



An introduction to neutron techniques in catalysis

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AJ O'Malley, SF Parker, K Refson, SE Rogers,
MW Skoda, S Yang, and T Youngs

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An Introduction to Neutron Techniques in Catalysis

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and T. Youngs



Johnson Matthey



An Introduction to Neutron Techniques in Catalysis

One of the goals of the UK Catalysis Hub at the Research Complex at Harwell (RCaH) (<http://www.rc-harwell.ac.uk/UKCatalysisHub>) is to promote the use of, and hence to better exploit, Central Facilities to advance studies in catalysis. To this end, a two day meeting titled “An Introduction to Neutron Techniques in Catalysis” was held at RCaH on the 3rd and 4th November 2014. The talks alternated between describing the various techniques available and success stories that showed how the methods have been used to study catalysts and catalytic systems. The emphasis was to answer the questions “what do we learn?” and “what is needed for a successful experiment?”

The meeting was very successful; it attracted 55 registrations, mostly PhD students and postdoctoral fellows but also included eight representatives from three chemical companies. Most of the participants had not yet carried out a neutron experiment. There were several requests for copies of the slides and the best way we could see to meet this need was to issue them as a RAL report. These are fully Open Access and available for download from the STFC ePubs archive (<https://epubs.stfc.ac.uk/index>).

We wish to thank the speakers for their contributions, Josie Goodall (Catalysis Hub), Emma Dingle (Elior) and Emma Roberts (STFC) for ensuring the smooth running of the meeting. The meeting would not have been possible without the generous sponsorship provided by the Catalysis Hub (*via* EPSRC grants EP/I019693/1 and EP/K014714/1), the STFC ISIS Facility and Johnson Matthey plc and we gratefully acknowledge their support.

Ian Silverwood (Catalysis Hub) and Stewart F. Parker (ISIS)

Meeting organisers



Johnson Matthey



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3rd November 2014

Welcome to the Rutherford Appleton Laboratory!

The Science and Technology Facilities Council (STFC) is responsible for managing large facilities worldwide. These include the Rutherford Appleton Laboratory (RAL), Daresbury Laboratory, Chilbolton Observatory, UK Astronomy Technology Centre and the Boulby Underground Science Facility in the UK, as well as a telescope site in the Canary Islands. STFC also manages the UK subscriptions to CERN, the ESRF and to the Institut Laue-Langevin (ILL) amongst others. On behalf of the UK government, it is also the major shareholder (86%) in Diamond Light Source Ltd, who run the UK's synchrotron located on the RAL site.

RAL hosts facilities that are used for space research, technology innovation, high power lasers used for fusion research and the OCTOPUS imaging cluster and the ULTRA cluster. These are a central core of lasers that can be used to image samples from single molecules to whole cells and tissues together with a range of ultrafast light sources for time resolved (down to femtosecond) studies. RAL is also the home of the ISIS Facility, a spallation neutron source that has revolutionised the field of neutron scattering. In combination with the ILL, users have access to techniques that reach from the Ångström to the micron and from attoseconds to microseconds.

ISIS uses neutrons for fundamental studies in physics, chemistry, materials science, earth science, engineering and biology. However, as a government funded facility, research that may be applied to the benefit of UK plc is also a goal. As a major driver of economic activity, studies in catalysis provide opportunities in both short and long-term research. Neutrons have been used for catalyst studies for over 40 years and this is a contribution that has continued at ISIS over its entire lifetime. Nonetheless, there are clearly areas of catalysis where neutrons are under-utilised. Our collaboration with the UK Catalysis Hub is an important way that we hope to grow the use of neutrons in catalysis and it is our belief that this meeting will spark ideas and projects that will make use of the neutron facilities that are available to you.



Professor Robert McGreevy
Director, ISIS



The UK Catalysis Hub:



Richard Catlow, Chris Hardacre, Matthew Davidson and
Graham Hutchings
+ 36 investigators from 30 UK Institutions

Catalysis Hub: Vision

- To establish a world-leading, comprehensive and coordinated programme of catalytic science in the UK.
- To develop new knowledge and promote innovation in and translation of catalytic science and technology.
- Enabling the UK to regain and retain a world leading position in catalysis.

The Catalysis Hub: Structure

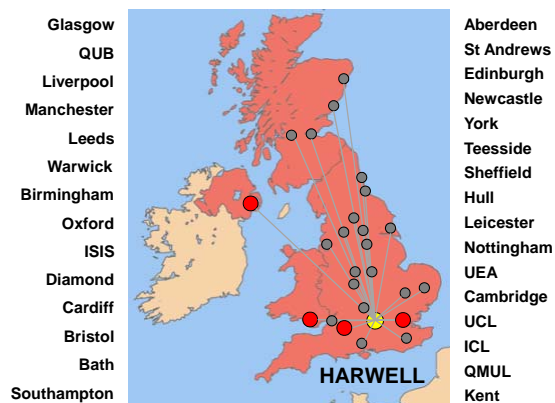
- Physical centre based in the Research Complex at Harwell, building on existing successful centre
- Network distributed throughout the UK
- Collaborative Teams to tackle major problems
- International visitors programme
- Outreach, dissemination and advocacy

Existing Base

- The hub was set up to build on an established base in the RCaH with EPSRC support and senior Research Fellow (Peter Wells)
- The original consortium has 11 teams with state of the art catalysis laboratories.
- The Hub extended this to 30 Universities spread across the UK and has attracted additional support from EPSRC and industry



The Catalysis Hub: Distribution



The Catalysis Hub: The Science

- Catalysis by Design
- Energy
- Environmental Catalysis
- Chemical Transformations
- (Biocatalysis)

Hub Science: Catalysis by Design

Initial Projects

- Probing the nature of active sites and mechanisms using synchrotron radiation (*Harwell Hub , Diamond, Belfast, UCL, Cardiff, Cambridge, Southampton*)
- Developments in neutron scattering to characterise absorbed species (*Harwell Hub, UCL, Belfast, Glasgow*)
- Active site design for effecting catalysis at the nano-scale (*Harwell Hub, Southampton, Cardiff, UCL*)
- Modelling of catalytic pathways and kinetics (*Cardiff, UCL, Harwell Hub + all partners*)
- Hierarchically structured porous catalysts (*UCL, Bath, Oxford, Southampton, Harwell Hub*)
- Microporous architectures with multifunctional active sites (*Southampton, Cardiff, UCL, Belfast, Bath, Harwell Hub*)

Hub Science: Environmental Catalysis

Initial Projects

- New advances in redox catalysis (*Cardiff, UCL, RCAH, Liverpool, Cambridge*)
- *Towards closing the chlorine cycle in large-scale chemical manufacturing processes* (*Glasgow, Cardiff, ISIS, Newcastle*)
- *Selective oxidation of alkanes* (*St Andrews, Imperial, Cardiff*)
- *Water treatment – combined hydrocarbon and nitrate removal* (*Cardiff, Aberdeen, UCL, Cambridge, RCAH*)
- *Particulate destruction* (*Cardiff, QUB, Newcastle*)
- *Autonomous Damage Repair* (*Bristol, Imperial, Bath, Aerospace Engineering, Bristol*)
- *Direct fixation of CO₂* (*Cardiff, UCL, RCAH*)
- *Functionalising C-H bonds with CO₂* (*St Andrews, Cardiff, Syngenta*)

Hub Science: Energy

Initial Projects

- Fuel Cells beyond methanol and ethanol – 3rd generation direct fuel cells using oxygenates as fuels (*Belfast, UCL, Cambridge, Southampton*)
- New Approaches to Reforming (*Newcastle, Cardiff, Belfast, Cambridge, Oxford*)
- Biofuels (*Cardiff, Belfast, Bristol, Newcastle, Birmingham, Glasgow*)
- Integrated system assessment (*Cardiff, UCL, Newcastle, Belfast*)

Hub Science: Chemical Transformations

Initial Projects

- Activation and Reaction of sp^3 Centres (*Bath, Bristol, Leeds, QUB, Manchester, Warwick, Liverpool, Oxford*)
- Selective Synthesis Gas Conversion (*Bath, Bristol, Imperial, Oxford, Sheffield, Cardiff, Liverpool, York*)
- New Catalysts and Processes for Oxygenated Polymers (*Bath, Bristol, Edinburgh, Imperial, Oxford*)
- Catalysis in Confined Environments (*Bath, Bristol, Imperial, Liverpool, Oxford, Sheffield*)
- Transition Metal-Free Catalysis (*Bath, Oxford, Cambridge, St. Andrews, Warwick*)
- Biocatalysis for High Value Transformations (*Bath, Oxford, York*)

Industrial Engagement

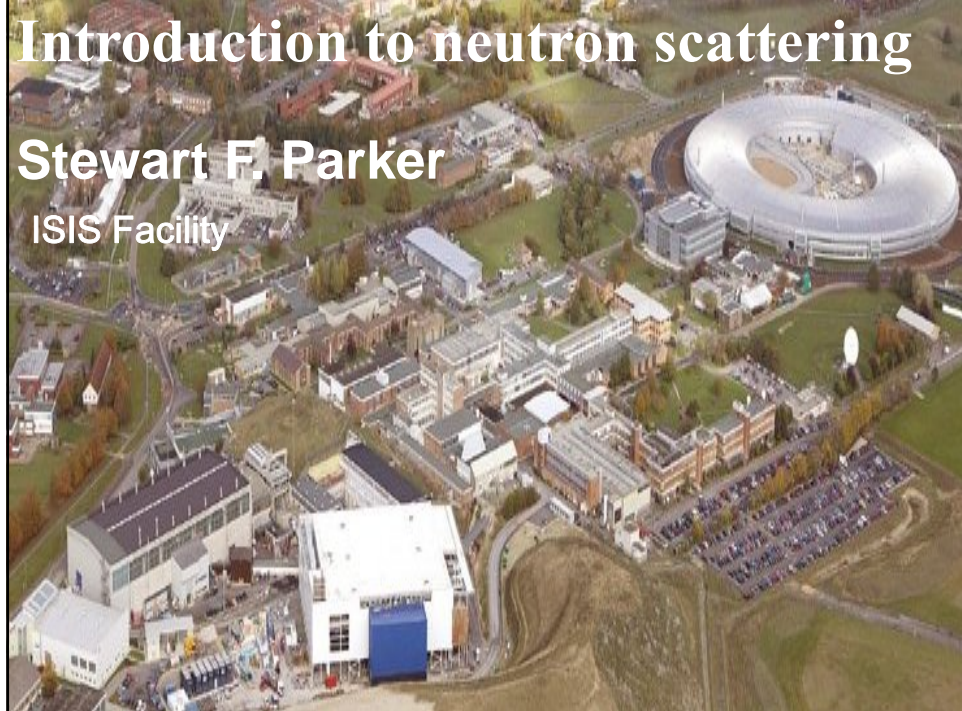


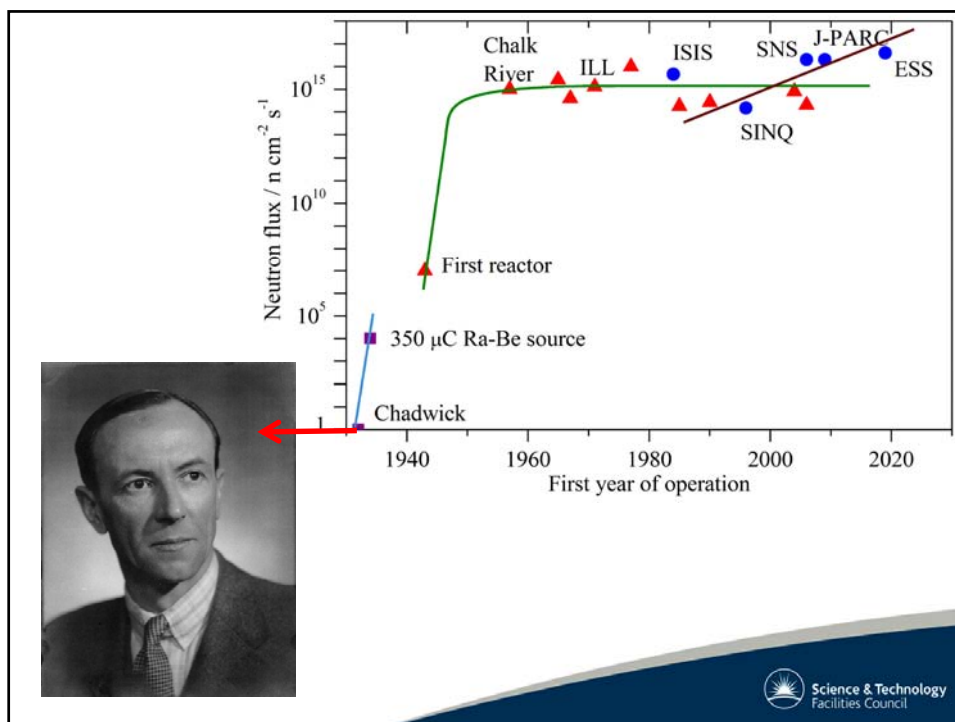
- Fundamental Catalytic science of high relevance to UK and global industry
- Engagement fostered by Advisory Board
- Engagement effected by joint projects, studentships etc.
- Extensive spin off activity anticipated.



