Science & Technology Facilities Council

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Proceedings of the Molecular Spectroscopy Science Meeting 2015

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Proceedings of the

Molecular Spectroscopy Science Meeting 2015

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Foreword

The 2015 edition of the *Molecular Spectroscopy Science Meeting* (MSSM2015) was held in Abingdon, United Kingdom at the end of January. This two-day meeting was jointly organized by the *ISIS Molecular Spectroscopy Group* (MSG) [1] and its *User Group* (the MSUG) [2]. This event provided a forum to discuss the latest science and associated infrastructure developments supporting growing research activities across molecular and materials science. To this end, the MSSM2015 programme was chosen to reflect current and emerging themes across the wide spectral range unique to ISIS, as well as growing and much-needed synergies between experimental studies and computational materials modelling. In five thematic sessions, we had the opportunity to hear the latest developments on *Catalysis & Energy*, *Soft Matter & Biology*, *Modelling & Simulation*, *Quantum Matter*, and *Nanostructured Materials*. Each thematic session was wrapped up by presentations from MSG members, highlighting recent and forthcoming developments at ISIS and the Harwell Campus. In addition to these, discussion sessions were led by Sylvia McLain (Oxford University) and Christoph Salzmann (University College London), our MSUG Chair and Representative, respectively. This formal timetable was complemented by lively breaks around food and refreshments, and a poster session at the end of the first day.

MSSM2015 began with a welcome from our MSUG Chair and updates of ISIS and the MSG, highlighting extensive work performed across ISIS during the 2014-15 shutdown, and plans on the horizon. These include, to name a few, the upgrade *ISIS Target Station I* [3], recent international reviews including those of TOSCA [4] and IRIS & OSIRIS [5], and the publication of a thematic issue following the *VI Workshop in Electron Volt Neutron Spectroscopy* in 2014 [7].

In the area of *Catalysis & Energy*, Joaquín Silvestre-Albero (Universidad de Alicante) presented exciting results on molecular uptake by activated carbons aimed at the design of novel materials for selective carbon-dioxide and methane capture. Maths Karlsson (Chalmers Tekniska Universitet) then reviewed the use of neutron and optical spectroscopies to explore the properties associated with charge transport in proton-conducting oxides. And Alex O'Malley (UK Catalysis Hub & University College London) told us about the stochastic dynamics of hydrocarbons in zeolites, with particular emphasis on how classical and quantum-mechanical computer simulations have been used to interpret and add value to neutron-scattering experiments. This session highlighted how these research lines will certainly benefit from ongoing projects to increase the neutron flux on TOSCA [8, 9] and MAPS [10], as well as the increased automation of sample-environment equipment for *in situ* and *operando* gas-adsorption and catalysis studies under conditions of practical and industrial relevance. Along a similar vein, collaborative efforts with the *UK Catalysis Hub* [11] at the Harwell Research Complex continue to be on the rise, as evidenced by this session as well as by a workshop held at the end of last year [12].

In *Soft Matter & Biology*, Maria Paula Marques (Universidade de Coimbra) showed how the interaction of palladium-based anti-cancer drugs with DNA can be explored via recourse to simultaneous neutron-Raman techniques, a capability unique to ISIS which has already led to fresh insights into new cancer therapies. Copious amounts of snow and bad weather in Northern England did not allow Mike Weir (University of Sheffield) to join us on this ocassion, to tell us about his work on polymer nanocomposites – Mike, we hope to have you with us next time! Holly Hedgeland (University College London) presented new results on molecular diffusion on graphitic surfaces using neutron and helium-3 spin-echo spectroscopies, techniques which certainly offer a number of unique and yet-to-be-tapped synergies. These presentations brought to the fore the increasingly important role played by Xpress and Rapid Access [13], ongoing efforts to provide high-throughput operation on IRIS & OSIRIS, recent instrument upgrades [14], and imminent developments following the recent review of these two spectrometers [5].

The last session of the first day was devoted to *Modelling & Simulation*, most certainly an overarching theme across MSS2015. Fernando Bresme (Imperial College London) showed how the properties of nanoscale interfaces under non-equilibrium conditions can be assessed and understood with state-of-the-art atomistic simulations, in some cases leading to rather counterintuitive effects such as the emergence of a net polarisation in liquid water upon the application of thermal gradients. Anne Guilbert (Imperial College London) extended this discussion to the temperature-dependent behaviour of conjugated polymers via a direct comparison of computational results with quasielastic neutron-scattering data. And Jeff Armstrong (Imperial College London & ISIS) presented new results using neutron scattering and molecular dynamics simulations aimed at a sound microscopic understanding of the thermal conductivity and order-disorder transitions in fullerene-based organic materials. In this context, we also note a number of recent developments within the MANTID framework [15], both to analyse neutron-scattering data across our instrument suite, as well as to compare these with the output of *in silico* studies [16, 17, 18].

Following an action-packed afternoon, the poster session before dinner counted with thirty contributions, primarily from early-career researchers. In addition to the main thematic areas of the meeting, posters on display also covered a number of parallel developments, including the implementation of Bayesian methods and the analysis of atomistic simulations within the MANTID framework, neutron-transport simulations to assess the performance of a silicon analyser as a high-resolution option for OSIRIS, the development of mass-selective neutron spectroscopy on VESUVIO, and new laboratory infrastructure at ISIS across biology, chemistry, and materials science [19]. The first day concluded with an enjoyable conference dinner, and the announcement of the award of the MSS2015 Poster Prize to Jemma Rowlandson (University of Bath & Centre for Sustainable Chemical Technologies), for a beautiful account of her PhD project *Analysis of Porosity in Activated Carbons – Reconciling Gas Sorption with Scattering Data.* We also had the opportunity to thank the *ISIS User Office* team, and Emma Roberts in particular, for all the hard work over the past few months to make it all happen. *Thank you Emma!*

MSSM2015 started its second day with a focus on *Quantum Matter*. Christoph Salzmann (University College London) captivated us with a survey of ice research across the complex (and poorly understood!) phase diagram of the water molecule using structural and spectroscopic probes. Roberto Senesi (Università di Roma – Tor Vergata) presented recent

VESUVIO studies on nuclear quantum effects of light (hydrogen) and not-so-light nuclides (oxygen). Beyond fundamental studies, this session also highlighted the unique capabilities of electron-volt neutrons to provide spectroscopic insights in a mass-resolved and element-specific manner, with emerging applications in the study of complex functional materials of technological relevance. Around mid-morning, Sara Fletcher (ISIS Impact Manager) provided a number of practical tips on how we could all contribute to the dissemination of our research to the wider public.

The last session of MSSM2015 was devoted to *Nanostructured Materials*. Heloísa Bordallo (Københavns Universitet) showed how neutron spectroscopy has been used to unravel the mysteries of cementitious materials at the nanoscale, a two-thousand-year-old challenge to both science and technology. This insightful presentation was followed by exciting studies on metal-organic supramolecular frameworks. Matthew Ryder (University of Oxford) explained how Terahertz neutron and synchrotron spectroscopies have revealed a number of hitherto unexplored dynamical phenomena in these nanostructured materials. Matthew Savage (University of Nottingham) presented comprehensive results on molecular adsorption in NOTT-300, a material that continues to attract much interest owing to its remarkable properties for industrial applications in gas-separation technologies. The meeting closed with a final discussion led by our MSUG Representative, followed by a well-deserved farewell lunch. This final discussion served to emphasize the increasing relevance of combining neutron-scattering techniques with other experimental probes and computational methods, to either tackle fundamental questions or engineer the functional behaviour of complex materials for practical applications.

With around 80 participants from around the world, over 20 presentations, and 30 posters, MSSM2015 was a resounding success, highlighting the merits and strengths of neutron spectroscopy in tackling a broad range of contemporary scientific challenges across molecular and materials science. Following this *Foreword*, these *Proceedings* contain further details about the event, including a detailed programme, a list of participants, numerous photographs, as well as electronic copies of all oral and poster contributions received to date.

In closing, we thank all participants for joining us last January, and encourage all of you to keep in touch. Over the next few months, we will continue to keep you up-to-date with the MSUG Newsletter *Good Vibrations* [2] and *we certainly look forward to seeing you again at the next (and surely vibrant!) MSSM.*

The Organising Committee
April 2015

References

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ISIS Molecular Spectroscopy Science Meeting

2015

29th & 30th January

The Cosener's House
Abingdon

The *ISIS Molecular Spectroscopy Group* will hold its next science meeting at the Cosener's House, Abingdon on the 29th and 30th of January 2015.

This year's meeting will focus on the following thematic areas

Catalysis & Energy
Nanostructured Materials
Modelling & Simulation
Quantum Matter
Soft Matter & Biology

Confirmed invited speakers include

Heloisa Nunes Bordallo, University of Copenhagen
Fernando Bresme, Imperial College
Joaquin Silvestre-Albero, Universidad de Alicante
Maths Karlsson, Chalmers University
Maria Paula Marques, Universidade de Coimbra
Christoph Salzmann, University College London
Roberto Senesi, Università di Roma – Tor Vergata

Keynote lectures will be followed by a number of oral presentations on a given thematic area. These slots are primarily intended for early-career researchers willing to present their work in the supportive atmosphere of our user group.

A poster session will also take place at the end of the first day. Anyone wishing to present his/her work is warmly invited to make a contribution. These are suited, but not limited, to undergraduate and early-stage doctoral students.

Those who wish to give an oral presentation or present a poster should submit the title on the registration website below. The Organising Committee will draw up the final program based on all submissions received.

Registration is now open and will close 30th November.

To register, please click here

We look forward to seeing you in January!

Sylvia McLain, Oxford University
Christoph Salzmann, University College London
Sanghamitra Mukhopadhyay, ISIS
Pedro Duarte Vaz, ISIS
Felix Fernandez-Alonso, ISIS

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Molecular Spectroscopy Science Meeting 2015
29-30 January 2015, Cosener's House, Abingdon

Thursday, 29 January

10:45	**Registration**
12:00	**Lunch**
13:00	**Welcome** *Sylvia McLain* ISIS Update *Philip King* MSG Update *Felix Fernandez-Alonso*
13:30	**Catalysis and Energy** (Chair: Paul Collier) Invited – Nanoconfinement effects on activated carbons *Joaquin Silvestre-Albero*
14:00	Invited – Neutron spectroscopy on proton conducting oxides *Maths Karlsson*
14:30	Contributed – Dynamics of hydrocarbons in zeolites as studied by computation and neutron scattering processes *Alex O'Malley*
14:45	Wrap-up *Stewart F. Parker*
15:00	**Discussion** *Sylvia Mclain*
15:15	**Refreshments**
15:45	**Soft Matter & Biology** (Chair: Sylvia Mclain) Invited – Shining the beam on drugs - from molecule to cell *Maria Paula Marques*
16:15	Contributed – Dynamics in polymer nanocomposites: nanotubes and graphene *Mike Weir*
16:30	Contributed – Surface diffusion through van der Waals landscapes and the importance of friction and the density of states *Holly Hedgeland*
16:45	Wrap-up *Franz Demmel*
17:00	**Modelling & Simulations** (Chair: Keith Refson) Invited – Computational studies of soft interfaces *Fernando Bresme*
17:30	Contributed – Temperature-dependent dynamics of poly-alkylthiophene conjugated polymers: a combined neutron scattering and simulation study *Anne Guilbert*
17:45	Contributed – The twin roles of Experiment and theory in making organic solar cells financially viable *Jeff Armstrong*
18:00	Wrap-up *Sanghamitra Mukhopadhyay*
18:15	**Rest break**
18:45	**Posters**
20:15	**Dinner**

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Molecular Spectroscopy Science Meeting 2015
29-30 January 2015, Cosener's House, Abingdon

Friday, 30 January

09:00	**Quantum Matter** (Chair: Matthew Krzystyniak) Invited – The many facets of ice research *Christoph Salzmann*
09:30	Invited – Quantum effects on the oxygen nuclei in light and heavy water *Roberto Senesi*
10:00	Wrap-up *Andrew Seel*
10:15	**Impact at ISIS** *Sara Fletcher*
10:30	**Refreshments**
11:00	**Nanostructured Materials** (Chair: Antonio Romerosa-Nievas) Invited – Stretching time: dynamics and functionality in hydrogen bonded systems *Heloísa Bordallo*
11:30	Contributed – Revealing physical phenomena in MOFs based on terahertz vibrations *Matthew Ryder*
11:45	Contributed – Determination of the binding modes of adsorbed gas molecules in porous hosts. *Matthew Savage*
12:00	Wrap-up *Svemir Rudic*
12:15	**Final Discussion** *Cristoph Salzmann*
12:30	**Lunch**

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Molecular Spectroscopy Science Meeting 2015
29-30 January 2015, Cosener's House, Abingdon
Poster list

Poster	Title
1	Data reduction and analysis using MANTID *Daniel Nixon*
2	Mechanical properties and lattice dynamics of isoreticular zirconium framework materials *Matthew Ryder*
3	Terahertz vibrations in metal-organic frameworks: from gate-opening phenomenon to shear-driven structural instability *Matthew Ryder*
4	FABADA into MANTID: a model selection case *Diego Monserrat*
5	Molecular structure of disorder metal organic polymers *Antonio Romerosa*
6	Application of inelastic neutron scattering to investigate the dry reforming of methane over bimetallic Ni-Co/Al_2O_3 catalyst *Xin Lao*
7	Comprehensive structure characterization of Ge quantum dots using X-ray absorption spectroscopy technique *Yuanpeng Zhang*
8	Inelastic neutron scattering as a characterization tool of C–H···O hydrogen bond dynamics *Mariela M. Nolasco*
9	Inelastic neutron scattering characterization of activated carbons *Antonio Noguera*
10	Calculation of thermal conductivity of different phases of ice using molecular dynamics *Irene Iriarte Carretero*
11	Spectroscopy without spectrometer – the sequel *Matthias Gutmann*
12	The phonon density of states in hybrid organic-inorganic PbS nanocrystal solids *Deniz Bozygit*
13	Deuteration laboratory in ISIS *Peixun Li*
14	Modelling thermal transport in functionalised nanoparticles *Niall Jackson*

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Molecular Spectroscopy Science Meeting 2015
29-30 January 2015, Cosener's House, Abingdon
Poster list

Poster	Title
15	Proton dynamics in deuterated and non-deuterated alkylammonium nitrate ionic liquids *Isabel Maria Vazquez Fernandez*
16	Vibrational characterisation of high surface area carbons through DRIFT, Raman and INS: an innovative approach *Andrea Lazzarini*
17	The ISIS materials characterisation laboratory *Gavin Stenning*
18	The ISIS hydrogen and catalysis laboratory *James Taylor*
19	Implementation of a silicon energy analyser on McStas: the way forward for OSIRIS *Jesús Pedro de Vicente*
20	Reduced carbon deposition over Ni-based bimetallic catalysts *Zheng Jian*
21	Combined INS and Raman study of the spectroscopic properties of the amorphous ices *Jacob Shephard*
22	CuH: a (nearly) 200 year old problem *Stewart Parker*
23	Thermo-orientation in polar fluids (Towards a microscopic understanding) *Jeff Armstrong*
24	The influence of adsorbed CO_2 on the dynamics of ZIF-7 *Pu Zhao*
25	Thermal conductivity calculation of different phases of water ice using molecular dynamics *Miguel Angel Gonzalez Gonzalez*
26	Mass-selective neutron spectroscopy beyond the proton *Matthew Krzystyniak*
27	Analysis of porosity in activated carbons: reconciling gas sorption with scattering data *Jemma Rowlandson*
28	Towards a better modelisation of carbon-based nanomaterials *Ricardo Fernandez-Perea*
29	The oxygen momentum distribution in water *Giovanni Romanelli*
30	High-resolution neutron spectroscopy for soft matter science *Victoria Garcia-Sakai*

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Non- parameteric analysis of
determination of
1. Zero point kinetic energy
2. Anisotropy or anharmonic
These can be implemented in
representation of the local
systems

DFT (GGA PW91) gives adsorption energy of 1.7 eV
1.1e net charge transfer from substrate gives anionic Cp
Small net polar covalent contribution involving HOMO and LUMO transferring charge both to and from substrate
ΔΦ ~ -1 eV
Same direction as for alkali metals
"Cushion effect" – electron depletion just above surface plane due to Pauli repulsion of π system induces a dipole moment towards the bulk of the metal
hcp
fcc
B
T
40 ± 3 meV

In an isotropic system:

Imperial College
Water at nanoparticle surfaces
Translational structure
HC layer
water
NPT – 1 bar, 298 K
Water interface
Nanoparticle interface
Bulk
Intensity (a.u.)
Frequency (cm⁻¹)
Shift of stretching modes to higher frequencies => compatible with experiments of the water-air interface using VSFS.
Scatena et al., Science 2001.
Disrupted; h-bond structure => Dangling h-bonds
Tay & FB: J. Mater. Chem.; J. Am. Chem. Soc.

Friction coefficient, η
Hops between both fc
DFT shows 55 meV b
MD simulations reproc
activation energies wit
Phys Rev Lett 106, 186101 (2011

Molecular Spectroscopy Science Meeting 2015

Welcome Session

Science & Technology Facilities Council
ISIS

Science & Technology Facilities Council
ISIS

ISIS Update

Philip King
ISIS Spectroscopy and Support Division

Molecular Spectroscopy Meeting, 29 Jan 2015

Science & Technology Facilities Council
ISIS

ISIS International Review (November 6-8 2013)

Chair: Prof. Joel Mesot (Director, Paul Scherrer Institute, Switzerland)

Committee: Prof. Sine Larsen (Copenhagen), Prof. Thomas Schulthess (ETH Zurich),
Dr. Mike Rowe (NIST Washington), Prof. Mike Klein (Philadelphia), Prof. Richard Jones (Sheffield)

"The Review Committee is extremely impressed by the development and performance of ISIS. In particular by the fact that ISIS has, since its creation, being able to create a culture of innovation that has had profound impact on and will continue to change the way neutron scattering is performed worldwide.

Very few research institutions have demonstrated similar drives toward innovation and spread of the resulting technological development."

Science & Technology Facilities Council
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Partnership with India

Letter of Intent signed between STFC and the Indian Government's Nano Mission

Access to ISIS for Indian scientists

Investment in ISIS instruments by India

Professor C.N.R. Rao, FRS, Chair of India's Nano Mission and Professor Robert McGreevy at ISIS earlier this month.

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Partnerships with India, China, South Africa

UK Government Newton funding to support researchers from India, China and South Africa

ISIS also has an MoU for collaboration with the Chinese Spallation Source currently being built.

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Partnership with Italy

Italy is one of ISIS' longest international partners

March 2014 saw our agreement with Italy renewed

The agreement is worth €15M over 6 years

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Partnership with Sweden and ESS

Agreement with Sweden to contribute to IMAT.

UK has committed to ESS construction costs

Sweden will contribute to ISIS operating costs over this period

This will also help to develop the Swedish neutron community

Funding enables ISIS to increase operating days . . .

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UK and ESS

UK ESS meeting for universities and industry held in December

Talks available from the STFC website

www.stfc.ac.uk/3249.aspx
(or search for ESS on STFC website)

UK-ESS Project Board will co-ordinate the UK's contribution to the ESS
(see STFC web page again)

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Long shutdown 2014/15

Part of 4 year maintenance cycle

Planned shut-down from Aug 2014 – March 2015

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New Main Control Room layout

Scary . . .

Getting there . . .

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Repairs to tank 1 tuning system

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Replacement of Extracted Proton Beamline magnets

Replacement of 30 year old systems that have developed water leaks and are becoming unserviceable

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Replacement of muon front-end magnets

Magnets have been installed since mid-1980s. Some date from 1960s

3 replaced in front-end

Rest of muon beamline to follow.

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TS2 Phase II Be reflector

New reflector required for Chipir and Larmor – also adds flexibility for the future

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TS2 Phase II - Larmor

Shutter opened March 20th.

Operational with new Instrument Control Programme (EPICS based)

SANS and reflectometry calibration standards run

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TS2 Phase II – ChipIr

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TS2 Phase II – IMAT

- 2 neutron imaging cameras ready
- 44m guide installed
- Blockhouse and sample positioner installed
- Commissioning first half of 2015

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TS2 Phase II – ZOOM

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WISH

Installation of Ar tanks to reduce scatter

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Mantid

- Continues to be developed as a data reduction and analysis framework across the neutron (and muon) instrument suite
- Mantid Training courses
  - NeutronTC and MuonTC
  - ILL NMI3 data analysis meeting
- New Contributors
  - PSI, ANSTO and Jülich (in addition to SNS, etc)

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Instrument reviews

Science & Technology Facilities Council
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ISIS Facility Development Studentships

First call for proposals, deadline 31 Oct 2014
Part-funding of studentships
Must have a facility development component

~60 Proposals received (10 available)
14 studentships co-funded

Science & Technology Facilities Council
ISIS

diamond

Joint ISIS – Diamond CDT Training School at RAL

Diffraction, Spectroscopy, Magnetism, Modelling and Theory

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Changes which may affect you

- Removal of **Programme Access**
- Encouragement of **Rapid** and **Xpress Access**
- **Direct Access** (deadline 16/4, 16/10) remains

- Changes to **consumable rules** for UK users

- Re-launch of **Experiment reports**

- See **ISIS website** for more details

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TS1 Upgrade

- Goals
  - at least twice the flux
  - low risk
  - improve operability/upgradeability
  - reduce background
- Baselining existing
  - Engineering
  - Neutronic performance
- Reviewed July 2014
- Feasibility complete spring 2015
- Commission 2018/19

Excellent agreement, measurement to modelling

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Long term plan

- Complete TS2 Phase II (2015)
- Upgrade TS1 target/moderators (2018/19); use to increase capacity
- Upgrade instruments (continuously) to increase capability
- Maintain accelerator sustainability programme
- Replace Linac Tanks 4 (2018) and 1 (2022?)
- Explore Linac upgrade possibility
- Explore all possibilities for a new facility; cost/benefit analysis; learn lessons from SNS, J-PARC, ESS

2013 2014 2015 2018 2020 2022 2025 2030 2033

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30 years of neutrons at ISIS

16 December 2014

Science & Technology Facilities Council
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UK Neutron and Muon Science and User Meeting 19-21 May 2015

- Tues 19 May – **Student day**
  - For the student community
- Wed 20 May – **Science day**
  - Functional materials
  - Magnetism and superconductivity
  - Biosciences and soft matter
  - Chemistry and catalysis
  - Engineering
- Thurs 21 May – **User meeting**
  - Updates from facilities (ISIS, ILL, ESS), research councils, etc

+ plenary talks
+ Willis Prize
+ student posters
+ dinner

+ 30 years of ISIS ops

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UK Neutron and Muon Science and User Meeting 2015

19-21 May 2015

Hinckley Island Hotel, Leicestershire

ISIS Molecular Spectroscopy Group Update

Felix Fernandez-Alonso

ISIS Molecular Spectroscopy Science Meeting
The Cosener's House, 29-30 January 2015

Science & Technology Facilities Council
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Farewell, Ashok

Welcomes and Good-bye

Also vacancy on
IRIS & OSIRIS
(recruitment in progress)

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Molecular Spectroscopy at ISIS

High energies

MAPS

Intermediate energies

Simultaneous diffraction & Raman

IRIS

OSIRIS

LET

Low energy

Science & Technology Facilities Council
ISIS

Xpress Access

Successfully running since 2006

Started Summer 2011

Enhanced automation in progress

Xpress has led directly to publication

VESUVIO soon

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2014 has been …

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… a busy year!

Science programme, now and in the years to come

Neutron instrumentation

Infrastructure developments

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International Review – TOSCA (with MAPS & MARI)

Science & Technology Facilities Council

Technical Report
RAL-TR-2013-015

TOSCA International Beamline Review

S Rudic, AJ Ramirez-Cuesta, SF Parker,
F Fernandez-Alonso, RS Pinna, G Gorini, CG Salzmann,
SE McLain, NT Skipper

December 2013

Executive Summary

For the past decade, TOSCA has set the standard for broadband vibrational spectroscopy with neutrons. Its primary strengths include user-friendly operation, full integration of computational materials modelling into its science programme, unrivalled sample-environment capabilities, and a high degree of complementarity with other spectroscopic techniques. It currently supports a thriving scientific community of non-traditional users of inelastic neutron scattering techniques from both academia and the industrial sector, as evidenced by an output of 150+ publications since 2008. For the first time in the history of the instrument, other leading neutron sources such as the JLL and the SNS intend to emulate its success by offering significantly higher count rates over the same spectral range with comparable resolution. For TOSCA to move forward in strategic research areas such as CO_2 capture and charge storage, a boost in incident flux via the provision of a neutron guide constitutes our highest priority at the present time. Other instrument developments on the horizon include the implementation of high count-rate inelastic detector modules, enhanced scientific infrastructure and an increase in diffraction capabilities.

epubs.stfc.ac.uk/work/11216706

The panel was impressed with the breadth and depth of the science being delivered…

… on an instrument that has kept a leading role in the field of inverted geometry spectrometers dedicated to chemical spectroscopy.

The scientific output … is outstanding (133 papers + 20 theses since 2008)

The panel agreed that the guide upgrade has to be taken up with the highest priority.

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TOSCA Upgrade – Primary Spectrometer

JPCS 554 012003 (2014)

Recent and future developments on TOSCA at ISIS

Stewart F. Parker,[1] Felix Fernandez-Alonso,[1,2] Anibal J. Ramirez-Cuesta,[1,3] John Tomkinson,[1] Svemir Rudic,[1] Roberto S. Pinna,[4] Giuseppe Gorini[4] and Javier Fernández Castañon[1,5]

[1] ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK
[2] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
[3] Present address: CEMD, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA
[4] CNISM, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, 20126 Milano, Italy
[5] Facultad de Ciencias, Universidad de Oviedo, Calvo Sotelo, 33007 Oviedo, Spain
[6] Present address: ILL, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble Cedex 9, France

EPJ 83 03013 (2015)

Monte carlo simulations of the TOSCA spectrometer: Assessment of current performance and future upgrades

Roberto S. Pinna[1,2], Svemir Rudic[1], Stewart F. Parker[1], Giuseppe Gorini[2] and Felix Fernandez-Alonso[1,3,*]

[1] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK
[2] CNISM, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, 20126 Milano, Italy
[3] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Engineering design & tendering on track.

Aiming for completion in 2016 (along with MAPS guide)

MAPS Upgrade

Increased (much-needed) flux for energy, catalysis, …

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Neutrons & Catalysis

Use of direct geometry established (25+% MAPS time).

