

DMM-II

Dynamics of Molecules
and Materials-II



ABSTRACTS

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DMM-II

Dynamics of Molecules and Materials-II



Programme

Abstracts

List of contributions

List of participants

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DMM-II

Dynamics of Molecules and Materials-II



PROGRAMME

Friday 5 July 2013

11h00 Registrations

12h00 Lunch

13h45 **INTRODUCTION** - Professor Stephen Clark, Head of the School of Chemistry of the University of Glasgow

CATALYSIS & ENERGY MATERIALS – 1

14h00-14h40 S. Parker* The use of direct geometry spectrometers for catalysis and molecular spectroscopy

14h40-15h00 R. Warringham Vibrational Analysis of an Industrial Fe-based Fischer-Tropsch Catalyst Employing Inelastic Neutron Scattering

15h00-15h30 B. Fultz* Polaron Dynamics in LiFePO₄

15h30-16h00 A. Borgschulte* Neutron scattering of hydrogen storage materials: from anharmonic vibrations to thermodynamics

16h00-16h30 Tea

INSTRUMENTS & DISCUSSION

16h30-16h50 A. Ivanov IN1-LAGRANGE on the Hot Neutron Source at ILL: New Spectrometer for Vibration Dynamics in Complex Materials

16h50-17h10 R. Mole Pelican: A cold neutron TOF spectrometer with polarisation analysis

17h10-17h30 J. Larese VISION Spectrometer at the Spallation Neutron Source

17h30-17h50 S. Rudić Recent and future developments on TOSCA

17h50-18h10 M. Johnson Modelling methods for INS

20h00 Dinner & beer

* *Invited speakers*

Saturday 6 July 2013

QUANTUM

- 9h00-9h30 A. Horsewill* Quantum Translator-Rotator Dynamics: INS investigations of the spin-isomers of H₂ and H₂O molecules trapped inside fullerene cages
- 9h30-9h50 L. Ulivi Quantum dynamics of hydrogen molecules in simple and binary clathrate-hydrates: measurements and computation
- 9h50-10h10 I. Natkaniec IINS and DFT studies of vibrational spectra of water retained in graphene oxide
- 10h10-10h30 J. Edge Inelastic Neutron Scattering of H₂ adsorbed in Laponite

10h30-11h00 Coffee

ENERGY MATERIALS – 2

- 11h00-11h30 H. Grothe* Inelastic Neutron Scattering and Neutron Diffraction of Nitric Acid Hydrates
- 11h30-12h00 S. Yang* Inelastic neutron scattering study on functional energy materials
- 12h00-12h20 S. Callear The structure and dynamics of hydrogen absorption in a metal alloy
- 12h20-14h45 J. Larese Inelastic Neutron Scattering (INS) Studies of Hydrogen Spillover on Pure and Pd decorated Metal Oxides

12h45-14h00 Lunch

MOLECULAR CRYSTALS & POLYMERS

- 14h00-14h30 S. Duyker* Unique vibrational mechanisms for negative thermal expansion in a series of metal-cyanide framework materials
- 14h30-14h50 S. Mukhopadhyay Investigation on Soft Vibrational Modes of Croconic Acid using Inelastic Neutron Scattering
- 14h50-15h10 E. Spencer Insights into the stability of γ -Al₂O₃ nanoparticles from Inelastic Neutron Scattering
- 15h10-15h30 D. Chudoba Vibrational spectroscopy of selected molecular crystals studied by means of density functional perturbation theory

15h30-16h00 Tea

BIOLOGY & POLYMERS

- 16h00-16h20 N. Tsapatsaris Polymorphism, Drugs and Neutrons: Is making more stable phases really that simple?
- 16h20-16h40 M. Appel Neutron spectroscopy of ferrocene and ferrocene containing polymers
- 16h40-17h00 F. Barroso Bujans Exploring vibrational modes of poly(ethylene oxide) confined in 2D and 3D with TOSCA spectrometer

17h00 DISCUSSION & CONCLUSION

20h00 Dinner & more beer

End of the workshop

* *Invited speakers*

Oral contributions

Friday 5 July 2013

CATALYSIS & ENERGY MATERIALS - 1

The use of direct geometry spectrometers for catalysis and molecular spectroscopy

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Inelastic neutron scattering (INS) spectroscopy has enabled vibrational spectra to be measured for over 50 years. Most studies have used indirect geometry spectrometers that are relatively straightforward to build and use and that provide spectra that are not dissimilar to infrared and Raman spectra [1]. In this talk we show the advantages of direct geometry spectrometers and their complementarity to indirect geometry instruments [2]. These instruments are able to access regions of low momentum transfer at relatively large energy transfer. This means that the C–H, N–H and O–H stretch regions can be exploited by INS spectroscopy for the first time. The instruments generally have very large detector area, which means that they are significantly more sensitive than the more commonly used instruments. They also allow the energy transfer as a function of momentum transfer to be examined. We describe the operational principles of the instruments and show how flux and resolution can be traded. We then demonstrate how the advantages of the instruments can be used to gain understanding of molecular systems in areas as diverse as hydrogen storage [3], hydrogen bonding [4] and fullerenes [5]. The instruments are starting to have a significant impact in studies of catalysts and this is illustrated with recent studies of hydrogen on fuel cell catalysts [6], methyl chloride synthesis [7], the deactivation of methane reforming catalysts [8] and a model carbon monoxide oxidation catalyst [9].

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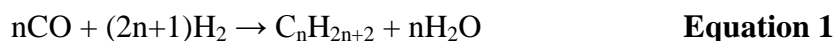
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Vibrational Analysis of an Industrial Fe-based Fischer-Tropsch Catalyst Employing Inelastic Neutron Scattering

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Fischer-Tropsch (FT) chemistry allows access to a wide range of hydrocarbon products via catalytic polymerisation of synthesis gas (syngas, **Equation 1**) over an iron or cobalt catalyst [1]. The resulting hydrocarbon products have a variety of applications, from providing feedstocks for the chemical industry to producing high purity diesel [2]. As the syngas reactant used for FT synthesis (FTS) can be derived from various resources such as coal, natural gas and biomass [3] it has been suggested the diesel produced by FT chemistry could mitigate global dependency on crude oil as an energy source in the future [4].



Since its development in the early 20th century to the present day, the actual active phase/species responsible for activity in iron based FT catalyst is still an issue of debate [5]. One of the reasons for the disparity of opinion is the variety of species that form during the process, including various iron oxides, iron carbides and hydrocarbonaceous species, making analysis of these systems non-trivial. Furthermore, as carbon is deposited on the surface of the catalyst, analysis using conventional surface spectroscopic methods such as infrared becomes increasingly difficult. In order to accurately describe the workings of an industrial Fe-based FT catalyst, a method is required that can probe the surface species that form during reaction. Inelastic neutron scattering (INS) has been utilised due to its ability to characterise hydrogen-containing species and to overcome the constraints discussed previously with infrared spectroscopy. An industrially reacted Fe-based FT catalyst sample was characterised using INS, temperature programmed oxidation (TPO), XRD, Raman, MALDI-TOF and DFT calculations [6]. The work contained in this presentation will discuss the first INS spectrum obtained for an industrially reacted Fe-based FT catalyst and will also highlight the applicability of INS towards the characterisation of surface species in industrially relevant catalytic systems.

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Polaron Dynamics in LiFePO_4

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The compound LiFePO_4 with an olivine structure is used as a cathode material in rechargeable Li batteries, but it is an insulator at low temperatures. Its low electrical conductivity is an issue for its use as an electrode. Polaron hopping is the mechanism of charge transfer between Fe^{2+} and Fe^{3+} ions in Li_xFePO_4 , and polaron hopping is the mechanism of electrical conductivity in LiFePO_4 .

Mössbauer spectrometry is sensitive to the valence of Fe, showing distinct spectral signatures of Fe^{2+} and Fe^{3+} at low temperatures. At higher temperatures, when the valence changes at rates of 1 to 100 MHz, these spectral components become blurred and merge together. The temperature dependence of this process can be used to obtain an activation energy for charge hopping in Li_xFePO_4 , and such measurements have been performed for several years.

In a new development, we studied polaron hopping in Li_xFePO_4 by making measurements on samples under pressure in a heated diamond-anvil cell. We measured synchrotron Mössbauer spectra on Li_xFePO_4 at the Advanced Photon Source. The spectra were analyzed for the frequencies of valence fluctuations using the Blume-Tjon model of a system with a fluctuating Hamiltonian. The polaron hopping frequencies were analyzed to obtain activation energies and activation volumes. The temperature of polaron hopping increased considerably under pressure, showing a positive “activation volume”. For samples of conventional bulk Li_xFePO_4 , the activation volume is approximately 6 \AA^3 at pressures to 17 GPa.