NEUTRON SCATTERING has a key role to play in
CATALYTIC SCIENCE







**ORNL 1943
TN, USA**



1994

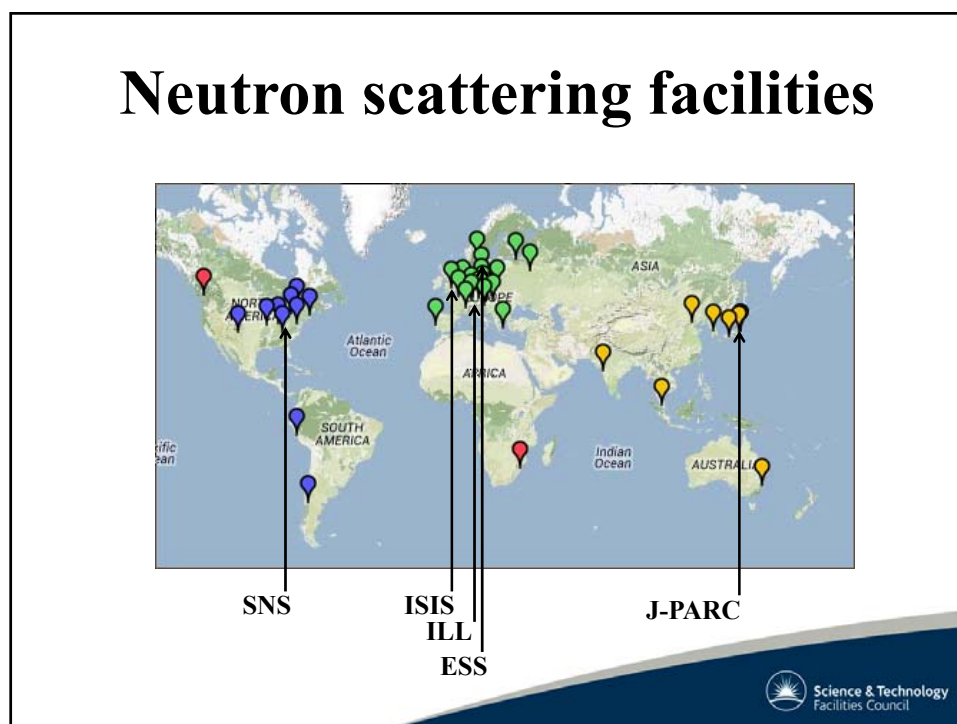


Clifford Shull (diffraction)

Bertram Brockhouse (inelastic)



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Getting access to facilities

Free at the point of use

Two proposal rounds per annum (spring and autumn)

Industry, academia is eligible to apply for beamtime (students cannot be a PI)

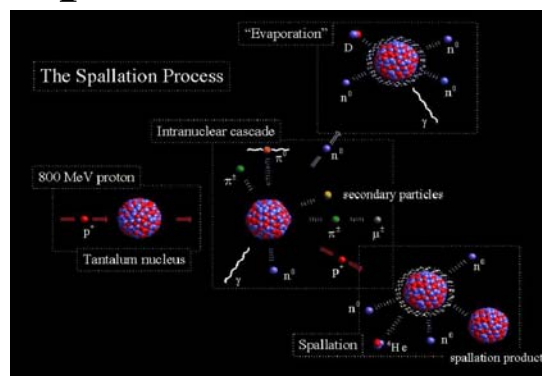
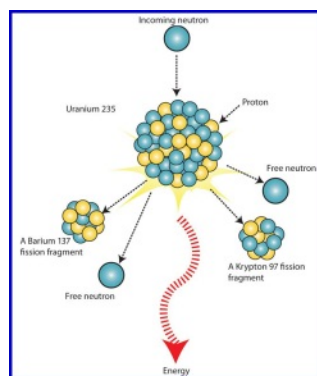
For ISIS/ILL experiments the facilities will pay travel, subsistence and contribution towards cost of preparation of samples for UK academic staff

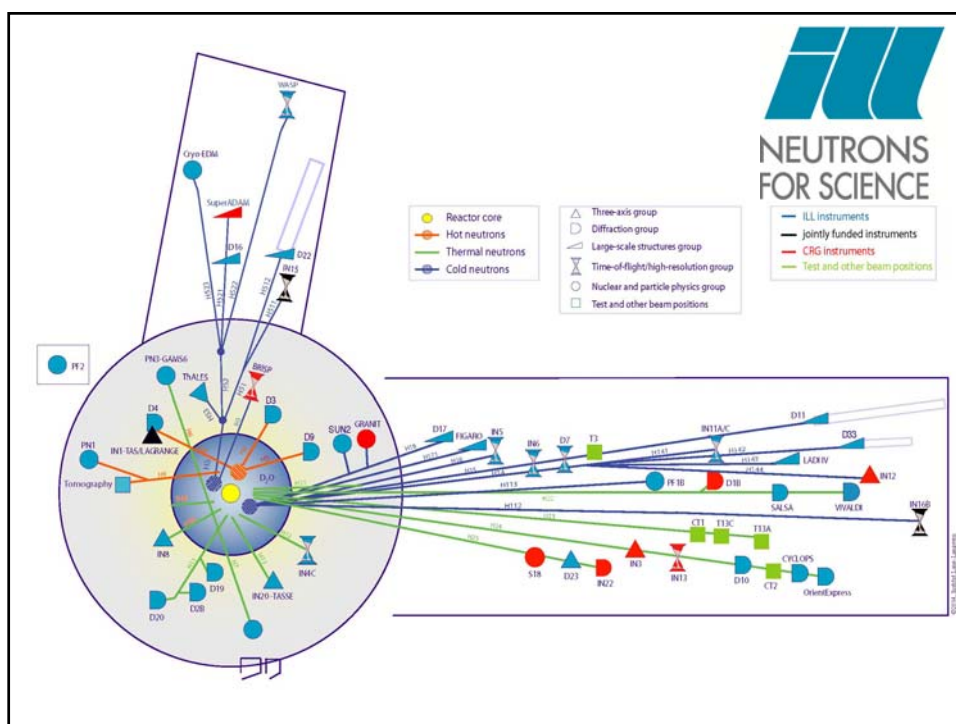
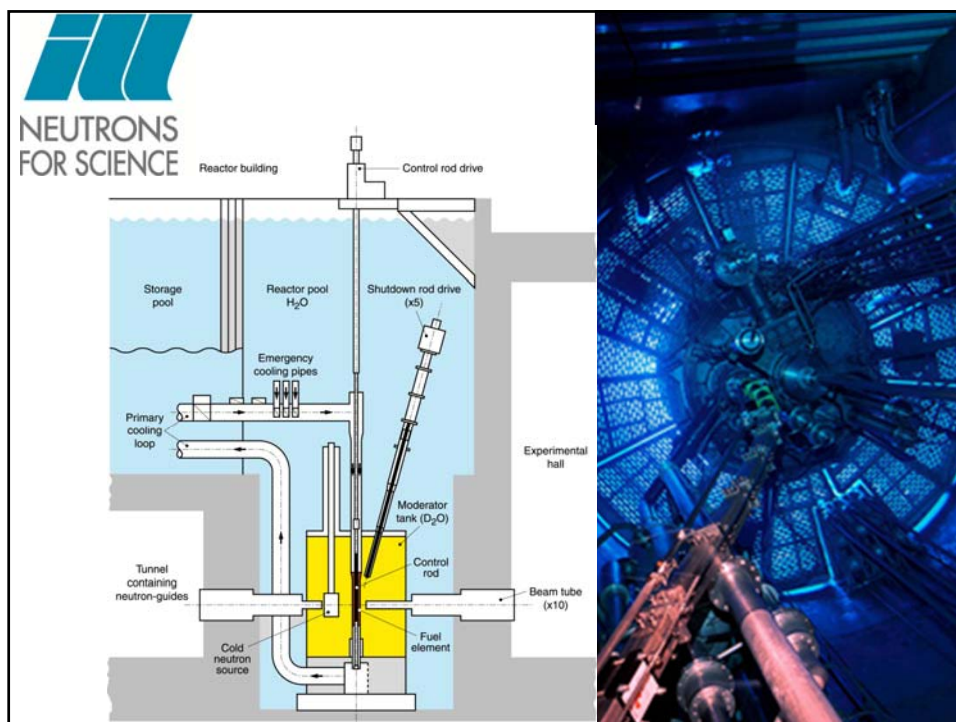
Condition of acceptance is that data is public domain (three year embargo) and publication is expected

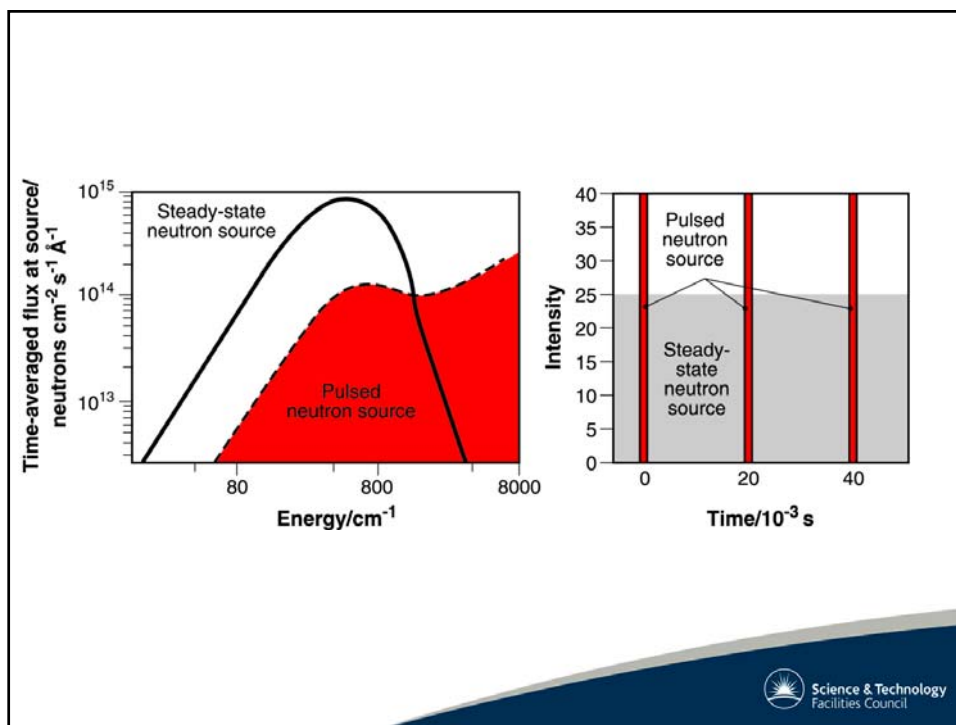
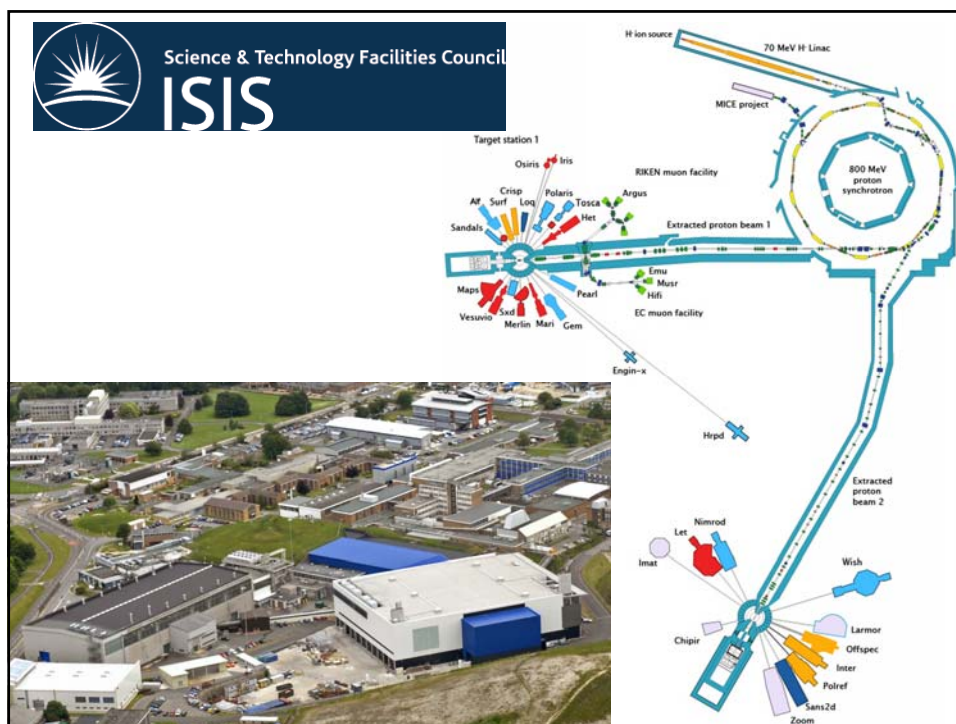
ISIS runs an Xpress system (nominally) available on all instruments



Reactors and spallation sources







Neutron properties

Mass of neutron \approx mass of hydrogen atom

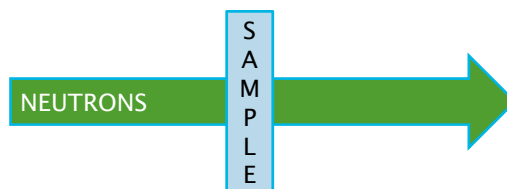
**Neutral particle: interacts weakly with matter
 \Rightarrow highly penetrating**

Magnetic moment (spin $\frac{1}{2}$): interacts with unpaired electrons

Neutrons tell you where atoms are and how they are moving!



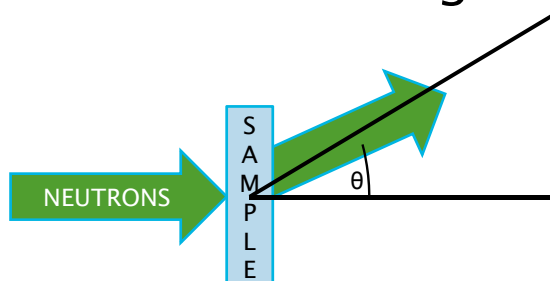
Neutron Interactions with Matter: Transmission



Majority of beam
Neutrons interact weakly with matter

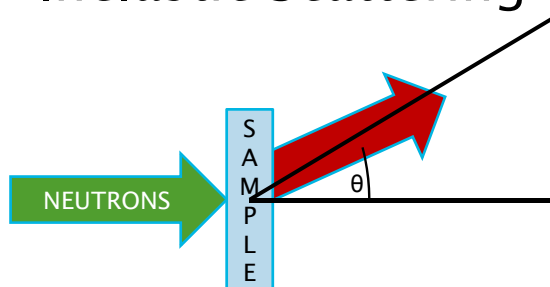


Neutron Interactions with Matter: Elastic Scattering



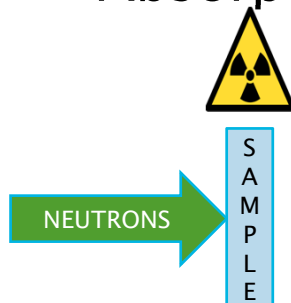
Neutrons can be scattered through an angle θ , without change to kinetic energy
Gives spatial information

Neutron Interactions with Matter: Inelastic Scattering



Neutrons can be scattered through an angle θ and transfer energy to/from sample
Describes dynamics of system

Neutron Interactions with Matter: Absorption



Some neutrons may be captured and join nuclei, generating (radioactive) isotopes

Safety



Radiation hazard is first to mind.