Exciting opportunities above and below molecular vibrations, total scattering, …

CatalysisHub

JM Johnson Matthey

Science & Technology Facilities Council ISIS

In Situ, Operando & Simultaneous Techniques

Science & Technology Facilities Council ISIS

International Review – IRIS & OSIRIS

Science & Technology Facilities Council

Technical Report
RAL-TR-2014-014

IRIS & OSIRIS International Beamline Review - Report Presented to the Panel

F Demmel, V Garcia Sakai, S Mukhopadhyay, SF Parker, F Fernandez-Alonso, J Armstrong, F Bresme, JP de Vicente, F Sordo, FJ Bermejo, CG Salzmann, SE McLain

November 2014

Executive Summary

IRIS & OSIRIS have led the way in high-resolution neutron spectroscopy using cold neutrons at pulsed spallation sources. Their main strengths lie in the provision of high spectral resolution over a wide dynamic range, synchronous high-resolution diffraction, low instrument backgrounds, a versatile range of sample environments, and user-friendly operation. These instruments currently support a productive scientific community using quasielastic and low-energy inelastic neutron scattering techniques, as evidenced by an output of 200+ publications since 2008. For *IRIS & OSIRIS* to move forward in both a *UK* and international context, full integration of computational materials modelling into our science programme constitutes the highest priority at the present time and would require further investment in staff and high-performance computing infrastructure. Additional instrument developments on the horizon include an increase in energy resolution and flux on *OSIRIS* using a silicon analyser and a new primary spectrometer, as well as a step change in the scientific remit of *IRIS* so as to provide high-throughput spectroscopic capabilities for emerging research themes in materials chemistry, soft matter, and biology.

epubs.stfc.ac.uk/work/12271760

Roadmap

Development	Year					
	2015	2016	2017	2018	2019	2020
ModelEng Phase I	*Staff recruitment with modelling expertise*	*SCARF upgrade & software development*	*Software and method development*	*Deployment & training*		
ModelEng Phase II				*Extension to other HPC initiatives*	*Extension to other HPC initiatives*	*Deployment & training*
OSIRIS Phase I	*Feasibility & design of new secondary*	*Secondary upgrade (Si111)*	*Secondary upgrade (Si111)*	*Start of operations with upgraded OSIRIS*		
OSIRIS Phase II			*Feasibility & design of primary*	*Primary upgrade: guide + pulse shaping chopper*	*Primary upgrade: guide + pulse shaping chopper*	*Start of operations with upgraded OSIRIS*
IRIS Phase I	*High-throughput QENS: sample environment*	*High-throughput QENS: sample environment, simultaneous techniques*	*High-throughput QENS: simultaneous techniques*			
IRIS Phase II		*Baselining & feasibility in context of TS1 upgrade*	*Feasibility & design of primary & secondary*	*Primary upgrade: guide + pulse shaping chopper*	*Primary upgrade: guide + pulse shaping chopper*	*Secondary upgrade e.g., Si311, QENS-SANS*

VESUVIO: Frontiers & Horizons

January 2014

ELECTRON-VOLT NEUTRON SPECTROSCOPY, WITHER GOEST THOU?

S. Fletcher,[1] A. G. Seel,[1] R. Senesi,[2] F. Fernandez-Alonso[1,3]
[1]ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
[2]Dipartimento di Fisica e Centro NAST, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy; Consiglio Nazionale delle Ricerche, CNR-IPCF, Sezione di Messina, Messina, Italy
[3]Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom

In January 2014, scientists from across the world came together in Abingdon (United Kingdom) for a two-day meeting on the latest developments in electron-Volt neutron spectroscopy (eVs) [1]. This international workshop was jointly organised by the ISIS Pulsed Neutron and Muon Source, the Consiglio Nazionale delle Ricerche, the Università degli Studi di Roma provided a comprehensive and up-to-date overview of eVs, with particular emphasis on the current science and instrumentation program on the VESUVIO spectrometer at ISIS [5]. The event also represented an opportunity to bring together experimental and theoretical communities interested in nuclear quantum dynamics in condensed matter and the application

Figure 1. Workshop participants during a brief lapse of (well-deserved?) orderly regime.

December 2014

VI Workshop in Electron Volt Neutron Spectroscopy: Frontiers and Horizons — IOP Publishing
Journal of Physics: Conference Series **571** (2014)

The Quantum Mechanics of Nano-Confined Water: New Cooperative Effects Revealed with Neutron and X-Ray Compton Scattering

G. F. Reiter[1], Aniruddha Deb[2]
[1]Physics Department, University of Houston, 4800 Calhoun Houston, Tx, 77204-5505
[2]Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

Mass-selective Neutron Spectroscopy Beyond the Proton

M. Krzystyniak[1,2], A.G. Seel [1], S.E. Richards[1,3], M.J Gutmann[1], and F. Fernandez-Alonso[1,3]
[1] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
[2] School of Science and Technology, Nottingham Trent University, Clifton Campus, Nottingham NG11 8NS, United Kingdom
[3] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.

Epithermal neutron instrumentation at ISIS

G. Gorini[1], G. Festa[1,2] and C. Andreani[2,3]
[1]Università degli Studi di Milano-Bicocca, Milan, Italy
[2]Università degli Studi di Roma Tor Vergata, Rome, Italy
[3]CNR-IPCF, Messina, Italy
[4]CNR-IFP, Milan, Italy

Measurement of proton momentum distributions using a direct geometry instrument

R. Senesi[1,2], A. I. Kolesnikov[3], C. Andreani[1,2]
[1] Università degli Studi di Roma Tor Vergata, Dipartimento di Fisica and Centro NAST, via della Ricerca Scientifica 1, Rome 00133, Italy
[2] CNR-IPCF Sezione di Messina, Messina, Italy
[3]Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States of America

Ab initio simulation of particle momentum distributions in high-pressure water

M. Ceriotti[1]
[1]Laboratory of Computational Science and Modelling, NQ Institute of Materials, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

And much more …

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Data Analysis

Technical Report RAL-TR-2014-005

How to use Mantid for low energy inelastic neutron scattering data analysis on indirect geometry instruments

Sanghamitra Mukhopadhyay

April 2014

Technical Report RAL-TR-2014-010

An Overview of the Recent Development of Indirect Inelastic Data Analysis in Mantid

Jackson, S

September 2014

VI Workshop in Electron Volt Neutron Spectroscopy: Frontiers and Horizons — IOP Publishing
Journal of Physics: Conference Series **571** (2014) 012009 — doi:10.1088/1742-6596/571/1/012009

VESUVIO Data Analysis Goes MANTID

S. Jackson[1,2], M. Krzystyniak[1,3], A.G. Seel [1], M. Gigg[1,4], S.E. Richards[1,3], and F. Fernandez-Alonso[1,5]

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[5] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

Technical Report RAL-TR-2014-009

VESUVIO Data Reduction and Analysis in Mantid

Jackson S

September 2014

Plenty of opportunities for extension

(see MANTID & FABADA posters)

Core capabilities across instrument suite under ***a single platform***

Science & Technology Facilities Council ISIS

In-Silico Neutron Spectroscopy

Materials Modelling

To fully exploit neutron data.

Current emphasis on time-dependent methods.

Tool deployment in progress.

Time-dependent

Time-independent

Python Interface

Experiments

Science & Technology Facilities Council ISIS

Keeping You Up to Date, Twice a Year

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www.scitech.ac.uk

Good Vibrations

The Newsletter of the ISIS Molecular Spectroscopy User Group (MSUG)

Volume 5, Issue 2 — September 2014

News

Welcome

Welcome to the final news-letter of 2014!

In this issue, we welcome two new faces who have recently joined the group: Dr. Pedro Duarte Vaz, instrument scientist on TOSCA; and Daniel Nixon from the University of Newcastle-upon-Tyne, sandwich student to work on Mantid Data Analysis Software.

Please join us in a warm welcome to both of them.

ISIS Molecular Spectroscopy Science Meeting 2015

29th & 30th January

The Cosener's House, Abingdon

We invite contributions in terms of oral or poster presentations from researchers willing to present their work in the supportive atmosphere of our user group.

Registration deadline is 30th November

Please register here.

We look forward to seeing you there!

Data Analysis and Mantid

Current developments of data analysis on Mantid have been summarised in two reports, one across all instruments and another on VESUVIO. A big thanks to Samuel Jackson, for all his work during his placement with us last year.

Inelastic Neutron-Scattering Database

The INS database has now increased to near 700 entries thanks to the efforts of a work experience student. Jack Parker. Have a look!

TOSCA Guide Project: Latest News

Tenders have been submitted for the design, manufacture, and supply of the shutter guide insert and surrounding shielding. A delivery schedule for the remainder of the guide is in preparation.

Simultaneous Neutron-Raman Spectroscopy Facility Upgrade

The Raman spectrometer used for simultaneous neutron/Raman studies has been upgraded. By replacing the laser rejection filters, transitions as low as 45 cm^{-1} are now readily observable. The addition of a second, software selectable, grating means that 1 cm^{-1} resolution spectra over the range 45 – 1800 cm^{-1} can be obtained with high signal-to-noise ratio. The ability to measure Raman and neutron data simultaneously from the same sample is a capability that is unique to ISIS. To date, it has been used on IRIS, OSIRIS, TOSCA, VESUVIO, as well as MAPS and SANDALS. It can be used on any instrument accepting a 100-mm diameter centrestick.

An Introduction to Neutron Techniques in Catalysis

A joint ISIS Catalysis Hub at RCaH workshop to be held on 3rd and 4th November 2014 at the Research Complex at RAL.

There will be a mixture of talks describing capabilities in neutrons and what can be learned from them, together with examples where neutrons have played a key role in catalysis studies. Further information and enrollment is available from the workshop website.

Please inform us of your publications arising from ISIS-related work.

Remember to include ISIS staff as co-authors on publications when deemed appropriate.

NEXT PROPOSAL ROUND REMINDER

Deadline October 16th.

Submit your proposal here

Science Highlights

- INS Study of the Molecular Properties of Pure Hydrogen Peroxide ...
- Investigation of a Nano-composite of Nanoparticles with Polyethylene Oxide Linear Chains.
- Magnetic Spectra in the Tri-diminished-icosahedron Fe_9 Nanocluster by INS
- Low-Energy Structural Dynamics and Constrained Libration in $LiNH_2$
- Modelling the Luminescence of Extended Solids

Forthcoming Conferences

- International Symposium on Chemical Theory for Complex Systems, Oct 30-31, Sweden.
- IMI Int. Conference on Comput. Phys., Jan 7-11, Singapore.
- Temporally and Spatially Resolved Molecular Science, Faraday Discussions 177, Jan 12-14, India.
- Frontiers of First-principles Simulations, Feb 1-5, Germany.
- MRS Spring Meeting, April 6-10, USA.

Further information: Molecular Spectroscopy Homepage · Group Members · IRIS · MAPS · OSIRIS · TOSCA · VESUVIO

Editor : Sanghamitra Mukhopadhyay (sanghamitra.mukhopadhyay@stfc.ac.uk)

Two issues per year

Spring & Autumn

To tell you about

- Projects & ISIS operations.
- Science highlights.
- Meetings & events.

Feedback always welcome

Science & Technology Facilities Council
ISIS

Meeting Format & Scope

Thursday, 29 January

10:45	**Registration**
12:00	**Lunch**
13:00	**Welcome** *Sylvia McLain* ISIS Update *Philip King* MSG Update *Felix Fernandez-Alonso*
13:30	**Catalysis and Energy** (Chair: Paul Collier) Invited – Nanoconfinement effects on activated carbons *Joaquin Silvestre-Albero*
14:00	Invited – Neutron spectroscopy on proton conducting oxides *Maths Karlsson*
14:30	Contributed – Dynamics of hydrocarbons in zeolites as studied by computation and neutron scattering processes *Alex O'Malley*
14:45	Wrap-up *Stewart F. Parker*
15:00	**Discussion** *Sylvia Mclain*
15:15	**Refreshments**
15:45	**Soft Matter & Biology** (Chair: Sylvia Mclain) Invited – Shining the beam on drugs - from molecule to cell *Maria Paula Marques*
16:15	Contributed – Dynamics in polymer nanocomposites: nanotubes and graphene *Mike Weir*
16:30	Contributed – Surface diffusion through van der Waals landscapes and the importance of friction and the density of states *Holly Hedgeland*
16:45	Wrap-up *Franz Demmel*
17:00	**Modelling & Simulations** (Chair: Keith Refson) Invited – Computational studies of soft interfaces *Fernando Bresme*
17:30	Contributed – Temperature-dependent dynamics of poly-alkylthiophene conjugated polymers: a combined neutron scattering and simulation study *Anne Guilbert*
17:45	Contributed – Understanding extremes in thermal conductivity (bridging experiment and simulation) *Jeff Armstrong*
18:00	Wrap-up *Sanghamitra Mukhopadhyay*
18:15	**Rest break**
18:45	**Posters**
20:15	**Dinner**

A forum to

Explore opportunities across:

- Science areas & expertise.
- Infrastructure & capabilities.

and have a good time!

Friday, 30 January

09:00	**Quantum Matter** (Chair: Matthew Krzystyniak) Invited – The many facets of ice research *Christoph Salzmann*
09:30	Invited – Quantum effects on the oxygen nuclei in light and heavy water *Roberto Senesi*
10:00	Wrap-up *Andrew Seel*
10:15	**Impact at ISIS** *Sara Fletcher*
10:30	**Refreshments**
11:00	**Nanostructured Materials** (Chair: Antonio Romerosa-Nievas) Invited – Stretching time: dynamics and functionality in hydrogen bonded systems *Heloisa Bordallo*
11:30	Contributed – Revealing physical phenomena in MOFs based on terahertz vibrations *Matthew Ryder*
11:45	Contributed – Determination of the binding modes of adsorbed gas molecules in porous hosts. *Matthew Savage*
12:00	Wrap-up *Svemir Rudic*
12:15	**Final Discussion** *Cristoph Salzmann*
12:30	**Lunch**

Molecular Spectroscopy Science Meeting 2015

Catalysis and Energy Session

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ISD plots of both alkanes from MD simulations
300 K
UCL
Octane
Dimethylhexane
Why??

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Nano-confinement Effects on Activated Carbons

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Molecular Spectroscopy Science Meeting-2015

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Introduction

Granular

Pellets

Carbon Cloth

Discs

Monoliths

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Introduction

Why carbon materials?

Slit-shaped micropores

Porosity can be tailored

Rather "inert" surface

Adsorption of non-polar species favoured,

Surface chemistry can be easily modified,

Many physical forms (granular, pellets, fibres, cloth, felt, monoliths, etc.)

⇩

Unparallelled flexibility

Introduction

Selectivity by molecular shape

J. Rouquerol et al, "Adsorption by powders and porous solids", 1999

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Can we design carbon materials for selective CO_2 capture?

Introduction

Carbon Dioxide Emissions

- Carbon Dioxide Sequestration (e.g. injection into deep underground reservoirs)

Requirements

Capture and concentration of CO_2 from large emission sources, such as power plants

!!!!CO_2 is accompanied by other gases: N_2, O_2, H_2O, NO_x, SO_x, particulate!!!!

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Objective

Synthesis of very high porosity CMS from petroleum residues for selective CO_2 adsorption vs. other molecules of similar molecular dimensions (N_2 and CH_4)

Synthesis of monolithic CMS without the use of a binder:

Sample preparation

440ºC, 1 MPa,
2-4 Hours.

Ball Milling

VR (vacuum residue)
DO (decanted oil)

Mesophase pitch
Ø≤500µm

MP-2 (2 h)
MP-4 (4 h)

VR-5; DO-10
VR-93; DO-88

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Sample preparation

440ºC, 1 MPa,
2-4 Hours.

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VR (vacuum residue)
DO (decanted oil)

Mesophase pitch
Ø≤500µm

MP-2 (2 h)
MP-4 (4 h)

VR-5; DO-10
VR-93; DO-88

Sample preparation

30 min, 300 rpm

Conforming Press
400 MPa

Activation
800ºC, 2 Hours

ACM

MP + KOH (1:x)
(VR-5, VR-93, DO-10, DO-88)

J.M. Ramos-Fernández et al., Carbon 46 (2008) 384

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Carbon Monoliths

Scanning Electron Microscopy

Activated carbons from petroleum pitch

N_2 adsorption isotherms at 77K

M. Casco et al., Carbon 67 230-235 (2014)

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Activated carbons from petroleum pitch

Textural properties

Sample	S_{BET} $m^2.g^{-1}$	V_{total} $cm^3.g^{-1}$	$V_{N2,DR}$ $cm^3.g^{-1}$	V_{meso} $cm^3.g^{-1}$	$V_{CO2,DR}$ $cm^3.g^{-1}$	Yield* wt%
VR5-1:1	1768	0.73	0.70	0.03	0.67	57
VR5-2:1	2432	1.05	0.91	0.15	0.80	57
VR5-2.5:1	2453	1.09	0.96	0.13	0.84	45
VR5-3:1	3126	1.45	1.05	0.40	0.73	49
VR5-4:1	3575	1.83	1.22	0.61	0.76	42
VR93-1:1	1548	0.64	0.61	0.03	0.64	64
VR93-2:1	2142	0.90	0.80	0.10	0.78	56
VR93-2.5:1	2772	1.22	0.99	0.23	0.84	55
VR93-3:1	3166	1.60	1.03	0.58	0.77	37
VR93-4:1	3407	1.77	1.06	0.71	0.75	44

*Yiel (wt%)= (dry carbon weigh/ precursor weigh)*100

M. Casco et al., Carbon 67 230-235 (2014)

Activated carbons from petroleum pitch

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M. Casco et al., Carbon 67 230-235 (2014)

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Activated carbons from petroleum pitch

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M. Casco et al., Carbon 67 230-235 (2014)

Carbon Monoliths

CO_2 adsorption isotherms at 298 K

M. Casco et al., Carbon 67 230-235 (2014)

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Carbon Monoliths vs powders

CO_2 adsorption isotherms at different temperatures

Carbon Monoliths

Immersion calorimetry into different liquids

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Carbon Monoliths

Carbon Molecular Sieves vs. Zeolites

Carbon Monoliths

Carbon molecular sieves vs. MOFs materials

J. Silvestre-Albero et al. ChemComm 47, 6840-6842 (2011)

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Carbon Monoliths

Carbon molecular sieves vs. MOFs materials

J. Silvestre-Albero et al. ChemComm 47, 6840-6842 (2011)

Carbon Monoliths

Carbon molecular sieves vs. MOFs materials

J. Silvestre-Albero et al. ChemComm 47, 6840-6842 (2011)

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Carbon Monoliths

Regeneration of the carbon molecular sieves

J. Silvestre-Albero et al. ChemComm 47, 6840-6842 (2011)

Carbon Monoliths

Kinetics of adsorption of CO_2, N_2 and CH_4 at 298 K

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Can we design carbon materials for selective CH_4 storage?

Methane Storage

	Pressure	Temperature	Delivery
LNG	atmospheric	112 K	600 v/v
CNG	210 atm	ambient	220 v/v
ANG	35 atm	ambient	210 v/v

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Petroleum-pitch based carbon monoliths

Effect of the KOH/pitch ratio

Petroleum-pitch based carbon monoliths

Excess adsorption isotherms

Old DOE's Target

M. Casco et al., Chem. Mater. DOI: 10.1021/cm5042524 *(2015)*

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Petroleum-pitch based carbon monoliths

Excess vs Storage

$$S' = n''_{exc} + \rho_{gas}\left(1 - \frac{\rho_{pack}}{\rho_{He}}\right)$$

S' =Storage amount
N"exc= excess amount

Petroleum-pitch based carbon monoliths

Carbon vs MOF

M. Casco et al., Chem. Mater. DOI: 10.1021/cm5042524 *(2015)*

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Petroleum-pitch based carbon monoliths

Carbon vs MOF: Effect conforming step

M. Casco et al., Chem. Mater. DOI: 10.1021/cm5042524 *(2015)*

Can we take advantage of confinement effects to grow synthetic hydrates?

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Natural Clathrates

1 CH_4:5.75 H_2O

1 L hydrate (s) = 168 L CH_4 (g)

permafrost

Synthetic Clathrates

CH_4 adsorption isotherms at 275 K

M. Casco et al., Nature Commun. (2015)

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Synthetic Clathrates

CH_4 adsorption isotherms at 275 K

M. Casco et al., Nature Commun. (2015)

Synthetic Clathrates

CH_4 adsorption isotherms at 275 K

M. Casco et al., Nature Commun. (2015)

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Synthetic Clathrates

CH_4 adsorption isotherms at 275 K

M. Casco et al., Nature Commun. (2015)

Synthetic Clathrates

CH_4 adsorption isotherms at 275 K

M. Casco et al., Nature Commun. (2015)

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M. Casco et al., Nature Commun. (2015)

Ineslastic Neutron Scattering

Rutherford Appleton Laboratory - ISIS (UK)

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Synthetic Clathrates

Ineslastic Neutron Scattering

M. Casco et al., Nature Commun. (2015)

Synthetic Clathrates

$1CH_4.5.75H_2O$
Literature for
Free water

Rw		nw	nx	nw/nx	$XCH_4.YH_2O$
unsaturated					
0.6		$3.33x10^{-2}$	$8.08x10^{-3}$	4.1	$1CH_4.4.1H_2O$
1.1		$6.11x10^{-2}$	$1.70x10^{-2}$	3.6	$1CH_4.3.6H_2O$
saturated					
1.8		$1.01x10^{-1}$	$2.76x10^{-2}$	3.7	$1CH_4.3.7H_2O$
supersaturated					
2.9	1.1	$6.11x10^{-2}$	$1.16x10^{-2}$	5.3	$1CH_4.5.3H_2O$
	1.8	0.1	$2.45x10^{-2}$	4.1	$1CH_4.4.1H_2O$
4.1	2.3	$1.28x10^{-2}$	$2.21x10^{-2}$	5.8	$1CH_4.5.8H_2O$
	1.8	0.1	$2.43x10^{-2}$	4.1	$1CH_4.4.1H_2O$

M. Casco et al., Nature Commun. (2015)

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Synthetic Clathrates

Synchrotron X-ray powder diffraction experiments

M. Casco et al., Nature Commun. (2015)

Conclusions

- ✓ *Appropriate selection of petroleum residue, activation degree and final conformation allows the preparation of carbon molecular sieves combining a highly developed porous structure together with a narrow pore size entrance*
- ✓ *Petroleum-pitch derived carbon molecular sieves combine a large adsorption capacity for CO_2 together with high selectivity versus molecules of similar dimensions as CH_4 and N_2*
- ✓ *When properly designed these carbon materials exhibit an excellent volumetric capacity (260 v/v at 10 MPa)*
- ✓ *Nanoconfinement effects on nanopores allow the fast nucleation and growth of methane hydrate structures with a final stoichometry that mimics natural chlatrates*

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Laboratorio de Materiales Avanzados

Thank you very much!!!
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Antelope Canyon-Reserva de los indios navajos (USA)

Neutron spectroscopy studies on proton conducting oxides

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A large family of different types of fuel cells has been developed - here are a few examples from Wikipedia

Direct borohydride fuel cell	Aqueous alkaline solution		70			Commercial
Alkaline fuel cell	Aqueous alkaline solution	10 – 100 kW	< 80	60–70%	62%	Commercial / Research
Direct methanol fuel cell	Polymer membrane (ionomer)	100 mW – 1 kW	90–120	20–30%	10–25%[46]	Commercial / Research
Reformed methanol fuel cell	Polymer membrane (ionomer)	5 W – 100 kW	250–300 (Reformer) 125–200 (PBI)	50–60%	25–40%	Commercial / Research
Direct-ethanol fuel cell	Polymer membrane (ionomer)	< 140 mW/cm²	> 25 ? 90–120			Research
Proton exchange membrane fuel cell	Polymer membrane (ionomer)	1 W – 500 kW	50–100 (Nafion)[47] 125–220 (PBI)	50–70%	30–50%[46]	Commercial / Research
RFC – Redox	Liquid electrolytes with redox shuttle and polymer membrane (ionomer)	1 kW – 10 MW				Research
Phosphoric acid fuel cell	Molten phosphoric acid (H_3PO_4)	< 10 MW	150-200	55%	40%[46] Co-Gen: 90%	Commercial / Research
Solid acid fuel cell	H^+-conducting oxyanion salt (solid acid)	10 W - 1 kW	200-300	55-60%	40-45%	Commercial / Research
Molten carbonate fuel cell	Molten alkaline carbonate	100 MW	600–650	55%	45-55%[46]	Commercial / Research
Tubular solid oxide fuel cell (TSOFC)	O^{2-}-conducting ceramic oxide	< 100 MW	850–1100	60–65%	55–60%	Commercial / Research
Protonic ceramic fuel cell	H^+-conducting ceramic oxide		700			Research
Direct carbon fuel cell	Several different		700–850	80%	70%	Commercial / Research
Planar Solid oxide fuel cell	O^{2-}-conducting ceramic oxide	< 100 MW	500–1100	60–65%	55–60%[46]	Commercial / Research

State of the art proton and oxide-ion conductors

Proton conducting perovskite type oxides

Structure (*e.g.* $BaZrO_3$)

Incorporation of protons

Proton conducting perovskite type oxides

Proton dynamics – over a large time-range – suitable for neutron spectroscopy

1. Vibrational motions, O-H stretches and wags
2. Local diffusional motions
3. Long-range translational diffusion

Proton conducting perovskite type oxides

ILL methods at the ILL: Figure replotted and modified after Jobic, et al, Microporous and Mesoporous Materials (2007)

Neutron spin-echo on $BaZr_{0.9}Y_{0.1}O_3H_{0.1}$

Intermediate scattering function obtained at IN15 at ILL (Q = 0.15-0.30 Å^{-1})

$I(Q,t)$ = FT[$G(r,t)$]

Karlsson et al., Chem. Mater. ***22*** *(2010) 740*

Neutron spin-echo on $BaZr_{0.9}Y_{0.1}O_3H_{0.1}$

Intermediate scattering function obtained at IN15 at ILL (Q = 0.15-0.30 Å^{-1})

Calculated I(Q,t)

Karlsson et al., Chem. Mater. ***22*** *(2010) 740*

NSE case study on proton conducting $BaZr_{0.9}Y_{0.1}O_3H_{0.1}$

"Long-range" diffusion constant obtained from different methods

Calculated I(Q,t)

- Comparable results, despite the different length scales (NSE: 20-40 Å; Conductivity: 1 μm).
- More "complicated" decay of *I(Q,t)* at larger Q-values may result from "local" structural effects (e.g. "trapping")

Karlsson et al., Chem. Mater. ***22*** *(2010) 740*

Proton trapping in barium zirconates

nature materials

ARTICLES

PUBLISHED ONLINE: 12 MAY 2013 | DOI: 10.1038/NMAT3638

Proton trapping in yttrium-doped barium zirconate

Yoshihiro Yamazaki[1,2]*, Frédéric Blanc[3], Yuji Okuyama[2], Lucienne Buannic[4], Juan C. Lucio-Vega[2], Clare P. Grey[3,4] and Sossina M. Haile[2]

Proton trapping in $BaZr_{0.8}Zr_{0.2}O_3H_{0.2}$

ARTICLES NATURE MATERIALS DOI: 10.1038/NMAT3638

Figure 1 | Proton trapping in BYZ20. a, Long-range proton diffusivity exhibits downward curvature, as expressed in equation (3) (red line) with parameters given in Table 1. Red circles and triangles denote, respectively, the proton diffusivity and the ambipolar diffusivity between proton and deuterium determined by a.c. impedance spectroscopy (ACIS). The trap-free proton diffusivity calculated from the proton–dopant association (trapping) model (blue line) matches that determined from a neutron spin-echo (NSE) experiment (blue open circles[11]). **b**, Apparent activation energies for proton diffusion and constant activation energy for association-free proton diffusion. **c**, Trapped and trap-free proton concentrations computed from the proton–dopant association model, equation (2) and the experimentally measured total proton concentration (see Supplementary Information for full description of analysis methodology).

Luminescence spectroscopy of Eu^{3+} in $BaZr_{0.9}Y_{0.099}Eu_{0.001}O_3H_{0.1}$

Luminescence emission spectrum

*Haro-Gonzales, Karlsson,Bettinelli et al., Solid State Ionics **247-248** (2013) 94-97*

Dopant – oxygen vacancy association

- Hydrated sample: only one $^5D_0$ -> $^7F_0$ band - > one local geometry, EuO_6.
- Dry sample: two $^5D_0$ -> $^7F_0$ bands -> Eu^{3+} (Y^{3+}) occupies two different local geometries: EuO_5 and EuO_6.

Luminescence spectroscopy of Eu^{3+} in $BaZr_{0.9}Y_{0.099}Eu_{0.001}O_3H_{0.1}$

Luminescence emission spectrum

*Haro-Gonzales, Karlsson,Bettinelli et al., Solid State Ionics **247-248** (2013) 94-97*

Dopant-proton association

- Significant shortening of the radiative lifetime of the excited state after hydration suggests quenching of the Eu^{3+} emission due to nearby O-H groups.