The activation volume is a measure the local atomic distortion required for the polaron to move between Fe sites, so its magnitude can indicate the rate-controlling process. The very large activation volume of $+6 \text{ \AA}^3$ is typical of ion diffusion, not that of isolated polarons (which are usually small and negative). We explain our results with strong correlations in the motions of polarons and Li^+ ions that alter the dynamics of both. The strengths of the interactions between polarons and ions are estimated by a Monte Carlo simulation of their coupled dynamics. This interpretation has practical implications. It is known that the Li^+ ions have one-dimensional channels for diffusion in olivine Li_xFePO_4 , and the ion diffusion is sensitive to impurities that block the ion channels. The wide scatter in reported electrical conductivity in Li_xFePO_4 likely reflects the interactions of polarons and Li^+ ions.

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Neutron scattering of hydrogen storage materials: from anharmonic vibrations to thermodynamics

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The change towards a sustainable energy society requires the development of novel energy materials. I will focus on the physics and chemistry of energy storage in complex hydrides as deduced from inelastic scattering of photons and neutrons. Starting with the archetypical compound LiBH_4 , the combination of infrared, Raman, and inelastic neutron-scattering (INS) spectroscopies on hydrided and deuterated samples reveals a complete picture of the dynamics of the BH_4^- ions as well as of the lattice [1]. Particular emphasis is laid on a comparison between experiment and theory, revealing significant discrepancy between the two approaches for vibrations with high anharmonicity, which is related to large vibrational amplitudes. The latter is typical for librational modes in molecular crystals and pseudo-ionic crystals such as complex hydrides. The presented strategy for anharmonic frequency corrections is then applied on $\text{AZn}_2(\text{BH}_4)_5$ ($A = \text{Li}, \text{Na}, \text{K}$), an unstable complex hydride. The measurements are compared to optical pump-probe infrared spectroscopy, giving the anharmonicity directly [2]. We speculate on the relevance of the results for the stability and kinetics of complex hydrides [3].

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INSTRUMENTS & DISCUSSION

**IN1-LAGRANGE on the Hot Neutron Source at ILL:
New Spectrometer for Vibration Dynamics in Complex Materials**

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The new secondary spectrometer IN1-LAGRANGE is dedicated to studies of high-energy excitations, such as molecular vibrations, in different classes of complex materials available as a rule in non-oriented forms (polycrystals, powders, glasses, composites, biological matter etc.). The instrument design is based on the space focusing of the neutrons scattered by the sample in a very large solid angle and then registered by a relatively small single counter. The analyzer is built from appropriately oriented pyrolytic graphite crystals set to reflect neutrons with a fixed central energy of 4.5 meV. The subtended solid angle is as high as ~2.5 Steradian with characteristic analyzer dimensions less than 1 meter. A cooled beryllium filter is put in the neutron scattering path in order to suppress higher-order reflections by the analyzer crystals. The new instrument demonstrates a very high sensitivity such that vibration spectra of samples with sub-milligram hydrogen content can be measured on a time scale of several hours. It is important that the use of single crystal reflection in the analyzer in combination with the reduced collimation of the incident monochromatic beam will permit experiments with relative energy resolution down to ~1%. The resolution/intensity optimization can be comfortably performed in a broad range with typical time for changing over from one instrument setting to another less than an hour. The secondary spectrometer LAGRANGE (LArge GRaphite ANalyzer for Genuine Excitations) fully benefits from the completed upgrade of the IN1 crystal monochromator with several double-focusing reflecting planes and the available incident neutron energies in the range ~ 5 - 1000 meV. The instrument performance is illustrated by selected examples of the recorded vibration spectra in different materials.

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Pelican: A cold neutron TOF spectrometer with polarisation analysis

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A new cold neutron time-of-flight inelastic neutron scattering instrument, Pelican, is currently being commissioned at the OPAL research reactor at ANSTO. The instrument is constructed to be of broad use with applications ranging from condensed matter physics, through to polymer science and soft condensed matter. It is however ideally suited to the study of molecular dynamics and vibrational spectroscopy. The use of large position sensitive detectors, gives approximately 0.8 steradian coverage, thus a large fraction of reciprocal space can be measured simultaneously, allowing for rapid data collections, as well as the study of single crystal samples. Polarization analysis has been implemented using a supermirror bender for polarization, while analysis will utilize Pastis coils and a wide angle ^3He cell. Although the use of polarisation analysis is more normally associated with the measurement of magnetic signals, one application of Pelican could be the experimental separation of the coherent and incoherent scattering contributions. In this contribution I will present the scientific background behind the instrument along with initial results from the commissioning experiments.

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VISION Spectrometer at the Spallation Neutron Source

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I will present a description of the spectrometer VISION currently in the commissioning phase at the Spallation Neutron Source at ORNL by briefly reviewing the history that served as a driving force for proposing a “best in class” neutron instrument for performing neutron vibrational spectroscopy and simultaneous structural characterization of novel and complex materials. The main advantage of locating an instrument like VISION at the SNS is that it offers the potential for more than two orders of magnitude greater flux on sample compared to existing instruments (worldwide), thereby making it possible to address scientific problems inaccessible today. I will review the design considerations and illustrate how those criteria were replicated in the as built spectrometer. The designed instrument includes diffraction detectors located at 90° and in the backscattering position and 14 identical PG focusing analyzer sections. I will conclude by presenting some examples of the current performance and the timeframe for general user experiments.

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Recent and future developments on TOSCA

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TOSCA is an indirect geometry time-of-flight spectrometer [1] optimized for the study of molecular vibrations in the solid state. It allows measurement of inelastic neutron scattering spectra in a large energy-transfer range, 0 to 8000 cm^{-1} , with a relative energy resolution of about 1.25% across the entire range. Recent developments include the capability to make simultaneous Raman scattering (over the range 100 - 3200 cm^{-1} with a resolution of 2 - 4 cm^{-1}) and neutron measurements at temperatures between 5 and 450 K. [2] The samples to be investigated are attached to one end of a custom-made centre-stick suitable for insertion into a 100 mm-bore cryostat. The other end of the center-stick is fiber optically coupled to a Renishaw inVia Raman spectrometer incorporating a 300 mW Toptica 785 nm wavelength stabilized diode laser. In addition to the inelastic detectors there are also two ³He filled detector tubes on the either side of the incident beam (scattering angle $\sim 178^\circ$) that monitor elastically scattered neutrons and enable modest resolution, $\Delta d/d \sim 3 \times 10^{-3}$, diffraction patterns to be recorded simultaneously with the inelastic spectrum. In doing so, diffraction detectors provide a check on the crystalline phase of the material and any changes to it as a function of alternation in the experimental conditions, e.g. temperature and pressure. The spectral range on TOSCA has recently been extended to -24 cm^{-1} *i.e.* to include the elastic line. This enables ortho-para conversion in hydrogen to be monitored and also provides overlap with the quasielastic neutron scattering spectrometers IRIS and OSIRIS. In order to achieve increased neutron intensity at the sample position Monte Carlo simulations for the development of a neutron guide on TOSCA have been performed. [3] The installation of the neutron guide would reduce accumulation time and enable studies of smaller samples.

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Modelling methods for INS

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Saturday 6 July 2013

QUANTUM

Quantum Translator-Rotator Dynamics: INS investigations of the spin-isomers of H₂ and H₂O molecules trapped inside fullerene cages

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With its ability to mediate transitions involving simultaneous changes in spin and spatial eigenstate, inelastic neutron scattering provides a unique experimental probe for investigating the dynamics of quantum rotors. The H₂ and H₂O molecules both possess ortho- and para-spin-isomers, namely quantum states that have correlated rotational and spin eigenfunctions arising from the antisymmetry requirement for the wavefunction under exchange of the pair of indistinguishable protons. The ground state in both molecules is the para- spin isomer with total nuclear spin zero; para-H₂ has even rotational quantum number, $J=0,2,\dots$, while ortho-H₂ has total nuclear spin $I=1$ and odd rotational quantum numbers $J=1,3,\dots$. Similar correlations arise for ortho- and para- states of the H₂O rotor but as an asymmetric top there are three quantum numbers for rotation.

