One major area of research is that of battery technology, in particular that technology which utilises electrolytic material. Such material is widely considered the future for battery advancement since it has the potential to provide outstanding performance in terms of reliability and safety. However, while numerous advantages are apparent, the polymer battery exhibits a much lower energy density than its standard 'metal' battery counterpart. When used in a battery, the polymer electrolyte is placed as an electronic separator between cathode and anode. Considerable research effort is focussed toward increasing the performance of both electrode and electrolyte and optimising the interface between them. Indeed, one key issue is to increase the ionic conductivity of the electrolytic material. However, while conductivity is strongly dependant upon molecular dynamics, the actual ionic conduction presently achieved is limited.

QENS studies at ISIS focus on the interplay of molecular dynamics and ionic conduction via the systematics of differing electrolytic material.

- *Biomaterials*

The interface between conventional materials physics and the bio-molecular sciences affords the opportunity for innovative research using neutron techniques. Broad research topics include: (a) structural bio-composites (dental material, biocompatible implants), (b) aqueous polymer/biopolymer gels for medical (ophthalmology) and bio-analytical applications (electrophoresis) (c) bio-mimetic material and processes (exploitation of bio-molecular templates)

At ISIS, work on bone mineralisation is already established and QENS is used regularly to study the dynamics of water in polysaccharide gels and the low-hydration response from disaccharides. Indeed, one particular challenge for QENS is to tackle functionally important ternary systems, i.e. bio molecular matrix + solvent + solute (the latter being a small, highly mobile molecule or slower macromolecular fragments such as the reptation of DNA). Such experiments are demanding on instrument time and need substantial biochemical resources to produce deuterated compounds.

Recent QENS work at ISIS on hydrogels illustrates some aspects of a project under (b) above. In brief, the bioavailability of drugs is as important as the synthesis of new pharmacologically active compounds. One bio-available drug delivery system (DDS) under investigation is the hydrogel. While synthetic biocompatible material eligible for DDS is limited, one that may be readily produced as a hydrogel is poly vinyl alcohol (PVA). PVA is already used in surgery as thread for stitches. However, by cross-linking PVA chains, a polymer network is formed. PVA based hydrogels are thermally stable and acid tolerant. However, they also retain water up to 99% of their total weight, water being confined inside the gel by the network formation. The drug release properties of any bio-available material depend on the diffusive behaviour of the 'caged' water. At ISIS, QENS is used primarily to investigate the diffusion characteristics of 'caged' water at temperatures supportive of biological function. However, for future applications, it is also necessary to synthesise hydrogels with enhanced physical/chemical stability. Nevertheless, to maintain biocompatibility, the cross linking mechanisms used to strengthen the hydrogel must not be chemically different to PVA. Such enhancements can be made and, consequently, systematic QENS studies are also performed at ISIS to investigate diffusion as a 'function' of hydrogel synthesis.

### ***Current limitations***

However, a common problem frequently encountered when investigating soft matter is that macromolecular material inherently exhibits a wide dynamic response. Consequently, complete understanding of all dynamic phenomena within a macromolecular system is often hindered by the limited energy window and resolution afforded by any one QENS spectrometer.

There are two main reasons for this. First, the majority of QENS spectra show non-exponential characteristics (i.e. the relaxation functions exhibit stretched exponential behaviour). Second, it is common that several processes within a material will exhibit dynamics on similar time scales. In both cases one requires a wide dynamic window and ultra high resolution in order to distinguish between differing relaxation phenomena. For example, for liquids and polymers in confined geometries there is great need to distinguish between the dynamically comparable "bound" (i.e. those interacting with the walls) and "free" (bulk-like) molecules.

It often proves necessary to use spectrometers from different neutron scattering facilities in order to map a complete dynamic range. For example, understanding local motion in diverse polymer systems, e.g. filled or cyclic polymers, requires use of IN10 at ILL (or IN16), NEAT at BENSC or Mibemol at LLB in addition to data collected from IRIS. It is readily apparent that such an approach is not only greatly time consuming but also elongates research programmes. Moreover, the successful treatment, and

subsequent theoretical interpretation, of experimental data collected from different spectrometers is far from trivial. At best, overlap between spectrometers can be achieved but at only limited momentum transfer values. Consequently, application of the correct model function to the data is a complex task.

A further concern when collating results from different instruments is that data collected during the assorted experiments might not be from the same sample. For example, situations may arise where there are concerns about the effect of thermal history or perhaps limited sample availability (i.e. due to costly selective deuteration procedures). In addition, when it becomes necessary to reproduce environmental conditions in situ on different beam lines then overlapping information becomes an increasingly difficult task.