Material	τ_{exp} (µs)	$\tau_{predicted}$ (µs)
$BaZr_{0.9}Y_{0.1}O_{2.95}$	470	431
$BaZr_{0.9}Y_{0.1}O_3H_{0.1}$	420	538

Proton diffusivity varies with dopant

Diffusivity in $BaZr_{0.9}M_{0.1}O_3$ (M = Y, In, Gd, Sc) – average structure the same (cubic)

Vibrational spectroscopy on "average" cubic $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0—0.75)

Raman spectroscopy on $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0—1)

Karlsson et al., Chem. Mater. ***20*** *(2008) 3480*

Strong Raman bands reveal local structural distortions

Literature data over proton conductivities

Composition	Conductivity /Scm^{-1}	
x = 0.10	$2.9 \cdot 10^{-5}$	
		9
x = 0.25	$2.6 \cdot 10^{-4}$	
		3
x = 0.75	$8.9 \cdot 10^{-4}$	

Neutron diffraction on hydrated $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0.50)

Deuterium sites in $BaIn_{0.50}Zr_{0.50}O_{2.50}(OD)_{0.50}$ determined with neutron powder diffraction (Ahmed *et al.*, *J. Alloys & Compds.*, 2008)

Fourier density maps at cuts of z = 0, showing missing positive scattering density attributed to D

INS (TOSCA) and IR on hydrated $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0—0.75)

Proton sites and hydrogen-bonding interactions in $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0—0.75) investigated with inelastic neutron scattering

Inelastic neutron scattering (O-H wag region)

Infrared spectroscopy (O-H stretch modes)

Karlsson et al., Phys. Rev. ***B*** *77 (2008) 104302*

INS (TOSCA) and IR on hydrated $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0—0.75)

MD calculations (G. Wahnström, Chalmers)

Infrared spectroscopy (O-H stretch modes)

Low-frequency bands - fundamentals or not?

Recent INS (Merlin) results on hydrated $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0.50)

- The maximum intensity occurs at higher Q-values for overtones and combination modes than for fundamental ones

  Roughly: Q ~ √2Q(fundamental)

  S. F. Parker et al, JACS (2003)
  J. Tomkinson et al, J. Chem. Phys. (2010)

<- Integration over slices in different energy ranges

Work in progress / L. Mazzei, S. F. Parker, D. T. Adroja, M. Karlsson

Recent INS (Merlin) results on hydrated $BaIn_xZr_{1-x}O_{3-x/2}$ (x = 0.50)

Preliminary analysis of the spectra suggests:

Band	Energy range	Q_{max}
A	91-115 meV	~8 Å^{-1} (wag)
B	125-145 meV	~9 Å^{-1} (wag)
C	150-170 meV	~10 Å^{-1} (wag)
D	180-210 meV	~11 Å^{-1} (2×A)
E	225-245 meV	~12 Å^{-1} (stretch)
F	280-300 meV	~13 Å^{-1} (stretch)
G	360-380 meV	~13 Å^{-1} (stretch)
H	410-440 meV	~14 Å^{-1} (stretch)
I	520-550 meV	~16 Å^{-1} (comb.)
L	560-600 meV	~17 Å^{-1} (comb.)
M	645-685 meV	~18 Å^{-1} (E+H)
…	… …	…

Case study on "average" cubic $BaIn_xZr_{1-x}O_{3-x/2}$

MD calculations

Infrared spectroscopy (O-H stretch modes)

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+ Many more

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MATERIALS SCIENCE
A CHALMERS AREA OF ADVANCE

Vetenskapsrådet

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Group (PhD students)

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Carin Österberg

Dynamics of hydrocarbons in zeolites as studied by computational and neutron scattering methods

Alexander O'Malley

Diffusion of Hydrocarbons in Zeolites

Zeolites most notable for use in the petrochemical industry as molecular sieves and as shape selective acidic catalysts

Understanding of diffusion processes essential

- Separation processes rely on significant differences in diffusion coefficients of the components.

- The rate limiting step of a catalytic process may be in diffusion of components to and from the active site.

Centre of mass distributions for butane (blue) and Methane (green) in silicalite

Difficult, as all this happens inside the zeolite. Computational methods such as molecular dynamics simulations are desirable

Neutron scattering methods for obtaining the diffusion coefficient

- The change of the spectral profile wrt neutron momentum transfer (Q) is related to the diffusion coefficient. (usually tracked from incoherent scattering of hydrogen atoms).
- Can probe the same length and time-scales similar to MD simulations.

$$\Delta\omega(Q)_{\text{inc}} = D_s Q^2$$

Can fit to models of diffusion such as "jump-diffusion models"

$$\Delta\omega(Q) = \frac{1}{\tau}\left(1 - \frac{\sin(Qd)}{Qd}\right)$$

MD simulations for obtaining the diffusion coefficient

Track the time evolution of a system by numerically solving the equations of motion for each particle (having chosen model carefully)

Calculate the mean-squared displacement WRT time, then self-diffusivity D_s

$$D_s = {}^1/_6 \lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle$$

Longer *n*-alkanes in silicalite: Up-to-date models giving close agreement with QENS

- C_8 – C_{20} in silicalite - directly compared with QENS studies by Jobic.
- Used the same loadings as experiment e.g. 1.56 mol/uc
- Use flexible frameworks and all-atom hydrocarbon models
- Same temperature range to calculate diffusion coefficients and activation energy.

Diffusion coefficients: Compare simple MD models, hierarchical simulations, current study

A plot of the calculated diffusion coefficients from the current MD simulations (O), MD simulations at infinite dilution [1] (▲), MD simulations using simpler models ( ), Hierarchical simulations (∗) and QENS studies (□) .

1. O'Malley, Alexander J., and C. Richard A. Catlow. "Molecular dynamics simulations of longer n-alkanes in silicalite: a comparison of framework and hydrocarbon models." *Phys. Chem. Chem. Phys.* 15.43 (2013): 19024-19030.

Activation energies: QENS, Hierarchical simulations, current MD simulations

A plot of the activation energy of diffusion with chain length, for the current MD study (•) , QENS studies (∗) and hierarchical simulations (□)

2. O'Malley, Alexander J., and C. Richard A. Catlow. "Molecular dynamics simulations of longer n-alkanes in silicalite: Up-to-date models giving close agreement with experiment." *Phys. Chem. Chem. Phys.* – Accepted 2014

Channel switching

- Channel switching from straight to sinusoidal channel system for octane only
- Seen only at 350 and 400 K, and only in channels containing multiple molecules
- Static energy calculations to understand energetics of switching

The effect of molecular shape on diffusion of octane isomers in zeolite Y

- Octane and dimethylhexane studied by QENS and MD in zeolite Y (Si/Al = 30) on OSIRIS
- Understand the difference in diffusion behaviour between the straight chain and branched isomer
- Still processing data from both methods to calculate diffusion coefficient…
- But some interesting parallels found from the MD…

Methanol and dimethylether in zeolite Y

- Understand diffusion component of methanol to dimethylether process
- Molecular dynamics in progress of methanol in zeolite Y same loading and Si/Al ratio
- Proposal submitted to study dimethylether in zeolite Y
- Will mix with deuterated methanol to look at diffusion of the product in the presence of the reactant.
- Different ratios of methanol to DME = different stages of the reaction

Diffusion of cyclic oximes in zeolite Y and SAPO-37

- The Beckmann rearrangement of cyclohexanone oxime is used to produce ε-caprolactam (the monomer for nylon-6).
- Can be performed at 130˚C in SAPO-37 but not zeolite Y. Interesting as they share the same structure, but have different compositions.
- QENS used to probe the diffusion close to reaction temperature of cyclic oximes in both systems.
- Q-dependencies as a function of temperature differ markedly between the two systems

Future work – binding of methanol to zeolite frameworks to form methoxy species
INS + embedded cluster simulations

- INS observations show binding of methanol to the framework to form methoxy species in ZSM-5, not zeolite Y.
- Embedded cluster simulations an improvement on DFT studies to calculate the barriers to this process between the 2 frameworks

Future work – Rotational motions of octane isomers in ZSM-5

$$S_{\mathrm{inc}}(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp(-i\omega t) I_{\mathrm{inc}}(Q,t)\, \mathrm{d}t$$

$$I_{\mathrm{inc}}(Q,t) = \langle \exp(iQ\cdot(\vec{r}(t) - \vec{r}(0))) \rangle$$

- Use of nMOLDYN to create theoretical QENS functions from MD to compare with previous OSIRIS experiment.
- Pair with translational studies to be performed at ILL

$$\bar{I}(Q,t) = \frac{1}{N}\sum_{i=1}^{N}\left\langle \frac{\sin(|Q||\vec{d}_i(t) - \vec{d}_i(0)|)}{|Q||\vec{d}_i(t) - \vec{d}_i(0)|} \right\rangle$$

Acknowledgements

- Prof. Richard Catlow, Dr Stewart Parker
- Dr Vicky Garcia-Sakai, Dr Sanghamitra Mukhopadhyay
- Dr Andrew Logsdail, Prof. Herve Jobic
- Dr Ian Silverwood, Dr Nikos Dimitratos
- M.E. Potter, Prof. R. Raja,
- Scott Rogers, Cath Brookes, Wilm Jones

Thank You

Catalysis and Energy - Wrap-up

Stewart F. Parker

MSG user meeting 29/30 Jan 2015

Science & Technology Facilities Council

Pd-based catalysts for hydrogenation of nitroarenes

Albers *et al*, J. Cat. 311 (2014) 153

Science & Technology Facilities Council

High-Pressure Experimental and DFT-D Structural Studies of the Energetic Material FOX-7

Computational study (validated by INS) shows phase change undetectable by diffraction.

Hunter *et al*, J Phys Chem 119 (2015) 2322
[doi: 10.1021/jp5110888]

Science & Technology Facilities Council

Fischer-Tropsch catalysis

Fischer-Tropsch: nCO + (2n + 1)H_2 → $C_nH_{(2n+2)}$ + nH_2O

UNIVERSITY of GLASGOW

Lennon *et al*, J. Cat. 312 (2014) 221
Angew Chem 52 (2013) 5608

MAPS upgrade

Gains small in main region of interest >2000 cm^{-1}
However: optimised 'B' chopper for <2000 cm^{-1}

Raman system upgrades

Lower wavenumber limit reduced to ~45 cm^{-1} by new laser rejection filters

Resolution improved to ~3 cm^{-1} over 45 - 1800 cm^{-1} by installation of a second grating

Ability to do gas dosing in progress

Installation of a green (532 nm) laser will allow access to C-H/N-H/O-H stretch with good resolution

System has been used on OSIRIS, TOSCA, VESUVIO, MAPS, SANDALS and (HRPD) and is potentially usable on any instrument that will accept a 100 mm centrestick

What else would you like to see?
DSC? UV-vis? Conductivity?
Or ....????

Molecular Spectroscopy Science Meeting 2015

Soft Matter & Biology Session

Science & Technology Facilities Council
ISIS

drug–glutathione binding – ¹H-HRMAS-NMR
Time course of [GSH] in human cells upon drug administration
osteosarcoma + 30 μM-cDDP or 12 μM-Pd₂Spm
3.0E+07
1.5E+07
0
[GSH]
0
12
24
36
48
Time (hours)
Pd₂Spm
control
cDDP-GS₂
Proteome Res. 13 (2014) 6033
SHARP

Shining the Beam on Drugs
from Molecule to Cell
Maria Paula
Marques
"Molecular Physical-Chemistry"
University of Coimbra PORTUGAL

A Tale of Two Drugs
an old drug – cisplatin
ISIS Meeting-2015 QFM-UC

A Tale of Two Drugs

a (hopefully) new drug – Pd_2Spm

on going research

Pt and Pd anticancer drugs

ISIS
- Stewart Parker
- John Tomkinson
- Victoria Garcia-Sakai
- Louise Hatter

diamond
- Diego Gianolio
- Giannantonio Cibin

Molecular Physical-Chemistry
Coimbra University PORTUGAL

- Maria Paula Marques
- Luís Batista de Carvalho
- Ana Lúcia Carvalho

cisplatin-like anticancer drugs

cisplatin
PLATINOL - 1971

carboplatin
PARAPLATIN - 1982
2nd generation

oxaliplatin
ELOXATIN - 1986
3rd generation

cisplatin-like

polynuclear polyamine complexes

particular structural features

different bridging polyamine ligands
different coordination patterns
different number of metal centres
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unique
interplay with DNA
ISIS Meeting-2015 QFM-UC

FROM
short-range
& intrastrand
adducts
TO
long-range
& interstrand
adducts
Pt
Pt
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broader spectrum
of
clinical activity
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GOALS

minimum
toxicity & resistance
optimised
cytotoxic activity
optimised
delivery
ISIS Meeting-2015 QFM-UC

increased
specificity & efficacy
ISIS Meeting-2015 QFM-UC

CD-encapsulation
delivery
&
targetting
structure
&
conf. behaviour
polymorphism
impact
on
intracellular
water
metabolic
impact
activation
pharmacodynamics
pharmacokinetics
interaction
with DNA
acquired
resistance
biodistribution
bioavailability
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Pd_2Spm
PdDap
ISIS Meeting-2015 QFM-UC

Pd(II)-amine complex formation
INS
Raman
δ (Cl-Pd-Cl)
ν (Pd-N)
δ (CCC)
δ (NH2)
δ (CH2)
ω (NH2)
t (CH2)
ω (CH2)
PdDap
Dap
δ (CH2)
ω (NH2)
δ (NH2)
0
500
1000
1500 cm-1
800
1200
1600 cm-1
Spec.Int.J. 27 (2012) 403; Biochem.Soc.Trans. 35 (2007) 374
ISIS Meeting-2015 QFM-UC

Pd(II)-amine complex formation
INS
Raman
δ (N-Pd-N)
δ (Cl-Pd-Cl)
ν (Pd-N)
δ (CCN)
δ (NH2)
δ (CH2)
Pd2Spm
Spm
ν (CN) + ν (CC)
t (CH2) + ω (CH2)
δ (CH2)
δ (NH2)
0
500
1000
1500 cm-1
800
1200
1600 cm-1
J.Inorg.Biochem. 108 (2012) 1
ISIS Meeting-2015 QFM-UC

simultaneous Raman & neutron scattering

cisplatin – conformational analysis

COMPLETE VIBRATIONAL ASSIGNMENT

ChemPhysChem 12 (2011) 1334

cisplatin – polymorphism
α
β
ISIS Meeting-2015 QFM-UC

Raman – cooling cycle
δ (Cl-Pt-N)
258
ν_{as}(Pt-N)
δ (NH_3)
beta
360 K
beta
298 K
alpha + beta
180 K
alpha + beta
150 K
alpha
80 K
alpha
5 K
very small amount of beta
0
250
500
750
1000
1250
1500
1750 cm-1
ISIS Meeting-2015 QFM-UC

INS – cooling cycle
γ´ (Cl-Pt-N)
δ (Cl-Pt-N)
β
β
ν_{as}(Pt-N)
alpha + beta
alpha + beta
alpha
alpha
150 K
120 K
80 K
50 K
5 K
250
500
750 cm-1
ISIS Meeting-2015 QFM-UC

cisplatin
polymorphic equilibrium = f(T)
Cooling cycle
marked hysteresis
Heating cycle
100
50
0
β cisplatin (%)
5
10
30
50
80
120
150
180
220
298
360
Temperature (K)
J.Phys.Chem. 117 (2013) 6421
ISIS Meeting-2015 QFM-UC

pharmacodynamics

interaction with DNA bases

ISIS Meeting-2015 QFM-UC

cDDP-G_2

cDDP-A_2

cisplatin-guanine binding – INS

Spec.Int.J. 27 (2012) 273

ISIS Meeting-2015 QFM-UC

cisplatin-adenine binding – Raman

New J.Chem. 37 (2013) 2691

ISIS Meeting-2015 QFM-UC

cisplatin-purine binding – EXAFS

(Pt–Cl) by (Pt–N) substitution

PCCP online DOI 10.1039/C4CP05183A

drug binding

DNA versus glutathione competition

pharmacokinetics

DRUG

INACTIVATION

cisplatin-glutathione binding – INS
(Pt–Cl) modes disappear upon glutathione binding & δ(N–Pt–S) is detected
τ (NH3)
δ (N-Pt-S)
δ (CCS)glut
δ (NCC)glut
cDDP-GS2
δ (CCS)
δ (CCS)
δ (CNH)
δ (CSH)
GSH
δ (Cl-Pt-Cl)
γ´ (Cl-Pt-N)
τ (NH3)
γ (Cl-Pt-N)
δ (Cl-Pt-N)
ν (N-Pt)
ρ (NH3)
cDDP
250
500
750 cm-1
PCCP online DOI 10.1039/C4CP05183A
ISIS Meeting-2015 QFM-UC

PdDap–glutathione binding – INS
ν (Pd–Cl)/δ (N–Pd–N) disappear & δ(N–Pd–S) is detected
δ (N-Pd-S)
ω (NH2)
δ (NH2)
PdDap-GS2
ν (Cl-Pd-Cl)
δ (N-Pd-N)
ω (NH2)
δ (NH2)
PdDap
0
250
500
750
1000
1250
1500
1750cm-1
ISIS Meeting-2015 QFM-UC

drug–glutathione binding – ^{1}H-HRMAS-NMR

18 days after drug administration – 80% cDDP-glutathione

only 20% free cisplatin

J.Proteome Res. 13 (2014) 6033

ISIS Meeting-2015 QFM-UC

drug–glutathione binding – ^{1}H-HRMAS-NMR

negligible binding to glutathione

drug concentration virtually unaffectd

J.Proteome Res. 13 (2014) 6033

ISIS Meeting-2015 QFM-UC

drug–glutathione binding – ^{1}H-HRMAS-NMR

DECREASED

GLUTATHIONE-MEDIATED

ACQUIRED RESISTANCE

for Pd_2Spm

relative stability of cDDP-purine adducts – EXAFS

stability →

cDDP-A_2

cDDP-G_2

PCCP online DOI 10.1039/C4CP05183A

delivery

cyclodextrin-encapsulation

stable inclusion complexes (IC)

increase availability at the main target (DNA)

cisplatin-HPβCD encapsulation – INS

from molecule to cell ... to bedside
cell
tissue
organism
POTENTIAL DRUG
patient
characterisation
ISIS Meeting-2015 QFM-UC

Obrigado

Surface diffusion through van der Waals landscapes and the importance of friction and the density of states

H. Hedgeland
University College London

B. A. J. Lechner, A. P. Jardine, G. Alexandrowicz,
P. Fouquet, B. J. Hinch, M. Sacchi, S. J. Jenkins, W. Allison and J. Ellis

Spin echo: window on atomic scale dynamics

Key to techniques:
Purple-optical
Blue-microscopy
Green-spectroscopy

Helium and neutron spin echo

Structure & dynamics: reciprocal space; real time

Measuring surface correlation

Spin echo time: $t = \frac{\gamma m^2 \lambda^3}{2\pi\hbar^2} \int B dl \propto \int B dl \Big/ E_i^{1.5}$

Within kinematic approx and for small ω:

$$P(\Delta\mathbf{K},t) \propto I(\Delta\mathbf{K},t) = \int G(\mathbf{R},t)\exp(i\Delta\mathbf{K}.\mathbf{R})d\mathbf{R}$$

$$\propto \int S(\Delta\mathbf{K},\omega)\exp(i\omega t)d\omega$$

Thermally activated surface dynamics

- Motion induced by thermal excitation
  - Modelled as "Adsorbate plus heat bath"
  - Langevin equation:

$$m\ddot{\mathbf{r}}_i = -\nabla V(x,y) - \eta m\dot{\mathbf{r}}_i + \xi_i(t) + \sum_{i\neq j} \mathbf{F}_{ij}$$

- Three aspects to the motion:
  - Energy Landscape
    - *STATIC FRICTION*.
  - Atomic scale friction
    - *KINETIC FRICTION*.
  - Interactions
    - *Co-operative effects*.

Benchmarking calculations

- Interactions:
  Pair-wise forces stabilise configurations with similar separation (de Gennes features) eg K/Cu(001)

• Guido Fratesi

Phys Rev B 80, 125426 (2009)

Aromatic adsorption – self-assembly of conjugated π systems

Benzene/graphite

- Activation energy: 17 ± 12meV
- Friction coefficient, **η = 2.2 ps⁻¹**

Nature Physics 5, 561-4 (2009)

Structures from lineshape analysis

- Cyclopentadiene C_5H_6/Cu(111)
- The molecule adsorbs dissociatively and *ionically*: $C_5H_6 \rightarrow (C_5H_5\text{-})_a$
- Behaviour differs from motion on a Bravais lattice

Single decay along [110]

Motion strongly activated

Double decay along [112]

Structures from dynamics

- Periodicity in $\alpha(\Delta \boldsymbol{K})$ indicates *motion on a lattice*.
- The double decay indicates a *non-bravias lattice*.
- Results correspond closely with equal occupation of fcc the Cu(111) s

Analytic model

Short and Long jumps along [112]

Equal jumps along [110]

Phys Rev B 89, 121405(R) (2014)

Cyclopentadienyl/Cu(111) – surface anion

- DFT (GGA PW91) gives **adsorption energy** of **1.7 eV**
- **1.1e⁻ net charge transfer from substrate** gives anionic Cp^-
- Small net polar covalent contribution involving HOMO and LUMO transferring charge both to and from substrate
- **ΔΦ ~ -1 eV**
- Same direction as for alkali metals
- "Cushion effect" – electron depletion just above surface plane due to Pauli repulsion of π system induces a dipole moment towards the bulk of the metal

- Friction coefficient, **η = 2.5 ± 0.5 ps^{-1}**
- Hops between both fcc & hcp hollow sites
- **DFT** shows **55 meV barrier** over bridge
- MD simulations reproduce **experimental** activation energies with barrier **40 ± 3 meV**

Phys Rev Lett 106, 186101 (2011); J Phys Chem C 115, 16134-1 (2011)

Pyrrole/Cu(111) – quantum influences

Experimental barrier: 50 ± 3 meV

Friction coefficient, **η = 2.0 ps^{-1}**

Angw Chem Int Ed 52, 5085-8 (2013)

Pyrrole/Cu(111) – quantum influences

- **Experimental barrier: 50 ± 3 meV**
- GGA **vdW DFT** gives bridge site adsorption with **15 meV** barrier over hollow sites

Angw Chem Int Ed 52, 5085-8 (2013)

- **ZPE adds 14-28 meV** – the larger of which is rate limiting
- Behaviour dominated by quantum contribution to total energy of vibrational ground state – internal modes

Thiophene/Cu(111) – jumping, rotating & flapping

- Change in activation energy with temperature
- Low temp (110 K) measurements reveal two process; 160 K shows a third

- vdW DFT shows S on top site, ring over fcc
- Effects of ZPE are negligible

- Friction coefficient, **η = 5 ± 2 ps^{-1}**

E_a (meV)	Jumping	Rotating	Flapping
Experiment	59 – 62	17 ± 2	11 ± 2
DFT	87 – 94	29	68

J Phys Chem Lett 4, 1953-8 (2013)

Aromatic adsorbates – benchmarking vdW DFT

Adsorbate	Substrate	DFT	DFT Barrier (meV)	Measured barrier (meV)	Friction coefficient (ps^{-1})
Cyclopentadienyl	Cu(111)	GGA PW91	55	40 ± 3	2.5
Pyrrole	Cu(111)	PBE + TS + ZPE	43	50 ± 3	2.0
Thiophene	Cu(111)	PBE + TS + ZPE	87 - 94	59 - 62	5.0

- "TS" DFT using Tkatchenko and Scheffler method (Phys Rev Lett 102, 073005 (2009))
- High friction in all three five-membered systems
  - Investigated using MD simulations with molecular degrees of freedom
  - Rotation about axis normal to substrate gives dominant contribution
  - More details: J Chem Phys 138, 194710 (2013)

Acknowledgements

The helium spin-echo method:

- Both atomic and molecular systems are accessible
- Uniquely sensitive to surface motion for pico- to nano-second regime
- Static and dynamic effects can be measured precisely allowing benchmarking of theoretical approaches

With thanks to the spin-echo team:

- **Cambridge**: W Allison, J Ellis, AP Jardine; SJ Jenkins
- **University of Reading:** M Sacchi
- **Lawrence Berkeley National Laboratory**: BAJ Lechner
- **Technion**: G Alexandrowicz
- **Institut Laue-Langevin**: P Fouquet
- **Rutgers**: BJ Hinch

Soft and Biomatter

Wrapped-up

Science & Technology Facilities Council
ISIS

Polymorphism in cisplatin anticancer drug

MPM Marques, R Valero (University of Coimbra, Portugal), SF Parker, J Tomkinson (ISIS) and LAE Batista de Carvalho (University of Coimbra, Portugal).

Instrument: Tosca **Support**: Portuguese Foundation for Science and Technology- PEst-OE/QUI/UI0070/2011, European Commission under the 7th Framework Programme through the Key Action: Strengthening the European Research Area, Research Infrastructures – Contract n°: CP-CSA_INFRA-2008-1.1.1 Number 226507-NMI3.

Cisplatin (cis-$(NH_3)_2PtCl_2$) is one of the most widely used anticancer agents, particularly towards testicular, head and neck tumours. Polymorphism, the ability to exist in more than one crystal form, is a key issue in pharmaceutical science since equilibrium between distinct polymorphs may affect the drug's properties and therapeutic effect. Cisplatin's polymorphic equilibrium between the two known alpha and beta species was elucidated by simultaneous Raman and INS spectroscopies, coupled to theoretical approaches. Alpha is predominant at very low temperatures (below ca. −170°C), while beta occurs at room temperature and higher. Both species coexist at intermediate temperatures, their relative population depending on the sample's history and follows a marked hysteresis. Simultaneous INS and Raman experiments, under exactly the same conditions, allowed a clear picture of cisplatin's polymorphic behaviour to be attained. Elucidation of the polymorphic equilibrium of this extensively used chemotherapy drug is paramount for optimising its pharmaceutical preparation, as well as transport and storage conditions.

Contact: pmc@ci.uc.pt
Further Reading: MPM Marques *et al.*, J.Phys.Chem. B **117** (2013) 6421.

Alpha and beta cisplatin polymorphs (INS and Raman spectra) and cisplatin-DNA interaction.

Penicillin's auto-catalytic self-activation

Z Mucsi (University of Toronto), GA Chass (Queen Mary University of London), P Ábrányi-Balogh (University of Szeged), B Jójárt (University of Szeged), DC Fang (Beijing Normal University), AJ Ramirez-Cuesta (ISIS), B Viskolcz (University of Szeged) and IG Csizmadia (University of Toronto).

Instrument: Tosca **Support**: EPSRC, UK (EP/H030077/1 & EP/H030077/2), Royal Society, UK (IE120096), National Natural Science Foundation of China (21073016), TÁMOP-4.2.2.A-11/1/ KONV-2012-0047, Hungary

Although penicillin is recognised as one of the great discoveries of the 2nd millennium, the appearance of resistant bacteria has significantly reduced its utility and viability. Continued characterisation of its structure and mechanism aids in the understanding and design of novel antibiotics with desired effects and great precision. Since its discovery by Fleming in 1928 and subsequent mass production, it has remained a mystery as to how penicillin escapes the body's hydrolytic effects, while maintaining its ability to hone-in on and disable the bacterial transpeptidase enzyme, efficiently blocking cell wall synthesis. To resolve this ability to switch from a non-active to a highly-reactive form, the dynamic structure-activity relationship of penicillin has been investigated by inelastic neutron spectroscopy, reaction kinetics, NMR and multi-scale theoretical modeling (QM/MM, DFT and post-HF ab initio). Results show that by a self-activating physiological pH-dependent two-step proton-mediated process, penicillin changes geometry to activate its irreversibly reactive acylation, facilitated by systemic intramolecular energy management and cooperative vibrations. This dynamic mechanism is confirmed by the 1st characterisation of a natural antibiotic by neutrons.

Contact: g.chass@qmul.ac.uk
Further Reading: Z Mucsi, *et al.*, Phys. Chem. Chem. Phys., **15** (2013) 20447-20455.

Trap composed of bait (to entice prey), sensor (detect prey), spring (energy reservoir) and mortal tool (kill prey). Components and systemic aspects are analogously reflected in penicillin's molecular structure.