In recent years remarkable complexes have been synthesised using 'molecular surgery' in which a small molecule such as H₂ or H₂O is permanently entrapped inside a fullerene cage, typically C₆₀. [1] In providing a practical example of an entrapped quantum particle, the system goes to the heart of quantum mechanics in displaying the wave-like nature of molecules. There is quantisation of both rotational and translational energy and the systems are proving to be invaluable as models for a quantum translator-rotator as well as for their intrinsic interest. [2 – 4]

In this paper, INS experiments conducted on IN4, IN5 and IN1-Lagrange at the Institut Laue-Langevin will be described. The samples studied have mass 50 – 120mg. The emphasis will be on low temperature investigations of the small molecule endofullerenes H₂@C₆₀, H₂@C₇₀ and H₂O@C₆₀. On IN1-Lagrange, high resolution spectra ($\approx 2\%$) have been obtained in the range 13 – 300 meV, while IN4 and IN5 permit detailed interrogation of the low-lying states <30 meV. In H₂@C₆₀ we observe splittings arising from the coupling of translational and rotational angular momentum while the effects of lowering the cage symmetry are studied with H₂@C₇₀. In H₂O@C₆₀, the electric dipole moment plays a role and the system provides the unique opportunity to study the H₂O molecule in isolation without hydrogen bonding.

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Quantum dynamics of hydrogen molecules in simple and binary clathrate-hydrates: measurements and computation

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Hydrogen gas and water may form clathrate hydrates either with themselves (simple clathrates) or together with a different substance (binary clathrates). The confinement of the hydrogen molecules is substantially different in the two cases: in binary clathrates hydrogen singly occupies the smaller dodecahedral cages, while in simple clathrates also the larger cages (hexakaidecahedral) are filled with several (up to four) hydrogen molecules. The dynamics of the two kind of molecules is qualitatively different. The Inelastic Neutron Scattering (INS) spectra of binary clathrate samples exhibit sharp bands arising from both the rotational transitions and the rattling modes of the guest hydrogen molecule [1]. They agree well with the rigorous fully quantum simulations, which account for the effects of the anisotropy, angular and radial, of the host cage on the microscopic hydrogen dynamics [2]. On the contrary, the INS spectrum of the hydrogen molecules in the large cages of simple clathrate samples, reported and discussed here for the first time, presents a very different shape, without sharp bands. The theoretical calculation of this spectrum is still an open problem. In this work we present data measured using two different neutron spectrometers, in order to derive their dependence on the momentum transfer, and to discuss their temperature dependence, the effects of the cage geometry, and the different features associated with the ortho-hydrogen and para-hydrogen species [3].

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IINS and DFT studies of vibrational spectra of water retained in graphene oxide

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Graphene oxide (GO) was synthesized in the Institute of General and Inorganic Chemistry RAS at Moscow by a modified Hummers method. The pristine GO was repeatedly washed with water and each time heated during 6 hours at 60°C. The powder sample, subjected to the INS study, was obtained from the aqueous dispersions of the pristine GO after a severe centrifugation and heating in a dry box for 6 days at 65-70°C. As shown, the prolongation of the drying procedure from 1 to 6 days does not change the composition of the final GO keeping it at the following level (mass %): C (58,0±1,0), H (1,5±0,5), O (39,0±1,0), N (0); the mole C/O composition constitutes ~ 2/1 [1].

The incoherent inelastic (IINS) and neutron powder diffraction (NPD) spectra at room temperature and 40K have been simultaneously measured on the NERA spectrometer [2] at the high flux pulsed reactor IBR-2M of the JINR at Dubna. A broad coherent reflection at ~0.69 nm in the NPD spectra of GO indicate that interplanar distance between graphene sheets is twice larger than in graphite and reflect amorphous structure of the sample. The IINS intensity of GO spectra exceeds more than one order of magnitude that one of the mass-equal (10 g) graphite, which exhibits the presence of hydrogen in the former case at the level according to chemical composition of investigated sample. The IINS spectrum shape allows its attributing to the scattering from confined water.

Computations of the amplitude-weighted-density of vibrational states (AWDOS) were performed in the framework of the all-electron generalized-gradient density functional theory (GGA-DFT) on basis of the medium-size GO cluster built of 25 conjugated rings. The single GO sheet was built according to the Lerf–Klinowski model supported by solid-state NMR studies [3]. The recently suggested Sheka-Popova model was obtained in due course of the computational synthesis of the graphene oxide polyderivatives [4]. Water retaining either in the vicinity of individual sheets or between two sheets has been considered. The obtained results allow for discussing water dynamics in GO.

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Inelastic Neutron Scattering of H₂ adsorbed in Laponite

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The inelastic neutron scattering (INS) spectra of molecular hydrogen physisorbed, at a range of loadings, in three forms of monohydrate laponite, have been analysed at low temperatures. The three forms are: research grade Na- & Ca-exchanged laponite and high surface charge (EL) grade Ca-exchanged laponite. The scattering is consistent with rotational transitions for a hindered dumbbell rotor in a double-minimum potential. A number of adsorption sites are revealed and the positions of the peaks show reasonable consistency across all temperatures and loadings for the same sample. All three samples have a weak site split by 3.2 meV. The Na and Ca ion-exchanged EL laponites have a range of sites at similar positions, the strongest being separated by 17 meV, indicating a rotational barrier height to rotation of about 4 kJ/mol. For some sites, the intensity ratios and separation of the degenerate and non-degenerate peaks from the free rotor transition at 14.7 meV, is consistent with adsorption to a point charge [1] and is likely to be H₂ adsorption to the partially hydrated cations, Na⁺ or Ca²⁺.

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ENERGY MATERIALS - 2

Inelastic Neutron Scattering and Neutron Diffraction of Nitric Acid Hydrates

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The IPCC report 2007 underlines the particular importance of aerosol particles for the water cycle and the radiation balance, and thus for the global climate.[1] The contribution of aerosols and clouds to radiative forcing might be comparable to the most important greenhouse gases like CO₂ but is much less understood. Nitric acid hydrates are important constituents of solid cloud particles in the lower polar stratosphere (Polar Stratospheric Clouds) and the upper troposphere (Cirrus Clouds). The exact phase composition of these particles is still a matter of controversy.[2] Especially, metastable modifications have, as recent measurements show, a particular relevance for the atmosphere, which have been ignored up to now.[3] Spectroscopic data for their detection are urgently needed and can be gathered with laboratory models.

Only recently we have recorded the FTIR and Raman spectra of all nitric acid hydrates, stable and metastable.[4,5] These data have been corroborated by X-ray diffraction measurements.[6] However, when interpreting the spectroscopic data it became evident that not all bands could be explained reasonably. Here, DFT calculations were extremely helpful,[7] but still the translational and librational bands were not fully understood. Hence, inelastic neutron scattering was employed in order to investigate this region.

For neutron scattering and neutron diffraction, samples were prepared ex-situ in an amorphous state and were transferred into a cryostat, where the sample has been annealed. Characteristic changes have been observed and have been correlated with the respective phase transitions. The structure of an unknown nitric acid hydrate has been discovered and solved and has in turn allowed the calculation of its vibrational spectra.

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Inelastic neutron scattering study on functional energy materials

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Understanding the molecular mechanism by which porous functional solids trap and separate small molecule gases is essential for the design and discovery of new materials for the selective capture of harmful gases (*e.g.* CO₂, SO₂) and for the energy-efficient separation of hydrocarbons (*e.g.* C₂H₂, C₂H₄ and C₂H₆). Within the field of carbon capture, materials functionalised with amine-groups show high selectivity and dominate this area of research, largely because of their potential to form carbamates *via* H₂N(δ⁻)—C(δ⁺)O₂ interactions thus trapping CO₂ covalently. However, the use of these materials is energy intensive and has significant environmental impact. We present in this lecture the development of several unique non-amine-containing porous solids with high selectivity to CO₂ and SO₂,¹⁻² together with their novel hydrocarbon separation properties.³ In particular, inelastic neutron scattering technique was used to probe the dynamics of the guest/host system. For example, NOTT-300, constructed from Al(III) ions and a tetracarboxylate ligand, incorporates hydroxyl groups within the pores and binds selectively to CO₂ and SO₂. NOTT-300 exhibits highly selective uptake of these two gases versus N₂, CH₄, H₂, CO, O₂, Ar, and *in situ* synchrotron powder diffraction and inelastic neutron scattering studies reveal that these hydroxyl groups bind CO₂ and SO₂ *via* the formation of O=C(S)=O(δ⁻)···H(δ⁺)—O hydrogen bonds, which are reinforced by the weak supramolecular interactions with C-H hydrogen atoms on the aromatic benzene rings (Fig. 1). The nature of the soft interaction here is distinct from that observed in the direct bond formation between the N-centre of amine groups and the electro-positive C-carbon centre of CO₂, which leads to very high isosteric heat of adsorption and results in a substantial energy penalty to release adsorbed CO₂ and SO₂. This offers important potential for the application of new capture systems basing on the soft binding of XO₂ (X=C, S) with formation of this “easy-on” and “easy-off” model.