The high-energy resolution backscattering instrument, HERBI, is designed to circumvent such experimental limitations.

## HERBI

Optimised for the narrow decoupled moderator pulse structure afforded by the second target station, and operating at 10Hz, HERBI will have access to a 100ms time frame.

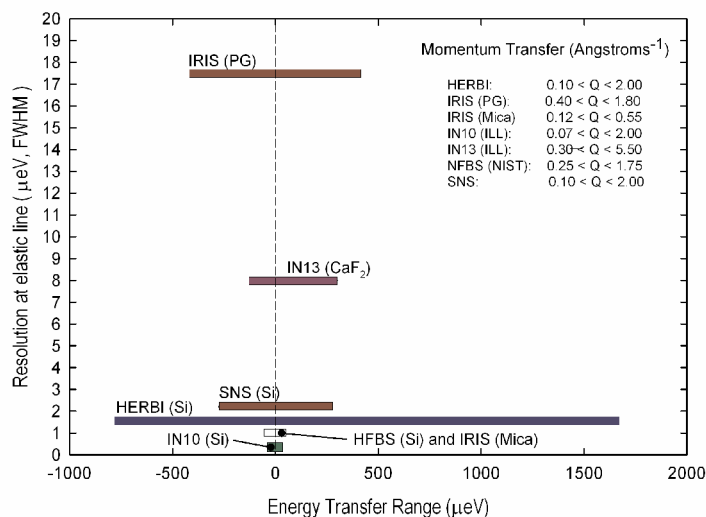


Figure 1: Comparison of energy transfer ranges accessible using different international backscattering spectrometers. The energy transfer range illustrated is that quoted alongside the highest instrument resolution. The analyser type is given in parentheses (PG=pyrolytic graphite)

Such a window will significantly improve upon the dynamic range accessible using IRIS. Indeed, coupled with ultra high µeV resolution and with access to a wide momentum transfer range HERBI will

extend considerably the capabilities of IRIS, giving a resolution comparable to that of the backscattering spectrometers IN10 (ILL) and IN16 (ILL) yet widening the energy range towards that accessible using direct geometry machines such as NEAT (BENSC) and Mibemol (LLB). With such prominent specifications, there is great opportunity to utilise the dynamic spectrum offered by HERBI in such a way that it should be possible to minimise the need for other QENS instruments.

Furthermore, access to a wide dynamic range allows access to a much wider temperature profile. Consequently, a more complete understanding of the temperature dependence of the different dynamic processes is apparent.

Figure 1 does illustrate that by using the muscovite mica analyser bank afforded by the IRIS spectrometer,  $1\mu\text{eV}$  resolution can be achieved, albeit with access to an extremely narrow energy transfer window ( $\pm 20\mu\text{eV}$ ). However, muscovite mica has an inherently high hydrogen content. Consequently, such analyser material contributes a sizable incoherent background component to any neutron spectra collected greatly reducing the sensitivity of the spectrometer. In the past, such a background component has been seen to hinder both QENS and INS studies. One study of note is the investigation of low energy excitations and dynamics in molecular magnet systems - systems for which high-resolution low energy transfer neutron spectroscopy is ideal.

In brief, molecular magnets are attracting increasing interest because they give rise to many new properties that are difficult to observe in 'classic' magnets based on metallic or ionic lattices. While initial synthetic effort was focused toward obtaining purely organic magnets, and reaching critical temperatures above room temperature, more recently chiral magnets have become the focus of attention alongside the design of material showing the coexistence of conducting or super conducting behavior and magnetic properties. Indeed, it has been observed that large, but finite, magnetic molecules which can be considered as zero dimensional magnetic materials may be perfect testing ground for theories treating quantum effects in mesoscopic magnets. On the other hand these molecules are still small enough to show large quantum effects, like tunneling of the magnetisation and quantum interference. It has also been discovered that slow relaxation of magnetization, not accompanied by long-range order, can also be observed in polymeric material allowing for the potentially exciting prospect of storing information in magnetic nanowires.

The use of a silicon analyser on HERBI will greatly reduce the background features presently encountered when using the mica analyser bank on IRIS and hence enhance the study of molecular magnets and similar systems. It is also worth mentioning that silicon is also not prone to potentially problematic background features arising from thermal diffuse scattering, an effect most apparent when using the IRIS pyrolytic graphite analyser bank.