Soft Confinement Nanoparticles

Macromolecules

Article

pubs.acs.org/Macromolecules

Microscopic Dynamics in Nanocomposites of Poly(ethylene oxide) and Poly(methyl methacrylate) Soft Nanoparticles: A Quasi-Elastic Neutron Scattering Study

D. Bhowmik,[†] J. A. Pomposo,[‡,∇,§] F. Juranyi,[∥] V. García-Sakai,[⊥] M. Zamponi,[#] Y. Su,[#] A. Arbe,[*,‡] and J. Colmenero[†,‡]

QENS Xpress

Started summer 2011

- Attracting new user communities (50%)
- Assessing experiment feasibility (30%)
- Completing experiments (20%)

Popular and successful

60+ samples and 20 new users

50% result in beamtime proposal

Gateway to QENS research at ISIS

High throughput operation

Automatisation and standardisation

Fully automated TLCCR system

- Parametric studies
- Rapid measurements before OSIRIS and LET detailed campaigns
- Link to nDDB initiative for biomolecules
- New communities, training
- S(Q,E) maps as a function of T, P, x

Science & Technology Facilities Council
ISIS

IRIS & OSIRIS International Beamline Review

https://epubs.stfc.ac.uk/work/12271760

ISIS

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ISIS

OSIRIS

The Future of IRIS

Science & Technology Facilities Council
ISIS

Molecular Spectroscopy Science Meeting 2015

Modelling & Simulations Session

Science & Technology Facilities Council
ISIS

Benchmarking calculations
LCN
Interactions:
Pair-wise forces stabilise
ations with similar
/de Gennes
K/Cu(001)
+ Guido Fratesi

Imperial College London

Computer Simulations of Soft Nanoscale interfaces

Fernando Bresme
Computational Chemical Physics Group
Department of Chemistry
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Imperial College London

Nanoscale interfaces

- Small size, 1 nm – 10's nm

~1-2 nm

Scientific Reports, 2015

- High interfacial curvature / high confinement => influences surface energies, transport properties (lubrication, heat transfer).

- Interfaces can modify their shape (soft): thermal fluctuations + adaptation to environment / external perturbations (responsive materials).

- Assembly of nanoparticles at fluid interfaces induced by capillary interactions

Advanced Materials 2014

Imperial College London

Nanoscale interfaces under non-equilibrium conditions

➢**Nanoscale thermal transport**: Energy conversion : Soret, Seebeck=> **thermo-phoretic devices**

Lervik & FB, Phys, Chem, Chem. Phys, 2014

➢"**Large**" thermal gradients => stronger effect

Imperial College London

SMALL interfaces and LARGE thermal gradients

➢ **Metallic (gold)** Nanoparticles/nanostructures => $10^{6\text{-}9}$ K/m *vs.* $10^{0\text{-}2}$ K/m

Reiner *et al.*, JACS (2013)

Nano Lett., 15, 553 (2015).

➢ **Gold functionalization** => modify hydrophobic / hydrophilic properties

➢ **Interfacial heat transport** = *f*(interfacial structure, dynamics & free energy)

Imperial College London

Water structure around core-shell nanoparticle surfaces

Au_{140} Butanethiol$_{62}$—3 nm

Imperial College London

Water at nanoparticle surfaces

Translational structure

NPT -- 1 bar, 298 K

Disrupted; h-bond structure => Dangling h-bonds

Shift of stretching modes to higher frequencies => compatible with experiments of the water-air interface using VSFS. Scatena *et al.*, Science 2001.

Tay & FB: J. Mater. Chem.; J. Am. Chem. Soc.

Imperial College London

How about bigger nanoparticles?

Increasing shell & keeping same core size

➢ Longer ligand => "softer" interface…

Imperial College London

Removing thermal fluctuations: Intrinsic profiles oil-water interface

Profile without thermal fluctuations => STRUCTURE

Mean profile Thermal fluctuations => NO STRUCTURE

$$\tilde{\rho}(z) = \left\langle \frac{1}{A}\sum_{i=1}^{N}\delta(z - z_i + \xi(\vec{r}_i)) \right\rangle$$

*FB, Chacon, Tarazona & Tay, Phys. Rev. Lett.
*FB, Chacon & Tarazona, Phys. Chem. Chem. Phys.

Imperial College London

Large thermal gradients and non-equilibrium effects

Reiner et al, JACS (2013)

With Edel and Maier (ICL), to appear in Nano Lett.

$10^{6\text{-}9}$ K/m

- **Large thermal gradients => novel coupling effects?**
- **Lehman=>** liquid crystals orientation under thermal gradients (1900)

Imperial College London

Non equilibrium thermodynamics theory

- Pure water: isotropic polarizable medium subjected to a heat flux.
- Linear flux-force relations:

o Displacement current:

$$\frac{\partial \mathbf{P}}{\partial t} = -\frac{L_{pp}}{T}(\mathbf{E}_{eq} - \mathbf{E}) - \frac{L_{pq}}{T^2}\nabla T$$

oHeat flux:

$$\mathbf{J}_q = -\frac{L_{qp}}{T}(\mathbf{E}_{eq} - \mathbf{E}) - \frac{L_{qq}}{T^2}\nabla T \qquad L_{pq} = L_{qp}$$

$$\mathbf{E} = \left(1 - \frac{1}{\varepsilon_r}\right)\frac{L_{pq}}{L_{pp}}\frac{\nabla T}{T}$$

induced electrostatic field

?

Computer simulations

Seebeck

$$E = -s\,\nabla T$$

FB, Lervik, Bedeaux and Kjelstrup, Phys. Rev. Lett. (2008)

Imperial College London

Computing heat transport in fluids– NEMD simulations

- Stationary Non-Equilibrium Molecular Dynamics (NEMD)

$$\nabla T \sim 10^{10}\,\mathrm{K/m}$$

*Tenembaum, Phys. Rev. A. (1983).

*Ikeshoji & Hafskjold, Mol. Phys. (1994).

*Romer, Lervik and FB, J. Chem. Phys. (2012) ** Thermostats

Imperial College London

Polarization of water under thermal gradients

Polar fluid + Thermal gradient => Polarization

NET=> $$\mathbf{E} = \left(1 - \frac{1}{\varepsilon_r}\right)\frac{L_{pq}}{L_{pp}}\frac{\nabla T}{T}$$

NEMD simulations of WATER

Reiner et al, JACS (2013)

With Edel and Maier (ICL), to appear in Nano Lett.

$10^{6\text{-}9}$ K/m=>$10^{5\text{-}8}$ V/m

***FB *et al.*, Phys. Rev. Lett., (2008) – MCFM water**

***Armstrong and FB, J. Chem. Phys. (2013) – SPC/E water**

Imperial College London

Enhancement of the thermal polarization

- Heat Flux + Dipole moment dynamic correlations => enhancement of the thermal polarization

Armstrong, Lervik and FB, J. Phys. Chem. B, 2013

Imperial College London

Computational Chemical Physics @ ICL

Niall, Jeff, Irene, Anna-Sofia, Silvia, Chris, Wendy, James, Ryan, Anders, Chris (NTNU/ICL); Miguel Angel, Drew; Stephen; Arthur; Angela

EPSRC Engineering and Physical Sciences Research Council

The Leverhulme Trust

European Commission

Imperial College London

Temperature-dependent dynamics of poly-alkylthiophene conjugated polymers

Anne A. Y. Guilbert

Poly-alkylthiophene polymers

Semi-crystalline polymer (10-20% crystalline)

Widely used in organic electronics:
- Organic transistors
- Organic photovoltaics

Dynamics potentially impact opto-electronic processes:
- absorption
- charge separation
- charge transport
- lifetime (coarsening of phase separation when blended with fullerenes)

Eight19 (Cambridge)

Quasi-elastic neutron scattering

- Focus on the Q-dependent loss in elastic intensity

Molecular Dynamics Simulation

Force field developed by Moreno *et al.* (*J. Phys. Chem. B* **2010**, *114*, 1591-1602)

Elastic Incoherent Structure Factor

Using nMoldyn3

Relaxation times

- Can calculate the self-part of the Van Hove of function
- Can tag specific subset of atoms
- Can manipulate the trajectories: recalculate the methyl atom positions taking the side chain as new reference

Relaxation times

Relaxation map

Can fit the relaxation time for the methyl rotation:

- T_a = 87 K +/- 14 K
- τ_0 = 25.9 fs +/- 2.5 fs

Elastic Incoherent Structure Factor

Elastic Incoherent Structure Factor

Motion geometry

Motion geometry

Mean-square displacement

$$EISF(Q,T) = \exp\left(-\frac{\langle R^2\rangle_T}{3}Q^2 + \frac{\alpha_2(T)\,\langle R^2\rangle_T^{\,2}}{18}Q^4\right)$$

Mean-square displacement

Conclusion

- MD simulations valuable tool

Acknowledgement

- Antonio Urbina, Jose Abad
  (Technical University of Cartagena)
- Carlos Díaz-Paniagua, Francisco Batallán
  (Instituto de Ciencia de Materiales de Madrid)
- Victoria García Sakai
  (ISIS Facility)
- Tilo Seydel
  (Institut Laue-Langevin)
- Jenny Nelson
  (Imperial College London)

Thank you!

Imperial College London

Understanding Organic Solar Cells

Experiment & Theory

Jeff Armstrong

Imperial College London

Computational Chemical Physics
Imperial College London

Heat-transport, Structure/dynamics of Complex materials

Imperial College London

Organic Solar Cells (Why is this technology alluring?)

-Light weight
-Flexibility
-Promise of cheaper fabrication
-Greater customisation

Allows more diverse applications

However all of this relies on achieving higher efficiencies (~15%)

Currently ~8%

Imperial College London

Bulk heterogeneous structures(BHJ):

What makes a good BHJ?:

-High exciton diffusion length
-Large donor acceptor interface area

PCBM (acceptor)

P3HT (Donor)

Imperial College London

P3HT/PCBM blends:

To understand their electron transport properties we must first understand their structure

Structure of pure PCBM?

Many factors influence the resultant structure of pure PCBM:

-Solvent preparation (e.g. chlorobenzene ortho-dichlorobenzene)

-Temperature of solvent removal

-And in simulation starting structure as well as equilibration conditions

Simulation: J. Mater. Chem., 2012, 22, 5434

Experiment: Chem. Phys. 2013, 427, 142-146

Imperial College London

How does blend morphology effect PCBM's structure?

-Both crystalline and amorphous domains have been seen experimentally

-We are dealing with a nano-composite, which can exhibit confinement effects

-Blend structure is again highly dependent on solvent preparation & thermal annealing

Imperial College London

Neutron experiment (temperature scan)

Broadening observed at ~360 K

Order/Disorder transition?
(similar to that seen in C60)

Imperial College London

Chosen model:

-Standard OPLS force-field

-C60 carbons are increased in size to match the C60 experimental density

-Unit cell taken as experimental crystal structure (Paternò et al)

-NPT runs 5ns with full box flexibility, stats gathered after 4ns

Imperial College London

C60-C60 (RDF)

No major change in C60 structure
(coordination is relatively unchanged)

Thermal expansion coefficient is $6.7 \times 10^{-5} K^{-1}$ compared to $6.5 \times 10^{-5} K^{-1}$ from experiment

Imperial College London

Chain-Chain (RDF)

Chains are able to access almost all of the cavity beyond 400K

Imperial College London

Mean-squared Displacement (Chain)

Increase in mobility at approximately T=400-500K

This can be clearly seen from the snapshots

Imperial College London

Possible mechanism for disorder transition?

-Strong electrostatic interaction between aromatic ring and C group

-Increasing chain flexibility with T

We can examine the effective binding energy of the aromatic ring and C

Also look at the dihedral torsional energy vs T

Imperial College London

Thank you for listening

Any Questions?

Modelling & Simulation

Felix Fernandez-Alonso
&
Sanghamitra Mukhopadhyay

ISIS Molecular Spectroscopy Science Meeting
The Cosener's House, 29-30 January 2015

Science & Technology Facilities Council
ISIS

Dynamics & Spectroscopy: Then and Now

1990s

The 'Ball-and-stick' Way

Two Decades On

In-silico Spectroscopy

Computational Modelling: Vibrations

Science & Technology Facilities Council

Technical Report
RAL-TR-2013-015

TOSCA International Beamline Review

S Rudic, AJ Ramirez-Cuesta, SF Parker,
F Fernandez-Alonso, RS Pinna, G Gorini, CG Salzmann,
SE McLain, NT Skipper

December 2013

The present

Usage of TOSCA by scientific discipline.

Recent advances in materials modelling have been at the heart of the success of TOSCA, with over half of its publications involving some form of modelling. The degree of sophistication of these methods has evolved from empirical ball-and-springs models to *ab initio* calculations of isolated molecules and, latterly, periodic DFT calculations across the entire Brillouin zone as well as the full inclusion of nuclear quantum effects. Such

The future

large (*i.e.*, ×10+), then replacing some of the forward-scattering analysers with these high-flux modules is advantageous, at a cost of ca. £200k.

Data acquisition is vital but so is its analysis. For systems with long-range order, TOSCA instrument scientists have been carrying-out state-of-the-art analysis for several years. There is a clear need to extend this paradigm to disordered materials, a task we intend to pursue primarily *via* scientific collaborations.

Both research areas targeted for growth (gas and charge storage) attempt to study hydrogenous and non-hydrogenous components simultaneously. While neutrons are ideal for hydrogen, they are less so for other

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Successes: periodic systems, phonon-based calculations (CASTEP, VASP)

Challenges: disordered media (catalysis, energy, liquids)

Neutron Spectroscopy of Framework Materials

PHYSICAL REVIEW LETTERS

Identifying the Role of Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization

Matthew R. Ryder,[1,2,3] Bartolomeo Civalleri,[4] Thomas D. Bennett,[5] Sebastian Henke,[5] Svemir Rudić,[2] Gianfelice Cinque,[3] Felix Fernandez-Alonso,[2,6] and Jin-Chong Tan[5,7]

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[4]*Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, via P. Giuria 7, 10125 Torino, Italy*
[5]*Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom*
[6]*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*

(Received 1 August 2014)

Beyond Vibrations: Nuclear Quantum Effects

Unique to ISIS

Great opportunity to link to state-of-the-art modelling

PIMD, quantum thermometry & MANSE …

Beyond Vibrations: Stochastic Phenomena

Challenges: disordered media, time-dependent methods to calculate transport properties (molecular dynamics), first-principles

Key: tool development, more computational power, your involvement in the process.

Roadmap

Development	Year					
	2015	2016	2017	2018	2019	2020
Modelling Phase I	Staff recruitment with modelling expertise	SCARF upgrade & software development	Software and method development	Deployment & training		
Modelling Phase II				Extension to other HPC initiatives	Extension to other HPC initiatives	Deployment & training
OSIRIS Phase I	Feasibility & design of new secondary	Secondary upgrade (Si111)	Secondary upgrade (Si111)	Start of operations with upgraded OSIRIS		
OSIRIS Phase II			Feasibility & design of primary	Primary upgrade: guide + pulse shaping chopper	Primary upgrade: guide + pulse shaping chopper	Start of operations with upgraded OSIRIS
IRIS Phase I	High-throughput QENS: sample environment	High-throughput QENS: sample environment, simultaneous techniques	High-throughput QENS: simultaneous techniques			
IRIS Phase II		Baselining & feasibility in context of TS1 upgrade	Feasibility & design of primary & secondary	Primary upgrade: guide + pulse shaping chopper	Primary upgrade: guide + pulse shaping chopper	Secondary upgrade: e.g., Si311, QENS-SANS

Recent Examples

Hydrogen bonding motifs in the organic ferroelectric croconic acid using CASTEP

Ab-initio MD simulations of molten salts

Simulations of protein building blocks (L-Alanine)

Ionic liquids
Diethyl-ammonium nitrate

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Bringing Theory & Experiment Together

MANTID

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Bringing Theory & Experiment Together

MD analysis: nMOLDYN + MANTID

Synthetic 'experimental' spectra from MD trajectories

First-principles: Added Value

Charge density difference

Electron localisation function

Understanding what electrons do, from where nuclei are (and do).

The Need for Increased Computational Power

Simulation box of 584 atoms,

First principles MD simulations,

1000 processors, 30ps trajectories

Matches experimental timescales

OSIRIS experiments & calculations on molten NaF

Comparison

On the Horizon: Larger Systems and for Longer

Dynamics in PCBM at high temperatures

About 500 atoms per unit cell

Barely possible with first-principles

In-Silico Neutron Spectroscopy

Materials Modelling

To fully exploit neutron data.

Model selection using neutron spectroscopic data.

Plenty of opportunities for your involvement.

Time-dependent

Time-independent

Python Interface

Experiment-driven model selection

Detailed model analysis (CDA, ELF, TD-AIM, …)

Experiments

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Molecular Spectroscopy Science Meeting 2015

Quantum Matter Session

Science & Technology Facilities Council
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Coupled O-H and O-D stretching modes of ice Isd
(a)
(b)
normalised intensity
Raman shift / cm⁻¹
Spectral differences between ice Isd and ice Ih exist.
The integrated peak areas are a measure for the extent of stacking disorder in ice.

The many facets of ice research

Dr Christoph G. Salzmann
Department of Chemistry
University College London
c.salzmann@ucl.ac.uk

Ice – a material of superlatives

- H_2O is 3rd most abundant molecule in the universe
- lower density than water
- first high-pressure polymorphs
- pressure-induced amorphisation
- polyamorphism
- important for a vast range of processes in geology, biology, chemistry, the atmospheric sciences and space research

C. G. Salzmann, P. G. Radaelli, B. Slater, J. L. Finney, **Phys. Chem. Chem. Phys.**, *13* (2011) 18468-18480

Structural classification of ice materials

1. Hydrogen order / disorder

Ice V / XIII phase transition at ambient pressure

ice V
(*A*2/*a*)

HCl doping

ice XIII
($P2_1/a$)

C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer, J. L. Finney, **Science**, *311* (2006) 1758

New hydrogen-ordered phases of ice – ices XIII, XIV and XV

ice XIV
($P2_12_12_1$)

ice XV
(*P*-1)

(1) Insights into defect dynamics in ice
(2) Geophysics of icy moons and planets

T. F. Whale, S. J. Clark, J. L. Finney, C. G. Salzmann, **J. Raman Spectrosc.**, *44* (2013) 290
C. G. Salzmann, P. G. Radaelli, E. Mayer, J. L. Finney, **Phys. Rev. Lett.**, *103* (2009) 105701
C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer, J. L. Finney, **Science**, *311* (2006) 1758

New hydrogen-ordered phases of ice – ices XIII, XIV and XV

(3) Benchmark structures for computer models of H_2O

experimental
K.D. Nanda, G.J.O. Beran, **J. Phys. Chem. Lett.**, *4* (2013) 3165

C. Knight, S. J. Singer, **J. Phys. Chem. B**, *109* (2005) 21040
J.-L. Kuo, W. F. Kuhs, **J. Phys. Chem. B**, *110* (2006) 3697

(4) Spectroscopy of H_2O

Hydrogen-ordered ices are the only condensed phases of H_2O with strictly defined selection rules.

T. F. Whale, S. J. Clark, J. L. Finney, C. G. Salzmann, **J. Raman Spectrosc.**, *44* (2013) 290

2. Stacking disorder

Stacking disorder in ice

W. F. Kuhs, D. V. Bliss, J. L. Finney, **J. Phys. Colloq. C1**, *48* (1987) 632-636.

Ice from supercooled water droplets (~232 K)

T. L. Malkin, B. J. Murray, A. V. Brukhno, J. Anwar, C. G. Salzmann, **Proc. Natl. Acad. Sci. USA**, *109* (2012) 1041-1045

Stacking disordered ice (ice Isd)

ice Isd

trigonal, *P*31*m*

Monte Carlo DIFFaX for ice V1.2 --- C.G. Salzmann (University College London)

DIFFaX (Treacy *et al.*) in a least-square environment

Refines stacking probabilities (up to 2nd order memory effects), lattice constants, zero shift and peak-profile parameters (*u*, *v*, *w*, *GL*)

Φ_C(zero order)=0.72, Φ_C(1st order)=0.677, Φ_C(2nd order)=0.670

Other ice Isd materials

Tendency to stay in cubic or hexagonal sequences
Still a long way to perfect ice Ic!

T. L. Malkin, B. J. Murray, C. G. Salzmann, V. Molinero, S. J. Pickering, T. F. Whale, *accepted*

Crystal morphology predictions

Stacking disorder becomes relevant below -15°C.

B. J. Murray, C. G. Salzmann, A. J. Heymsfield, S. Dobbie, R. R. Neely, C. J. Cox, *submitted*

The mystery of snow flakes with three-fold symmetry

FIG. 3. Examples of trigonal ice crystal shapes observed in the cirrus layer.

B. J. Murray, C. G. Salzmann, A. J. Heymsfield, S. Dobbie, R. R. Neely, C. J. Cox, *submitted*

Differences between ice Ih and Isd

Different crystal morphologies and light scattering properties
Prismatic faces of ice I*sd* are 'rougher' (→ surface chemistry).
Ice I*sd* has a higher vapour pressure than I*h*.
Growing realisation that stacking disorder in ice has profound consequences on its chemical and physical properties.

The spectroscopic signature of stacking disorder in ice

Subtle structural differences and local density fluctuations in the ice I family beyond the first coordination shell.

Can we detect stacking disorder in ice spectroscopically?

Urgent demand for lab studies as well as for remote applications.

Coupled O-H and O-D stretching modes of ice Isd

Spectral differences between ice I*sd* and ice I*h* exist.

The integrated peak areas are a measure for the extent of stacking disorder in ice.

T. H. G. Carr, J. J. Shephard, C. G. Salzmann, **J. Phys. Chem. Lett.**, *5* (2014) 2469-2473

Correlations with results from other techniques

New technique available for characterising ice I*sd* in the lab but also for remote or even telescopic applications.

T. H. G. Carr, J. J. Shephard, C. G. Salzmann, **J. Phys. Chem. Lett.**, *5* (2014) 2469-2473

3. Amorphous ice

Making amorphous ice in the lab

Structural relaxation of low-density amorphous ice

A gradual structural relaxation process takes place upon heating LDA.

Due to the coupled nature of ν(OH) spectroscopic changes reflect structural change on an extended length scale.

J. J. Shephard, J. S. O. Evans, C. G. Salzmann, **J. Phys. Chem. Lett.**, *4* (2013) 3672-3676

Decoupled μ(OD) stretching modes of ASW (FT-IR)

Decoupled μ(OD) modes are sensitive to local structure

Local structural changes start immediately.

Shortening of the average O-O distance and narrowing of the O-O distance distribution.

Process is separate from crystallisation and does not seem to reach completion before crystallisation.

Difficult to reconcile with a glass transition to the liquid

J. J. Shephard, J. S. O. Evans, C. G. Salzmann, **J. Phys. Chem. Lett.**, *4* (2013) 3672-3676

Acknowledgement

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Ben Murray, Tamsin Malkin, Thomas Whale

Durham

John Evans, Stewart Clarke

Science & Technology Facilities Council ISIS

THE ROYAL SOCIETY

EPSRC Engineering and Physical Sciences Research Council

The Leverhulme Trust

Momentum distribution and mean force from VESUVIO experiments

Roberto Senesi

Università degli Studi di Roma Tor Vergata , Dipartimento di Fisica and Centro NAST; CNR-IPCF

Why (Nuclear) Quantum Effects

Nuclear quantum effects in ordinary substances are common in the macroscopic world

Originate from microscopic properties of atoms and molecules

Uncertainty principle and quantum statistics, zero point energy

Why (Nuclear) Quantum Effects

PRL **110,** 065701 (2013) PHYSICAL REVIEW LETTERS week ending 8 FEBRUARY 2013

Role of Quantum Effects in the Glass Transition

V. N. Novikov[1,2] and A. P. Sokolov[1,2,3]
[1]*Department of Chemistry and Joint Institute for Neutron Sciences, University of Tennessee, Knoxville, Tennessee 37996, USA*
[2]*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[3]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*
(Received 23 July 2012; published 5 February 2013)

It is shown that quantum effects lead to a significant decrease of the glass transition temperature T_g with respect to the melting temperature T_m, so that the ratio T_g/T_m can be much smaller than the typical value of 2/3 in materials where T_g is near or below ~60 K. Furthermore, it is demonstrated that the viscosity or

Effect on glass formation

PNAS

Unraveling quantum mechanical effects in water using isotopic fractionation

Thomas E. Markland[a] and B. J. Berne[b,1]
[a]Department of Chemistry, Stanford University, Stanford, CA 94305-5080, and [b]Department of Chemistry, Columbia University, New York, NY 10027

Contributed by B. J. Berne, February 28, 2012 (sent for review February 2, 2012)

When two phases of water are at equilibrium, the ratio of hydrogen isotopes in each is slightly altered because of their different phase affinities. This isotopic fractionation process can be utilized to analyz that equi

(9), as well as the ability to use heavy solvents in two-dimensional-IR and NMR spectroscopies, where deuteration is assumed not to dramatically alter the structure or dynamics observed. How-

PRL **108,** 193003 (2012) PHYSICAL REVIEW LETTERS week ending 11 MAY 2012

piri-
e its

Effect on water's movement in the world's climate.

Anomalous Nuclear Quantum Effects in Ice

B. Pamuk,[1] J. M. Soler,[2] R. Ramírez,[3] C. P. Herrero,[3] P. W. Stephens,[1,4] P. B. Allen,[1] and M.-V. Fernández-Serra[1,*]
[1]*Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800, USA*
[2]*Dep. de Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[3]*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas (CSIC), Campus de Cantoblanco, 28049 Madrid, Spain*
[4]*Photon Sciences Directorate, Brookhaven National Lab, Upton, New York 11973, USA*
(Received 18 November 2011; published 9 May 2012)

One striking anomaly of water ice has been largely neglected and never explained. Replacing hydrogen (^{1}H) by deuterium (^{2}H) causes ice to expand, whereas the normal isotope effect is volume contraction with

Effect on ice expansion

Why "Effects"?

PNAS

Quantum nature of the hydrogen bond

Xin-Zheng Li, Brent Walker, and Angelos Michaelides[1]
London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, United Kingdom

Edited by Michael L. Klein, Temple University, Philadelphia, PA, and approved February 23, 2011 (received for review November 9, 2010)

Hydrogen bonds are weak, generally intermolecular bonds, which hold much of soft matter together as well as the condensed phases of water, network liquids, and many ferroelectric crystals. The small mass of hydrogen means that they are inherently quantum mechanical in nature, and effects such as zero-point motion and tunneling must be considered, though all too often these effects are not considered. As a prominent example, a clear picture for the impact of quantum nuclear effects on the strength of hydrogen bonds and consequently the structure of hydrogen bonded sys-

although a negative Ubbelohde effect has also been observed (20, 21). In H-bonded liquids analogous issues have been discussed. In liquid hydrogen fluoride (HF), for example, density-functional theory (DFT) simulations predict that when QNEs are accounted for the first peak of the F-F radial distribution function (RDF) sharpens and shifts to a shorter F-F distance (15). The implication of this increase in structure in the liquid is that the H-bond is strengthened upon inclusion of QNEs. In contrast, similar simulations for liquid water show that the

1. There is no general description of the effect of quantal motion in molecular systems.
2. The changes with respect to classical descriptions can vary in different qualitative and quantitative manners- depends on the system, phase, temperature, etc...
3. These effects have to be measured at the atomic/molecular level.

Example: OH bond in ice (L. Lin et al., PRB (2011))

Potential energy surface of the proton along the OH bond in ice
Square modulus of the proton wave function

The Fourier Transform of

$$|\Psi|^2$$ is

$$n(p)$$ Momentum distribution

The width (variance) of $n(p)$ is

$$\langle E_K \rangle = \frac{\langle p^2 \rangle}{2M}$$ Kinetic energy

The value in ice, averaged over directions, is about 150 meV
This is mostly quantum zero point energy!!
at T=270 K, the classical contribution is 1/100 of this…

Momentum distribution of the proton is a probe of the local environment ….