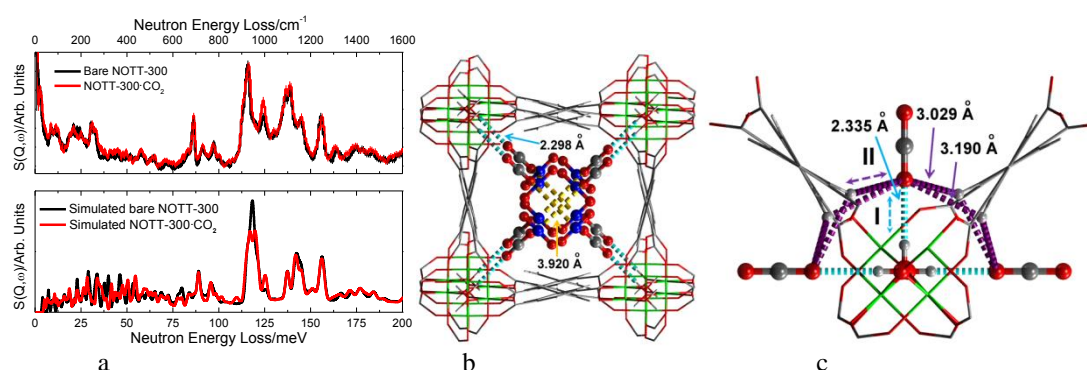


Figure 1. (a) *In situ* inelastic neutron scattering spectra; (b) optimised CO₂ positions in the pore channel (b,c). The adsorbed CO₂ molecules in the pore channel are highlighted in ball-stick model. The carbon atom of second site of CO₂ is highlighted in blue.

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The structure and dynamics of hydrogen absorption in a metal alloy

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Hydrogen storage is one of the most important technological issues to be resolved in the move towards a sustainable hydrogen-based economy. Despite significant advances, no materials have been discovered that have substantially improved overall performance over the current generation of transition metal hydrides. In this presentation, results from neutron scattering studies (including neutron diffraction, inelastic neutron scattering and quasi-elastic neutron scattering) of hydrogen absorption and desorption in a prototypic metal hydride under realistic operating conditions are discussed. These *in operando* measurements mimic the hydrogen cycling behaviour in the current generation of polymer electrolyte fuel cell vehicles. Our results explain the nature of hydrogen absorption and desorption in two prototypic Ti-V-Cr-Mo transition metal hydride systems and also the capacity limitations that develop on prolonged cycling of these materials [1].

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Inelastic Neutron Scattering(INS) Studies of Hydrogen Spillover on Pure and Pd decorated Metal Oxides

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We will discuss our recent investigations using INS and quasielastic neutron scattering QENS to examine the interaction of hydrogen with pure and metal decorated metal oxide materials, specifically Al₂O₃, ZnO and MgO. These find widespread use as energy materials especially as oxidation and hydrogenation catalysts. Our studies are geared toward illuminating the microscopic details of the process(es) that underlie the phenomena often referred to as “hydrogen spillover” in order to identify what, if any, role it plays in the catalytic cycle. The term “hydrogen spillover” refers to the diffusion of hydrogen from a surface capable of disassociating H₂, onto the surface of an adjoining solid. One of the characteristics of this diffusing hydrogen is that it possesses an electron capable of pairing with an unpaired free radical electron on an adjacent surface noted above, that spillover of hydrogen from a metal to a metal oxide or carbon surface is primarily of interest because most commercial catalysts consist of nanometer sized metal clusters supported on either high surface area metal oxides or carbon, and many catalytic reactions involve hydrogen. More recently, a number of experiments have been performed to determine if hydrogen spillover offers a potentially useful route for improving the storage capacity of various metal decorated high surface area carbon nanomaterials. It appears that rather than clarifying the microscopic details of the hydrogen spillover concept these experiments added to the confusion concerning the presence and role of the spillover process. Because hydrogen spillover is the fastest of the many spillover processes (e.g. oxygen spillover), and because H₂ adsorption is a commonly used method to measure the surface area of supported metal catalysts, it is an important process to understand and clarify.

We will present recent INS observations that show that hydroxyl formation on these metal oxide supports takes place only when the metal catalyst is present even at low temperatures. Spectral signatures in both the rotational and vibrational portions of the INS signals underscore this behavior. QENS data establishes that there is substantial translational diffusion at temperatures well below 50K. Similarities and differences of the various support materials will be highlighted. Implications for improving the catalytic performance of these materials will be presented.

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MOLECULAR CRYSTALS & POLYMERS

Unique vibrational mechanisms for negative thermal expansion in a series of metal-cyanide framework materials

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Negative thermal expansion (NTE, contraction upon heating) is a comparatively rare phenomenon that is found in a growing number of materials, most commonly arising from low-energy transverse thermal vibrations of the atomic or molecular bridges between metal ions. The main application for NTE is in compensating for the commonly inconvenient positive thermal expansion (PTE) displayed by the vast majority of solids. The discovery of new families of material that exhibit this property, and the elucidation of the mechanisms that underpin their behavior, is important both in extending the field and in allowing the tailoring of thermal expansion properties desired for such applications.

We present a study of the NTE behavior in the anhydrous $\text{LnCo}(\text{CN})_6$ ($\text{Ln} = \text{La-Lu}$) series of coordination frameworks.[1] Using variable-temperature X-ray and neutron powder diffraction, we measure some of the largest NTE yet reported over a broad temperature range (100-500 K). The degree of NTE in the series scales with the radius of the Ln ion, with effective linear coefficients of thermal expansion ranging from $-14.62(4) \times 10^{-6} \text{ K}^{-1}$ for $\text{LaCo}(\text{CN})_6$ to $-9.05(3) \times 10^{-6} \text{ K}^{-1}$ for $\text{LuCo}(\text{CN})_6$. This trend is a result of differences in the coordinative bond strength across the Ln series, with weaker bonding for the larger ions leading to greater framework flexibility and lower energy transverse thermal vibrations. Combined INS and computational analysis identifies an unusual NTE-contributing mode in which the trigonal prismatic LnN_6 unit twists about its axis at relatively low energies. The incorporation of locally unstable coordination geometries within a framework material, achieved in this case topotactically from the hydrated crystal phases and stabilized by the lattice connectivity, yields a more complex mechanism than the previous rigid-unit descriptions used for other mono- and diatomic-bridged materials, and represents a new approach for the strategic design of NTE materials.

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Investigation on Soft Vibrational Modes of Croconic Acid using Inelastic Neutron Scattering

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Croconic Acid ($C_5O_5H_2$) is the first single component organic molecule which shows room temperature ferroelectricity in its solid state form [1]. In crystalline form, croconic acid molecules are arranged in hydrogen bonded sheets connected through hydrogen bonded hinges. Apart from its technological applications in organic electronics devices, ferroelectricity in croconic acid is a subject of investigation, because of its single component ferroelectricity. In organic materials ferroelectricity often depends on charge transfer between chemically distinct donor-acceptor pairs [2], which is possible only in presence of more than one molecular component. The atomistic level knowledge of hydrogen bonding in croconic acid is required to understand this mechanism.

The vibrational properties of solid state materials are often used to understand ferroelectricity in inorganic materials [2]. We employed neutron diffraction experiment on SXD at ISIS to understand the crystalline structure of this molecular crystal and inelastic neutron spectroscopy (INS) on LAGRANGE at ILL and TOSCA at ISIS to understand its vibrational properties. The experimental data were analysed using state-of-the-art calculations based on plane wave pseudo potential density functional theory (DFT) to understand the nature of hydrogen bonds in this material [3].

Two distinct vibrational peaks have been identified related to two types of hydrogen bonds present in the solid. Motions of these hydrogen bonds in different directions are dominant in the INS spectrum. Further investigations using temperature dependent INS investigation showed these modes as soft modes. The vibrational energies of the hinge position and terrace position hydrogen ions soften by 4% and 3.5%, respectively, with change in temperature from 5K to 300K.

We predicted that these hydrogen ions had dominant role in the ferroelectric properties of the crystal.