HERBI will exhibit an extremely well defined and temperature independent resolution function; exact knowledge of which is paramount for fruitful and complete data interpretation.

Finally, the ability to extend the spectrometer's energy transfer window to 20meV with minimal degradation of instrument resolution will prove a most advantageous feature of this next generation instrument. Resolution versus energy transfer is given in Figure 2. One current area of research that will benefit greatly from such an attribute is the study of hydrogen storage.

- *Molecular adsorption*

A detailed knowledge of the energetic molecular hydrogen interactions with solid surfaces is an area of extraordinary importance. One major idea currently being explored is the use of adsorbed hydrogen as hydrogen storage at low temperatures to be used as fuel. Also in many catalytic reactions and processes, the hydrogenation process involves the interaction of hydrogen molecules with active centres located in porous material matrices, i.e. zeolites etc. Dihydrogen is an almost free rotor in the solid state and in the ground state has a fully spherical distribution, the main feature is a very strong rotational line located at 14.7 meV. In the presence of a surface or when interacting with a potential, this rotational line is split. The nature of the interaction determines the amount of splitting and the relative intensity of the resulting peaks. It has been used successfully in characterising the interaction potential in substituted CoALPO's and for the study of hydrogen adsorbed on nanotubes. On TOSCA, however, and in the case of strongly interacting systems, the splitting drives some peaks below 3 meV; an energy transfer regime not accessible on the spectrometer at present. It is clear that high resolution (i.e. several orders of magnitude better than that currently available on TOSCA), a well-defined resolution function and a sizable energy transfer window are required for successful band deconvolution. HERBI offers the user such characteristics. The knowledge of the potential energy surface also provides a test bed for the quality of DFT calculations of molecular hydrogen adsorption on surfaces.

It is visibly apparent that HERBI will allow significant developments to be made within the remit of scientific research envisaged on TSII

## HERBI – TECHNICAL OVERVIEW

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The HERBI instrument is a near back-scattering crystal analyser inverted geometry spectrometer. It is designed to provide ultra high-energy resolution over a very large region of ( $Q$ ,  $\omega$ ) space. The design of the instrument is such that it is optimised for operation at 10Hz on Target Station 2 and views the decoupled narrow methane moderator. The instrument sits at the end of a long (120m) super mirror guide ( $m=3$ ). The guide is curved just enough to ensure there is no direct line of sight from the moderator to sample position. Two disc choppers (running at 2 to 10 Hz), situated near to the target station, define the incident wavelength band of neutrons and prevent frame overlap.

The secondary spectrometer consists of a 5m diameter evacuated vessel inside which sit the analysers and position sensitive detector (PSD) banks - the latter located slightly below the horizontal scattering plane ( $2\theta_B=176^\circ$ ). One half of the instrument vessel houses a silicon (111) analyser bank while the other accommodates an array of silicon (311) analyser crystals. The latter is intended to extend the momentum transfer range accessible. The Si(111) crystal analysers will provide very high-energy resolution, 1.5 $\mu$ eV (fwhm) at the elastic line. Moreover, the dynamic range for the Si(111) analyser is extremely wide due to the fact that HERBI will make full use of the 100ms time frame afforded by the operation of the second target station. Suppression of higher order reflections necessary to achieve a wide dynamic window will be achieved using a beryllium filter situated in the scattered beam between sample and analyser. Instrument specifications are summarised as follows:

Analyser Reflection	Analysing Energy (meV)	$\Delta E$ ( $\mu$ eV)	E-range (meV) at 10Hz	Q-range ( $\text{\AA}^{-1}$ )
Si (111)	2.08	1.5	- 0.77 to 1.65 <sup>a</sup>	0.1 to 2.0
Si (311)	7.635	10	- 4 to 23 <sup>b</sup>	0.6 to 3.8

<sup>a</sup> Standard energy window accessible when operating at 10Hz. It is possible to extend this range out to 20meV with minimal degradation of resolution by slowing the choppers. Resolution versus energy transfer is illustrated below

<sup>b</sup> Standard energy window accessible if contamination from Si(933) is eliminated