…or a probe of the force acting on the proton

How to measure proton momentum distributions using the VESUVIO spectrometer at ISIS

$$\mathbf{p_n} - \mathbf{p_n'} = \hbar \mathbf{q}$$ Change of neutron momentum in the scattering process

$$\hbar\omega = \frac{(\mathbf{p_n} - \mathbf{p_n'})^2}{2M} + \frac{(\mathbf{p_n} - \mathbf{p_n'})\cdot\mathbf{p}}{M}$$ Change of neutron energy in the scattering process
Only on VESUVIO!

Inelastic neutron scattering at
High energy-high momentum transfer
Probe a particular excitation
---the free particle recoil---:

$$\hbar\omega = \frac{\hbar^2 q^2}{2M}$$

$$S(\vec{q},\omega) = \hbar \int d\vec{p}\; n(\vec{p})\; \delta\left(\hbar\omega - \frac{\hbar^2 q^2}{2M} - \frac{\vec{p}\cdot\hbar\vec{q}}{M}\right)$$

How to measure momentum distributions using the VESUVIO spectrometer at ISIS

R. Simmons (1984)

The scattering is centred at recoil energies and broadened by distribution of momenta (**p**)

$$\mathrm{h}\omega = \frac{\mathrm{h}^2 q^2}{2M} = \mathrm{h}\omega_r$$

Use the coupling between energy and wave vector transfer, then represent the scattering intensity in terms of *y*

$$y = \frac{M}{\mathrm{h}^2 q}(\mathrm{h}\omega - \mathrm{h}\omega_r) = \frac{\mathrm{h}p}{\mathrm{h}} \cdot \hat{q}$$

$$S(\vec{q},\omega) = \hbar \int d\vec{p}\; n(\vec{p})\; \delta\left(\hbar\omega - \frac{\hbar^2 q^2}{2M} - \frac{\vec{p}\cdot\hbar\vec{q}}{M}\right) = \frac{M}{\hbar q} J(y,\hat{q})$$

$$J(y,\hat{q})$$ Is centred at zero and is broadened by n(***p***)

Referred to as **NEUTRON COMPTON PROFILE**

How to measure momentum distributions using the VESUVIO spectrometer at ISIS-II

Note: in real experiments there is an additional broadening due to resolution and small deviations from the purely "impulsive " regime

$$F_I(y,q) = [J(y) + \Delta J_I(y,q)] \otimes R_I(y,q)$$

How do we measure momentum distributions and kinetic energies of..?

Electrons, using ID16 at ESRF

Compton profile of Na; p- resolution≈13%
S. Huotari et al, PRL 105, 086403 (2010)

$$q = \vec{p} \cdot \hat{q}$$

Protons, using VESUVIO at ISIS

Neutron Compton profile of water; p-resolution≈14%
A. Pietropaolo et al, PRL 100, 127802 (2008)

$$y = \frac{\vec{p}}{\hbar} \cdot \hat{q}$$

Properties of the Neutron Compton profile

In an isotropic system:

$$\int_{-\infty}^{\infty} y^2 \; J(y)\, dy = \sigma^2 = \frac{2M}{3\hbar^2}\langle E_K \rangle \qquad n(p) = -\frac{1}{2\pi y}\frac{d\,J(y)}{dy}\bigg|_{y=p}$$

$$f(x) = -\frac{Mx}{\hbar^2}k_B T + \frac{\int_0^{\infty} dy\; y\,\sin(xy)\,J(y)}{\int_0^{\infty} dy\,\cos(xy)\,J(y)}$$

Mean force: average force acting on the proton along coordinate x

L. Lin et al, PRL (2010)

The shapes of Neutron Compton profiles is directly related to potential and mean force

Example

FIG. 7.1. Two different curves are given which have the same zero, first and second moment

These curve shapes look very different but have the same area, same center, same width (variance--- <Ek>)

Experiment: proton in lysozyme (egg white), *RS et al PRL (2007)*

The shapes at two temperatures (180 K – protein does not work) and (290 K protein works) have the same area, same center, same variance (<Ek>), but different underlying potentials…

Shape analysis usually carried out using nonlinear fitting of the profiles.
Can be done numerically, in a non parametric way:

• Determine σ and <Ek> by numerical integration

$$\int_{-\infty}^{\infty} y^2 \, J(y) \, dy = \sigma^2 = \frac{2M}{3h^2} \langle E_K \rangle$$

•Correct for deviations from impulsive approximation ΔJ(y,q) and resolution R(y,q)

•Derive the momentum distribution by numerical calculation of

$$n(p) = -\frac{1}{2\pi y} \frac{d\,J(y)}{dy}\bigg|_{y=p}$$

•Derive the mean force by numerical calculation of

$$f(x) = -\frac{Mx}{\hbar^2} k_B T + \frac{\int_0^{\infty} dy \; y \sin(xy) \, J(y)}{\int_0^{\infty} dy \cos(xy) \, J(y)}$$

Shape analysis -non parametric way:

• Determine σ and <Ek> by numerical integration

Two samples of ice at the same temperature, one doped with KOH 0.01 mol/l

Shape analysis non parametric way:

•Derive the momentum distribution by numerical calculation of

$$n(p) = -\frac{1}{2\pi y}\frac{dJ(y)}{dy}\bigg|_{y=p}$$

Shape analysis non parametric way:

•Derive the mean force by numerical calculation of

$$f(x) = -\frac{Mx}{\hbar^2}k_B T + \frac{\int_0^\infty dy\, y \sin(xy)\, J(y)}{\int_0^\infty dy \cos(xy)\, J(y)}$$

NOTE: if f(x) is a straight line, then underlying potential is harmonic and isotropic

These appear anisotropic with small anharmonicities (quasiharmonic)

FULL ANALYSIS IS UNDERWAY

Conclusions

Non- parameteric analysis of Neutron compton profiles allow to provide a first order determination of

1. Zero point kinetic energy
2. Anisotropy or anharmonicity of the underlying potentials and forces

These can be implemented in fitting-based line shape analyses to obtain robust representation of the local environment of protons, deuteronse, etc.. In molecular systems

Team

Carla Andreani (group leader); RS, Alexandra Parmentier, Giovanni Romanelli

-Mean force, theory: R. Car, L. Lin, J. Morrone, M. Parrinello

Conclusions- 2. Operate in conjunction with INS experiments from TOSCA, MARI, MAPS,..Single particle proton excitations in molecules and local effective potentials-

Measure single-particle Excitation, es. 0 to 1

↓

Assume an underlying parabolic potential

↓

Gaussian proton wave function

↓

Gaussian proton momentum distribution (multivariate in 3D)

Conclusions- 2. Operate in conjunction with INS experiments from TOSCA, MARI, MAPS,..Single particle proton excitations in molecules and local effective potentials-

"True potential"

Measure single-particle Excitation, es. 0 to 1

↓

~~Assume an underlying parabolic potential~~

↓

~~Gaussian proton wave function~~

↓

~~Gaussian proton momentum distribution (multivariate in 3D)~~

Science & Technology Facilities Council

~~Wrapping Up Quantum Matter~~

VESUVIO

Science & Technology Facilities Council

Come and Do a VESUVIO Experiment..?

VESUVIO

$$S(\mathbf{q},\omega)_{IA} = \hbar \int \underbrace{n(\mathbf{p})}_{\text{Momentum Distribution}} \delta\left(\underbrace{\hbar\omega - \frac{\hbar^2 q^2}{2M}}_{\text{Mass-spec}} - \underbrace{\frac{\hbar}{M}\mathbf{q}\cdot\mathbf{p}}_{\text{Spectroscopic}}\right) d\mathbf{p}.$$

Science & Technology Facilities Council

Our Scientific Themes

^4He, ^3He

Proton dynamics (excluding H_2O)

Protons in H_2O

Deuterium dynamics

M>4, MANSE

Science & Technology Facilities Council

MANSE

Table 1. Programme of the *VI Workshop in Electron Volt Neutron Spectroscopy.*

Monday 20th January	
13:00	Welcome and Particulars
13:05-13:15	**Spectroscopy with Epithermal Neutrons** Felix Fernandez-Alonso, ISIS
Session 1	*Nuclear Quantum Effects*
13:15-13:55	Quantal Nuclear Motions in Condensed H-Bonded Systems Carla Andreani, [illegible]
13:55-14:35	The Quantum [illegible]no-Confined Water: New Cooperative Effects Revealed with Neutron and X-Ray Compton Scattering George Reiter, Houston
Session 2	*DINS Beyond the Proton*
14:55-15:35	MANSE and [illegible] Matthew Kr[illegible]
15:35-15:55	Origins of Mechanical Toughness in Bio-Cement During Setting Gregory Chass, Queen Mary University of London
15:55-16:15	Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water Upon Melting Giovanni Romanelli, Rome
Session 3	*Measurement and Instrumentation*
16:20-16:50	Epithermal Neutron Detection at ISIS [illegible]
16:50-17:10	[illegible]
17:10-17:35	Direct and Inverse Geometry Instruments for Proton Momentum Distribution Studies Roberto Senesi, Rome
Tuesday 21st January	
Session 4	*Theoretical Horizons and Calculation*
09:00-09:40	Inexpensive Evaluation of the Quantum Kinetic Energy and Particle Momentum Distribution by First-Principles Simulations Mich[illegible]
09:40-10:05	Coll[illegible] Ice Christoph Drescher-Grau, Bochum
10:05-10:30	Simulation Studies of Hydrogen-Bonded Ferroelectrics Thor Wikfeldt, Reykjavik/Stockholm
10:50-11:15	Interaction Induced Localisation of Protons: Temperature and Superfluid Helium Solvation Effects Lukasz Walewski, Bochum
11:15-11:40	Nuclear Quantum Effects in Enzyme Catalysis From Momentum Distributions Dan Major, Bar-Ilan
13:30-15:30	**Open Discussion**

Water

MANSE

Instrumentation

Computation

VESUVIO GOES SOCIAL

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If you would like to know more…

Journal of Physics: Conference Series

Table of contents

Volume 571

2014 « previous issue next issue »

VI Workshop in Electron Volt Neutron Spectroscopy: Frontiers and
20–21 January 2014, Abingdon, UK

Over the Horizon: Future Roles of Electron Volt Neutron Spectroscopy

Nuclear quantum effects in a 1-D model of hydrogen bonded ferroelectrics

Ab initio simulation of particle momentum distributions in high-pressure water

VESUVIO Data Analysis Goes MANTID

New prospects of VESUVIO applied to measurements in water mixtures

Measurement of proton momentum distributions using a direct geometry instrument

The VESUVIO Spectrometer Now and When?

Epithermal neutron instrumentation at ISIS

The Harmonic Picture of Nuclear Mean Kinetic Energies in Heavy Water

Mass-selective Neutron Spectroscopy Beyond the Proton

The Quantum Mechanics of Nano-Confined Water: New Cooperative Effects Revealed with Neutron and X-Ray Compton Scattering

The VI Workshop in Electron Volt Neutron Spectroscopy: Frontiers and Horizons

A.G. Seel,[1] R. Senesi,[2,3] and F. Fernandez-Alonso[1,4]

And come to the VII Workshop!

What We're Aiming For…

But is that all?

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Aiming Higher
("Suck it and see" / "What the Heck")

Proton dynamics ☺

- (Proton) Number Density
- γ-resonance spectroscopy (dopplerimetry)

Anything else with eV neutrons

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Dopplerimetry

(go and see Matthew's poster)

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Molecular Spectroscopy Science Meeting 2015

Impact at ISIS

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Impact at ISIS

Sara Fletcher
ISIS Impact Manager
www.isis.stfc.ac.uk

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What is Impact?

- Depends who you talk to!
- Financial
- Quality of life
- Inspiring the next generation
- Media coverage
- Scientific impact
- Who is your audience?

Science & Technology Facilitie
ISIS

Eight Great Technologies

David Willetts

Policy Exchange

Funders

- Impac
- Impac
- Impac
  range
- Timeli

"EDF Energy used it to research the performance of materials in nuclear power stations, enabling them to extend the working life of two nuclear power stations by five years – a very significant gain of extra electricity."

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3 July 2013 Last updated at 17:21

300 Share

Glowing tags to reveal hidden prints

By Paul Rincon
Science editor, BBC News website

Scientists have described a new system for visualising "hidden" crime scene fingerprints.

Despite several enhancement techniques already in use, only about 10% of fingerprints from crime scenes are of sufficient quality to be used in court.

The technique is based around fluorescent chemical "tags" and works on metal surfaces, meaning it could be used on knives, guns or bullet casings.

Details were outlined at the **Faraday Discussions** lecture series in Durham.

"Notwithstanding DNA, fingerprints are still the major source of identification in criminal investigations," co-author Prof Robert Hillman, from the University of Leicester, told BBC News.

"When someone asks: 'Haven't we been doing this for a century, why do we need another method?' Our answer is: 'To image the 90% we don't currently get'."

Although the technique currently works only with metallic objects, Prof Hillman said these were "quite signficant" forensically - especially in

The technique, demonstrated here on stainless steel, produces a negative image of the print

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Adam Jones column
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Public engagement and schools

- Provoke
- Relate
- Reveal
- Facilities and demos

- Open week 2015!

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What do we want from you?

- Evidence of impact
- REF submissions
- Scientific publications – ideally at acceptance stage
- To understand what you do and why

Sara Fletcher
ISIS Impact Manager
sara.fletcher@stfc.ac.uk

Charvy Narain
charvy.narain@stfc.ac.uk

UTRECHT
UNIVERSITY

Molecular Spectroscopy Science Meeting 2015

Nanostructured Materials Session

Science & Technology Facilities Council
ISIS

chemically bound water
Length Scales
supercooled to 260K.

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EUROPEAN SPALLATION SOURCE

Stretching time: dynamics and functionality in hydrogen bonded systems

Heloisa N. Bordallo

bordallo@nbi.ku.dk

Molecular Spectroscopy Science Meeting 2015 29-30 January 2015, Cosener's House, Abingdon, UK

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Hydrogen dynamics using Inelastic and Quasi-Elastic Neutron Scattering

The Niels Bohr Institute, Science

Drug polymorphism

Bio-nanocomposite: breast cancer drug delivery

Unpublished

Liquid mobility in confinement

Museum of Modern and
Contemporary Art (Nice)

H_2O/D_2O
Tomato seedling
5 min
20 min
40 min
D_2O

4 mins
8 mins
20 mins

Elodea cells in NaCl.

500µm

Sample 6
0.5 Å⁻¹
1.25 Å⁻¹
S(Q,t) / S(Q,0)
Time (ns)

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Michelle Rodrigues
UNICAMP

Laurie P. Aldridge
ANSTO

Johan Jacobsen
NBI-ESS

Mark Telling

Local

Collapsed motorway bridge affecting traffic

Minor miracle that no-one was hurt

The police said they still werent sure why the bridge collapsed, but that a team of engineers were investigating (Photo: Scanpix)

September 29, 2014 09:58

The collapse of a bridge onto the Copenhagen-Helsingør motorway has suspended the movement of traffic along the road in north Zealand.

DR dk

Sukkerrør kan bane vejen for 'grøn' og stærk cement

Jacobsen, J. et al. Sci. Rep. **3** (2013) 2667.

Hydration Process

Kimberly Kurtis, School of Civil Engineering Georgia Institute of Technology Atlanta, Georgia

Structure of cement… deciphering the puzzle…

After the war, Bernal resumed his professorial duties at Birkbeck, setting up the Biomolecular Research Laboratory in 1948. As well as groups working on organic crystals and proteins, he had others working on computers, the structure of cements (buildings and building materials were a life-long interest), and the structure of water. Rosalind Franklin later joined him to start work on virus structure, which she continued with Aaron Klug.

Cracks – Most significant, can be created by removal of water.

Capillary Pores - Not significant if paste not cracked, well cured and has water to cement ratio less than 0.42.

Gel Pores - In well made concrete rate limiting factor!

NIST model - Fraction of connected capillary pores.
Bentz and Garboczi, Cem. and Conc. Res. **21**, 325 (1991).

Pore-Water Structure: Model

Gel pores
Diameter < 10nm
Act like water reservoir

w/c=0.42 &100 days older samples:
Powers Brownyard's model
gel pore water only!

Chemically bond water

Capillary pores
Diameter > 10nm
Discontinuous for w/c < 0.42

Water mobility in concrete

Largest volume of manufactured material produced on Earth: **1 ton for every person.**

Over **1 trillion dollars** is invested in concrete production…

That is about **1000 ESSs** per year! Compare this with…

Worldwide **semiconductor industry: 213 billion U$ /year** and the **bank bailouts in the US: 2.7 - 3.6 trillion U$**

The **cement industry produces 5-7% of global CO_2** emissions, which is linked to climate change!!!

Diffusion Model

$$\Gamma_T(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0} \quad \text{and} \quad D_t = \frac{L^2}{6\tau_0}$$

17966 J. Phys. Chem. B 2006, 110, 17966−17976

Water Dynamics in Hardened Ordinary Portland Cement Paste or Concrete: From Quasielastic Neutron Scattering

Heloisa N. Bordallo,[*,†] Laurence P. Aldridge,[‡] and Arnaud Desmedt[§]

Diffusion Model

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Diffusion Model

Pastes made under different conditions :significantly different diffusivities !

17966 *J. Phys. Chem. B* **2006**, *110*, 17966−17976

Water Dynamics in Hardened Ordinary Portland Cement Paste or Concrete: From Quasielastic Neutron Scattering

Heloisa N. Bordallo,[*,†] Laurence P. Aldridge,[‡] and Arnaud Desmedt[§]

Hindered Water Motions in Hardened Cement Pastes Investigated over Broad Time and Length Scales

Heloisa N. Bordallo, Laurence P. Aldridge, Peter Fouquet, Luis Carlos Pardo, Tobias Unruh, Joachim Wuttke, and Fabiano Yokaichiya

ARTICLE

reorientational motions≃0.3ns

Bulk water can be supercooled to 260K.

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Glassy Nature of Water: Ultra-confinement

White spheres are hydrogen atoms, red are water oxygen, purple are layer oxygen, green are silicon, light blue are layer calcium, and yellow are interlayer calcium. Water molecules are highlighted with a larger size compared to the other elements in the model.

Glassy Nature of Water in an Ultraconfining Disordered Material: The Case of Calcium–Silicate–Hydrate
Mostafa Youssef, Roland J.-M. Pellenq, Bilge Yildiz
Journal of the American Chemical Society **2011** *133*, 2499

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Glassy Nature of Water: Ultra-confinement

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SCIENTIFIC REPORTS

Page views 11,865

OPEN

SUBJECT AREAS:
ENGINEERING
MATERIALS FOR DEVICES

Nano-scale hydrogen-bond network improves the durability of greener cements

DR dk

18. SEP. 2013 KL. 06:30

Sukkerrør kan bane vejen for 'grøn' og stærk cement

Use of Bagasse Ash in Concrete

- Compressive Strength[6]

Cement Replacement (%)	3 Day Strength (MPa)	7 Day Strength (MPa)	28 Day Strength (MPa)
0	20	27	36
5	22	30	42
10	27	35	43
15	28	35	42
20	27	35	40
25	25	32	35
30	20	25	32

[6]Amin, Noor-ul. "Use of Bagasse Ash in Concrete and its Impact on the Strength and Chloride Resistivity."*Journal of Materials in Civil Engineering*. (2010): n. page. Web. 1 Jun. 2012. <http://scitation.aip.org/getpdf/servlet/GetPDFServlet?filetype=pdf&id=JMCEXX000001000001000194000001&idtype=cvips&doi=10.1061/(ASCE)MT.1943-5533.0000227&prog=normal>.

Elastic Incoherent Neutron Scattering

Why are greener cements better?

Diffusion results

	τ_0	D_t
Bulk Water	1.57±0.12	2.49±0.07
OPC Γ	2.1±0.3	2.5±0.4
OPC Γ	32.3±0.5	0.28±0.04
M700 Γ	2.21±0.02	2.49±0.02
M700 Γ	41.9±0.3	0.16±0.01

Both samples contain bulk-like water

The glass-like water is more restricted in the M700 cement

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Why are greener cements better?

Diffusion results

	τ_0	D_t
Bulk Water	1.57±0.12	2.49±0.07
OPC Γ	2.1±0.3	2.5±0.4
OPC Γ	32.3±0.5	0.28±0.04
M700 Γ	2.21±0.02	2.49±0.02
M700 Γ	41.9±0.3	0.16±0.01

Both samples contain bulk-like water

The glass-like water is more restricted in the M700 cement

Why do we want to provide large **Q-range coverage?**

Jacobsen, J. et al.. Sci. Rep. **3** (2013) 2667.

The enigma of dental cements

The National Health Service in England and Wales has reported an annual expense of approximately £320 million in dental restorative work. In Denmark, the public expense on oral care reached €455 million in 2005.

Conventional dental X-rays

X-rays tomography

Neutrons tomography

Benedict Lenhoff, BSc thesis, Johan Jacobsen, Solveig Hedal and Casper Madsen MSc thesis

Objective: control the the liquid (proton) mobility

Hydration Process with Neutrons!

Peterson, Fratini, and many others...

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Hydration process: How does it happen?

- ☑ hydration of the glass particles & release of cations
- ☑ hydrated cations react with the carboxylic group (COO^-): polyacid chains
- ☑ polymeric chains are cross-linked

Benetti, A.R et al. To appear in Sci. Rep. (2015).

Temperature & Time effects: What else can we learn?

IRIS
17μeV

Benetti, A.R et al. To appear in Sci. Rep. (2015).

MIRACLES: Stretching time at ESS

Ruep Lechner – ESS

Ana R. Benetti
Odontology Faculty – KU

Markus Strobl
ESS

Mark Telling
ISIS

Nikolay Kardjilov

Murillo L. Martins, Postdoctoral SwB
Everton C. dos Santos, NTNU-NBI
Marcella C. Berg, NBI-ESS
José Enelditon M. Pereira, SwB
Rosanna Ignazzi, MSc with the ILL
Casper Madsen, MSc
Martin Kjærulf Rasmussen, BSc

Department of Engineering Science

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Revealing physical phenomena in MOFs based on terahertz vibrations

Matthew R. Ryder

Molecular Spectroscopy Science Meeting - 30th January 2015

matthew.ryder@eng.ox.ac.uk

Department of Engineering Science

UNIVERSITY OF OXFORD

Outline of Talk

- Introduction to Metal-Organic Frameworks (MOFs)
- Why MOFs are Important
- Recent Project: THz Vibrations of MOFs
  - Materials
  - Methods
  - Results
- Summary

What are Metal-Organic Frameworks?

- MOFs are microporous crystalline materials.

Ref: Video made by BASF

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Why are MOFs important?

- They can possess extremely high internal surface areas (up to ~10,000 $m^2\ g^{-1}$).
- With just small changes to the building blocks, we can tweak their structure and properties.
- As a result they can become ideal for a multitude of applications.

Ref. M. R. Ryder and J.C. Tan. "Nanoporous metal organic framework materials for smart applications." Mater. Sci. and Tech. 30, 1598 (2014)

Project: THz Vibrations of MOFs

- Materials
  - ZIF-4, ZIF-7 and ZIF-8
- Methods
  - Inelastic Neutron Scattering (INS)
  - Synchrotron Infrared (IR) Spectroscopy
  - Density Functional Theory (DFT)
- Results
  - Lattice Dynamics

M. R. Ryder, *et al.*, Phys. Rev. Lett. 113, 215502 (2014)

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Zeolitic Imidazolate Frameworks (ZIFs)

Chemical compositions and physical data of ZIF structures				
ZIF-n	Composition	Crystal Space Group	Network Topology	Solvent Accessible Volume, %
ZIF-4	$Zn(Im)_2$	*Pbca*	cag	34.31
ZIF-7	$Zn(bIm)_2$	$R\bar{3}$	SOD	26.57
ZIF-8	$Zn(mIm)_2$	$I\bar{4}3m$	SOD	50.38

Inelastic Neutron Scattering (INS)

Spectral Regions

I. 3100-3200 cm^{-1}
- Aromatic C-H Stretching

II. 960-1600 cm^{-1}
- C-C and C-N Stretching
- C-H Bending

III. 420-945 cm^{-1}
- Aromatic Ring Deformations

IV. 0-330 cm^{-1} (0-10 THz) - THz Modes
- Collective Lattice Dynamics

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Synchrotron Infrared (IR) Spectroscopy

Spectral Regions

- 600-700 cm^{-1}
  - Ring Deformations
- 260-330 cm^{-1} (8-10 THz)
  - Zn-N Stretching
- However, the exciting modes are the collective lattice modes…

ZIF-4 - Soft Mode 7 cm^{-1} (0.2 THz)

- Phase transition possibly instigated through the shearing of the 4MR.
- The deformed framework results in a greater solvent accessible pore volume.

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ZIF-4 - Gate Opening 33.1 cm^{-1} (1 THz)

- Larger but fewer solvent accessible pores.

ZIF-7 - Soft Mode 21.8 cm^{-1} (0.65 THz)

- The phase transition of ZIF-7 has been confirmed experimentally.

Zhao *et al*, Chem. Mater. 26, 1767 (2014)

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ZIF-7 - Breathing 21.8 and 49.0 cm^{-1}

- 21.8 cm^{-1} (0.65 THz)
  - Spiral Motion
  - 4MR Shearing
- 49.0 cm^{-1} (1.47 THz)
  - Ligand Wagging

ZIF-8 - Soft Mode 18.9 cm^{-1} (0.57 THz)

- Shows possible phase transition, with the same deformed 6MR as ZIF-7-II.

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ZIF-8 - Shear Deformation 21.6 cm^{-1}

- The 4MR shear mode at 21.6 cm^{-1} (0.65 THz) could explain the mechanical instability witnessed when the material is subjected to ball-milling.

ZIF-8 - Gate Opening 33.4 cm^{-1} (1 THz)

- The gate opening mechanism of ZIF-8 has been confirmed experimentally.

Experimentally Confirmed

Moggach *et al*, Angew. Chem. Int. Ed. 2009

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Summary

- High-resolution neutron and synchrotron vibrational spectroscopy in conjunction with DFT can offer new insights into understanding fundamental lattice dynamics and mechanics of framework materials.
- Collective vibrations and low-energy THz modes elucidate possible unique physical mechanisms: gate-opening and breathing, soft modes (possible phase transitions) and the onset of shear-induced framework instability.
- An undiscovered new phase of ZIF-8 and possibly ZIF-4 have been suggested.
- A selection of the physical phenomena discussed have recently been observed experimentally confirming the validity of the proposed approach for unravelling lattice dynamics.

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TOSCA: an update

Svemir Rudic, Stewart Parker, Pedro Duarte Vaz, Felix Fernandez Alonso

ISIS, STFC, RAL, Chilton, Didcot, UK

Sample changer - upgrade

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The elastic line on TOSCA

10 Hz Chopper

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Double disc chopper

- The existing drive assembly is replaced by a system designed for disc chopper.
- TOSCA can run effectively when TS1 is at either 40 or 50 Hz.
- To be installed Feb 2015.

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TOSCA neutron guide

TOSCA neutron guide

Science & Technology Facilities Council

Acknowledgements

ISIS Choppers Design Group: Clive Smith, Peter Galsworthy

ISIS Instruments Design Group: Simon Waller, Daniel Zacek

Thank you.

Molecular spectroscopy group user representatives:
Sylvia McLain (Oxford)
Christoph Salzmann (UCL)

Please send us feedback, ideas etc!

Discussion points:

(1) Neutrons *plus* other in-situ techniques?
(2) What is the future of the field? Which instruments do we need?

"We still don't understand many of the most fundamental questions. How can we investigate complex materials?"

"As scientists we have an obligation to tackle the important problems of our time."