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Insights into the stability of γ -Al₂O₃ nanoparticles from Inelastic Neutron Scattering

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Alumina (Al₂O₃) exhibits complex polymorphism at the nanoscale and surface energies play a pivotal role in determining the relative stabilities of the phases as a function of particle size. Coarse crystalline alumina exists as the α form (corundum) under standard conditions but when the surface area of the particles exceeds the threshold value of ~ 125 m²/g the γ form (spinel) becomes energetically more stable [1,2]. It is known that surface water (both chemi- and physisorbed) is essential for stabilising alumina nanoparticles and we report here inelastic neutron scattering (INS) studies of four hydrated nanoparticles with differing pore diameters ranging from 4.5 to 27.2 nm. Low temperature INS spectra were collected over the 0–200 meV energy range on the TOSCA spectrometer at ISIS (Oxford, UK) and INS spectra over the 0–600 meV energy range were collected on SEQUIOA at the SNS (Oak Ridge, USA). By combining both calorimetric and INS techniques we have explored in detail the thermodynamic properties of γ -Al₂O₃ nanoparticles and evaluated the dynamical behaviour of the stabilising water layers confined to their surface. From this comprehensive study the following key conclusions can be drawn: (i) As frequently observed in metal oxide nanoparticle systems the γ -Al₂O₃ surface is terminated by multi-coordinated chemically bound OH and H₂O species, and further stabilised by physisorbed molecular water; (ii) The C_p data support the hypothesis that cation vacancies are occluded within the γ -Al₂O₃ lattice, although their concentration and distribution are unknown; (iii) Neither the water content of the alumina nanopowder nor the inter-particle distance impacts on the thermodynamic properties of the γ -alumina nanoparticles; (iv) The water species confined to the alumina surfaces are strongly bound by an extensive network comprising both covalent and hydrogen bonds. These interactions act to restrict the motion of these groups, and consequently the energy distribution of the rotational and translational modes of the surface water are modified relative to ice-Ih.

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Vibrational spectroscopy of selected molecular crystals studied by means of density functional perturbation theory

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Density functional perturbation theory (DFPT) has recently become a state-of-art method for studying the vibrational dynamics of condensed matter, pushing out the limits of static quasi-harmonic approach.

An extensive validation of DFPT method for the prediction of solid-state vibrational spectra of selected complex molecular systems has been performed, including polymorphic forms of resorcinol, coumarine's iodonic derrivatives, hydroxypyridines and others.

Plane-wave generalized gradient approximation (GGA) of density functional theory has been widely tested with high numerical accuracy. Multiple exchange-correlation functionals in combination with norm-conserving pseudopotentials were probed along with semiempirical corrections for London forces.

The critical view on the performance of the quoted theory in the prediction of the structural properties and vibrational spectra of molecular crystals has been drawn. The special impact has been given to optical vibrational spectroscopy, showing pros and cons of selected methodology.

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BIOLOGY & POLYMERS

Polymorphism, Drugs and Neutrons: Is making more stable phases really that simple?

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Controlling polymorphism in pharmaceutical drugs is a long-standing challenge in formulation science. A well-known example is paracetamol, $C_8H_9NO_2$, a representative of an active pharmaceutical ingredient composed of aromatic polyfunctional molecules with characteristic proton donor-receptor pairs.

The marketed phase I crystallises in the monoclinic space group $P2_1/a$ with corrugated molecular layers that do not slip easily over each other. In contrast, phase II, which is orthorhombic, has relatively planar layers that can slip over each other without difficulty with the added advantage of better dissolution.

Despite the high compressibility and bioavailability of phase II, phase I is still the marketed form. Here we present, for the first time, inelastic neutron scattering measurements for the two crystalline polymorphs measured at 300K at pressures from ambient up to 1 GPa. Under a pressure of *ca* 400 MPa the form II polymorph, which was stable for more than one year, exhibits an unexpected marked shift and dampening of the entire low energy libron manifold.

The results indicate anisotropic weakening of the potential surface in the denser form II and are discussed in relation to the difference of the behaviour of the hydrogen-bonded environment for each polymorph [1]. Our results have repercussions in the understanding of conformational flexibility and are a prelude for further studies on, until now, unexplored paracetamol polymorphs

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Neutron spectroscopy of ferrocene and ferrocene containing polymers

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Ferrocene is an organometallic complex consisting of two cyclopentadienyl rings with an iron atom sandwiched in between. When oxidized, the ferrocene unit exhibits a magnetic moment. We are interested in the study of polymers containing ferrocene and their possible suitability as magnetic 'soft control' materials, where microscopic properties are influenced by external magnetic fields.

Our investigations combine high resolution neutron backscattering spectroscopy, neutron time of flight spectroscopy and vibrational spectroscopy, probing molecular dynamics in a wide range.

In our quasielastic studies, we mainly focus on the ring rotation dynamics of the ferrocene molecule in bulk and when attached to a polymer chain, in its neutral and oxidized state. While previous experiments favor a 5-fold jump diffusion model for the rotation dynamics of ferrocene [1], our data shows higher consistency with 10-fold jumps. We are currently employing complementary DFT calculations in order to strengthen these observations. Moreover, we find that oxidation of the ferrocene molecule leads to a significant increase in the mean jump rate which is corroborated by the DFT calculations.

Vibrational spectra of ferrocene and several ferrocene containing polymers have been recorded using neutron spectroscopy on Lagrange at the ILL. They reveal a shift of several vibrational modes of the ferrocene complex when it is oxidized and/or part of a polymer chain. We aim to use these experiments together with DFT calculations in order to provide more insight into the constraints exerted on the ferrocene complex in the polymeric materials.

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Exploring vibrational modes of poly(ethylene oxide) confined in 2D and 3D with TOSCA spectrometer

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Confined macromolecules at a nanometer scale exhibit a fascinating and unexpected dynamic behavior. Upon a decrease of confining dimensions down to the nanoscale, properties such as glass-transition and melting temperatures are often observed to deviate quite significantly from those of the bulk material. In this study we use high-resolution inelastic neutron scattering (INS) to assign specific vibrational modes of poly(ethylene oxide) (PEO) affected by two-dimensional (2D) and three-dimensional (3D) confinement upon intercalation in the interlayer space of graphite oxide (GO) [1-3] and in the micro and mesopores of partially coalesced amorphous carbon nanoparticles (AC-Np), respectively. INS data were collected on the TOSCA spectrometer located at the ISIS Facility, Rutherford Appleton Laboratory, UK.

Upon polymer intercalation, drastic changes in the thermal response of PEO confined in 2D and 3D spaces were found, such as the suppression of crystallization and glass transition. By means of INS, we found that PEO is accommodated in a layer of thickness ~ 3.4 Å within the GO substrate by adopting a preferential planar zigzag (trans–trans–trans, *ttt*) conformation, in no way resembling the characteristic $7/2$ helical structure of the bulk crystal. In AC-Np, the PEO chains are partitioned into micropores and mesopores. The confinement of the polymer within the micropores constraints the chain dynamics as observed by a reduction of ΔC_p at the glass transition compared to the bulk polymer. Instead, mesopore confinement leads to less restricted chain conformations by forming loops and tails, which contribute to the emergence of weak cooperative dynamics associated with the observed glass transition. INS data unequivocally show that chain conformations are distinctly different from those characteristic of the semicrystalline bulk, and rather similar to those of PEO confined in the interlayer space of graphite oxide. Clear signatures of *ttt*, *tgt*, *tgg*, and *ggg* chain conformations are observed for PEO confined in AC-Np, as a result of the presence of trains, loops and tails.

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Poster contributions

Nuclear spin conversion of H₂O@C₆₀

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Encapsulation of small molecules within fullerene cages such as C₆₀ and C₇₀ (endofullerenes) has allowed for the study of molecules in isolation. [1] Endofullerenes enable trapped molecules to be arranged in a lattice structure where they are free to rotate and translate within the cage without any form of chemical bonding. When the entrapped molecule is H₂ the inter-fullerene interactions are virtually negligible, revealing themselves only at the very lowest temperatures. When the entrapped molecule is H₂O, the system provides the almost unique opportunity to study water molecules in isolation without hydrogen bonding. [2] However, unlike H₂, H₂O possesses an electric dipole moment, so the properties of the H₂O@C₆₀ complex are characterised by interactions between the electric dipoles in different cages.