Mainly due to induced β and γ .

Activity depends on instrument and elemental (isotopic) composition.

Hazard managed by combination of physical interlocks and protocols.

Annual dose for ISIS employee less than that from living in Cornwall!

Major risks arise from larger scale of experiments.

Cells plus centresticks may be heavy and awkward.

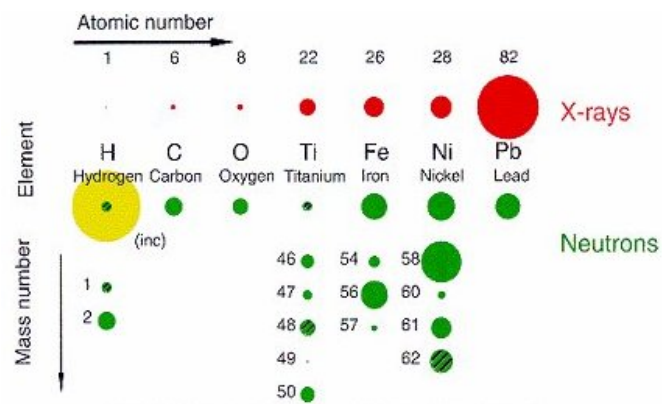
Quantities of solvents needed may be much larger than commonly used.

Often several litres liquid N_2 needed to cool or load samples.

Hazards managed by risk assessments and education.

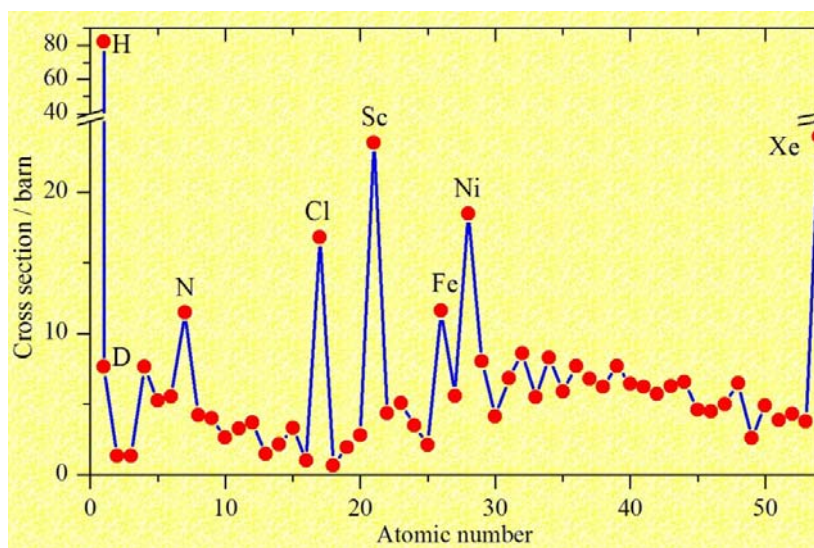
If in doubt, ask your local contact!

Neutrons and Photons



H and D have vastly different scattering powers for neutrons

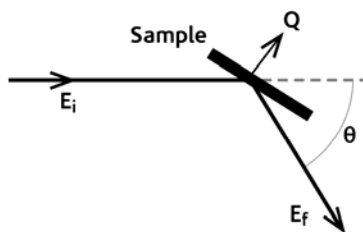
Used in SANS, neutron reflectometry and total scattering to manipulate refractive index profile or 'contrast'



Scattering in

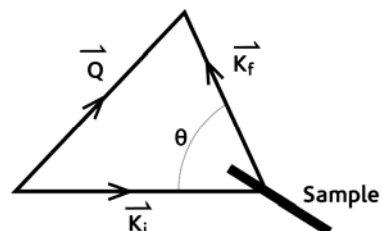


Real space



(a)

Reciprocal space



(b)

$$E_T = E_i - E_f$$

$$E_T = 0 \text{ Elastic scattering}$$

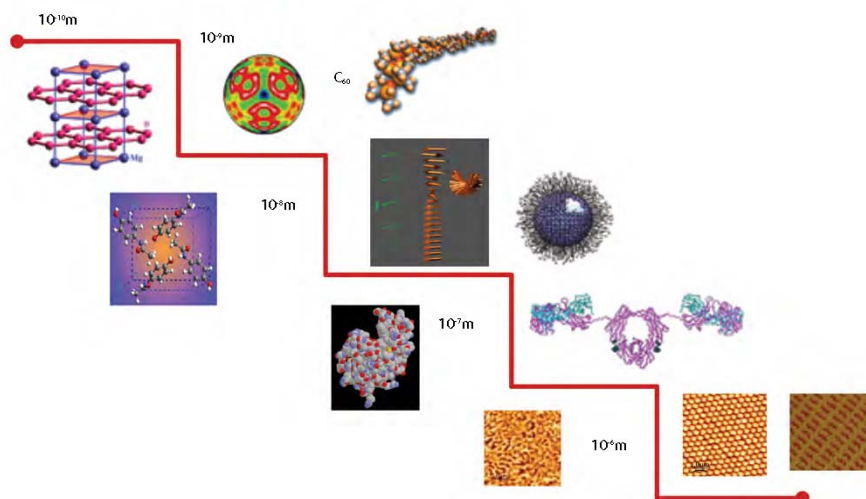
$$E_T \neq 0 \text{ Inelastic scattering}$$

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

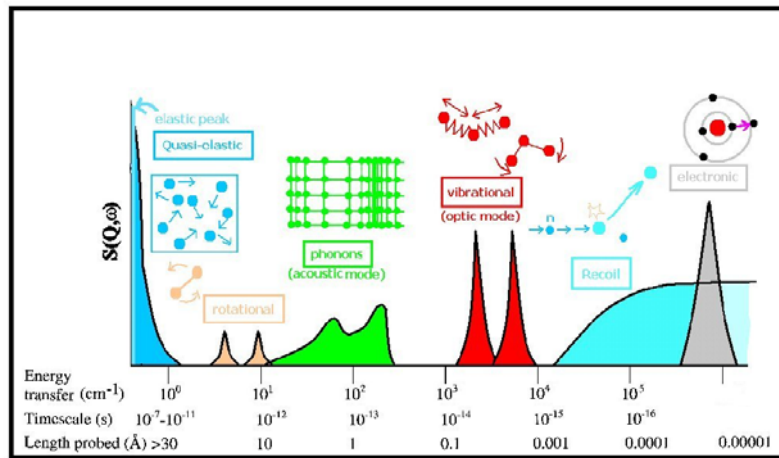
$$k = \frac{2\pi}{\lambda}$$



Neutrons can study length scales from Å to μm



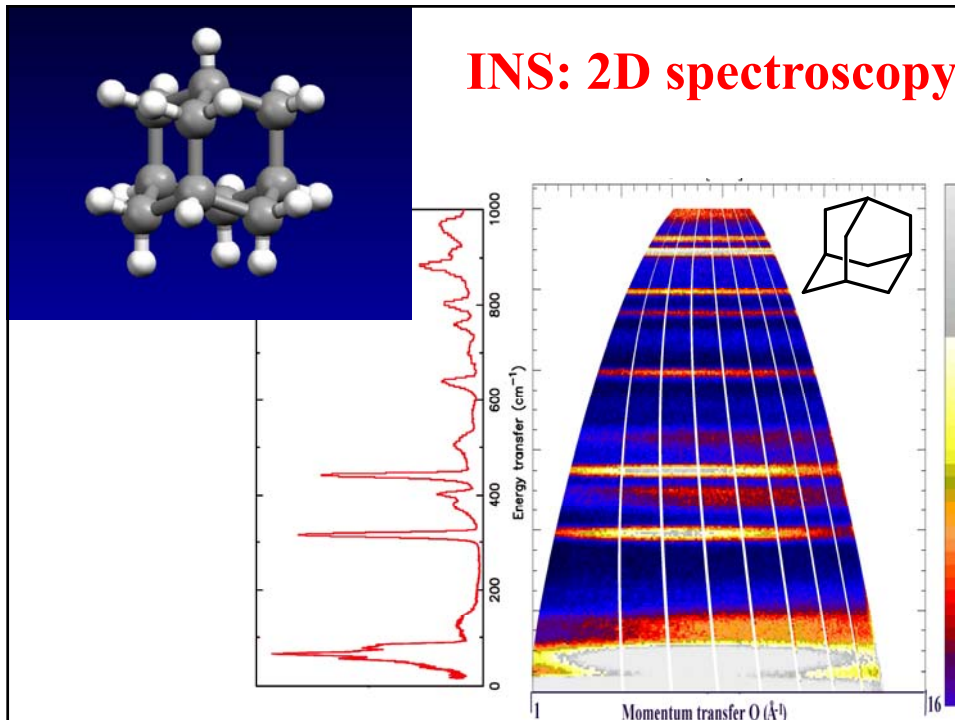
Inelastic neutron scattering



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INS: 2D spectroscopy



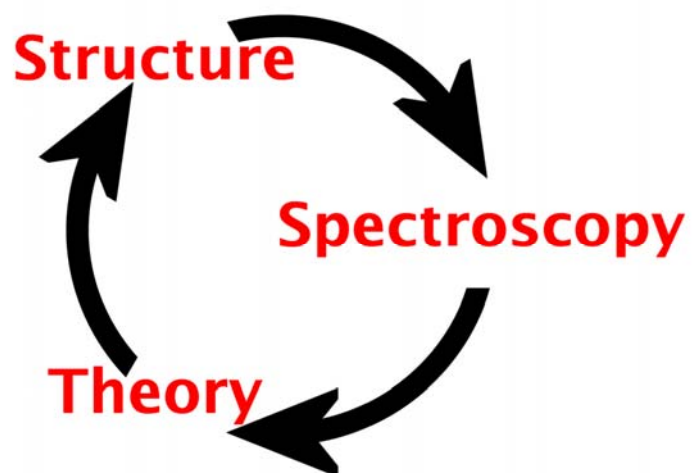


Atomic Force Microscope (AFM), Rigaku SmartLab X-Ray Diffractometer/Reflectometer

Physical Property Measurement System (PPMS), Single Crystal X-Ray Diffractometer

Magnetic Property Measurement System (MPMS), Thermo Gravimetric Analysis (TGA)

X-Ray Fluorescence Spectrometer (XRF)



Low- & High-energy Neutron Spectroscopy

Beyond Molecular Vibrations

Felix Fernandez-Alonso

Molecular Spectroscopy Group
ISIS Pulsed Neutron and Muon Source
&
Department of Physics & Astronomy
University College London

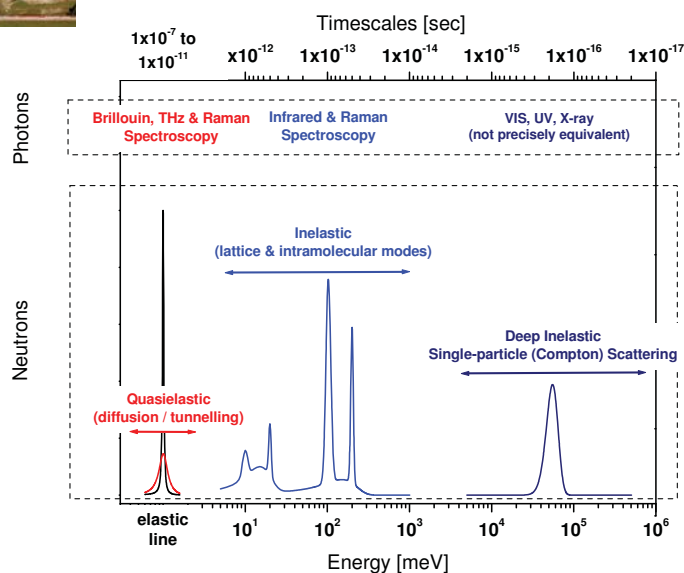
Introduction to Neutron Techniques in Catalysis
Harwell Research Complex
3-4th Nov 2014



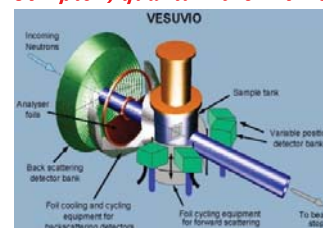
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Neutron Spectroscopy: Overview



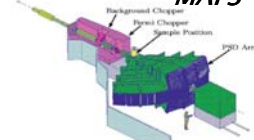
High energy
Compton, quantum thermometry



TOSCA



MAPS



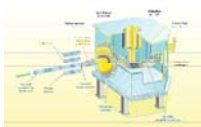
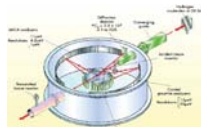
Intermediate energy (Raman)