Imperial College
Water at nanoparticle surfaces
Translational structure
HC layer
water
Radial Distance (Å)
NPT -- 1 bar, 298 K
Water interface
Nanoparticle interface
Intensity (a.u.)
Bulk
Frequency (cm-1)
Shift of stretching modes to higher frequencies => compatible with experiments of the water-air interface using VSFS.
Scatena et al., Science 2001.
Tay & FB: J. Mater. Chem.; J. Am. Chem. Soc.
SHARP

How to measure proton momentum distributions using the VESUVIO spectrometer at ISIS
Change of neutron momentum in the scattering process
Change of neutron energy in the scattering process
Only on VESUVIO!
Inelastic neutron scattering at High energy-high momentum transfer
Probe a particular excitation ---the free particle recoil---:
$\hbar\omega = \frac{\hbar^2 q^2}{2M}$

Universitat d'Alacant
Universidad de Alicante
Synthetic Clathrates
Ineslastic Neutron Scattering
a)
Methane in carbon
Methane Clathrate 40 bar
Methane Clathrate 60 bar
energy transfer [meV]
b)
Methane in clathrate
5 K
20 K
45 K
intensity [a.u.]
energy transfer [meV]
M. Casco et al., Nature Commun. (2015)

Proton conducting perovskite type oxides
Structure (e.g. BaZrO3)
Incorporation of protons
BaZrO3
1. Doping
BaZr1-xInxO3-x/2
2. Hydration
BaZr1-xInxO3Hx

Molecular Spectroscopy Science Meeting 2015

Poster Presentations

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ISIS

DATA REDUCTION AND ANALYSIS USING MANTID

Science & Technology Facilities Council
ISIS

INTRODUCTION

MANTID is a data reduction, analysis and visualisation toolkit for various neutron and muon techniques, this poster gives an overview of its use in the reduction and analysis of neutron scattering data on the indirect inelastic spectrometers at the ISIS facility; IRIS (QENS), OSIRIS (QENS), TOSCA (INS) and VESUVIO (EVS), the analysis of reduced data (in S(Q, w)) from instruments at other facilities such as BASIS and VISION at the SNS as well as it's use in loading simulation data from 3rd party software.

SIMULATION

MolDyn:
Allows import of S(Q, w) and F(Q, t) simulations from nMOLDYN.
Option to symmetrise, crop and convolve with resolution for S(Q, w) workspaces.

DensityOfStates:
Calculates phonon densities of states using the output of a CASTEP simulation.
Option to broaden parks to a given FWHM.
Option to calculate a partial density of states given a list of ions.
Option to scale the contributions of individual ions by their scattering cross sections.

REDUCTION

ENERGY TRANSFER: Conversion of the raw time of flight data to energy transfer using [delta]E = 1/2 m [(L1/t1-2)^2 – (L2/t2)^2].
Where L1 is moderator to sample distance, L2 is sample to detector distance, t1 is the time of flight between the moderator and sample, t2 is time of flight between sample and detector and mn is the mass of a neutron.
Options to sum spectra into groups and normalise to the calibration file.

CALIBRATION:
Correction for detector efficiency and analyser reflectivity, ensuring correct intensity variation over all Q.
RESOLUTION:
Sums all spectra to give the resolution curve in energy transfer.

DIAGNOSTICS:
Performs integration over a time range to get the number of counts as a function of spectrum number for a sample run.

TRANSMISSION:
Calculates the sample transmission as a function of wavelength using the monitor raw data for the sample and background/container run.

SQW:
Converts data which is a function of angle & energy, I(theta,w), into a function of momentum transfer and energy, S(Q,w).

MOMENTS:
Calculates n^th moment of an S(Q, w) workspace.

SYMMETRISE:
Takes an asymmetric reduced file and makes it symmetrical about x=0 by reflecting a portion of the positive energy range such that emin = -emax.

ANALYSIS

ELWIN & MSD FIT:
Performs integration over a specified energy range for each spectrum/Q-value in a series of runs. Default range is the resolution width thus giving elastic intensity.
Fit log(elastic_intensity) vs Q^2 to get the mean square displacement as a function of the run number or temperature.

FURY & FURY FIT:
Uses the fourier transform technique to reduce the equation for measured spectrum I(Q, w) = S(Q, w) convolute R(Q, w) to I(Q, t) = S(Q, t) x R(Q, t), thus deconvolving the resolution.
Fit I(Q, t) to either 1 exponential, 2 exponentials, 1 stretched exponential or 1 stretched and 1 regular exponential.

CONV FIT:
Fit S(Q, w) to either 0, 1 or 2 Lorentzians and a Delta function.

CORRECTIONS:
Calculate the absorption corrections for the sample and, if present, container.
The sample shape can be either a flat plate or a cylinder.
The cross-sections may be input either manually or derived by giving the chemical formula.
Apply the corrections to give the corrected sample scattering, If the corrections file is not specified a simple subtraction is performed.
A scaling factor may also be applied to the container.

BAYES

RES NORM:
Creates a normalisation workspace by fitting each spectrum in the measured resolution data with the resolution function created by Calibration.
The fitted parameters are intensity and a stretch factor for the width.

QUASI:
Lorentzians: Fit data with up to 3 Lorentzians using Bayesian statistics taking into account the resolution. The relative probability is given for each fit of 0 to 3 Lorentzians.
Stretched exponential: Fits the function exp(-sigma*t^beta) to give the parameters sigma & beta.

STRETCH:
A special case of the Stretched Exponential program which plots goodness of fit values over a grid of sigma and beta values to show the correlation between the parameters.

JUMP FIT:
Fit the Q variation of the widths to 4 models: simple Fick Diffusion, Chudley-Elliott model, Hall-Ross model and Teixeira's model for water.
The input can be the fitted widths of either ConvFit or Bayes Quasi.

VESUVIO SUPPORT

Support for the VESUVIO electron volt spectrometer has been added by means of the required algorithms and fit functions required to analyse the data based on the neturon Compton scattering technique.
Namely, most significant additions in supporting VESUVIO are the GaussianComptonProfile and GramChalierComptonProfile fitting functions and CalculateMSVesuvio algorithm for calculating multiple scattering corrections.

NEW FEATURES IN RELEASE 3.3

MULTI DATA FITTING
Allows fitting of multiple spectra using common fitting parameters.

TRANSMISSION TAB ON INDIRECT TOOLS:
Calculates total scattering and transmission for indirect geometry spectrometers by inputting sample cross-sections, chemical formula & thickness
To be used before an experiment to decide on optimum sample thickness.

EXPORTING PYTHON SCRIPTS FROM INDIRECT USER INTERFACES:
Allows the processing steps for a specific tab to be exported to a Python script which can then be laoding back into Mantid and modified.

SUMMARY

Development of MANTID in the near future (from the inelastic perspective) will focus on better integration for the analysis of VESUVIO data and creation of a user interface similar to Indirect Data Reduction to provide a simple interface to the corrections and fitting routines.
Another main focus will be the use of simulation data within MANTID, there is already planned work for the next release to improve the loaders for and analysis routines using nMOLDYN, Sassena and CASTEP simulation data.

Further information and download links for MANTID are available at http://www.mantidproject.org

Mechanical Properties and Elastic Anisotropy of Isoreticular Zirconium Framework Materials

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Introduction

The MIL-140 series are a topical group of porous zirconium (Zr) dicarboxylate based metal-organic frameworks (MOFs). In this work, we have employed density functional theory (DFT) to investigate the detailed elastic behaviour of all four MIL-140 structures.

Fig. 1. Structures of (a) MIL-140A, (b) MIL-140B, (c) MIL-140C and (d) MIL-140D, where the inorganic building units (ZrO polyhedra, shown in green) form 1D chains along the c axis. Color scheme zirconium: green; carbon: gray; oxygen: red; nitrogen: blue; hydrogen: white. The dashed blue lines represent one unit cell.

Young's Modulus

Fig. 2. 3-D representation of the Young's modulus (E) of MIL-140A, where E_{max} is lying on the [001] axes and E_{min} is found in the proximity of the [100] axes.

- All MIL-140 structures are highly anisotropic.
- The general shape of the 3-D elastic response is consistent for each material.
- Increasing the length of the linker lowers the Young's modulus.

Units are in GPa

	MIL-140A	MIL-140B	MIL-140C	MIL-140D
E_{min}	11.3	9.6	4.8	3.0
E_{max}	142.0	126.5	114.0	99.2
AE	12.6	13.2	23.8	33.1

Shear Modulus

Fig. 3. Shear modulus (G) representation of MIL-140B, where the colour coding: blue and green denotes the maximum and minimum moduli respectively, for each (θ, ϕ, χ) point in 3-D spherical coordinates.

- The trend in both maximum and minimum shear moduli are the same as for the Young's modulus.
- Same high values of anisotropy.

Units are in GPa

	MIL-140A	MIL-140B	MIL-140C	MIL-140D
G_{min}	3.2	2.7	1.3	0.8
G_{max}	36.9	32.7	28.7	26.8
AG	11.5	12.1	22.1	33.5

Linear Compressibility

Fig. 4. Linear compressibility (β) representation of (a) MIL-140A, (b) MIL-140B and (c) MIL-140C, where green and red signifies positive and negative values of linear compressibility respectively.

- Does not display the same linear trend in maximum and minimum values.
- Large positive and negative values for MIL-140C due to the flexibility of the linker.

Units are in TPa^{-1}

	MIL-140A	MIL-140B	MIL-140C	MIL-140D
β_{min}	-3.0	0.2	-10.7	1.1
β_{max}	27.8	23.8	54.8	35.4

Poisson's Ratio

- All MIL-140 structures possess directions of negative Poisson's ratio.
- The negative values are located on the [001] axes.

Fig. 6. Poisson's ratio (ν) representation of MIL-140D, where blue signifies the maximum Poisson's ratio and green and red denote the positive and negative minimum Poisson's ratios respectively.

	MIL-140A	MIL-140B	MIL-140C	MIL-140D
ν_{min}	-0.13	-0.15	-0.29	-0.61
ν_{max}	1.11	0.98	1.16	1.37

Summary

- We have demonstrated that DFT (B3LYP) can be used to elucidate the complex elastic behavior of MIL-140 frameworks.
- The maximum and minimum Young's moduli and shear moduli display comparable trends and as a result the extent of anisotropy is almost identical.
- Negative linear compressibility has been reported for both MIL-140A and MIL-140C, suggesting that the rotational flexibility of the linker plays a significant role.
- We show that all MIL-140 structures show negative Poisson's ratios (auxeticity) and that the extent of the behaviour is increased from MIL-140A to MIL-140D.

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Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Instability

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Introduction

Zeolitic imidazolate frameworks (ZIFs) represent a major subfamily of metal-organic frameworks (MOFs). ZIFs combine the thermal and chemical stability of inorganic zeolites with the rich topological diversity and pore size tunability characteristic of MOFs. The structures of ZIFs comprise of tetrahedral metal centres (Mn^{+} = Zn^{2+}, Co^{2+}, Li^{+}, B^{3+}) bridged by imidazolate-derived linkers.

In this work, we have investigated the vibrational properties and fundamental elasticity of three distinct ZIF structures, by the combined use of *ab initio* density functional theory (DFT) [1] in conjunction with neutron and synchrotron spectroscopy.

Fig. 1. Structures of (a) ZIF-4, (b) ZIF-7, and (c) ZIF-8, in which the inorganic building units are represented by the ZnN_4 tetrahedra (in purple). Middle panel shows the imidazole-based organic building units that are bridging the adjacent ZnN_4 inorganic tetrahedra. Right panel depicts the complex pore morphologies and solvent accessible volumes (SAV, denoted by yellow surfaces). Here hydrogen is omitted in the framework structures for clarity. Color scheme adopted is zinc: purple; carbon: gray; nitrogen: blue; hydrogen: white.

Inelastic Neutron Scattering (INS)

Fig. 2. INS spectra in the regions of (a) 0-200 cm^{-1} with linear scaling to highlight the fine features, and logarithmic scaling for (b) 200-4,000 cm^{-1}. Comparison of experimental (in blue) and DFT theoretical spectra (in red) for ZIF-4, ZIF-7, and ZIF-8. The theoretical spectra include overtones to the 10th order.

- INS results show excellent agreement between experiment and theory.
- Double peak located ~ 600 cm^{-1} in both spectra is due to Zn-N vibrations.
- Theoretical spectra include overtones to the 10th order.

Synchrotron Infrared (IR) Spectroscopy

Fig. 3. IR spectra in the region 25-700 cm^{-1} region: (a) Experimental spectra of three ZIFs, and comparison of experimental and theoretical (DFT) spectra for (b) ZIF-4 and (c) ZIF-8. An empirical 10.0 cm^{-1} FWHM Lorentzian line shape has been applied to the theoretical data to aid in comparison.

- IR results show excellent agreement between experiment and theory.
- The peaks in the 275-325 cm^{-1} region for all structures are due to Zn-N stretches.
- Intensity variation witnessed around 700 cm^{-1} is explained by the beam splitter used.

DFT Calculations (PBE-D)

Fig. 4. Low-energy THz vibrations of ZIF-4 viewed normal to the 4- and 6-membered ring (MR) orientations. (a) Phase transition mechanism facilitated by lattice distortion from the shearing of 4MR, in which negative shear stresses -τ generate elongated 6MR, and vice versa. (b) Gate-opening mechanism, red arrows designate collective dynamics that resulted in a increased pore cavity.

- The mode resembling a new phase of ZIF-4 results in a greater accessible pore volume.
- This mechanism, in conjunction with the gate-opening mode could explain the anomalous gas adsorption.

- For ZIF-7 we have discovered at least four distinctive modes associated with gate-opening and/or framework breathing motions, located at 0.65, 1.47, 2.01 and 4.61 THz. Two examples are illustrated in Fig. 5(b) and (c).

Fig. 5. Low-energy lattice dynamics in ZIF-7. (a) Phase transition in agreement with recent experiment. (b) Breathing mode accommodated by collective 6MR spiral 'screw' motion accommodated by 4MR shearing. (c) Breathing mode *via* synchronous flapping of the organic linkages.

- We have discovered that a low-frequency mode is observed that may explain the phase transition observed when ZIF-8 is subject to a high pressure.
- The new phase we predicted on the basis of terahertz vibrations strongly resembles that of the ZIF-7-II phase (Fig. 5(a)).
- We further identified a gate-opening mode, explaining why such a lattice motion can facilitate the process of gas adsorption.

Fig. 6. Low-frequency lattice dynamics in a sodalite cage of ZIF-8, corresponding to its cubic unit cell. (a) Phase transition via elongation of 6MR topology. (b) Shear deformation of 4MR. (c) Gate opening of pore apertures.

Summary

We demonstrate that high-resolution neutron and synchrotron vibrational spectroscopy in combination with *ab initio* density-functional theory opens up new opportunities to understanding fundamental lattice dynamics of nanoporous ZIF and MOF materials.

Our work shows, for the first time, that collective vibrations and low-energy THz modes offer insights into many possible and competing pathways governing unique physical mechanisms in ZIFs, including gate-opening and breathing phenomena, phase transitions, and onset of shear-induced structural instabilities.

The results are very promising as a selection of these physical phenomena have recently been observed experimentally, confirming the validity and robustness of our computational approach.

The methodologies being developed here can be employed for studying other families of MOFs and associated framework materials, especially for predicting and tuning their multifunctional properties central to emerging technological applications [2].

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FABADA into MANTID: A model selection case

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THE METHOD

Bayes Theorem (*applied to fitting*)

Relates the probability that an hypothesis is true given a set of data P(H|Data) (what we want)

with the probability that you get some data, given an hypothesis P(Data|H) (What we measure)

P(H) is the prior knowledge about your hypothesis, P(Data) is a normalization constant

$$P(H|Data) = \frac{P(Data|H)\,P(H)}{P(Data)} \propto P(Data|H)$$

T. Bayes

...in our case, no prior information will be supposed

Bayesian versus Frequentist

(related to fitting)

Frequentist	Bayesian
We get „values" for parameters ($P_i \pm \varepsilon_i$) and for χ^2	We get Probability Distribution Functions (PDF) for parameters **and for χ^2**
Supposes a single minimum for χ^2 (P_i) and quadratic in all parameters	No suppositions are needed
Model selection only possible if conditions above are fulfilled	Model selection always possible, taking only data into account.
Least Square can get stuck in local minima	Fitting procedure does not get stuck

What is hidden behind the ubiquitous χ^2 ?

If we *suppose* a Gaussian probability distribution of data (D_i) around the values calculated with a fitting function (H_i), with a determined combination of parameters (your hypothesis):

$$P(H|Data) = \prod_{i=1}^{i=Ndata} P(H|Data_i) = \prod_{i=1}^{i=Ndata} \frac{1}{\sigma_i\sqrt{2\pi}} e^{-\frac{(H_i-D_i)^2}{2\sigma_i^2}}$$

Let's define now the likelihood as P(H|Data), then its logarithm:

$$\log L \propto \sum_{i=1}^{i=Ndata} -\frac{(H_i-D_i)^2}{2\sigma_i^2} = -\chi^2/2$$

Therefore, χ^2 is a measure of the likelihood of our hypothesis. But, in fact the supposition that data (D_i) are distributed as a Gaussian centered in the calculated values (H_i), is only valid for high count rates. ***For low count rates we should use the Poisson distribution, and then***:

$$\log L = \sum_{i=1}^{i=Ndata} \log[P(H|Data_i)] = \sum_{i=1}^{i=Ndata} \log\left[\frac{e^{-H_i} H_i^{D_i}}{D_i!}\right] \propto \sum_{i=1}^{i=Ndata} [-H_i + D_i \cdot \log H_i]$$

Fortunately, spectrometers have usually high enough count rates, and the χ^2 approximation is true. However, understanding what is χ^2 allows us to use different suppositions about how our data are distributed. Therefore, what is hidden behind χ^2 is nothing more than **...PROBABILITY!**

Bayes at work: The Markov Chain Monte Carlo Method

Finding the best fit to data means finding the maximum Likelihood, which in the case of Gaussian distribution is finding the minimum in the $\chi^2(P_i)$ function, where P_i are the values for every parameter of the fitting function.

If we have a set of parameters (P_i^{old}) and we randomly generate a new set of parameters (P_i^{new}), we will accept this new set with a probability:

$$\frac{prob(P_i^{new}/Data)}{prob(P_i^{old}/Data)} = e^{-\frac{(\chi^2_{new}-\chi^2_{old})}{2}}$$

Therefore we "explore" the surface $\chi^2(P_i)$ having into account the probability that data are described by the fitting function (or hypothesis), similar to a Monte Carlo simulation where Energy is χ^2 and error is temperature. That has some advantages:

All $\chi^2(P_i)$ compatible with data are explored, **without** making any assumption about how the minimum in $\chi^2(P_i)$ depends on parameters (even not supposing that here is a single minimum!)

Correlations between parameters are naturally taken into account.

We obtain the Probability Distribution Function (PDF) of parameters (containing much more information that simply $P_i \pm \varepsilon_i$)

Model selection is easily done **without** making any assumption on $\chi^2(P_i)$, and obtaining (again) a PDF, which can reveal more than one minimum in $\chi^2(P_i)$,i.e. more than one description of data.

A CLASSICAL EXAMPLE[1] : How many lines are there?

1.- D. S. Sivia and C. J. Carlile J. Chem. Phys. 96 (I), 1 January (1992).

QENS data generated with 3 lines

Syntethic QENS data have been generated so that three processes describe the material dynamics. Generated data has been convoluted by a Gaussian resolution. Fittings were performed using FABADA into MANTID framework.

Model Selection

We obtain the markov chain containing all possible values of χ^2 and parameters compatible with data and error. Model selection is performed by the maximum of χ^2 PDF not by the minimum χ^2 . We see that the bayesian approach correctly obtains that the most probable number of lorentzians is 3.

Parameter estimation

*We obtain **Probability Distribution Functions (PDF)** for each parameter P, instead of P±δP. As an example we show the PDF's associated to two parameters:*

The PDF can be "nice" (Gaussian)..

Or can be non-gaussian, resulting in a non-symmetric error bar

*But **no supposition** has been made for them (in classical fittings it is **imposed** to be a Gaussian)*

Parameter correlation

We can quantify correlation between variables using the mutual information: $MI = S(x) + S(y) - S(x,y)$

Where $S(x) = \sum_{\forall x} P(x)\ln P(x)$ and $S(x,y) = \sum_{\forall x,y} P(x,y)\ln P(x,y)$

We calculate MI for all combinations of two parameters

*Mutual information has also in to account **non linear correlations**!!*

Technical details: *L.C. Pardo et al. Phys. Rev. E. 84, 046711 (2011); L.C Pardo et al. J. Phys.: Conf. Ser. 325, 012006 (2011)*
Real data fits: *The program has been already used in many application ranging from astronomy (G. Sala et al.The Astrophysical Journal, 752:158, 2012), to QENS data (M. Rovira-Esteva et al. Phys. Rev. B 81(9) 092202, 2010), diffraction (M. Rovira-Esteva et al. Phys. Rev. B 84, 064202, 2011) or dielectric spectroscopy (J. C. Martínez et al. J. Phys. Chem. B 114 6099, 2010)*

Molecular structure of disordered Ru-Ru-Co polymers

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During the last years the Romerosa's group of the university of Almeria have generalized the synthesis of a new family hetero-organometallic polymers where PTA (1,3,5-triaza-7-phosphadamantane) is acting as bidentate, bridging ligand.[1]
Herein we present a structural study by means of simultaneous Raman and inelastic neutron scattering (INS) spectroscopy of the organo-heterometallic Ru Ru Co based polymer $\{[\{(PTA)_2CpRu\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2\}\text{-}\mu\text{-}CoCl_3\text{-}]\bullet[(PTA)_2CpRu\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2]\bullet 16\ H_2O\}_n$ (1a) and of its dehydrated derivative $\{[\{(PTA)_2CpRu\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2\}\text{-}\mu\text{-}CoCl_3\text{-}]\bullet[(PTA)_2CpRu\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2]\}_n$ (1b).
Upon dehydration 1a loses its crystallinity and gives the amorpous 1b. Surprisingly the loss of crystallinity is not followed by any change in the macroscopical features of the single crystals (transparency, shape, brilliance). When, as in this case, diffraction methods cannot be used for a structural elucidation, Raman and INS together with DFT calculations showed up to be a very powerful method to characterize disordered systems.

Figure 2. Molecular packing of 1a. The highlighted areas contain the most characteristic structural features, whose vibrations are shown in figures 3 and 4.

Figure 1. Dehydration of polymer 1a.

Figure 3. Top: single crystal X-ray diffraction of 1a (hydrogens and solvent molecules omitted for clarity).Bottom: INS and Raman spectra of 1a and 1b at 10K measured on TOSCA.
It is appreciable how in both INS and Raman spectra, the terahertz region of 1a and 1b is almost identical, meaning that the polymeric structure is not lost after dehydration.

Figure 4. The water molecules hosted in 1a tunnels, are actively sustainig the packed structure through a web of hydrogen bonds. The signal of water, which remains after subtraction of 1b to 1a INS spectra, can be associated with hydrogen bonding of water with PTA, as showed by calculated vibration frequencies (B3LYP/3-21G).

Figure 5. PC (Figure 5a) and NC (Figure 5b) stretches of the PTA ligand. Raman and INS spectra ofo 1a and 1b measured on TOSCA at 10K. Symmetric stretches are associated with N and P centred umbrella motions, which make the INS signal more intense with respect to the asymmetric stretches. We found all the signals splitted with respect to the starting material $[\{(PTA)_2CpRu\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2\}OTf$ (dashed line) sdue to the cobalt coordination and the water hydrogen bonding.

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Application of inelastic neutron scattering to studies of CO_2 reforming of methane over bimetallic Ni-Co/Al_2O_3catalyst

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Introduction

❖ CO_2 dry reforming of CH_4 (DRM) on Ni^0-based catalysts plays important roles for energy and environment sustainability since it converts two major greenhouse gases into valuable Syngas while Ni^0 catalysts suffer from surface carbon deposition (coking).

❖ Ni-based bimetallic catalysts usually exhibit enhanced DRM performance while their metal interaction and coking-resistance nature remain unclear.

❖In this work, we developed bimetallic Ni-Co/Al_2O_3 catalysts with varying Ni/Co ratios via an innovative synthesis strategy and comparatively investigated their DRM performance under accelerated coking reaction conditions. The deposited carbon species and the nature of Ni-Co bimetallic effects were unveiled Inelastic Neutron Spectroscopy combined with other characterisation techniques.

XRD Analysis

Fig.1 XRD patterns of reduced Ni/Al_2O_3, Ni-Co/Al_2O_3 and Co/Al_2O_3 catalysts

Table 1 The structure parameters of metallic Ni-Co alloy, Ni and Co species on the catalysts

Sample	Metal Lattice Parameter (nm)	mean crystallite size (nm)
Ni/Al_2O_3	0.352	26.86
8Ni2Co/Al_2O_3	0.353	24.37
4Ni6Co/Al_2O_3	0.353	26.67
Co/Al_2O_3	0.354	27.71

❖ Ni-Co alloys were formed in broad Ni/Co ratio range as evidenced by the gradual shift of metal Bragg diffraction shown in Fig.1.

Fig.2 XRD patterns of spent Ni/Al_2O_3, Ni-Co/Al_2O_3 and Co/Al_2O_3 catalysts

❖ Graphitic carbon was observed from XRD patterns of Ni and 8Ni2Co/Al_2O_3 catalysts while negligible on samples with higher Co concentration, suggesting Co-rich alloy catalysts are more resistant to coking.

Temperature-programmed Reduction

Fig. 3 The H_2-TPR profiles of fresh Co/Al_2O_3, Ni-Co/Al_2O_3 and Ni/Al_2O_3 catalysts

❖ Multi-stage reduction was observed for the monometallic and bimetallic catalyst precursors. The high-temperature reduction was not significantly influenced by cobalt.

❖The reduction of NiO species was shifted gradually to lower temperature as increasing Co concentration in the bimetallic catalysts, suggesting that metallic Co could promote NiO reduction.

TPO analysis

Fig.4 TPO profiles of Ni/Al_2O_3, 8Ni2Co/Al_2O_3, 4Ni6Co/Al_2O_3, and Co/Al_2O_3 after 6 h DRM

❖ Two types of carbon species were lay down on the surface of the catalysts.

❖Total amount of carbon deposition decreased as increased Co content, revealing Co can depress coking.

❖ The lower reaction temperature accompanying with increasing Co content indicated that Co changed carbon species deposited on the surface of corresponding catalysts..

Raman analysis

Fig. 5 Raman spectra of coke deposits over spent catalysts after 6 h reaction.

❖ G band, locating at 1580cm^{-1} was attributed to single crystal graphitic carbon, while D band centering at 1320cm^{-1} arose from structure imperfection, including defective existence, polycrystalline graphite and other carbonaceous materials.

❖ The intensity and bandwidth of G band became weaker as improving Co content, indicating that Co may depress formation of graphite but cannot reduce amorphous C.

Low-Energy INS Spectra Analysis

Fig. 6 INS spectra of reacted catalyst after 6 h reaction of a 1 : 1 mixture of CH_4 and CO_2 at 898 K using the MAPS spectrometer operating an incident neutron energy of 2017 cm^{-1} (the C–H and O–H stretch region).

❖ INS results evidenced carbonaceous species were formed on the spent catalysts;

❖The weak band centered at 1170 cm^{-1}, assigning to an aromatic in-plane C–H bending mode, while small peaks locating at 1430 cm^{-1} attributing to a C–H deformation modes, respectively.

High-Energy INS analysis

Fig. 7 INS spectra of catalysts after 6 h dry-reforming reaction (CH_4:CO_2 =1 : 1 vol) at 898 K using the MAPS spectrometer with incident neutron energy of 4048 cm^{-1}(the fingerprint region).

❖ The peaks centering at 3652~3700 cm^{-1} was assigned to the vibration of hydroxyl group resided on the catalyst support;

❖ A very small feature observed at 2900 cm^{-1} on the Co/Al_2O_3 due to C–H stretch of residual aliphatic hydrocarbon, and the vibration of aromatic C-H vibration was observed at 3031cm^{-1} in the Ni/Al_2O_3.