H₂ and H₂O are quantum rotors which both exhibit nuclear spin isomerism, possessing para (total nuclear spin I=0) and ortho (I=1) species. Nuclear spin conversion of H₂ molecules is known to be absent or not observable in other endofullerenes complexes such as H₂@C₆₀ and H₂@C₇₀. [3] However, ortho-para conversion between the spin isomers of H₂O@C₆₀ is observed on a timescale of hours to days depending on the temperature.

We have investigated the conversion between the nuclear spin isomers of H₂O using INS and NMR experiments which have been performed at the Institut Laue-Langevin, Grenoble and the University of Nottingham. Conversion is observed in NMR experiments via the diminishing amplitude of the signal with time. In INS experiments, the conversion can be observed from the increase and decrease in peaks originating from para- and ortho- H₂O respectively. Besides being able to measure the conversion rate from the change in the intensity of the peaks over time, we are also able to identify the origin of the transitions. Together with the extremely narrow linewidth observed from the INS spectrum of endofullerenes and knowing that para to para transitions are forbidden, we are able to map out the energy level diagram of H₂O@C₆₀ with high degree of accuracy.

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Dynamics of methyl groups of isomers of dimethylpyridine studied by INS and computational methods

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Dimethylpyridines (DMP), commonly known as lutidines, form six structural isomers depending on positions of methyl groups bonded at pyridine ring, namely, three at *meta*: 2,4-DMP, 2,6-DMP and 3,5-DMP, two at *ortho*: 2,3-DMP and 3,4-DMP, and one 2,5-DMP at *para* positions. They were studied by optical spectroscopy [1] and calorimetric [2] methods in order to demonstrate consistency between vibrational assignment and some physical properties like methyl group rotational barriers, standard entropies and heat capacities derived with these methods. More recent research of crystal structures of six isomers of dimethylpyridine [3], allows now for the calculations of vibrational spectra and rotational barriers of methyl groups in crystals by advanced quantum chemistry methods. Neutron spectroscopy is especially useful for study dynamics of methyl groups and we present inelastic incoherent neutron scattering (IINS) spectra of all isomers of dimethylpyridine measured on the NERA spectrometer [4] at the IBR-2 high flux pulsed reactor at Dubna.

The low temperature IINS spectra have been used as a test of calculated vibrational density of states (VDOS) of isolated molecules, as well as of dimers and trimers bonded by C-H...N interactions. Torsional vibrations of methyl groups calculated for isolated molecules of the *meta* and *para* isomers have significantly lower frequencies than corresponding bands observed in the IINS spectra, while for the *ortho* isomers their calculated frequencies are correctly reproduced by IINS spectra of crystalline samples. External hindrance of methyl group rotations by the C-H...N interactions between molecules is well reproduced by calculated librational frequencies for linear clusters. Essential shift of methyl libration frequencies of isolated molecules to their frequencies in condensed states is even done by vibrational spectra of the DFT optimized dimer clusters. Periodic DFT calculations of optical frequencies were performed for comparison hindrance of methyl rotations in crystals. Calculated frequencies of methyl librations for *meta*-dimethylpyridines have slightly higher values than those experimentally observed in the IINS spectra. Calculated frequencies of the out-of-plane and in-plane vibrations of methyl groups in crystals of dimethylpyridines reproduce well their positions and width at corresponding IINS bands.

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**IN1-LAGRANGE on the Hot Neutron Source at ILL:
New Spectrometer for Vibration Dynamics in Complex Materials**

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The new secondary spectrometer IN1-LAGRANGE is dedicated to studies of high-energy excitations, such as molecular vibrations, in different classes of complex materials available as a rule in non-oriented forms (polycrystals, powders, glasses, composites, biological matter etc.). The instrument design is based on the space focusing of the neutrons scattered by the sample in a very large solid angle and then registered by a relatively small single counter. The analyzer is built from appropriately oriented pyrolytic graphite crystals set to reflect neutrons with a fixed central energy of 4.5 meV. The subtended solid angle is as high as ~2.5 Steradian with characteristic analyzer dimensions less than 1 meter. A cooled beryllium filter is put in the neutron scattering path in order to suppress higher-order reflections by the analyzer crystals. The new instrument demonstrates a very high sensitivity such that vibration spectra of samples with sub-milligram hydrogen content can be measured on a time scale of several hours. It is important that the use of single crystal reflection in the analyzer in combination with the reduced collimation of the incident monochromatic beam will permit experiments with relative energy resolution down to ~1%. The resolution/intensity optimization can be comfortably performed in a broad range with typical time for changing over from one instrument setting to another less than an hour. The secondary spectrometer LAGRANGE (LArge GRaphite ANalyzer for Genuine Excitations) fully benefits from the completed upgrade of the IN1 crystal monochromator with several double-focusing reflecting planes and the available incident neutron energies in the range ~ 5 - 1000 meV. The instrument performance is illustrated by selected examples of the recorded vibration spectra in different materials.

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ISIS Glasgow Catalyst Panel

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Virtually all reactions that are carried out industrially use a catalyst to increase the rate of reaction. Over time, there is a build-up of a carbon-rich overlayer on the catalyst. This may have any effect from being essential to the way the catalyst works to killing it stone dead. Our research goal (funded by the EPSRC) is to use a range of techniques, including neutron spectroscopy, to understand how the overlayer modifies the catalyst. The ISIS Glasgow Catalyst Panel [1] was designed to produce the type of overlayers that are present on the catalysts that are used for two increasingly important industrial processes. The first of these is methane reforming [2-4] which is used to make hydrogen, this uses a nickel catalyst and the overlayer is produced from the reaction of methane with an oxygen-containing gas (either carbon dioxide or steam). Industrially the hydrogen is mostly used to make ammonia (for fertiliser production) and methanol (used as a solvent and as a reactant in other processes). The other reaction is the Fischer-Tropsch process which makes long chain hydrocarbons (i.e. petrol and diesel) from carbon monoxide and hydrogen and uses an iron catalyst [5].

The ISIS Glasgow Catalyst Panel (IGCP) is the next stage development of a previous panel that has proved highly successful. This third generation design has built on the knowledge gained to produce a compact, portable system. The panel was manufactured and supplied by Swagelok to ISIS's design specification and specific requirements. ISIS also offers a portfolio of catalyst flow cells of various design geometries to be used in conjunction with the panel in neutron friendly materials.

Acknowledgments

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Crystal structure, inter-molecular interactions and vibrational spectroscopy of di- and tri-halogeno-trimethylbenzenes

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The crystal structure and vibrational spectroscopy of twelve halogeno-mesitylenes is presented. The symmetrical compounds $C_9H_9I_3$, $C_9H_9Br_3$ and $C_9H_9Cl_3$ are triclinic below 293 K, above a monoclinic disordered phase appears before the melting. The structure studied by neutron diffraction gave the presence probability of methyl protons at 14 K [1]. The asymmetrically substituted compounds: $C_9H_{10}I_2$, $C_9H_{10}Br_2$, $C_9H_{10}Cl_2$, $C_9H_9ClI_2$, $C_9H_9Cl_2I$, $C_9H_9BrI_2$, $C_9H_9Br_2I$, $C_9H_9ClBr_2$, $C_9H_9Br_2Cl$ were studied by X-ray diffraction. Their structures are monoclinic and disordered at 293 K. An ordering appears in some cases at 100 K. The experimental conformation is compared to that obtained by DFT calculations for isolated molecules using the MPW1PW91 functional in the Gaussian package. The agreement is very good, but small deviations may appear for the methyl orientation ($C_9H_9I_3$ [1]). The packaging energy due to van der Waals interactions was studied using 6-exp atom-atom UNI potentials. This showed that, in all crystal phases, the molecules may easily jump by $2\pi/3$ or even $2\pi/6$ in their molecular plane. This was confirmed by H, D and ^{13}C NMR.

For all these molecules there are 57 normal modes of vibration. More than 40% of the frequencies have wavenumbers smaller than 700 cm^{-1} and are well detected by INS. They were calculated by DFT using the harmonic and also the an-harmonic models [1, 2]. The results were compared to those of the Raman, IR and INS spectra obtained below 30 K. No scaling seems necessary for frequencies below 800 cm^{-1} . DFT calculated PED give a good idea of the intra-molecular motions. This study shows also how each degenerated normal mode in $C_9H_9X_3$ is split in $C_9H_9X_2Y$. There are disagreements between theory and experiment only for the normal modes with frequencies calculated below 150 cm^{-1} and concerning the torsion modes of methyl groups. This is explained by the fact that the DFT computations do not take into account the methyl spins. These modes corresponds to tunnelling transitions studied with neutron backscattering spectrometers [3]. It will be shown how the tunnel gaps are sensitive to the crystal environment.