'Chemical' resolution

IRIS

OSIRIS

LET



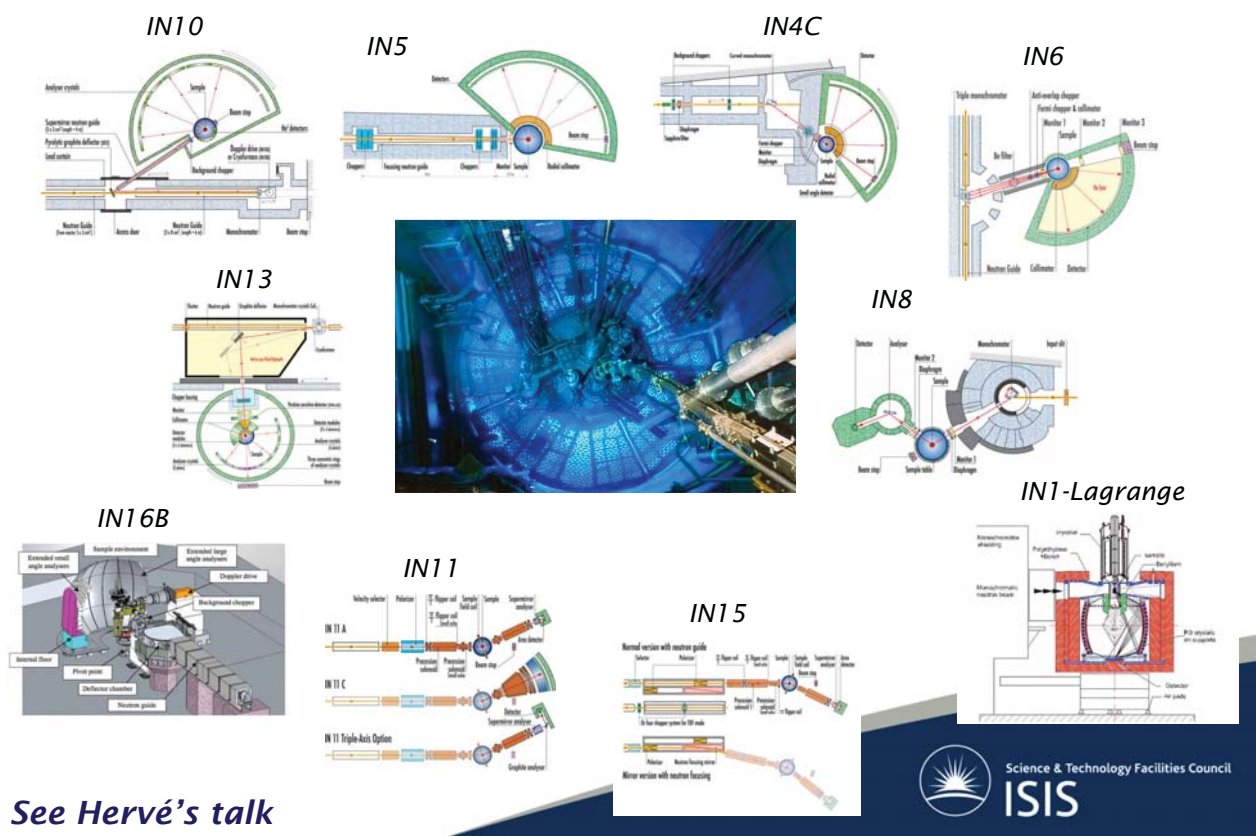
Low energy
(Brillouin, THz)

Simultaneous diffraction
Direct link to theory

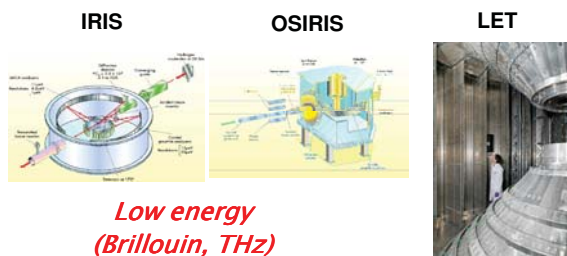
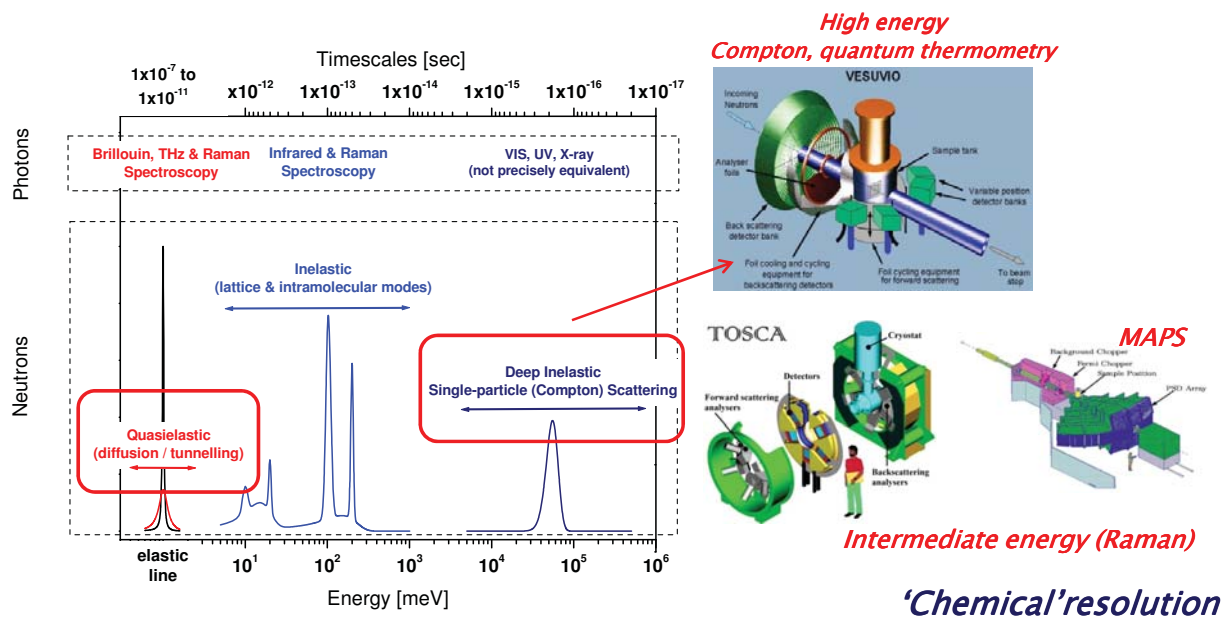


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Neutron Spectroscopy at ILL



Below and Above Molecular Vibrations



Simultaneous diffraction
Direct link to theory

Low and High Energies: An Operational Definition

Use the H₂ molecule as ‘yardstick’

- H-H stretch is highest-known vibrational frequency for a molecule:
 - $\omega_{vib} = 4400 \text{ cm}^{-1} = 550 \text{ meV} = 133 \text{ THz}$
 - **High energies** > ω_{vib}

Spallation sources (ISIS) can access up to 100-200 eV.

- H₂ rotational constant (free molecule) also highest known.
 - $B_{rot} = 58.8 \text{ cm}^{-1} = 7.35 \text{ meV} = 1.8 \text{ THz}$
 - **Low energies** < $2B_{rot} = 15 \text{ meV} = 3.6 \text{ THz}$ (rotational band head)

*With neutrons, access to sub-THz frequencies is routine.
Reactor sources (ILL) best for cold neutrons.*



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Hydrogen: A Very Special Case

Nuclide	σ_{coh}	σ_{inc}	Nuclide	σ_{coh}	σ_{inc}
¹ H	1.8	80.2	V	0.0	5.0
² H	5.6	2.0	Fe	11.2	0.4
C	5.6	0.0	Co	0.8	4.8
O	4.2	0.0	Cu	7.5	0.6
Al	1.5	0.0	³⁶ Ar	77.9	0.0

ppm H detection possible (impossible with X-rays).

Most examples will focus on H (except high energy) .

Beyond H: also within our reach

**Ongoing instrument upgrades to make these routine,
e.g., CO₂ sequestration**



Science & Technology Facilities Council
ISIS

For Much More

**NEUTRON SCATTERING -
FUNDAMENTALS**

Edited by
**FELIX FERNANDEZ-ALONSO
DAVID L. PRICE**

VOLUME 44
EXPERIMENTAL METHODS IN THE PHYSICAL
SCIENCES

Treatise Editors
THOMAS LUCA TORO
ALBERT C. PARR
KENNETH BALDWIN

The logo consists of the letters 'AP' in a stylized, bold, serif font, enclosed within a circle. The 'A' and 'P' are joined together.

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1.1.2.37 Neutron Scattering and X-ray Scattering	12	2.1.32 Cold Neutron Sources	140
1.1.2.38 Neutron Scattering and X-ray Scattering	12	2.1.33 Cold Neutron Sources	140
1.1.2.39 Neutron Scattering and X-ray Scattering	12	2.1.34 Cold Neutron Sources	140
1.1.2.40 Neutron Scattering and X-ray Scattering	12	2.1.35 Cold Neutron Sources	140
1.1.2.41 Neutron Scattering and X-ray Scattering	12	2.1.36 Cold Neutron Sources	140
1.1.2.42 Neutron Scattering and X-ray Scattering	12	2.1.37 Cold Neutron Sources	140
1.1.2.43 Neutron Scattering and X-ray Scattering	12	2.1.38 Cold Neutron Sources	140
1.1.2.44 Neutron Scattering and X-ray Scattering	12	2.1.39 Cold Neutron Sources	140
1.1.2.45 Neutron Scattering and X-ray Scattering	12	2.1.40 Cold Neutron Sources	140
1.1.2.46 Neutron Scattering and X-ray Scattering	12	2.1.41 Cold Neutron Sources	140
1.1.2.47 Neutron Scattering and X-ray Scattering	12	2.1.42 Cold Neutron Sources	140
1.1.2.48 Neutron Scattering and X-ray Scattering	12	2.1.43 Cold Neutron Sources	140
1.1.2.49 Neutron Scattering and X-ray Scattering	12	2.1.44 Cold Neutron Sources	140
1.1.2.50 Neutron Scattering and X-ray Scattering	12	2.1.45 Cold Neutron Sources	140
1.1.2.51 Neutron Scattering and X-ray Scattering	12	2.1.46 Cold Neutron Sources	140
1.1.2.52 Neutron Scattering and X-ray Scattering	12	2.1.47 Cold Neutron Sources	140
1.1.2.53 Neutron Scattering and X-ray Scattering	12	2.1.48 Cold Neutron Sources	140
1.1.2.54 Neutron Scattering and X-ray Scattering	12	2.1.49 Cold Neutron Sources	140
1.1.2.55 Neutron Scattering and X-ray Scattering	12	2.1.50 Cold Neutron Sources	140
1.1.2.56 Neutron Scattering and X-ray Scattering	12	2.1.51 Cold Neutron Sources	140
1.1.2.57 Neutron Scattering and X-ray Scattering	12	2.1.52 Cold Neutron Sources	140
1.1.2.58 Neutron Scattering and X-ray Scattering	12	2.1.53 Cold Neutron Sources	140
1.1.2.59 Neutron Scattering and X-ray Scattering	12	2.1.54 Cold Neutron Sources	140
1.1.2.60 Neutron Scattering and X-ray Scattering	12	2.1.55 Cold Neutron Sources	140
1.1.2.61 Neutron Scattering and X-ray Scattering	12	2.1.56 Cold Neutron Sources	140
1.1.2.62 Neutron Scattering and X-ray Scattering	12	2.1.57 Cold Neutron Sources	140
1.1.2.63 Neutron Scattering and X-ray Scattering	12	2.1.58 Cold Neutron Sources	140
1.1.2.64 Neutron Scattering and X-ray Scattering	12	2.1.59 Cold Neutron Sources	

Where Atoms Are



First question: what is the structure of a molecule or complex?

- Usual situation: no long-range order (no Bragg peaks).
- Spectroscopy is a local probe for disordered media -- also total scattering techniques, see Tristan's and Chris' talks.
- It constitutes an important fraction of what vibrational spectroscopy does (regardless of probe, photon or neutron).
- Spectroscopy can give more than average structure (e.g., energetics and motion).

Where atoms are ... from what they do

Polymer Intercalation in Graphene-related Materials

www.rsc.org/softmatter

Soft Matter, 2011, 7, 7173

COMMUNICATION

Polymers under extreme two-dimensional confinement: Poly(ethylene oxide) in graphite oxide†

Fabienne Barroso-Bujans,^{a,c} Felix Fernandez-Alonso,^{b,c} Silvana Cerveny,^d Stewart F. Parker,^b Angel Alegria^{a,c} and Juan Colmenero^{a,c,d}

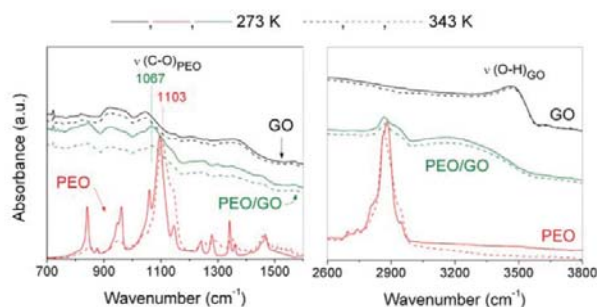
Received 13th April 2011, Accepted 31st May 2011
DOI: 10.1039/c1sm05661a

CARBON 50 (2012) 5232–5241

Tunable uptake of poly(ethylene oxide) by graphite-oxide-based materials

Fabienne Barroso-Bujans^{a,c}, Felix Fernandez-Alonso^{b,c}, Jose A. Pomposo^{a,d,e}, Eduardo Enciso^f, Jose Luis G. Fierro^g, Juan Colmenero^{a,e,h}

Optical (FTIR+Raman)



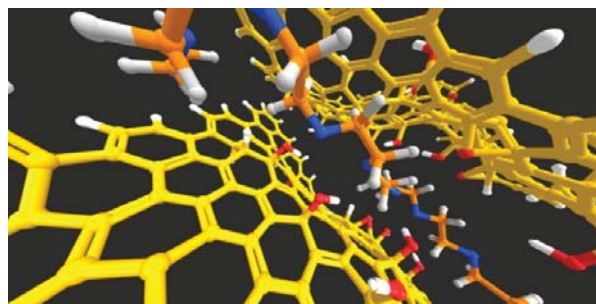
TOSCA Xpress: Soft Matter Comm 7 7173 (2011).