❖The C-H vibration in alloy catalysts shifted to low wavenumber, revealing that cobalt favored the deposited aromatic carbonaceous to evolve into aliphatic mode;

❖The C-H peak areas declined as increasing Co content, revealing Co dominated the anti-coking property of the alloy catalysts in DRM.

Conclusions

❖ Carbon deposition closely related to the cobalt concentration in the bimetallic catalysts that are more resistant to coking in dry reforming due to Ni-Co interaction in the alloy.

❖ Different carbonaceous species distributed over various metal surface, suggesting that carbon formation is related with electronic and geometric structure of surficial metal.

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UNIVERSITY OF Southampton

Science & Technology Facilities Council Rutherford Appleton Laboratory

INELASTIC NEUTRON SCATTERING AS A CHARACTERIZATION TOOL OF C-H··· O HYDROGEN BOND DYNAMICS

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In the last few years, the role of the C–H···O hydrogen bonds in crystal engineering and molecular recognition processes has aroused considerable interest [1], and evidence has been accumulated to show that C–H···O hydrogen bonds play a significant role in determining molecular conformation [2], in molecular recognition processes [3], in the stabilization of inclusion complexes [4], and even in the activity of biological macromolecules [5].

Vibrational spectroscopy is a useful tool for the study of weak intermolecular interactions. In particular, Raman spectroscopy has been successfully used to characterize the nature and properties of C–H···O bonds [6-9]. The presence of hydrogen-bonded dimers can be inferred from the changes in frequency and shape of the bands assigned to the donor and acceptor groups. However, in the study of hydrogen bonds, both far-IR and Raman spectra present limitations in what concerns the low wavenumber modes, such as the H···O stretching mode (νH···O). Inelastic Neutron Scattering (INS), due to its particular sensibility to the vibrational motions of the hydrogen atoms, presents unique capabilities to assess this question. This work reports the study of C–H···O hydrogen bonds in model organic compounds such as dihydrocoumarin and cyclopentanone.

Raman Spectroscopy

The Raman spectrum of cyclopentanone, in the carbonyl stretching mode (νC=O) region, presents a band envelope composed of two individual bands. The presence of this pair of bands can be interpreted in terms of a intermolecular association through hydrogen-bonding to the carbonyl oxygen atom. The higher wavenumber band component is assigned to the free carbonyl group, and the lower wavenumber band component is assigned to the hydrogen bonded carbonyl group.

Raman spectra in the νC=O region. Solutions of dihydrocoumarin in CCl_4, with mole fractions ranging from x=1 to x=0.01.

The presence of at least three bands under the band envelop is evident.

Inelastic Neutron Scattering (INS)

In order to inspect whether and to what extent the interactions through C-H···O can be reflected in the low frequency vibrational modes the INS technique was applied. The cross-section of ^1H dominates in relation to other nuclei, so in INS spectra only the modes with contribution from H atoms are observed.

INS spectra of cyclopentanone solutions in CCl_4. The bands marked with arrows present concentration-dependent intensities, an effect ascribed to the presence of a self-association equilibrium based on C-H···O hydrogen bonds.

Comparison of experimental INS spectra of dihydrocoumarin solutions in CCl_4 and simulated INS spectra for monomer and dimer. The simulation was obtained using the a-CLIMAX program and ab initio vibrational modes. Some intensity patterns of pure and diluted solutions can be related with dimer and monomer spectra, respectively.

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Inelastic Neutron Scattering Characterization of Activated Carbons

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Background

• Hydrogen has been proposed as an energy vector to chemically store energy from renewable sources to be used in mobile applications or to power the grid. The aim is to reduce oil and gas consumption, helping towards the reduction of emission of global warming gases as well as improving air quality. However, hydrogen storage issues, such as low gravimetric storage density needs to be addressed. One possible solution could be to use nanoporous materials to physically adsorb hydrogen at low temperatures and moderate pressures.

Scope

• Get a better understanding of how hydrogen interacts with nanoporous materials and its state. This will help designing better materials in the future.
• Check for further evidence of solid-like hydrogen (detected by the appearance of a peak at 14.7 meV) in several nanoporous materials (activated carbons), determine which intrinsic properties contribute to the appearance of this phenomena and to test the model we use.
• 4 Activated carbons (TE7_20, TE3, AX-21 and OLC-1750) have been tested at 0 and 1 bar of hydrogen by using INS in TOSCA, located in ISIS, Rutherford Appleton Laboratories, Oxfordshire, UK.
•Materials were previously characterized and tested with hydrogen at high pressures by using an ASAP 2020 and an HTP-1.

INS and hydrogen data:

•Each material was previously re-degassed under vacuum at 150 °C overnight and tested at 0 and 1 bar for 12 h at 77 K in TOSCA. The materials were previously tested with hydrogen at 77 K.

AX-21 INS plots at 0, 1 and 1-0 bar at 77 K (-3 to 500 meV) and hydrogen adsorption test plots at different pressure ranges at 77 K

Modelling

• The experimental excess H_2 uptake is modelled using a method developed at the University of Bath.
• This considers that H_2 adsorbate has a constant density, ρ_A, with the remaining pore space containing bulk hydrogen with density ρ_B.
• The link between these two densities is represented by a pore filling equation, θ_A; we use the Tóth isotherm for this.

$$n_E = (\rho_A - \rho_B)\theta_A V_P \qquad n_A = \rho_A \theta_A V_P = n_E + \rho_B \theta_A V_P$$

$$n_T = \rho_A \theta_A V_P + \rho_B V_P (1-\theta_A) \qquad \theta_A = bP/[1 + (bP)^c]^{1/c}$$

Where:
V_P: pore volume
n_E^{max}: maximum hydrogen excess
P_E^{max}: pressure at which the maximum excess is found
P_E^0: pressure at which the excess is predicted to be 0
n_A^{max}: maximum amount of hydrogen predicted to be in the material, being the pores fully filled with adsorbate

Graph showing key parameters. experimental points (black), excess isotherm (n_E, blue), absolute (n_A, red) and total modelled isotherms (n_T, green), including prediction bands (dashed lines).

Characterization and data analysis

•The materials were characterized by using nitrogen
•The area in region around the 14.7 meV (background subtracted) was fitted to a Gaussian to determine the area
•The hydrogen isotherms at high pressure were fitted to the model to predict the adsorbate density within the pore

AX-21 1-0 bar at 77 K data (10-20 meV range) area

Material:	14.7 meV area peak (Gauss):	BET ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Microporous pore volume (DR) ($cm^3 g^{-1}$)	Pore diameter (Å) (DFT, N_2)
TE3	0.9561 ± 0.0742	1567 ± 21	1.24	0.73	5.1, 8.1, 12 and 15
OLC-1750	0.0605 ± 0.0109	321 ± 0.66	1.29	0.13	11
AX-21	0.4533 ± 0.0243	2524 ± 47	1.82	1.97	5, 6.8, 8.3, 12, 16 and21
TE7_20	0.7510 ± 0.0436	1234 ± 7	1.33	0.52	5, 6.8, 12 and 15

Characterisation table and area fitting results

Material:	ρ ± error (DR) ($kg\ m^{-3}$)
TE3	78.39 ± 0.25
AX-21	69.04 ± 1.00
TE7_20	67.14 ± 0.78

Predicted adsorbate density by using the model fixing the experimental pore volume (DR)

Pore diameter vs area from the 14.7 meV peak signal for each of the 4 activated carbons

Conclusions

While more materials need to be tested, initial observations are that:

• Results back up the existence of solid-like hydrogen in different activated carbon materials due their pore sizes (ranged between 5 and 6.8 Å), observed by the appearance of the 14.7 meV peak when tested at 77 K and 1 bar.

• OLC-1750, a material with micropores at 11 Å shows no solid-like hydrogen, probably due to weaker van der Waals forces than smaller pores.

•TE3 has the highest 14.7 meV peak signal, being also the material with highest modelled adsorbate density. It shows the narrowest pore distribution and highest pore volume at the lowest pore sizes, confirming the relationship between pore size and solid-like hydrogen signal.

• AX-21 shows however the highest hydrogen uptake and a lower predicted adsorbate density. This shows that it stores hydrogen less efficiently but compensates by having a much higher microporous volume than the other carbons.

Acknowledgements

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Science & Technology Facilities Council

ISIS Deuteration Facility

Peixun Li, Marek Jura

ISIS, Rutherford Appleton Laboratory, STFC, UK, OX11 0QX, peixun.li@stfc.ac.uk

The ISIS Deuteration Facility has now been established and is operational, currently accepting user's proposals. The aim of the facility is to provide ISIS users access to deuterated materials for ISIS experiments. For more information or deuterated materials inquiry, please contact deuteration facility manager Dr Peixun Li directly on peixun.li@stfc.ac.uk.

The Routine Deuterated Materials

Alkyl group (R)	R-OH	R-Br	R-N(CH$_3$)$_3$Br	-N(CD$_3$)$_3$Br	RSO$_3$Na	RSO$_4$Na	(R)$_4$-NCH$_3$Br	RSiCl$_3$
C_8D_{17}	✓	✓	✓	✓	✗	✓	✗	✗
C_9D_{19}	✓	✓	✓	✓	✗	✓	✗	✗
$C_{10}D_{21}$	✓	✓	✓	✓	✓	✓	✗	✗
$C_{11}D_{23}$	✓	✓	✓	✓	✓	✓	✓	✗
$C_{12}D_{25}$	✓	✓	✓	✓	✓	✓	✓	✓
$C_{13}D_{27}$	✓	✓	✓	✓	✓	✗	✓	✗
$C_{14}D_{29}$	✓	✓	✓	✓	✓	✗	✓	✗
$C_{16}D_{33}$	✓	✓	✓	✓	✗	✗	✓	✓
$C_{18}D_{37}$	✓	✓	✓	✓	✗	✗	✓	✓
$C_{22}D_{45}$	✓	✓	✓	✓	✗	✗	✓	✓
2-(C_7D_{15})C_9D_{19}	✓	✓	✗	✗	✗	✗	✗	✗

Alkyl group (R)	ROH	RhE$_3$	RhE$_4$	RhE$_5$	RhE$_6$
C_8D_{17}	✓	✓	✓	✓	✓
C_9D_{19}	✓	✓	✓	✓	✓
$C_{10}D_{21}$	✓	✓	✓	✓	✓
$C_{11}D_{23}$	✓	✓	✓	✓	✓
$C_{12}D_{25}$	✓	✓	✓	✓	✓
$C_{13}D_{27}$	✓	✓	✓	✓	✓
$C_{14}D_{29}$	✓	✓	✓	✓	✓
$C_{16}D_{33}$	✓	✗	✗	✓	✓
$C_{18}D_{37}$	✓	✗	✗	✗	✓

Deuteration Facility

Deuteration laboratory

Deuteration reactor

Non-routine materials

We have made, and are in a position to make, many other perdeuterated and partially deuterated surfactants (e.g. several of the gemini cationic series). We have also made samples of protonated surfactants that are not commercially available. We are occasionally able to make these available on a similar basis to the compounds in the Tables on a collaborative basis.

Case Deuterated Materials Study

Partial deuterated modification of several of the Tweens series

(*Langmuir*, **2014**, *30* , 9741–9751, *J. Phys. Chem.* **B 2014**, 118, 4867–4875).

Proton dynamics in Deuterated and Non-Deuterated alkylammonium nitrate ionic liquids

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INTRODUCTION

Ionic liquids are of interest to chemistry and material sciences because of their designer properties. Protonated ionic liquids (PILs) are excellent proton carriers in fuel cell electrolytes. PILs are formed by the transfer of a proton from a Brønsted acid to a Brønsted base, which means they have a proton available for the formation of hydrogen bonding. Hydrogen bond is a strong directional inductor compared to the interaction of other forces, as Van der Waals interactions, and it has a high relevance in ionic liquid features. But, there is a lacuna in our knowledge of these compounds. In order to separate out different types of molecular motion and understand the contribution of individual hydrogen groups on the N and C atoms, we have studied the proton transfer in a structurally simples alkylammonium nitrate ionic liquids, $[CH_3NH_3][NO_3]$ and $[(CH_3)_2NH_2][NO_3]$ and the partially deuteriated analogues, $[CH_3ND_3][NO_3]$ and $[(CH_3)_2ND_2][NO_3]$.

EXPERIMENTAL

Ionic liquids

a)

b)

Figure 1. Schematic representation of the chemical structure of Methylammonium nitrate (a) and Dimethylammonium nitrate (b)

Instruments

Figure 2. Target Station 1 at ISIS

Figure 3. IRIS. High-resolution spectrometer at ISIS

RESULTS AND CONCLUSIONS

A)

B)

C)

D)

✓ **Methylammonium nitrate**

F)

✓ **Dimethylammonium nitrate**

E)

✓ **Methylammonium nitrate deuterated**

G)

✓ **Dimethylammonium nitrate deuterated**

A)B) Phase transitions of methylammonium nitrate and dimethylammonium nitrate, respectively.
C) Variation of Integrated Elastic Intensity with temperatures of dimethylammonium nitrate and its analogue deuterated.
D)E) QENS spectrum of a completely protonated methylammonium nitrate sample, measured between -240 °C and 115 °C and its analogue deuterated, respectively.
F)G) QENS spectrum of a completely protonated dimethylammonium nitrate sample, measured between -240 °C and 80 °C and its analogue deuterated, respectively.

QENS spectra give qualitative information on the dynamic behaviour of the ionic liquids studied. There is a strong elastic signal, due to the existence of slow dynamic processes. In addition to elastic scattering, even at the lowest temperature probed -240 °C, a broad quasielastic component is observed. The quasielastic component is temperature dependent: molecular motion becomes faster [as indicated by the progressive broadening of the $S(Q,v)$ data] with increasing temperature. From the variation of integrated elastic intensity with temperatures (C), we find that the nature of molecular motions are temperature dependent, and the difference between elastic intensity of analogues protonated and deuterated, is higher with the increasing temperature.

FUTURE WORK

I have submitted a proposal following the results discussed in this poster . Aim of this proposal is to perform a temperature dependent QENS study of ethylammonium nitrate and its partially deuteriated analogue ($[Et_DNH_3][NO_3]$), which will permit to characterise the classical hopping mechanism in the picosecond time domain.

CONTACT

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Vibrational characterisation of high surface area carbons through DRIFT, Raman and INS: an innovative method

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Material and Issues

High-surface-area carbons are industrially relevant materials whose properties depend on morphology, texture and surface features. For catalysis they are usually employed as supports for noble metal nanoparticles; their surface morphology and functionalization are fundamental to confer the desired properties to the deposited nanoparticles (shape, size distribution, surface coverage). This class of materials usually have surface areas up to 1500 $m^2 \cdot g^{-1}$ and a total pore volume of about 1 $ml \cdot g^{-1}$. The detailed characterization of this class of materials is a fundamental step for understanding their potential in a variety of applications. Unfortunately, many characterization techniques, and in particular spectroscopies, are difficult to be applied on carbons, due to the intrinsic strong interaction of carbons with electromagnetic radiation.

Objectives

We want to define structural and surface properties of high-surface-area carbons with the help of a multitechnique approach, based on the synergic combination of three vibrational spectroscopies: 1) Inelastic Neutron Scattering (**INS**); 2) back-scattering **Raman** spectroscopy; 3) FT-IR diffuse reflectance spectroscopy (**DRIFT**).

Experimental

2 different samples of activated carbons (**CW** and **chemi**), provided by Chimet S.p.A., were analysed:

	CW	chemi
Activation	Steam, High T	H_3PO_4, High T
Particle size (μm)	28,3	22,5
Surface area ($m^2 \cdot g^{-1}$)	1000	1500
Total pore volume ($ml \cdot g^{-1}$)	0,6	1,1

INS spectra were collected at ISIS on TOSCA instrument in a 0-4000 cm^{-1} range over 8 h of accumulation. *Raman* spectra were collected averaging 20 acquisition of 50 s per each using a Renishaw inVia Raman microscope instrument equipped with 514 nm and 244 nm lasers. *DRIFT* was collected with a ThermoFisher Smart accessory averaging 1024 spectra on a Nicolet 6700 instrument, at 4 cm^{-1} of resolution; data are reported in Kubelka-Munk.

Inelastic Neutron Scattering (INS)

This technique eliminates the problem of radiation interaction and is sensitive to vibrations involving hydrogen including species, which are abundant on carbons surface. Data for both samples (weighted on the sample mass) show vibrational modes related to H atoms: a band at 3060 cm^{-1} due to ν(C-H) stretching; a broad band between 1000 and 1500 cm^{-1} due to δ(C-H_n) bending modes; the bands between 900 and 700 cm^{-1} due to δ(C-H) vibrations out of plane. In addition, we observe a sharp band (*) at 950 cm^{-1}, which is still under debate. Finally δ(O-H) of some ligand (4) is present between 500 and 600 cm^{-1}. The 2 spectra are very similar, except for intensity, which can be explained only partially in terms of surface area; chemi has more terminations than CW, although qualitatively they are the same.

Raman spectroscopy

This technique, differently from FT-IR spectroscopy, is sensitive also to vibrational modes that do not involve a change in the dipole moment, and measures the radiation coming from the disexcitation of electronic transitions of different chemical species. For this reason outcomes are strongly affected by the excitation energy.

The spectra collected give us the following information:

- for both samples G peak does not disperse in function of λ, a typical behaviour of nano-graphitic domains;
- in both cases, green laser excitation source let appear the I peak at 1150 cm^{-1}. This peak is typical of sp^3 phase of ta-C in coexistence with sp^2 phase;
- in UV-Raman, D peak is present for chemi only, suggesting it has a larger topological disorder;
- In Vis-Raman, I(D)/I(G) is different for CW and chemi, but the explanation is not straightforward.

FT-IR diffuse reflectance spectroscopy (DRIFT)

This technique is sensitive to vibrations involving a dipole change and, collecting backscattered radiation, partially avoids the problem of strong absorption by the sample.

From IR spectra is possible to identify the following species in both samples: a band around 1600 cm^{-1} due to ν(C=C) stretching of conjugated sp^2 bonds; a broad band centered at 1250 cm^{-1} related to δ(C-H_n) bending modes; a series of bands between 900 and 700 cm^{-1} (3 for chemi, 2 for CW) associated to vibrations out of plane δ(C-H) of condensed aromatic rings edges; mainly for chemi, a band at 1710 cm^{-1}, related to δ(C=O) stretching mode. Vibrational modes related to H-containing species are visible also with INS technique, with exception for the band at 950 cm^{-1}.

The spectra of the 2 samples are qualitatively similar, but have a different intensity, suggesting that chemi is more defective than CW.

Conclusions

Matching the data coming from these techniques is possible to affirm that: **1) Raman gives us an idea about topological disorder of the samples; 2) DRIFT reveals low differences in terminations for CW and chemi samples, spectrum intensity directly depend on defectivity of the samples; 3) INS spectra, sensible only to sample mass and element cross section, show the same kind of termination for both samples too, but intensities are not fully explained in terms of surface area.** The techniques used, when considered individually, fail to provide a complete picture about the samples; our aim was also to provide a characterisation methodology able to fully understand the different aspect of this fundamental materials.

Science & Technology Facilities Council
ISIS

Materials Characterisation Laboratory

Dr Gavin Stenning

The MCL is part of the ISIS support lab team to provide support for beamline experiments. The Materials Characterisation Laboratory boasts a wide range of instrumentation, detailed below, for determining sample structure, screening and purity, as well as studying physical properties of materials. For more information or to book instrument time please contact Lab Manager Dr Gavin Stenning directly on gavin.stenning@stfc.ac.uk

X-ray Diffractometer

•Rigaku SmartLab X-ray diffraction system
•Uses SmartLab Guidance software to assist with experiment
•Can be used for thin film and powder diffraction
•Can be configured as a reflectometer
•Variable temperature stages (12-1200 K).

Powder XRD

XRD Patterns show rhomobohedral phase contaminant transforms completely to monoclinic phase at low temp

Bull *et al.*, J Phys Condensed Matter *in press*

Single Crystal Diffractometer

•Oxford Diffraction Gemini Single Crystal Diffractometer
•Available for sample screening, structure analysis and other crystallographic experiments
•Goniometer incorporates rotatable beam stop and 120x magnification video microscope
•Open flow liquid nitrogen (90-300K) and liquid helium (<10-90K) available

X-ray Reflectivity

XRR combined with PNR showing variable thickness EuO thin films Barbagallo *et al.*, Phys. Rev. B 84, 075219, 2011

Microscopy

MFM images of a 400-nm-pitch as-grown square ice array.

Langridge, *et al.*, Nature Physics 7, 75–79 (2011)

Physical Property Measurement System

•Quantum Design PPMS-9
•To carry out measurements including heat capacity, resistivity, VSM and ACMS, AC Transport.
•Helium-3 cooled for operation to 0.5K
•9 Tesla magnetic field

Magnetic Property Measurement System

•Integrates SQUID detection system and precise temperature control unit
•Max Sample Size: 9mm
•Field Uniformity: 0.01% over 4cm
•Temperature Range: 1.8 – 400K
•Maximum Field Strength: 7 Tesla
•Offers DC or RSO transport

Single Crystal XRD

X-ray crystal Structure of an Indium Chloride Thioether Complex

Jura *et al.*, Chemistry of Materials 25, 1829–1836, 2013

Magnetometry

Thin film of Nb on Si grown by sputtering. Hystersis showing development of superconducting thin films for RF cavities

S. Wilde *et al.*, IPAC Conference, 2014

Atomic Force Microscope

•Vecco – Dimension 3100 Scanning Probe Microscope
•Accepts Samples up to 200mm for standard and advanced SPM imaging
•Can be used in Magnetic Force Microscopy (MFM) mode to map magnetic force gradient above sample surface

X-ray Fluorescence

XRF data was used to accurately determine $KNbO_3$ levels of doping in a BiFeO3 series of samples studied for multiferroic behaviour on the WISH Instrument

J Mater Chem C, 2, 3345-3360, 2014

X-ray Fluorescence Spectrometer

•PANalytical Epsilon XL
•Performs non-destructive quantitative analysis of elements from sodium to uranium
•Suitable for concentrations down to ppm levels

Science & Technology Facilities Council
ISIS

Dr James Taylor
and James Crosland

ISIS Hydrogen and Catalysis Laboratory

The hydrogen and catalysis lab at ISIS offers a range of equipment optimised for the study of hydrogen storage materials and catalysts. It features appropriate ventilation for working with pressurised H_2 gas and other flammable gasses. Instrumentation is available to characterise H_2 storage materials including adsorption and desorption isotherms, porosity measurements and H_2 uptake. Spectroscopic equipment is also available for sample characterisation. For more information please contact Dr James Taylor (james.taylor@stfc.ac.uk).

Bruker Vertex 80v FTIR

The Vertex is a high resolution IR spectrometer, featuring evacuated optics to eliminate atmospheric moisture absorptions for high sensitivity and stability.

- Specac liquid flow cell with operation up to 250˚C and a Pike gas flow cell
- Optimised for use in mid-IR
- DigiTect MCT liquid nitrogen cooled detector
- Resolution >0.2 cm^{-1} sufficient for ambient pressure gas phase & RT measurements

Hiden Isochema IGA

The Hiden Isochema IGA gravimetric analyser will precisely measure the magnitude and kinetics of vapour-phase samples at controlled temperatures and pressures.

- Operation from -196 to 1000˚C and UHV to 20 bar
- Can be used in conjunction with close-coupled MS
- A second instrument is situated in the experimental halls for analysis during beamline experiments

Bruker Senterra Raman

The Senterra is a high performance Raman microscope spectrometer. It allows measuring spatially resolved Raman spectra and combines this information with high-quality microscopic images of the sample.

- Operation up to 1000˚C with hot stage (vacuum stage available)
- Spatial resolution of less than 1 micron
- Multiple laser wavelengths including 785, 633 and 532 nm

Hiden Isochema HTP (IMI)

The Isochema HTP is a volumetric and thermal desorption H_2 storage analyser. For investigations from surface area determination, high pressure studies, gas storage and separation to high pressure catalysis.

- Operation from 77 to 773 K
- Standard methods or entirely user-defined experiments
- Multi-gas control
- Analysis software with end point detection for sorption processes, reaction kinetics and sample pre-treatment

Recent Innovations

The development of effective hydrogen storage mediums is a significant hindrance to the adoption and development of H_2 as a sustainable energy source. Recent work carried out here at ISIS has shown that in-situ hydrogen generation may be accomplished by catalytic cracking of NH_3 via a stoichiometric decomposition and regeneration cycle of $NaNH_2$. A simple flow reactor setup was used to achieve conversion efficiencies of up to 99.2%. Many catalysts can effectively crack ammonia to release the hydrogen, but the best ones are very expensive precious metals. This new method is different and involves two simultaneous chemical processes rather than using a catalyst, and can achieve the same result at a fraction of the cost. The results show promise that one day ammonia-based transportation should be achievable on a large scale.

W. I. F. David *et al.*, *J. Am. Chem. Soc.*, **2014**
DOI: 10.1021/ja5042836

Comparison of NH3 conversion as a function of reaction temperature (between 250 and 650 ° C) for the blank 46.9 cm3 reactor and 0.5 g of NaNH2, silica/alumina-supported nickel, and alumina-supported ruthenium, at an NH3 flow rate of 60 sccm. The data were fitted to a sigmoidal distribution.

Implementation of a Silicon Energy Analyser on McStas: The Way Forward for OSIRIS

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2.- Instituto de Fusión Nuclear - UPM (SPAIN) 3.- ISIS Facility, Rutherford Appleton Laboratory (United Kingdom)

Introduction

OSIRIS at ISIS is a high-resolution low-energy neutron spectrometer with simultaneous diffraction capabilities. At present, OSIRIS achieves high spectral resolution via the use of a pyrolytic (PG) graphite analyser in near-backscattering geometry in the secondary spectrometer. This analyser occupies half of a 5-m^3 vacuum vessel and it is cooled down to 10 K for optimal performance. In this work, we explore how the spectroscopic performance of OSIRIS could be enhanced via the use of an additional silicon analyser located on the vacant side of the instrument. To this end, we have implemented a new analyser module using the McStas code. This module overcomes current limitations to attain an accurate description of large-area energy analysers of arbitrary shape, thereby paving the way for detailed neutronic studies of indirect neutron spectrometers at pulsed spallation sources.

The analyser pixel model

Silicon is a cubic structure crystal. Its natural growth has a low degree of freedom. Hence silicon crystals achieve better spectral resolution than PG crystals when used as an analyser since they reflect a narrowest neutron energy distribution.
The following table collects silicon crystal-parameters used in the simulations.

Parameter	Value
Lattice spacing	5.43071 Å
Mosaicity	0.1 "
D-spacing spread	1.86e-5
Absorption cross section	0.171
Incoherent cross section	0.004

FROM: Journal of Neutron Research 17 (2014) pp. 63-74

We have focused our interest on the 111-planes of the silicon crystal. These planes reflect neutrons with an energy of 2.08 meV (6.27 Å) at backscattering geometry.

Current limitations

McStas code provides some methods to simulate a large-area energy analyser of arbitrary shape but there are some limitations. One method is to modelate every analyser pixel as an individual McStas crystal component. Then the components must be placed along the arbitrary shape. This is a robust method when the number of crystal is not too high. Otherwise it fails due to *out of memory error* since a common analyser could have thousands of pixels. The other method is to provide an *off* or *ply* geometry externally to the code. This second method is easy to implement. But the crystal lattice-vectors do not follow the curvature of the geometry. Hence 111-planes will not reflect neutrons of 2.08 meV of energy. Therefore another methods need to be developed in order to simulate a large-area energy analyser.

A new method for large-area energy analysers

A new method to approach the large-area energy analyser model of McStas was developed. This method modifies the neutron rays according to the shape of the analyser. It moves and rotates the trajectory of every neutron emerging from the sample. Only a *Single_crystal* component (one analyser pixel) is placed in front of the sample. The aim is that every neutron hits this crystal component (see the figure below). Once the neutron is reflected by the crystal its trajectory is moved and rotated again to its original position in the analyser shape.