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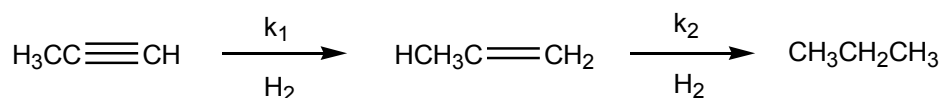
Characterisation of hydrocarbonaceous overlayers important in metal-catalysed selective hydrogenation reactions

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Hydrocarbonaceous overlayers are important in controlling selectivity profiles of metal-catalysed hydrogenation reactions [1]. However, as the overlayer is invariably impervious to investigation by infrared spectroscopy, the nature of the overlayer is often poorly understood. A recent series of experiments using the MAPS and MERLIN spectrometers at ISIS have established that INS can indeed be used to obtain the vibrational spectrum of this important entity. This presentation describes a recent series of experiments where propyne hydrogenation over a commercial grade alumina-supported Pd catalyst was selected as a suitable reaction system for which to evaluate the suitability of INS in this role.



The reaction conforms to a consecutive process, with partial hydrogenation to propene (k_1) preceding full hydrogenation to propane (k_2) [3-7]. Figure 1 shows INS spectra (2000-4400 cm^{-1}) recorded using the MAPS spectrometer. Figure 1(a) presents the spectrum of the activated catalyst, where a broad feature centred at 3594 cm^{-1} is assigned to unresolved (O-H) stretching modes of alumina hydroxyl groups. The spectrum after 6 hours continuous reaction at 323 K, with ethene, propane and propene identified as reaction products, is shown in Figure 1(b). A new feature centred at 2956 cm^{-1} is readily assigned to the C-H stretch of retained hydrocarbonaceous species. The difference spectrum (Figure 1(c)) shows that the $\nu(\text{C-H})$ mode ranges from 2850-3063 cm^{-1} , indicating the mostly aliphatic nature of the overlayer and this is supported by the quantification of the carbon and hydrogen on the surface. It is this species that is thought to be controlling hydrogen supply, which is then influencing the extent of hydrogenation [6]. Curvefitting the difference spectrum 1c, shows that there is also a broad feature at 3260 cm^{-1} assigned to a population of strongly hydrogen-bonded hydroxyls. Figure 1(c) represents a milestone and establishes that INS can be used to access these important aspects of high specification heterogeneous catalysts.

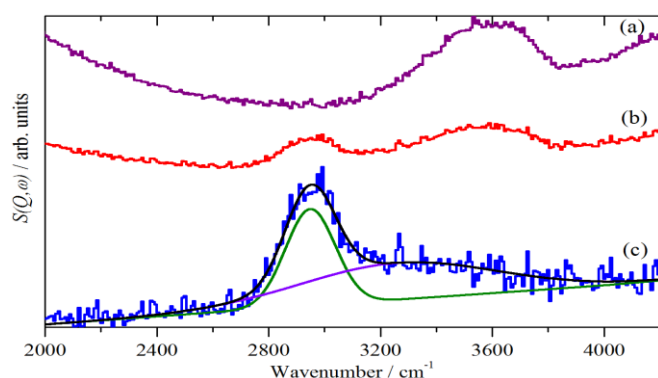


Figure 1: INS spectra (recorded on MERLIN with $E_i = 4840 \text{ cm}^{-1}$) of (a) the Pd(5%)/Al₂O₃ catalyst after activation, (b) the catalyst after carrying out six hours of the propyne hydrogenation reaction, (c) the scaled difference spectrum ($\times 4$ ordinate expanded relative to (a) and (b)) with curve resolved components and the total fit.

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Giant spin fluctuations and their effect on the first order magnetic transition in the itinerant ferromagnet, $\text{LaFe}_{13-x}\text{Si}_x$

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The $\text{LaFe}_{13-x}\text{Si}_x$ system ($x < 1.6$) has a first order ferromagnetic, FM, to paramagnetic, PM, transition that is tunable in magnetic field and ends at a (tri)critical point (H_{crit} , T_{crit}) beyond which it is second order. In this large family of materials T_c can be easily tailored by changing the Fe content or by hydrogenation and $\text{La}(\text{Fe},\text{Si})_{13}$ has attracted huge interest due to its potential for room temperature magnetic cooling.[1] One of the key fundamental issues is that despite the magnetic transition being strongly first order, there is almost no magnetic or thermal hysteresis (an advantage for cooling applications).

We are able to isolate the heat capacity at the phase transition (i.e. excluding contributions due to latent heat) using a novel microcalorimetry method.[2] For $x < 1.6$ we observed that a giant increase in the heat capacity evolves as the system approaches the tricritical point.[3] We argue that this enhancement of the heat capacity is due to anomalously large spin fluctuations that are enabled by a multiple minima energy landscape.[4] To test this theory we employed inelastic neutron scattering.

Initial measurements with MARI were performed on the $x=1.2$ composition in order to isolate the energy and $|Q|$ of interest. We found that enhanced scattering occurred below T_c at low $|Q|$ ($< 0.5 \text{ \AA}^{-1}$), which collapsed toward the elastic line as the temperature was increased. We confirmed that this was not due to spectral broadening at increasing temperatures by taking scans at several temperatures above and below T_c .

The results obtained so far suggest that enhanced magnetic scattering occurs at T_c . Further work will involve isolating this range of interest and exploring how it is affected by changes in the state variables H , T , and P .

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Parameters of the NERA spectrometer for cold and thermal moderators of the IBR-2M pulsed reactor

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The inverted geometry time-of-flight spectrometer NERA for simultaneous investigation of elastic and inelastic neutron scattering was constructed on the 109 m basis flight of channel 7 of the IBR-2 reactor at the JINR in Dubna. Spectrometer parameters were optimized for the thermal neutrons spectrum of water moderator working at the temperature of 330K [1]. During the modernization of IBR-2 reactor in years 2006 – 2012 a new source of cold neutrons with the operating temperature range of 90 – 30 K was installed in sector of the 7-10 channel numbers. A new moderator, an organic glass of mesitylene and m-xylene solution, was selected as a result of investigation of methyl groups dynamics and structural studies of solid phases of methyl compounds of benzene [2], done on NERA spectrometer at IBR-2 reactor. The cold moderator causes of incident neutron spectrum shift to longer wavelength (Fig. 1). In complex with water moderator allows to effectively use thermal and cold neutrons in range of wave-lengths up to 7 Å, which is limited by the length of basis flight and the frequency of reactor pulses equal 5 Hz.

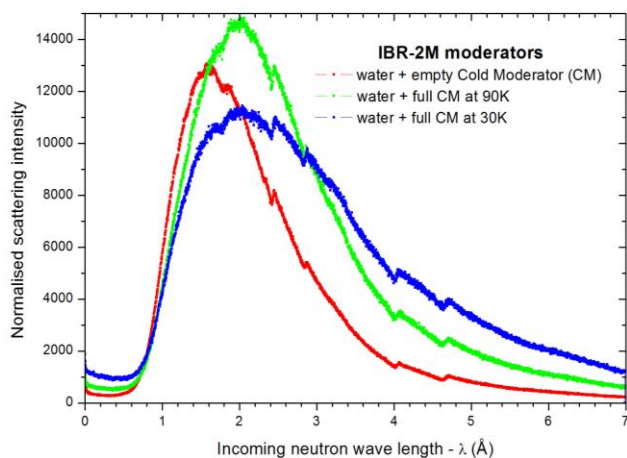


Fig. 1. NERA – Vanadium elastic scattering.

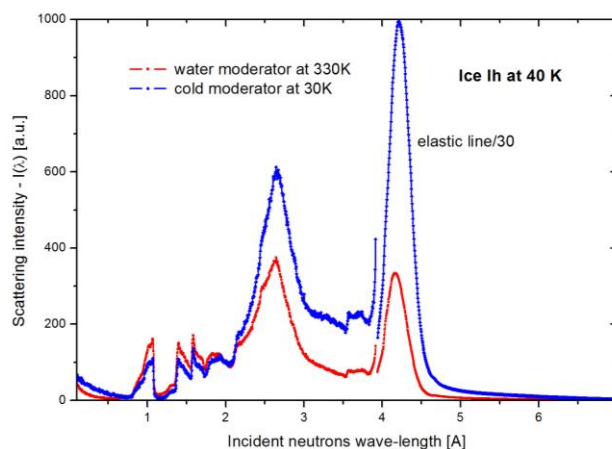


Fig. 2. NERA - Ice Ih inelastic scattering.