ACS Macro Lett 1 550 (2012).

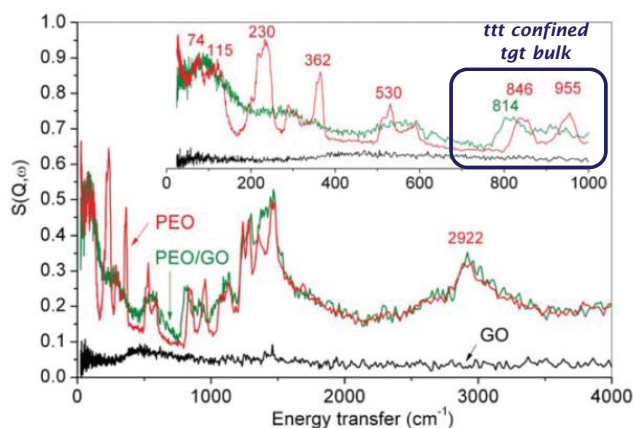
Macromolecules 45 3137 (2012).

Carbon 50 5232 (2012).

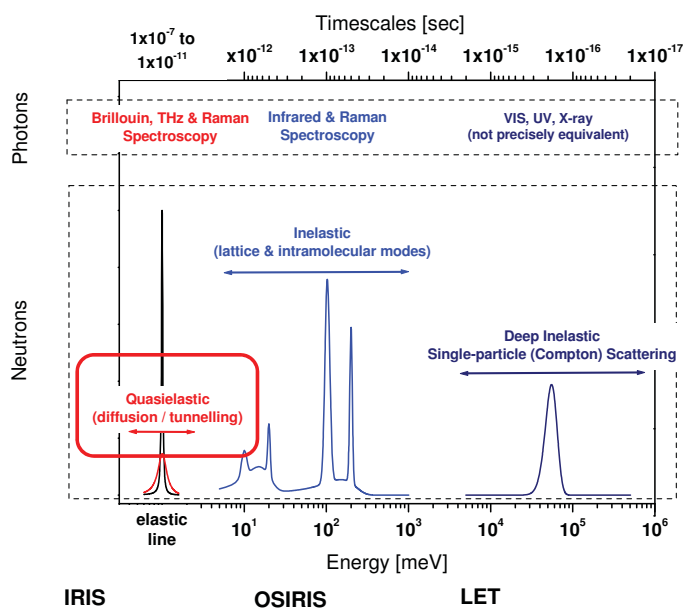
Soft Matter 9 10960 (2013).



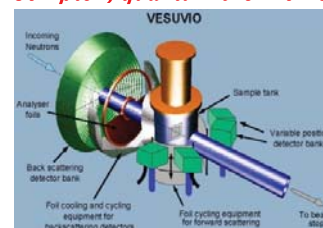
Intercalate conformation: only with neutrons



Below Molecular Vibrations



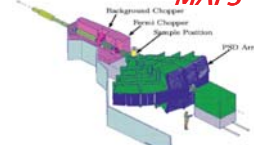
High energy
Compton, quantum thermometry



TOSCA



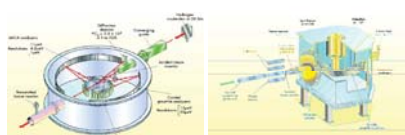
MAPS



Intermediate energy (Raman)

'Chemical' resolution

Simultaneous diffraction
Direct link to theory



Low energy
(Brillouin, THz)



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Spectroscopy:

Where Atoms Are *and Do*

Lower energies: larger (supramolecular) objects.

Recall: $\omega_{vib} = \sqrt{\frac{k}{\mu}}$



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THz Spectroscopy of MOFs

(in press)

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 Civalieri,⁴ Thomas D. Bennett,⁵ Sebastian Henke,² Svenir Rudić,² Gianfelice Cinque,³ Felix Fernandez-Alonso,^{2,6} and Jin-Chong Tan^{1,4}

¹Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom

²ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom

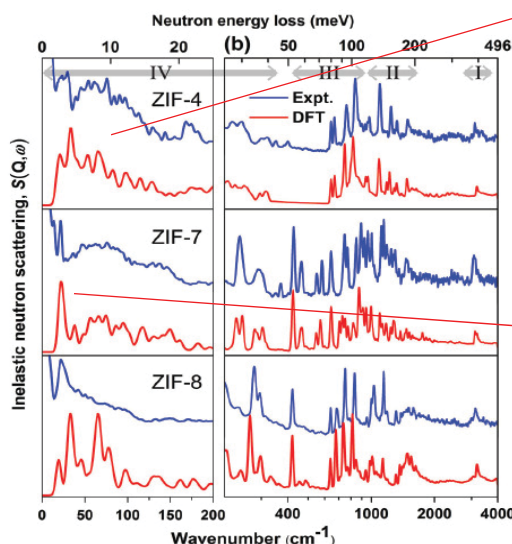
³Diamond Light Source, Harwell Campus, Didcot, Oxford OX11 0DE, United Kingdom

⁴Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, via P. Giuria 7, 10125 Torino, Italy

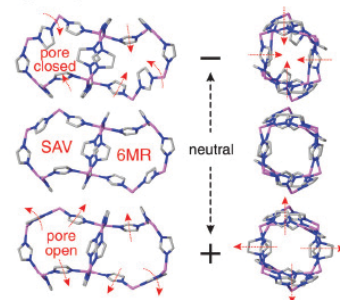
⁵Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom

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

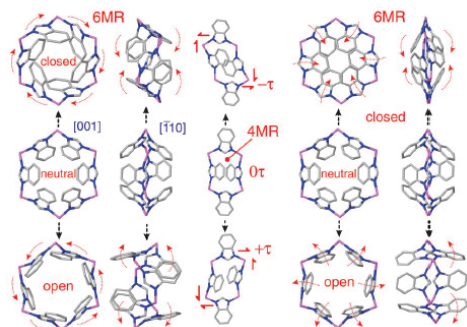
(Received 1 August 2014)



Gate-opening mechanism at ~1 THz



Breathing & shearing at 0.654 THz



Where Atoms Are *and Do*

Low energies also give access to:

Quantum tunnelling in H_2 , CH_4 , hydrocarbons, methyl groups in many materials like polymers, ...

No classical counterpart (not vibrations per se)



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Molecular Tunnelling on Surfaces



VOLUME 87, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 2001

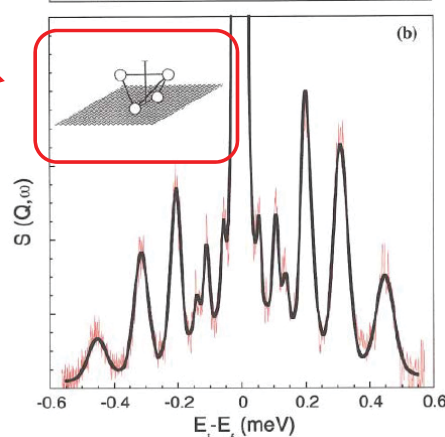
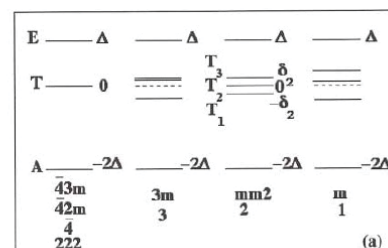
Tracking the Evolution of Interatomic Potentials with High Resolution Inelastic Neutron Spectroscopy

J. Z. Larese,^{1,*} D. Martín y Marero,² D. S. Sivia,² and C. J. Carlile^{2,3}
¹Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973
²ISIS, Rutherford Appleton Laboratory, Didcot, United Kingdom
³Institut Laue Langevin, Grenoble, France
 (Received 27 October 2000; published 26 October 2001)

Structure of CH_4 films on $MgO(100)$ surfaces

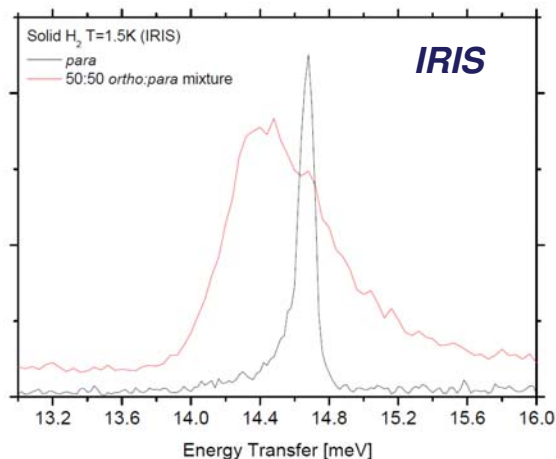
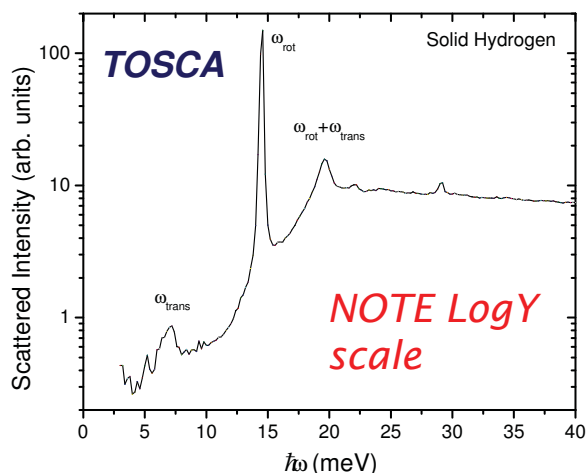
TABLE I. Comparison of model calculations (Ref. [10]) with fits to data in Fig. 1(b) using Bayesian analysis. Model calculations use molecule-to-surface distance of 3.30 \AA and molecular field of 21.8 cm^{-1} and level diagram ($mm2$, 2).

Transition	Model (μeV)	Experiment (μeV)
$E \rightarrow T3$	59	56.6 ± 0.5
$T2 \rightarrow T1$	110	108.2 ± 0.4
$T3 \rightarrow T2$	134	139.7 ± 0.7
$E \rightarrow T2$	193	200.0 ± 2.1
$T1 \rightarrow A$	212	218.0 ± 3.7
$T3 \rightarrow T1$	Not Allowed	Not Observed
$E \rightarrow T1$	300	306.2 ± 0.4
$T2 \rightarrow A$	322	324.0 ± 2.5
$T3 \rightarrow A$	456	450.4 ± 0.7



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Rotations in Molecular Hydrogen



- $(0 \rightarrow 1)$ rotational transition purely incoherent (optically forbidden).
- Very sensitive to local environment (energy barriers)

www.isis.stfc.ac.uk/instruments/tosca/ins-database/

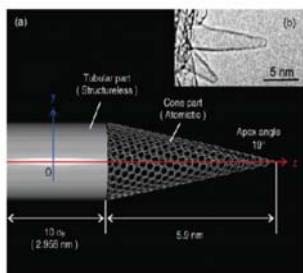
in Handbook of Nanophysics,
eds. KD Sattler, vol. 5 (2010).



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H₂ Rotations in Carbon Nanostructures

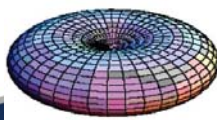
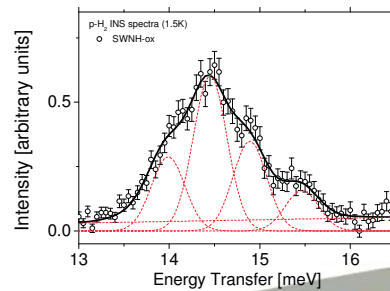
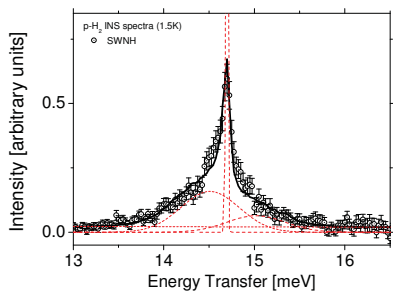
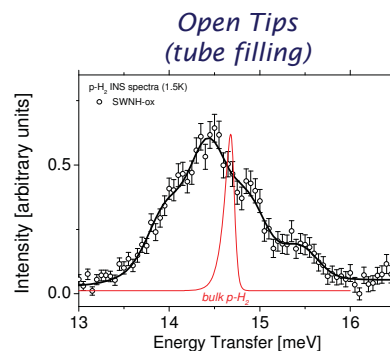
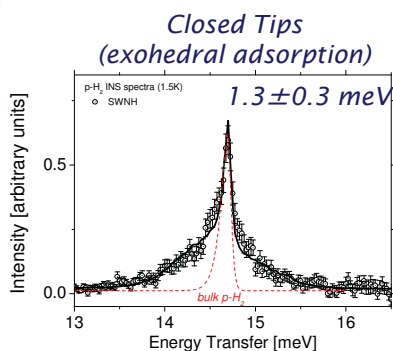
PHYSICAL REVIEW LETTERS
PRL 98, 215503 (2007)
week ending
25 MAY 2007
Nature of the Bound States of Molecular Hydrogen in Carbon Nanoforms
F. Fernandez-Alonso,^{1,2,4} F.J. Bernabeu,^{1,2} C. Cabrillo,¹ R. O. Loutfy,³ V. Leon,⁴ and M.L. Subong⁵
¹ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
²Instituto de Estudios de la Materia, C.S.I.C., and Dept. Electrodinámica y Electromagnetismo, Universidad del País Vasco/EHU, P.O. Box 644, E-48940 Leioa, Spain
³MBE Corporation, 7000 South Kasha Road, Tucson, Arizona 85736, USA
⁴Centre de Recherche sur la Matière Condensée, CNRS—Université d'Orléans, 1 rue de la Ferrière, 45071 Orléans Cedex 2, France
(Received 5 January 2007; published 25 May 2007)



- Case of extreme confinement (surface areas > 1000 m²/g).

- Cylindrically symmetric environment: molecular alignment parallel to surface.