The High Energy Resolution Backscattering Instrument - HERBI

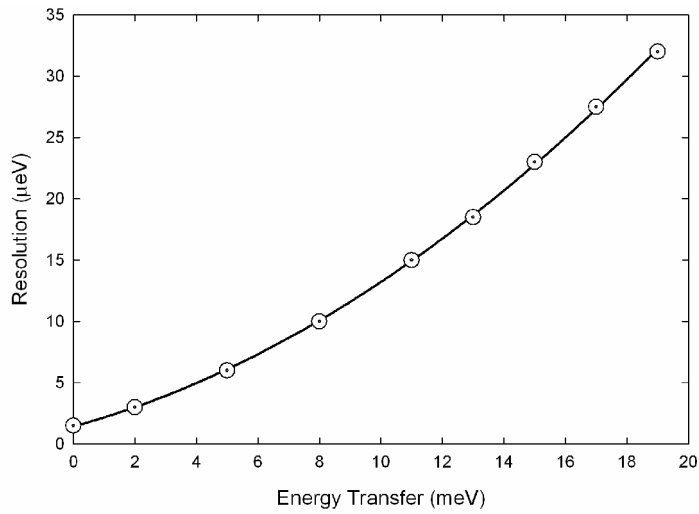


Figure 2: Resolution (FWHM) vs. Energy Transfer for Si(111)

It is estimated that the neutron flux at the sample position will be similar to that of IRIS (possibly slightly better) i.e. approx  $1 \times 10^7$  n/cm<sup>2</sup>/s. This figure is based on the design specifications that the neutron guide will be an m=3 super mirror of width, and height, 10cm.

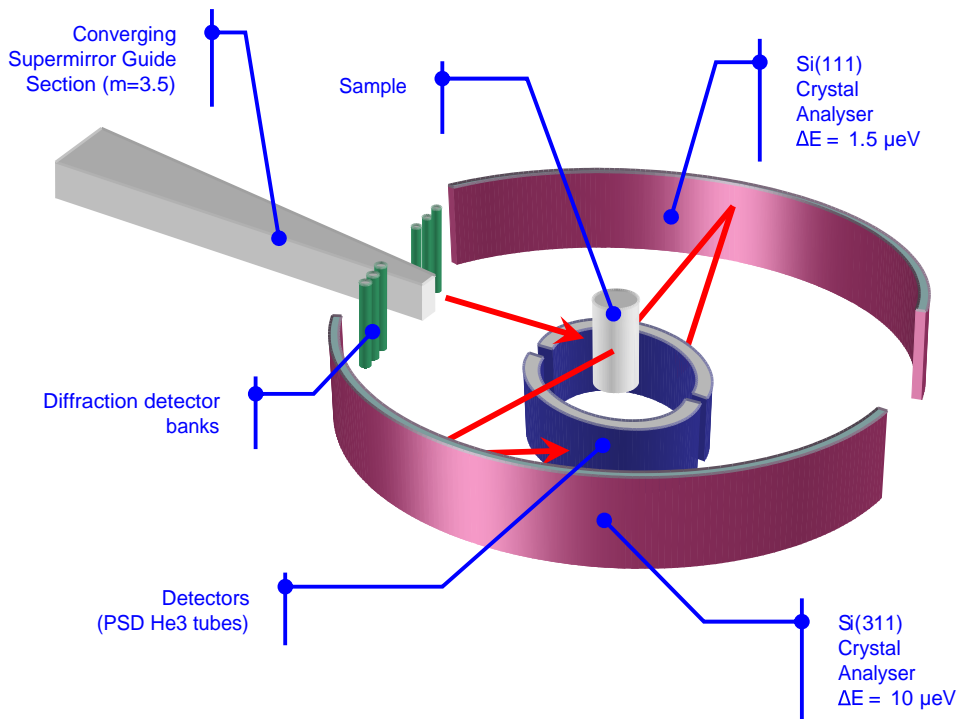


Figure 3: The HERBI spectrometer

*The High Energy Resolution Backscattering Instrument - HERBI*

Furthermore, the count rate at the detector for HERBI will be approximately 25% that obtained when using the IRIS pyrolytic graphite 002 reflection (this is not taking into account the effect of the extended dynamic range). Consequently, HERBI will not only allow access to a energy transfer window several orders of magnitude wider than that accessible when using the mica 002 reflection on IRIS (i.e. the reflection associated with the highest instrument resolution, 1 $\mu$ eV) but it will also exhibit a count rate 6-7 times greater!

Finally, by using a bank of  $^3\text{He}$  PSDs it will be possible to tune the final resolution of the instrument to match the user's requirements - the user being able to modify the active length of each detector and thereby alter the resolution and intensity of the analysed signal. This feature is aided by the fact that the design of the profile of the analyser is such that the analyser 'focuses' different resolutions onto different areas of the PSD. Consequently, the user will be able to trade intensity for resolution (and vice-versa) both during the experiment and afterwards during subsequent data analysis.