Inelastic incoherent neutron scattering (IINS) spectra for 10 ml of water at 40K, normalized to 1 hour of measurement at the average power of the reactor $W = 2$ MW, are shown in Fig.2. An elastic peak of scattered neutron energy analysers for $\lambda = 4.2$ Å, corresponding to Bragg reflection at 45° angle from the pyrolytic graphite – PG(002), is an optimal variant of measuring IINS spectra. Calculations of the spectrometer resolution, depending on the reflection angle of PG (002) analysers, in order to optimize measurements of IINS spectra and quasielastic neutron scattering (QENS) for a cold source, were performed. Experimental IINS, QENS and neutron powder diffraction (NPD) spectra of standard samples obtained for thermal and cold spectra of incident neutrons are compared and discussed.

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Characterising the size and shape of cholesteric liquid- crystal polymers in solutions as a function of pH (pH-jump) by SANS

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The current paradigm for the development of non-viral DNA delivery vectors is to model viral assembly and gene transfer by incorporating functional groups that enable particular assembly and transfer steps. Cationic polymers or lipids are used to condense DNA into small virus-like particles able to protect DNA from inactivation by blood components, from degradation by extracellular nucleases, extravascularization of the particle across small openings (fenestrae) in endothelial barriers (for intravascular administration routes), and cellular endocytosis.

Functional groups are incorporated into synthetic vectors to enhance cell targeting, endosomal escape, and nuclear targeting of the DNA to be delivered. Cationic polymers or lipids which are good at condensing DNA tend to be toxic or have poor biodistribution. The intravascular route of administration, an attractive approach for wide spread delivery, is particularly plagued by toxicity as well as biodistribution problems. 1, 2.

Several non-permanent polycations possessing substantial buffering capacity below physiological pH, such as lipopolyamines and polyethylenimines, are efficient transfection agents per se, i.e. without the addition of lysosomotropic bases, or cell targeting, or membrane disruption agents. These vectors have been shown to deliver genes as well as oligonucleotides both in vitro and in vivo. Their efficiency relies on extensive endosome swelling and rupture that provides an escape mechanism for the polycation/DNA particles 3.

Synthetic Cholesteric Liquid Crystal Polymers (ChLCP), having the mesogenic rigid group along the helical main chain but different side chain length, have been synthesised in our laboratory, through a stereoselective polycondensation reaction 4, 5 and functionalized with nitrogenated groups.

These ChLCPs are multifunctional materials - biocompatible against macrophages and fibroblasts cellular lines and optically active. They have been extensively characterized⁶, both as thermotropic and lyotropic, conferring interesting macromolecular properties to these compounds indicative of potential application in the biological and engineering field.

We have also shown that these ChLCP are able to interact with biomacromolecules such as lipids, both neutral and cationic, and nucleic acids. Their structures in the complexes, identified by synchrotron radiation source 7, 8, 9, have been applied successfully as non-viral vectors in gene therapy 10, 11, 12.

Small-angle neutron scattering (SANS) has been used to investigate the pH-dependent conformational change of our cationic ChLCP synthesised biopolymer mimics based on Cholesteric Liquid Crystals 4, 5 to advance in the knowledge of these materials of biotechnical interest with potential applications as non-viral vectors for Gene Therapy.

pH can be used as a signal to promote the efficient delivery of biomacromolecules or DNA to the correct intracellular compartment when polymers are used as delivery systems in Gene Therapy 10-12. The pH of an endosome is lower than that of the cytosol by up to two pH units, depending on the stage of endosomal development.

In this experiment we have measured each sample in D₂O as a function of pH at a polymer concentration of 7 mg/ml. Each pH point corresponded to conditions that the polymer would be expected to encounter during endocytic internalization (pH 7.4-3).

The radius of gyration of the ChLCP was determined as a function of the pH, the aim being to correlate changes in polymer conformation with membrane activity. With increasing pH the polymer radius of gyration increased to a maximum R_g , before subsequently decreasing once more.

Our results have so far been analyzed using a combination of model fits to the scattering curves (SANDRA program). We see a variation of R_g that appears to match our hypothesis that there is a coil expansion on passing from neutral pH (cytosol) to an acidic pH (endosomal and lysosomal) environments.

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Vibrational spectrum and Hydrogen adsorption on a PtCl₂-functionalised UiO67 metallorganic framework

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Microporous materials have proven to be highly valuable materials for industrial applications as petrochemistry, catalysis, and selective separation. In this regard, metal organic frameworks (MOFs) give new possibilities in the design of both geometrical shape and chemical properties of the internal surface allowing for very high pore volumes and surface areas [1,2]. Moreover, they are in principle able to display novel functionalities, potentially exploitable for a number of applications in catalysis, as sensors, in gas separation, and/or storage [3]. Here, we present preliminary results on the vibrational behavior of a functionalised UiO-67, MOF. Here two C of adjacent ring of 1/6 of the 4,40 biphenyl-dicarboxylate (BPDC) linkers are substituted with N species and functionalized with PtCl₂, creating a square planar coordination for the metal center. These exposed metal species are considered to induce enhanced adsorption properties during gas dosing. For this reason, the evolution of rotational transition of H₂ molecule (15 meV) during hydrogen uptake has been followed by inelastic neutron scattering up to 25 bar pressure on the IN4 Instrument at ILL.

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Hydrogen on graphene investigated by inelastic neutron scattering

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Graphene appears as a very promising base material for many technological applications, from nanoelectronics to hydrogen storage field [1]. Although, up to now, several of these applications were not feasible because of the lack of large-scale production of high-quality graphene sheets, the recent development of methods for chemically separating the graphite planes, made possible the synthesis of gram-scale amount of graphene [2]. This has opened the door for experimental investigation of graphene by using techniques that are usually reserved to bulk systems, as neutron scattering.

For the first time, we investigated chemically synthesized graphene samples by inelastic neutron scattering. We focused our attention in studying the interaction between hydrogen and carbon planes, in order to test the potentiality of graphene as a base material for hydrogen storage devices and hence to clarify the physical mechanism underlying the hydrogen storage process. In fact, thanks to the large hydrogen scattering cross section, neutrons are the perfect tools for studying hydrogen in materials and materials for hydrogen storage as well [3].

Chemically synthesized defective graphene samples, either in the pristine form or after thermal treatment in hydrogen flux, were measured on both the hot-neutron Beryllium-filter IN1-BeF Spectrometer and the thermal neutron time-of-flight IN4 spectrometer at Institut Laue Langevin, in Grenoble (France). The two sets of data were combined in order to investigate with good resolution the Vibrational Density of States (vDOS) in a wide energy range (0-250meV). The experimental vDOS of as-prepared graphene shows localized peaks, which can be ascribed to C-H bending modes [4]. When compounds are exposed to hydrogen flux at high temperature, not only this vibrational signature is noticeably enhanced, but also additional features appear in the spectrum. On one side, this reveals the extraordinary capability of defects in dissociating the molecule of hydrogen and then trapping atomic hydrogen, up to very high temperatures; on the other side it suggests the existence, in hydrogenated graphene, of almost two different hydrogen populations: the first one located at the edges and the other one at the single-atom in-plane vacancies. This hypothesis is supported by ab-initio DFT calculations, performed using the VASP code.

Finally, we will present on our recent advances. In particular, we are currently studying graphene-based compounds, in which carbon planes are chemically manipulated and decorated with metal atoms, in order to tune the binding energies between hydrogen and the graphene planes themselves.

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Inelastic neutron scattering and theoretical investigation of L-aspartic and L-glutamic acid, and their derivatives

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Amino acids are basic structural units of proteins which play an essential role in virtually all biological processes. Out of twenty proteinogenic amino acids, L-aspartic acid and L-glutamic acid have one amino group and two carboxylic acid groups, and among other functions serve as neurotransmitters in the brain, and participate in the metabolism of biological systems.[1] While the crystal structure of L-aspartic acid [2] and L-glutamic acid [3,4] have been determined and their infrared and Raman vibrational spectra recorded [5,6], the properties of their methylated and acetylated derivatives are less well known. Inelastic neutron scattering (INS) is a useful and established technique to explore vibrational spectra of solid state samples. When complemented with computational studies of optimized geometries and corresponding vibrational frequencies one can learn more about structures, interactions and dynamics of the systems involved. In this work we present our initial INS studies of the vibrational spectra of L-aspartic acid and L-glutamic acid at 10 K while their conformational preferences as well as those of their methylated and acetylated derivatives were investigated with the help of theoretical calculations.

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