- Orientational barriers are a few meV (4x than nanotubes).



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H₂ in Metal-doped Carbon Nanostructures

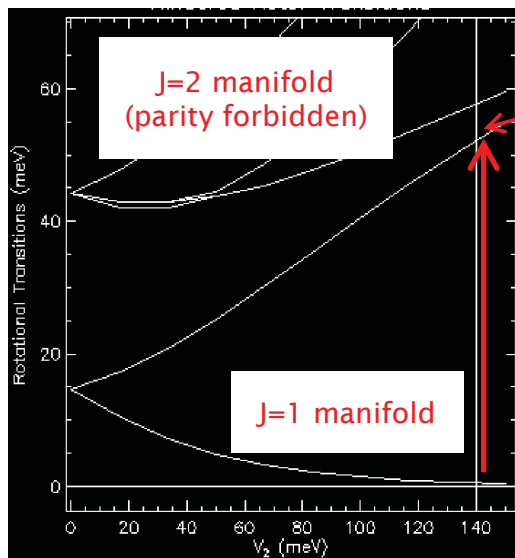


PRL 101, 126101 (2008) PHYSICAL REVIEW LETTERS week ending 19 SEPTEMBER 2008

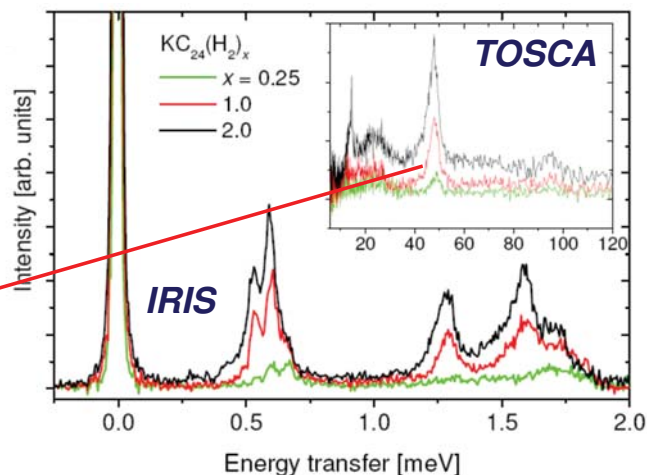
Quantum Delocalization of Molecular Hydrogen in Alkali-Graphite Intercalates

Arthur Lovell,^{1,*} Felix Fernandez-Alonso,^{1,*} Neal T. Skipper,² Keith Refson,³
Stephen M. Bennington,^{1,3} and Stewart F. Parker¹

¹ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
²Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom
³Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
(Received 7 March 2008; published 18 September 2008)



H₂ pinned along quantization axis.



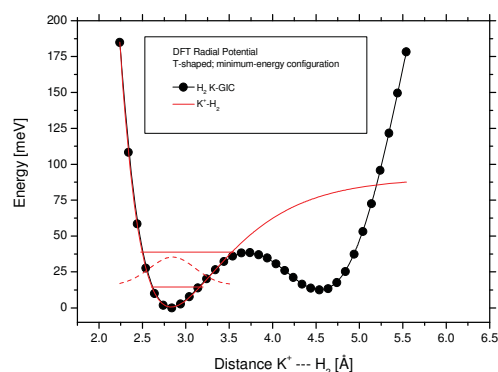
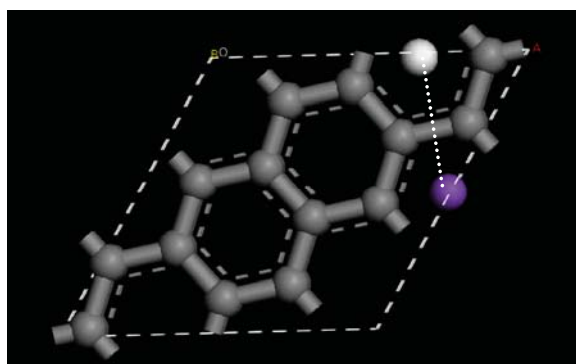
Orientational barriers ~30x than carbon-only materials

Structure & energetics



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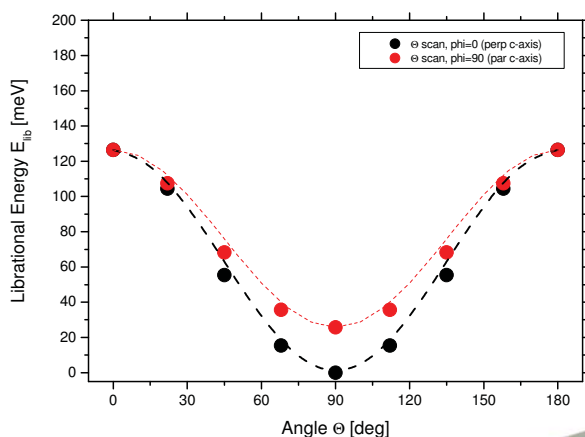
First-principles: Potential Energy Landscape of H₂ in K-GIC



Orientational potential:

$$V(\Theta, \phi) = V_{\Theta} \left[1 - \left(1 - \frac{V_{\phi}}{V_{\Theta}} \sin^2 \phi \right) \sin^2 \Theta \right]$$

Right barrier height towards ion ($V_{\Theta}=125$ meV).
Small modulation ($V_{\phi}=25$ meV) due to graphite planes.



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Nature of Metal-H₂ Interactions

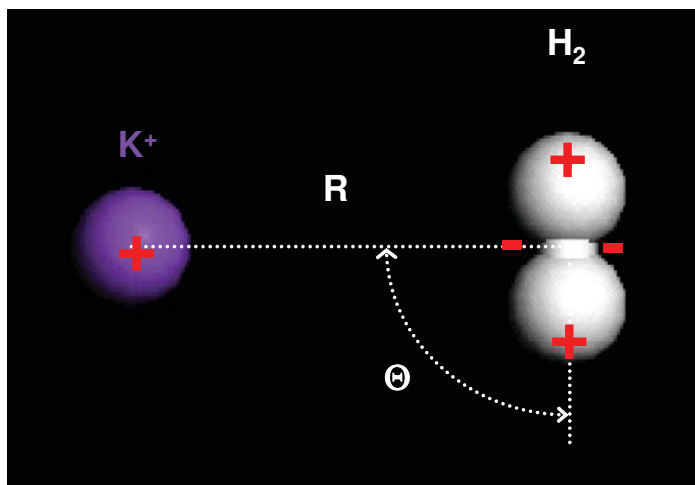
Ion-permanent quadrupole
(T-shaped complex)

$$V_Q(R, \Theta) = \left[\frac{Q_{H_2}}{R^3} \right] P_2(\cos \Theta)$$

Ion-induced dipole
(linear complex)

$$\begin{aligned} Q_{H_2} &= 0.460 \text{ au} \\ \alpha &= 5.179 \text{ au} \\ \alpha_{par} &= 6.305 \text{ au} \\ \alpha_{per} &= 4.578 \text{ au} \end{aligned}$$

$$V_\alpha(R, \Theta) = - \left[\frac{1}{R^4} \right] \left[\frac{\alpha}{2} + \frac{1}{3} (\alpha_{par} - \alpha_{per}) P_2(\cos \Theta) \right]$$



For the H₂ molecule: quadrupole term dominates.

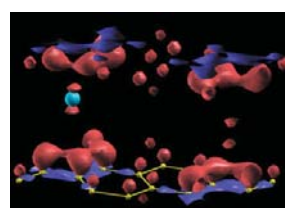
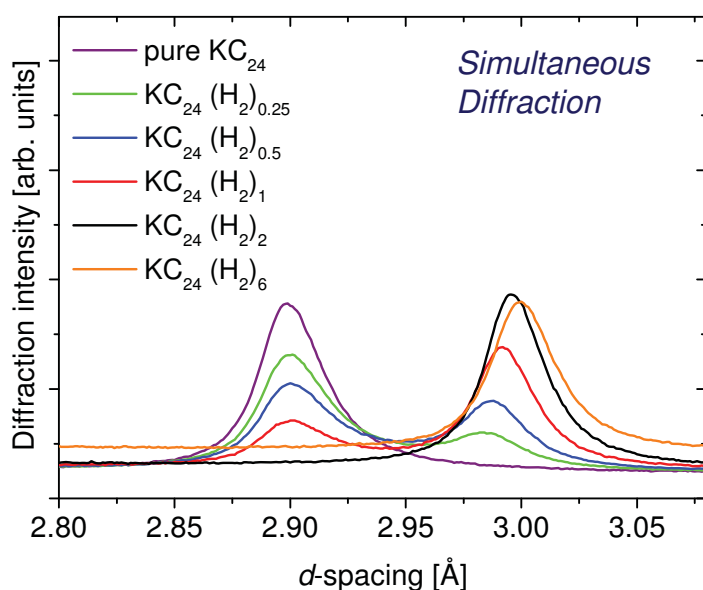
Bond activation minimal
(induced dipole interactions small)



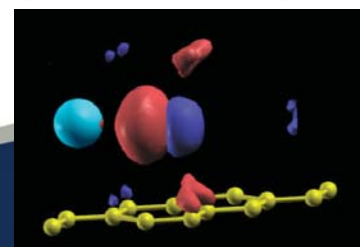
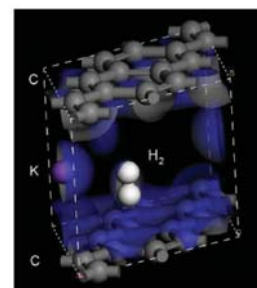
Science & Technology Facilities Council
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The Free Lunch: Substrate is not a Passive Bystander

Gallery expansion along c-axis is ~0.3Å as we take up hydrogen.

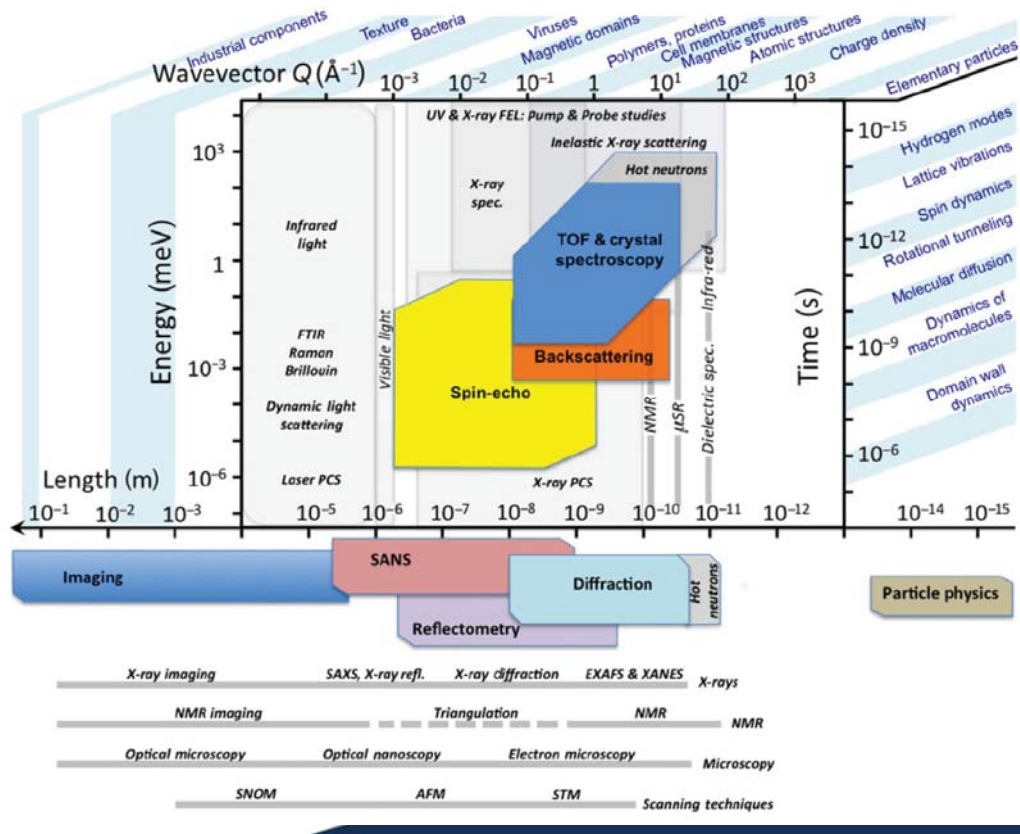


DFT
Modelling



Phys Rev Lett **101** 126101 (2008)
J Chem Phys **129** 224701 (2009)
Handbook of Nanophysics, eds. KD Sattler, vol. 5 (2010)

Where Atoms Are and Do: Neutrons



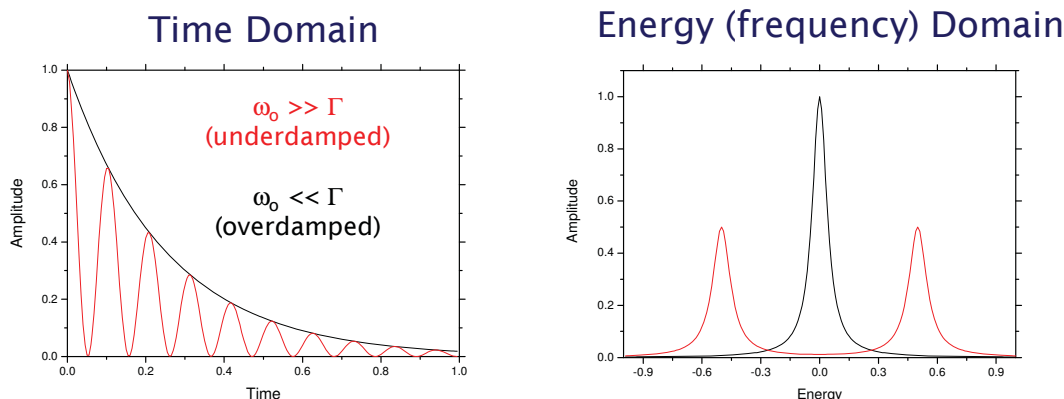
Beyond Vibrations: Atomic & Molecular Transport



Science & Technology Facilities Council
ISIS

“Inelastic” vs “Quasielastic”

Spectral peaks characterized by a frequency ω_0 and damping Γ (decay)



- Underdamped motions: ‘proper’ spectroscopic peaks, e.g., H₂ molecule rotations & vibrations.
- Overdamped motions: not enough time to define period of oscillation
 - Centered at zero frequencies (elastic scattering of probe – e.g., neutrons).
 - Broadening proportional to damping.
 - Example: diffusion in a crowded environment.