This method allows to simulate large-area energy analysers.

Testing the method

The new method was checked with a set of *Single_crystal* components arranged on spherical slices. The attached figures show the comparisson for four different arragements. The plots show a good agreement with the current methods.

The new analyser method in OSIRIS

The figure on the right shows the energy distribution of neutrons reflected by a silicon spherical analyser at OSIRIS. The analyser is composed of 283 columns and 40 rows of 1 cm x 1 cm pixels at backscattering geometry. The FWHM of the distribution is 3.2 μeV (the moderator time amission uncertanty is not taken into account). Figures below show how a large-area analyser focus the reflected neutrons over a small region where the detectors should be placed. Top figure is for the backscattering geometry while bottom figure is for a near-backscattering geometry.

Conclusions

A McStas method to simulate a large-area energy analyser was developed. It was applied to the OSIRIS instrument model. Following points are emphasised.

- In cases where it is comparable with current methods, the new method achieves up to a **30:1 speed ratio** over other options.
- The new method allows to simulate the complete analyser geometry that it is useful for:
  - → **Simulate the total intensity** recorded on detectors.
  - → **Simulate the cross trajectories** of the neutrons inside the vessel.
  - → The momentum of neutrons emerging from the guide results in an **asymmetry of the reflected neutrons emerging from the analyser pixels**. Therefore the simulation of a complete analyser lets to take this phenomenon into account.

TODO: To test other closed-quadric-surfaces like ellipsoids. To give McStas component form to the new method.

ISIS Molecular Spectroscopy Science Meeting, 29th & 30th January 2015, The Cosener's House, Abingdon

The spectroscopic properties of the amorphous ices: A combined INS and Raman study

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Figure 1 (a) Density and **(b)** radial distribution functions, *G*(*r*), of LDA, uHDA and vHDA. Adapted from Loerting *et. al.*. [3] and Salzmann *et. al.*. [5]

Scheme 1 preparation of uHDA, LDA and vHDA. [1][2]

Structural properties

- There are several named types: low (LDA), unannealed high (uHDA) and very high (vHDA) density amorphous ice are considered here. Their formation from ice I is indicated in **Scheme 1**. [1][2]
- **Figure 1(a)** indicates differences in their density with pressure. [3] The amorphous ices are metastable with respect to crystalline phases. The pressure-density plot indicates the density of the most highly annealed amorphous material that it is possible to produce before crystallization.
- **Figure 1(b)** indicates differences in local structure, modeling has indicated the differences to be caused by the presence of interstitial water molecules in uHDA and vHDA but not in LDA.[4]

Spectroscopic properties

- **Figure 2(a and b)** show inelastic neutron scattering (INS) spectra recorded on MARI. Features are due to rigid body H_2O translations (mainly acoustic), librations, bending and stretching vibrations.
- **Figure 2(c)** shows Raman spectra. There are features due to H_2O translations and OH stretching vibrations.
- **Figure 3** shows the position of INS and Raman peak maxima for the amorphous ices plotted with density [6].
- Differences between INS and Raman spectra arise due to the different interaction of light and neutrons with the ices. Whilst INS spectra reflect the H-projected density of vibrational states, Raman spectra are also effected by the change in polarizability of the specific vibration.

Figure 2(a and b) INS and **(c)** Raman spectra of LDA, uHDA and vHDA.

Figure 3 Variations in INS and Raman peak maxima with density.

Are amorphous ices related to liquid water ?

- To answer this question we must consider if the transitions between low and high density amorphous ices are representative of transitions between two distinctly different liquid states ? Also, if their formation from crystalline ices is through thermodynamic melting phenomena or mechanical collapse ? [7]
- The comparison of INS and Raman data shown here indicates clear trends with density. increases in peak position are caused by the weakening of hydrogen bonds. Decreases in intensity of Raman active rigid body translational modes with increasing density indicates a less symmetric environment in vHDA and uHDA relative to LDA. The bandshape and trends observed here may point towards LDA having a local ice I structure but for uHDA and vHDA to have a different (less symmetric) structural motif.

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UCL · Durham University · Università di Roma Tor Vergata · The Royal Society · Science & Technology Facilities Council ISIS · EPSRC Pioneering research and skills

Imperial College London

Thermo-orientation in polar fluids

(Towards a microscopic understanding)

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Introduction:

As advances in technology push the scales of electronic devices to ever smaller domains, it has become of great importance to understand heat transport at small scales in an effort to manage the waste heat produced by such devices. Water is a working fluid in not many industrial processes and so understanding its thermal properties is of particular interest. We employ both non-equilibrium molecular dynamics (**NEMD**) and equilibrium **Green-Kubo**, simulations in order to investigate the particularly novel phenomena of **thermo-orientation**, which has been shown to be present in both polar and non-polar fluids**(1),(2)**.

FIG.1

The above figure shows the NEMD simulation setup we employ, whereby the regions shown in red and blue are subjected to velocity rescaling to enforce a "hot" and "cold" temperature respectively, thus driving the system into a steady state temperature gradient.

Heat/Polarisation coupling:

Thermal coupling effects are predicted from non-equilibrium thermodynamics (**NET**) and have been seen in many simulations **(1-4)**. When considering thermo-orientation in a polar fluid, we are interested in the coupling between the heat-flux **J_q** and the polarisation **P**. The resulting force flux relations are shown in **Eqn.1**(**left**), along with the resulting equation in the case of a time independent polarisation (**right**). We have previously performed simulations to show that the dependence on the dielectric constant is very small consideration in the cases we study. The range of thermodynamic states is shown on the phase diagram below (**Fig.2 left**). From each simulation the average electric field is calculated at different points along the axis of applied temperature gradient(**Fig.2 right**).

EQN.1

$$\mathbf{J_q} = -\frac{L_{qp}}{T}(\mathbf{E_0} - \mathbf{E}) - \frac{L_{qq}}{T^2}\nabla T$$

$$\frac{\partial \mathbf{P}}{\partial t} = -\frac{L_{qp}}{T}(\mathbf{E_0} - \mathbf{E}) - \frac{L_{qq}}{T^2}\nabla T$$

$$\mathbf{E} = \left(1 - \frac{1}{\epsilon}\right)\frac{L_{pq}}{L_{pp}}\frac{\nabla T}{T}$$

FIG.2

(Left) The liquid branch and critical point of water from experiment and simulation (SPC/E) are shown in black and red respectively. The equation of state for each NEMD simulation is also shown, where the colours orange, purple and blue show increasing temperature gradients.

(Right) The electric field at various points along the z-axis for a representative simulation (P=2000 atm, T=725 K). The colours black red and blue show separate simulations, with increasing temperature gradients.

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Thermo-orientation:

The electric field is then compared at a common state point for each thermal gradient, thus allowing the calculation of **L_{pq}/L_{pp}** through **Eqn.1**, as shown in **Figure.3**. Interestingly we observe a minimum at around **725 K**,corresponding to a maximum in the magnitude of the orientation at this temperature.

FIG.3

(Left) The electric field as a function of temperature gradient for temperatures; 500 K, 575 K, 650 K, 725 K, 800 K and 1000 K.

(Right) L_{pq}/L_{pp} as a function of temperature.

Microscopic interpretation

We performed equilibrium simulations, firstly to extract the Debye relaxation time , which along with **Eqn.2** (Derived from the Debye approximation), allows us to calculate **L_{pp}** and thus **L_{pq}**, from our NEMD results. We have then shown that the maximum overlap in the Fourier Transform of the heat-flux autocorrelation function and Polarisation auto-correlation function occurs at **725 K**, i.e. the same temperature at which we observe the largest magnitude in the cross correlation of heat and mass flux. The reason that this increases to a maximum and then declines is due to the opposing shift in the time-scales of both the heat-flux and polarisation. At the temperature of 725 K the two time-scales optimally match giving the largest cross correlation. It can be seen from the Fourier analysis of the velocity auto-correlation functions that the change in structure of water upon heating results in a shift from **librational modes** to **diffusive behaviour** and it is this which causes the change in heat-flux character of the system.

EQN.2

$$\mathbf{P}(t) = \kappa \mathbf{E}\left(1 - e^{-t/\tau}\right)$$

$$L_{pp} = \frac{\kappa T}{\tau}$$

FIG.4

(Top right) Lpp and Lpq as a function of temperature.

(Bottom left) The Fourier transform of the heat-flux auto-correlation (solid lines), polarisation auto-correlation (dashed lines) and the total overlap of the two functions as a function of temperature (inset figure).

(Bottom right) The Fourier transform of the velocity autocorrelation function.

The colour scheme for various temperatures is as was used in Fig.3.

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Thermal Conductivity of Different Phases of Ice: A Molecular Dynamics Study

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We have used the **TIP4P/Ice**[1] water model to study the thermal conductivity (TC) of Ice Ih, VI, VII and a high pressure plastic phase (Fig.1). We use two approaches to compute the thermal conductivity; **Equilibrium Molecular Dynamics (Green-Kubo method)** and **Non-Equilibrium Molecular Dynamics.** We report results of the vibrational density of states, which provide a direct link to experiments, and highlights the different vibrational behaviour of the ice phases investigated here. Our results show that state of the art classical models strongly underestimate the thermal conductivity of the phases investigated here, except for ice VI, where we find quantitative agreement with experimental data.

Green-Kubo Method

We have calculated the thermal conductivity of the different ice water phases using the Green-Kubo[2] method, which relies on the computation of the fluctuations of the heat current $\mathbf{J}(t)$. Linear response theory gives the following equation for the thermal conductivity in 3D:

$$\lambda = \frac{1}{3k_B V T^2}\int_0^\infty \langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle dt$$

where V is the volume of the system, $\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle$ is the heat current autocorrelation function (HCAF), t is the time, T is the temperature, and k_B is Boltzmann's constant. The heat current vector is defined by:

$$\mathbf{J}(t) = \sum_{i=1}^{N} E_i \mathbf{v}_i + \frac{1}{2}\sum_{i\neq j=1}^{N} (\mathbf{F}_{ij}\cdot\mathbf{v}_i)\mathbf{r}_{ij}$$

Where the sum is performed over the total number of particles in the system, N. E_i and $\mathbf{v}_i$ are the energy and velocity of particle i, while $\mathbf{F}_{ij}$ and $\mathbf{r}_{ij}$ are the interparticle force and separation vectors. Our Molecular Dynamics simulations have been carried out with the LAMMPS[3] package. Thermal conductivities for each ice phase at different conditions are collected in Table1.

TIP4P/Ice

r_{OH} (Å)	∠HOH, deg	σ (Å)	ε / k (K)	q(O) (e)	q(H) (e)	q(M) (e)	r_{OM} (Å)
0.9572	104.52	3.1668	106.1	0	0.5897	-2q(H)	0.1577

Figure 1 Diagram of water model[4] and phase diagram showing unit cells[5] of phases Ih, VI & VII

Non-equilibrium Molecular Dynamics

In NEMD, a temperature gradient is applied by adding a heat source and a heat sink and then computing the heat flux, therefore mimicking an actual experiment (Fig.2). The equation below is the macroscopic continuity equation for the heat flux for this simulation geometry.

$$J = \frac{\pm\Delta U}{2\delta t A} = -\lambda\frac{\partial T}{\partial x}$$

Where J is the heat flux, ΔU is the internal energy added(+) and removed(-), δt is the timestep, A is the cross-sectional area of the box, λ is the thermal conductivity and dT/dx is the temperature gradient applied (~10^{10} K/m).

Size effects[6] need to be taken into account in NEMD methods for systems where the phonon mean free path length is comparable to the length of the box. Therefore, calculations were performed for different sizes of simulation box and then extrapolated to the bulk situation using a finite size scaling method.

Fig 2 showing NEMD simulation cell [7]

Table 1 Thermal conductivity of Ice Ih, VI, VII and plastic phase.

Ice phase	T/K	p/bar	ρ/g cm^{-3}	λ_{EMD}	λ_{NEMD}
Ih	99	49	0.928	1.9±0.1	-
Ih	151	24	0.922	1.43±0.06	-
Ih	197	74	0.916	1.29±0.06	1.2±0.1
Ih	267	-50	0.906	1.22±0.07	-
VI	299	21700	1.376	1.79±0.08	-
VII	302	75200	1.688	4.6±0.3	-
VII	316	99700	1.748	5.7±0.3	4.8±0.6
VII	412	99600	1.701	4.4±0.2	-
Plastic	419	100050	1.702	4.3±0.3	-

We have extracted O-O RDFs which show the different structures of phases Ih, VI and VII. The phonon density of states spectra obtained from Velocity Autocorrelation Functions (VACFs) are compared with experimental results from neutron diffraction[9] at low frequencies.

A plastic phase, where the hydrogens are disordered but the oxygen atoms arrange themselves in an fcc lattice, has been reported for several water models[10], but has not yet been found experimentally. The RDF and phonon spectra show the difference between the structures. The calculated thermal conductivity for both phases is very similar (VII-4.4±0.2 & plastic-4.3±0.3)

O-O Radial Distribution Functions

Phonon DoS for Ih

Phonon DoS for ice VI

O-H Radial Distribution Functions

Phonon DoS for VII & plastic

Phonon DoS and H-H VACF (inset)

CONCLUSIONS 1) Rigid non-polarizable models underpredict the TC of ice Ih and ice VII **2**) The computed TC for ice VI agrees with available experimental data **3**) Our results show qualitative agreement with available experimental data in low energy transfer region **4**) The thermal conductivity of ice VII and plastic ice is very similar. This result suggests that hydrogen bonding does not play a significant role in determining the TC of high pressure phases.

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Mass-selective Neutron Spectroscopy Beyond the proton

Science & Technology Facilities Council
ISIS

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VESUVIO: NCS – mass-selective spectroscopy of Doppler-broadened nuclear recoil peaks

Under Plane Wave Impulse Approximation (IA)

[7 eV < ω < 90 eV and 70 Å^{-1}< q < 200 Å]

$$\hbar\omega = \frac{\hbar^2}{2M}Q^2$$

$$S(q,\omega) = \left(\frac{1}{4\pi\omega_R T^*}\right)^{1/2} \exp\left(\frac{-(\omega-\omega_R)^2}{4\omega_R T^*}\right)$$

$$T^* = \int \omega Z(\omega) \coth\left(\frac{\omega}{T}\right) d\omega$$

Going beyond lithium: simultaneous NMDs of H, C and O in the squaric acid across the order-disorder phase transition at T=373K

Structural comparisons between antiferroelectric squaric acid (top) and ferroelectric croconic acid (bottom).
S Horiuchi et al. Nature 463, 789-792 (2010) doi:10.1038/nature08731

Lattice parameter for h-SA (inset: H-bond lengths).

Simultaneous NMDs measurement of H, C and O in the squaric acid across the order-disorder phase transition

Forward scattering with stoichiometric fixing

PIMD, K. T. Wikfeldt and A. Michaelides J. Chem. Phys. 140, 041105 (2014)

Half-width of four Raman bands of h-SA

Outlook: eV spectroscopy with really heavy nuclei using neutron resonant absorption followed by prompt gamma emission.

Take-home messages:

1. **VESUVIO uses NCS as a unique 'nuclear wave function diffractometer' and nuclear quantum thermometer;**
2. **NCS results obtained using VESUVIO can be used to benchmark modern *ab initio* nuclear quantum dynamics calculations and go beyond usual ab initio structure and function prediction techniques to deliver information about subtle nuclear quantum delocalisation;**
3. **In addition to ND for ordered structures, VESUVIO uses NCS to monitor local dynamics of different nuclei simultaneously across phase transitions into liquid, molten crystal and gas phases in a manner that is unaffected by the Debye-Waller factor.**

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Analysis of porosity in activated carbons

Reconciling gas sorption with scattering data

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1. Introduction

Nanoporous activated carbons have been demonstrated to be useful for a multitude of applications including biomedical, organic solvent recovery and energy storage, due to their propensity for adsorbing and sequestering molecules. The selectivity of these carbon materials is due to the size of their internal pores. Here we compare analysis of the pore structure of a range of nanoporous carbon materials using small angle X-ray and neutron scattering as well as analysis of nitrogen sorption isotherms at 77 K, to investigate the comparability of these analysis methods.

TiC - Carbide Derived Carbons

Figure 1: *Synthesis of TiC-CDCs.* [1]

Structure of TiC-CDCs changes with temperature, as show in Figure 1.

Figure 2: *TEM images of TiC-CDCs.* [2]

Sample	Cl_2 (°C)	H_2 (°C)
TiC-CDC 600	600	600
TiC-CDC 800	800	600
TiC-CDC 900	900	600
OLC	1750	-

Onion - Like Carbons (OLC)

Figure 3: *TEM image of OLC.*

Samples supplied by Dr Volker Presser, Leibniz Institute of New Materials, Germany.

2. Nitrogen sorption measurements

N_2 sorption isotherms at 77 K were obtained for TiC-CDC samples at different chlorination temperatures; 900°C, 800°C, 600°C, 400°C and the OLC sample. Application of the DFT and NLDFT models to the sorption isotherm was used to obtain a pore size distribution (PSD). Models assume an infinite slit-pore geometry.

Figure 4: *Nitrogen sorption isotherms for TiC-CDC samples. Markers are hollow for adsorption branches and solid for desorption branches.*

NLDFT Model	
TiC-CDC	Average pore diameter (Å)
600	13.7
800	12.0
900	28.6

DFT Model	
TiC-CDC	Average pore diameter (Å)
600	12.8
800	14.1
900	27.2

Figure 5: *Pore size distributions (PSD) obtained by application of the NLDFT (left) and DFT (right) pore filling model.*

Volume-weighted average pore size was calculated from pore size distributions. Deviations of average pore size between the different models (NLDFT and DFT) was evident.

3. Small angle scattering measurements

Room-temperature small angle X-ray scattering (SAXS) data collected on I22 at the Diamond Light Source, UK and small angle neutron scattering (SANS) data from SANS2D at ISIS, UK were simultaneously refined using the IGOR software.

TiC-CDC Cl_2 temperature (°C)	Radius of gyration (Å)
600	8.6
800	11.7
900	15.2

Figure 6: SAXS (circles) and SANS (triangles) profiles from TiC-CDCs chlorinated at different temperatures; 600°C (blue), 800°C (red) and 900°C (black). Solid lines are best fit to the Gibaud model, which takes into account macro and micropore radius.

SAXS/SANS analysis shows increasing average pore diameter with chlorination temperature. Volume-weighted average pore size from PSD analysis was compared with SAXS/SANS analysis. A clear deviation between PSD models and small angle scattering measurements was observed.

Summary

- The information from small angle scattering is useful for analysis of materials with homogeneous pore dimensions.
- Gas sorption analysis allows greater definition of pore size distributions, but results depend greatly on models used.

Conclusions

- Pore sizes from gas sorption are often quoted as absolute values; these should instead be considered characteristic.
- Supporting data from other methods, such as small angle scattering, is recommended when quoting a pore size obtained via gas sorption analysis.

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Engineering and Physical Sciences Research Council

Towards a better modelisation of carbon-based nanomaterials

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The strong indications of the untapped potential of Carbon-based nanostructured materials as next-generation sorbents come mainly from simulation and theoretical work [1]. Dispersive interactions among the various carbon nanostructures (graphene, nanotubes, etc) as well as with guest molecules (H_2, CO_2, etc) are at the core of the relevant physical mechanisms involved. However, the vast majority of the "in-silico" studies rely on effective pairwise descriptions of the dispersive forces (Lennard-Jones). Recent developments of new van-der-Waals DFT functionals [2] provide a convenient starting point to attain a more accurate representation. By making recourse of the SCARF-RAL cluster we have calculated the energy barriers involved in a specific type of stacking fault in graphite using a dispersive DFT functional. The calculations agree well with the experimental data but, the comparison with the standard pairwise potential calculations reveals a discrepancy of an order of magnitude. We show here our ongoing study of the limits as well as of possible improvements of classical pairwise modelisations of the interlayer interactions.

Intrinsic type-II stacking fault in graphite (sliding of graphite structure along adjacent graphene layers)

It is reproduced by tilting the supercell of large scale DFT simulations using CASTEP and the PBE+D functional on the SCARF-RAL cluster. Calculated energy barriers consistent with experiments [3].

Comparison with classical simulation using the empirical Brenner-Stuart potentials

The LJ in Brenner-Stuart requires a long range interaction (Verlet cut of 4.7 σ) to obtain a smooth barrier and even so the barrier is about an order of magnitude lower !!!

A normal Verlet Cut-off increase the barrier while making it jagged

Barrier dominated by nearest layer interaction

We assumed:

- Different interaction between adjacent and nonadjacent layers
- The Mie(n,6) potential family,

$$E = C\epsilon\left[\left(\frac{\sigma}{r}\right)^{3n\epsilon} - \left(\frac{\sigma}{r}\right)^{3\epsilon n\epsilon}\right] \qquad r < r_c$$

Pairwise potentials determined by fitting to Castep calculations for the expansion of

- 2 layers
- 3 layers
- Graphite

in A-A stacking to facilitate calculations (all the layers are equivalent)

The best fit is obtained with Mie (14,6)

Fit with a Mie(14,6) fixing the interaction between adjacent layers to the above 2-layers Mie (14,6) fit

The interactions previously calculated yields a good estimation of the A-A "graphite" expansion

Pairwise potentials resulting from fitting

Recalculated energy barriers:

Mie(n > 12, 6) potentials rise the sliding barrier substantially and reduce the Verlet cut (2.9 σ)

However, the barrier heigh is still very far from target

Nonetheless, barrier heights even above the Castep calculation can be obtained by restricting the interaction to nearby neighbours but with a strong non analytic behaviour

Conclusions:

- The dispersive interactions are modulated by intermediate layers.
- Simple pairwise potentials are not a good representation of dispersive forces.
- The usual Verlet cut-off gives a very inaccurate representation of the interlayer interaction.
- The results strongly suggest the necessity of an extension of the potentials beyond purely pairwise interactions.

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The Oxygen momentum distribution in Water

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Molecular Spectroscopy Science Meeting 2015

1) The Quantum Nature of Water

Water is a strange as much as a simple molecule. An investigation of the quantum effects across its melting, as well as the effects of the isotope substitution H→D can shed light on its complex phase diagram and anomalies.

Quantum mechanics provokes a zero-point-energy motion affecting the nuclei in the molecule. The mass dependence of the Schroedinger equation brings to strong isotope effects in the nuclear dynamics.

2) Neutron Compton Scattering

Mass selection

When the energy and momentum transfer are high with respect to the binding energies of the system, the $S(q,\omega)$ simplifies in a sum of free recoiling peaks, one for every mass in the sample.

VESUVIO is a time of flight (t.o.f.) indirect geometry spectrometer using epithermal neutrons to measure nuclear momentum distributions and kinetic energies. It has about 200 detectors in both forward and backward scattering.

3) The experiment

The backscattering detectors present a better mass-separation and no signal from hydrogen. Each signal is proportional to the number of atoms × their neutron cross section.

4) y-scaling

The West variable

The y_M mass-dependent variable allows the coherent sum of the momentum distribution of the mass M

$$y_M = \frac{1}{\hbar}\vec{p}\cdot\hat{q} = \frac{M}{\hbar q}\left(\omega - \frac{\hbar q^2}{2M}\right).$$

5) Compton Profiles

After the subtraction of the empty cell and the multiple scattering, the neutron Compton profile $J(y)$ can be fitted through a model distribution.

...or the Compton profile and the spurious container contribution can be fitted simultaneously.

6) Results

The Mean Kinetic Energy

When the NCPs are fitted with Gaussian functions, the square of the fitted standard deviation σ can be directly related to the nuclear Mean kinetic energy

$$\int_{-\infty}^{\infty} y^2 J(y)\, dy = \sigma^2 \rightarrow \langle E_K \rangle = \frac{\hbar^2\sigma^2}{2M}$$

	Light water		Heavy water	
	$\langle E_K \rangle$ [meV]	T [K]	$\langle E_K \rangle$ [meV]	T [K]
Liquid	51 ± 3	276	61 ± 3	280
Solid	56 ± 3	270	60 ± 4	274

Oxygen in ice is more energetic than in water!

Through the y-scaling it is possible to isolate the Oxygen momentum distribution and obtain a value for the mean kinetic energy.

For the experiment on D_2O a multivariate Gaussian could highlight the anisotropy of the momentum distribution (see G. Romanelli, M. Ceriotti, D.E. Manolopoulos, C. Pantalei, R. Senesi, C. Andreani, J. Phys. Chem. Lett. 4 (19) (2013) 3251).

The Oxygen mean kinetic energy largely differs from a MB prediction, but it is larger than the predictions from first-order quantum harmonic models.

The kinetic energy for Oxygen in liquid light water is higher than in ice: there are strong contributions from translational network modes.

High-resolution Neutron Spectroscopy for Soft Matter Science

Science & Technology Facilities Council
ISIS

Understanding Organic Materials for Photovoltaic Devices

Efficacy of photovoltaic devices depend on nanostructure and relaxations of organic molecules such as P3HT and PCBM.

Paternó *et al.*, Chem. Phys. **83** (2015); J. Mat. Chem. C. Commun. **1**, 5619 (2013)

Polymers under Confinement

INS shows unusual and novel properties of confined poly(ethylene oxide) chains in graphite oxide and graphene sheets.

Barroso-Bujans *et al.*, ACS Macro Letters **1**, 550 (2012)

Towards Stronger and Greener Cements

Pore structure modification decreases water mobility and permeability in cement pastes blended with sugar cane ash compared to that in ordinary Portland cement.

Jacobsen *et al.*, Nature Scientific Reps. **3**, 2667 (2013)

Designing Intelligent Nanovectors for Targeted Drug Delivery

Diffusion of water is key for controlled drug release in biodrgradable polymer-based hydrogels or lipid-encapsulated nanovectors.

Ghugare *et al.*, Macromol. Symp, **329**, 27 (2013); Chiapponi *et al.*, J. Phys. Chem. B **116**, 12915 (2012)

Flexibility, Key Alongside Structure, for Protein Function

Comparison of ps-ns dynamical modes in proteins points to a structure dependent flexibility .

Telling *et al.*, Soft Matter Comm. **8**, 9529 (2012); Chem. Phys. S.I. **8**, 9529 (2012)

Explaining Anaesthesia: Partitioning of Ethanol into Lipid Membranes

Ethanol increases membrane permeability with ethanol and water found in hydrophobic core. Pre-phase transition enhanced and motional hindering in gel phase only.

Toppozini *et al.*, Soft Matter **8**, 11839 (2012); Toppozini *et al.* Chem Phys **83** (2015)

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MANSE
Be
N
B C
O F
Li
Tof (μm)

UNIVERSITY OF COPENHAGEN
Cracks - Most significant, can be created by removal of water.
Capillary Pores - Not significant if paste not cracked, well cured and has water to cement ratio less than 0.42.
Gel Pores - In well made concrete rate limiting factor!
Fraction Connected
Degree of hydration
Bentz and Garboczi, Cem. and Conc. Res. 21, 325 (1991).

Shape analysis no
•Derive the mean force
by numerical calculation of
$f(x)$
x [Å]

hermally activated surface dynamics
LCN
• Motion induced by thermal excitation
• Modelled as "Adsorbate plus heat bat
• Langevin equation:
$m\dot{\mathbf{v}}_i = -\nabla V(x,y)$
$\alpha(\Delta K)$
ΔK
C_6H_6/Graphite
log(t)
$\alpha(K)$ / sec^{-1}
CO/Cu(001)
ΔK<110>
ΔK<100>
SHARP

Imperial College
Water at nanoparticle surfaces
Translational structure
HC layer
water
O
H
NPT -- 1 bar, 298 K
Intensity (a.u.)
Water interface
Nanoparticle interface
Bulk
(cm⁻¹)
Disrupted; h-bond structure => Dangling h-bonds
Shift of stretching modes to higher frequencies => compatible with experiments of the water-air interface using VSFS.
Scatena et al., Science 2001.
Tay & FB: J. Mater. Chem.; J. Am. Chem. Soc.

Tha
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