Note: transition from ‘INS’ to ‘QENS’ is continuous (e.g., with temperature)



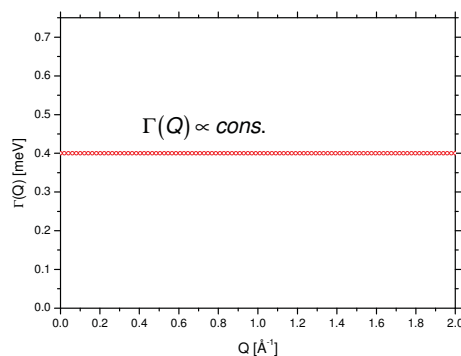
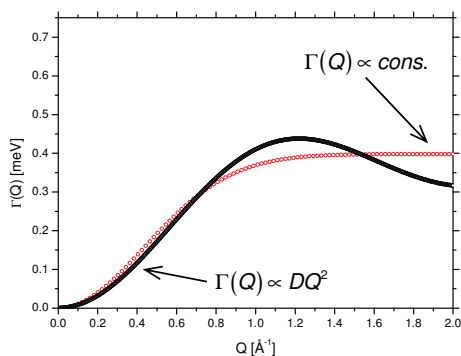
Science & Technology Facilities Council
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The Added Dimension (Neutrons Only)

If neutron Q range matches characteristic length scales of motion R ($Q \sim 1/R$), then QENS broadening Γ will be sensitive to it.

Two limits of interest:

- Translational diffusion: motion of molecular center of mass.
- Localized diffusion: motion about the molecular CM



Lorentzian line shape :
$$\frac{\Gamma(Q)}{E^2 + \Gamma^2(Q)}$$



Science & Technology Facilities Council
ISIS

Molecular Transport in Hydrogen Fluoride

PRL 98, 077801 (2007)

PHYSICAL REVIEW LETTERS

week ending
16 FEBRUARY 2007

Observation of Fractional Stokes-Einstein Behavior in the Simplest Hydrogen-Bonded Liquid

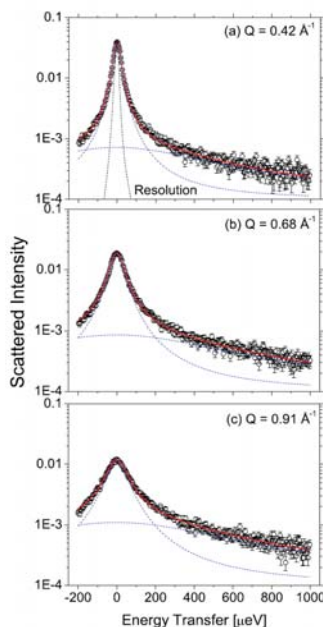
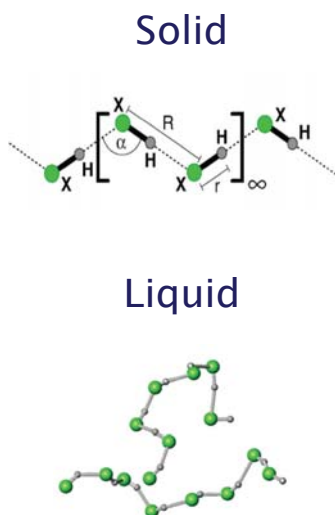
F. Fernandez-Alonso,^{1,*} F. J. Bermejo,^{2,†} S. E. McLain,¹ J. F. C. Turner,³ J. J. Molaison,³ and K. W. Herwig⁴

¹ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

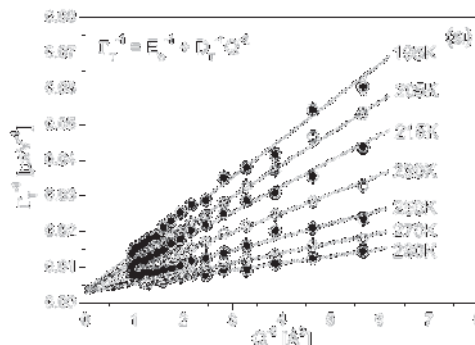
²CSIC-Instituto Estructura de la Materia y Department of Electricity and Electronics, University Basque Country, P.O. Box 644, Bilbao 48080, Spain

³Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600, USA

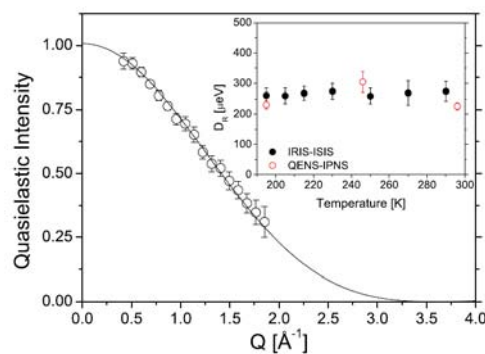
⁴Spallation Neutron Source, Oak Ridge National Laboratory, Scarboro Road, Oak Ridge, Tennessee 37830, USA
(Received 24 October 2006; published 14 February 2007)



Translational Diffusion



Rotational Diffusion



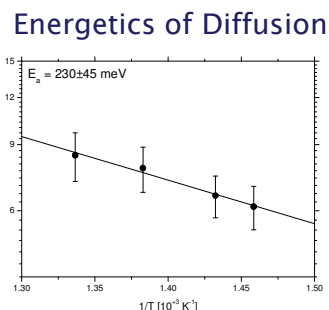
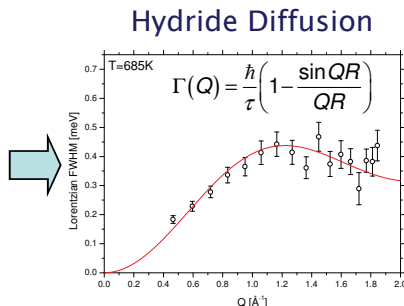
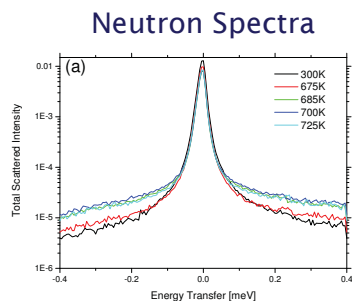
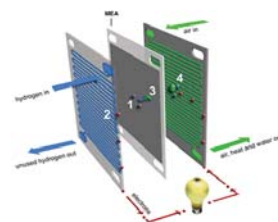
Mass & Charge Transport: Fuel-cell & Battery Materials

COMMUNICATION

Adv. Mater. 2006, 18, 3304–3308

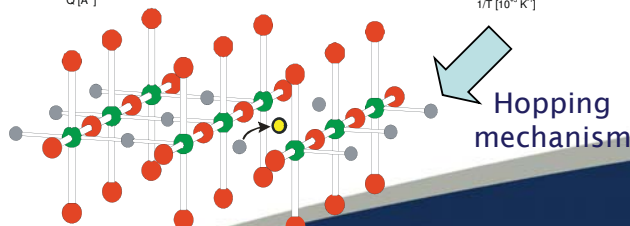
Observation of Hydride Mobility in the Transition-Metal Oxide Hydride $\text{LaSrCoO}_{3.7}$ **

By Craig A. Bridges, Felix Fernandez-Alonso, Jon P. Goff, and Matthew J. Rosseinsky*



Order-of-magnitude increase in conductivity compared to other proton conductors.

Only way to obtain microscopic diffusion directly



Diffusion of Organic Contaminants in Hydrated Clays

Chemical Geology 230 (2006) 182–196

The structure and dynamics of 2-dimensional fluids in swelling clays

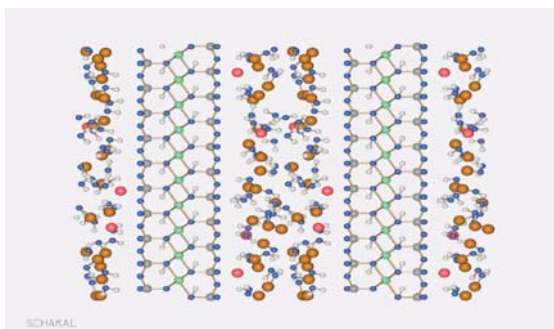
Neal T. Skipper ^{a,*}, Peter A. Lock ^a, James O. Titiloye ^b, Jan Swenson ^c,
Zakaria A. Mirza ^a, W. Spencer Howells ^d, Felix Fernandez-Alonso ^d

^a Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

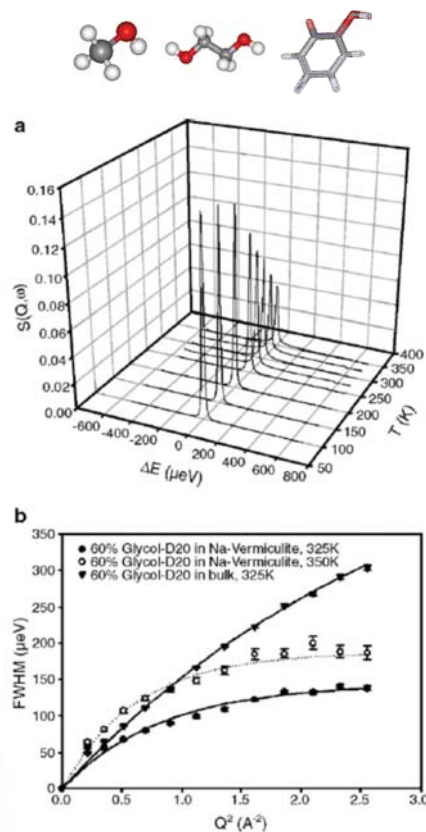
^b Department of Chemical Engineering and Applied Chemistry, Aston University, Birmingham, B4 7ET, UK

^c Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^d ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK



- Diffusion of organic molecules close to bulk solutions: unexpected high mobility inside clay.
- Pressures and temperatures in order to emulate geophysical environments a few Km in depth.

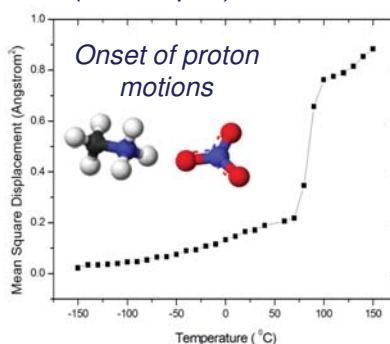
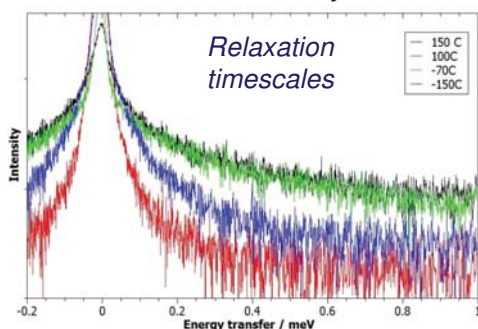


Vibrations and Elastic Scattering

- Well-defined vibrations lead to modulation of elastic-line intensities
- Debye-Waller factor (as in diffraction):
$$I(Q) = e^{-\frac{r^2 Q^2}{3}}$$
- “Elastic-window” scans: T-dependence of mean-square displacement.

Atom-specific (H) ‘neutron calorimetry’ with spatial and temporal resolution – quick measurements, backbone of Xpress programme

Methylammonium nitrate (ionic liquid)



KR Seddon et al

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ISIS

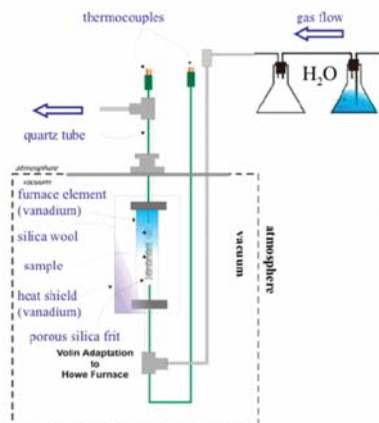
Solid Electrolytes under Operating Conditions

J. Phys. Chem. C 2007, 111, 6574–6580

Proton-Containing yttrium-doped barium cerate: A Simultaneous Structural and Dynamic Study by Neutron Scattering

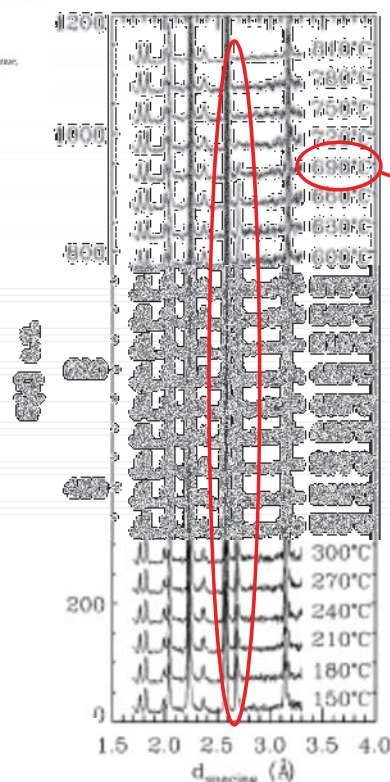
N. Malikova,^{1,2,4} C.-K. Loong,² J.-M. Zanotti,³ and F. Fernandez-Alonso^{5,7}
 Intense Pulsed Neutron Source Division, Argonne National Laboratory, 9700 S. Cass Avenue,
 Argonne, Illinois 60439, Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay,
 91191 Gif-sur-Yvette cedex, France, and ISIS Facility, Rutherford Appleton Laboratory,
 Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

Yttrium-doped Barium Cerate (perovskite-type)



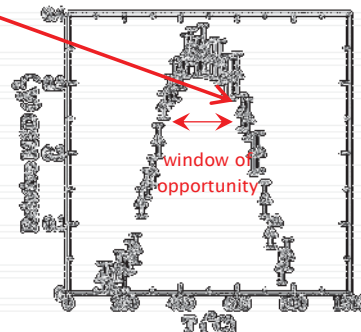
Experimental conditions
to emulate operating fuel cell

Simultaneous Diffraction



Rhombohedral → cubic
phase transition

MSD - Proton Mobility



Dehydration & proton
mobility occur
before phase
transition at 700C

More on this in ...

Hervé Jobic's and Alex O'Malley's talks ...



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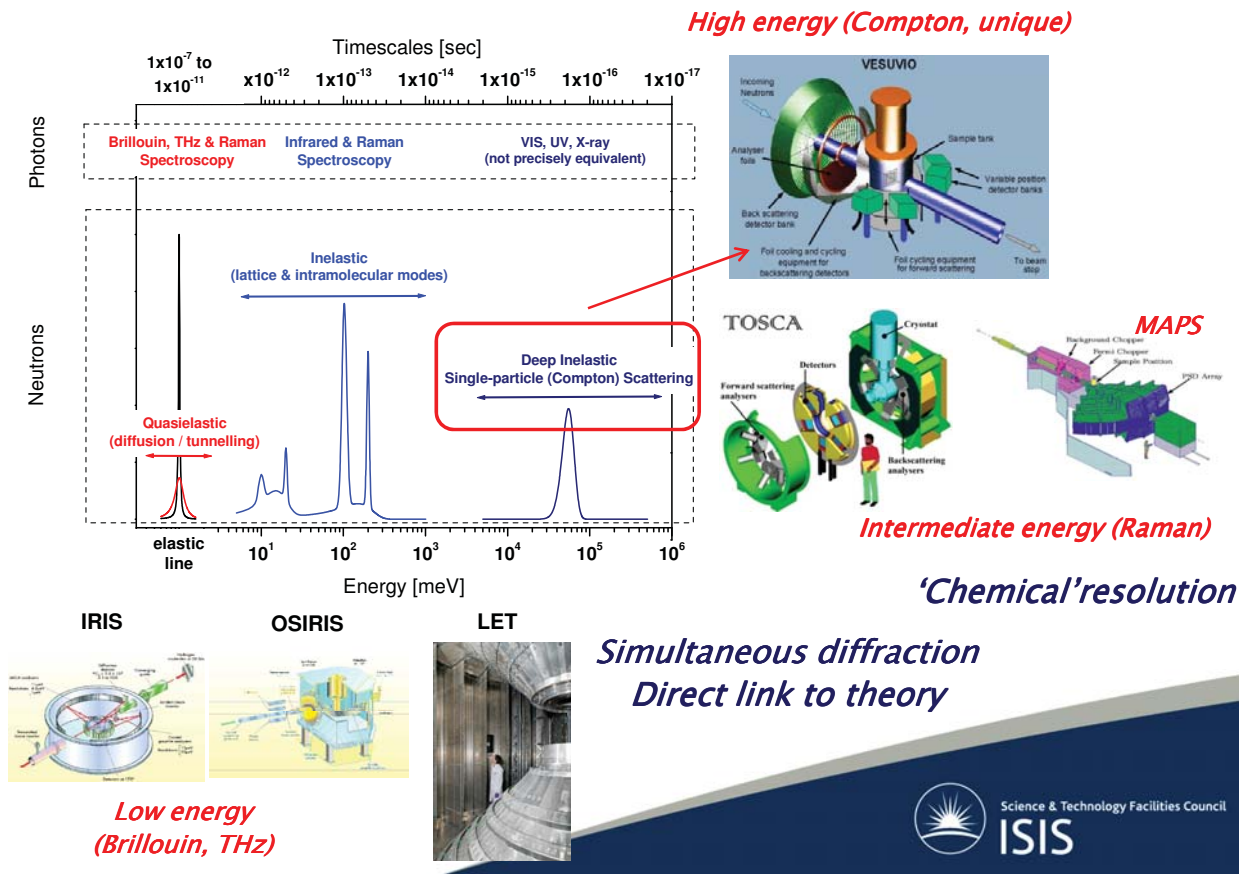
ISIS



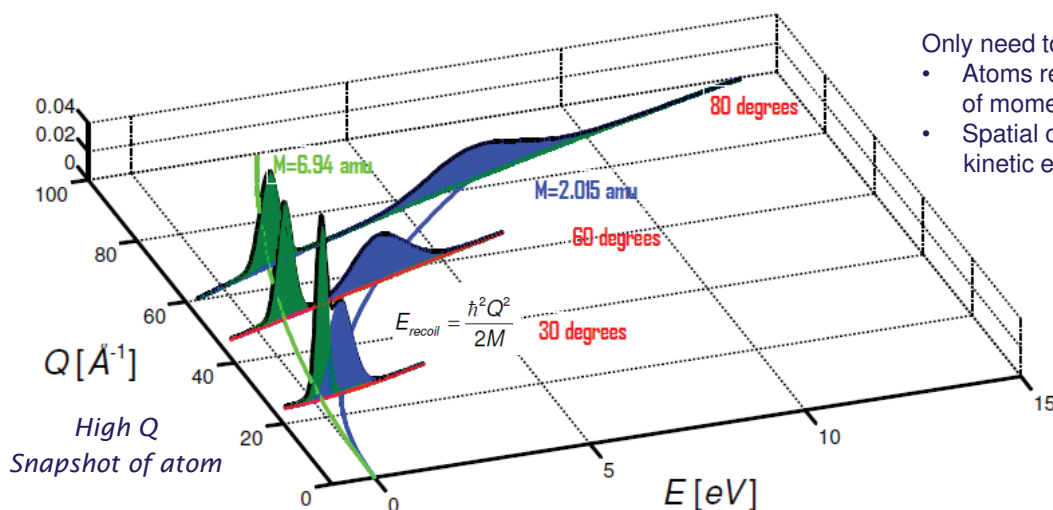
Science & Technology Facilities Council

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Above Molecular Vibrations: Atoms



MASS-selective Neutron SpECTroscopy - MANSE



Atomic Quantum Thermometry:

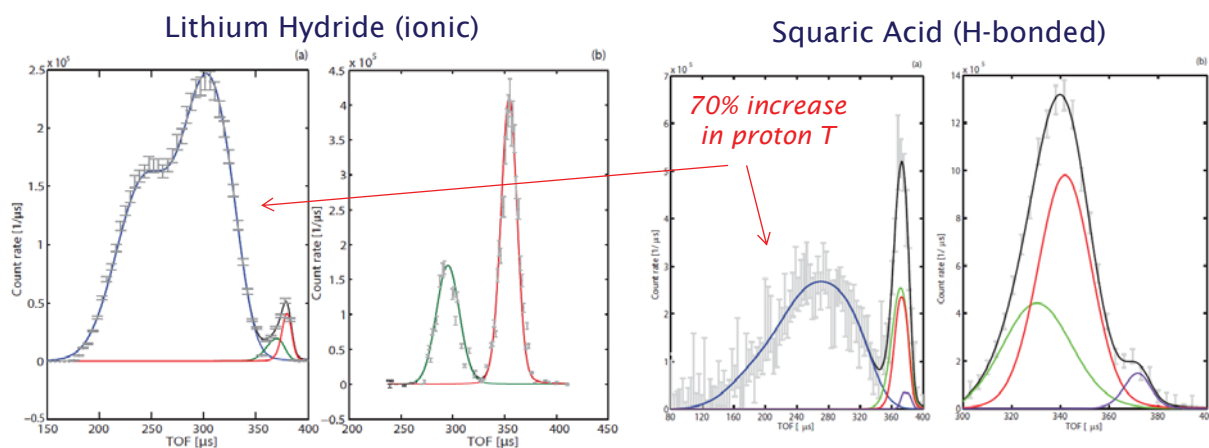
- Mass selectivity from atomic recoil (kinematics).
- Width of recoil peaks: kinetic energy or 'chemical temperature' of an atom (binding).
- Already demonstrated up to 20 amu.

PHYSICAL REVIEW B 88, 184304 (2013)
Mass-selective neutron spectroscopy of lithium hydride and deuteride: Experimental assessment of the harmonic and impulse approximations

Maciej Krzysztyniak* and Selena E. Richards
School of Science and Technology, Nottingham Trent University, Clifton campus, Nottingham NG11 8NS, United Kingdom
and ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

Andrew G. Seal and Felix Fernandez-Alonso[†]
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
(Received 26 July 2013; revised manuscript received 22 October 2013; published 19 November 2013)

MANSE: Unique Chemical Information from Recoil Data



(in press)

- Two modes of operation (similar to xtallography):
 - Coarse resolution (forward scattering, H)
 - High resolution (backscattering)
- Peak integration: head count with sub-ppm sensitivity for H.
- Sensitive to chemical environment (temperature) around an atom, a consequence of binding forces and dimensionality of bonding network.
- Mass resolution could be improved further.

Mass-selective Neutron Spectroscopy Beyond the Proton

M. Krzystyniak^{1,2}, A.G. Seel¹, S.E. Richards^{1,2}, M.J. Gutmann¹, 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

¹ ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX.

² School of Science and Technology, Nottingham Trent University, Clifton Campus

³ Department of Physics and Astronomy, University College London, Gower Street, London

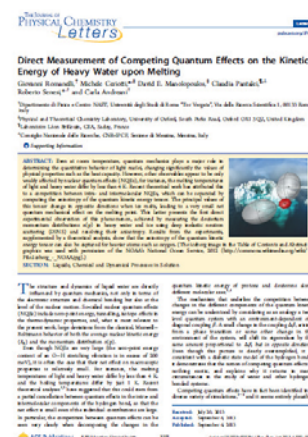
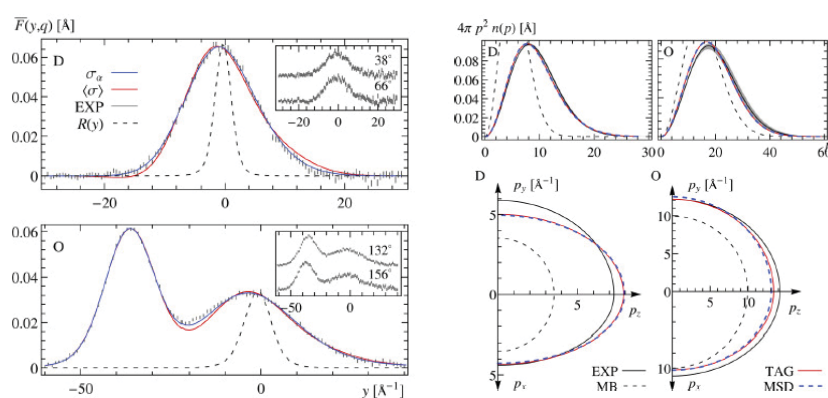
WC1E 6BT, United Kingdom



Science & Technology Facilities Council

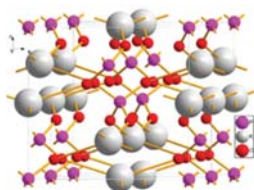
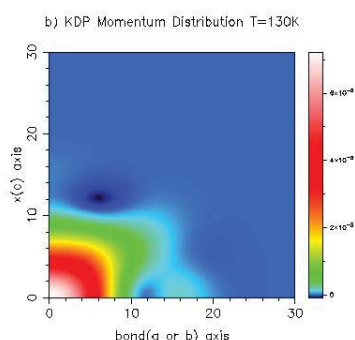
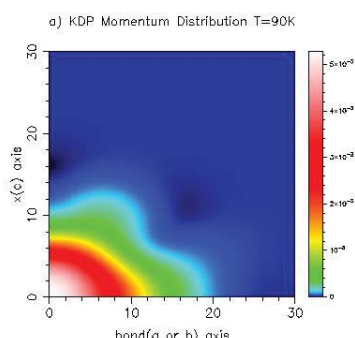
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Beyond Recoil Widths: Nuclear Quantum Effects and the Melting of Heavy Water



- Intra and intramolecular nuclear quantum dynamics of D and O: detailed line shape analysis gives nuclear momentum distribution (not just width).
- Use of state-of-art first-principles methods (PIMD) to be quantitative.
- Direct benchmark of theoretical methods.

High-energy Neutrons as the Ultimate *Wavefunction Diffraction*

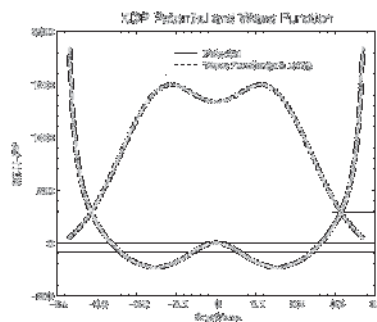
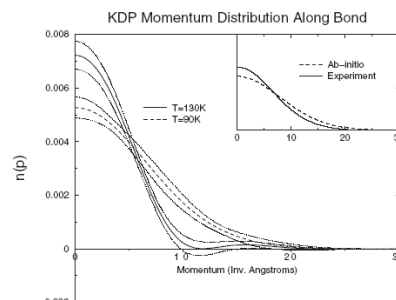


$$n(p) \propto \left| \int \Psi(\vec{r}) e^{i\vec{p}\cdot\vec{r}} d\vec{r} \right|^2$$

Young's double-slit experiment on the proton

$$V(\vec{r}) = E - \frac{\int \left(\frac{p^2}{2m} \right) \sqrt{n(\vec{p})} e^{i\vec{p}\cdot\vec{r}} d\vec{p}}{\int \sqrt{n(\vec{p})} e^{i\vec{p}\cdot\vec{r}} d\vec{p}}$$

Requires single crystals



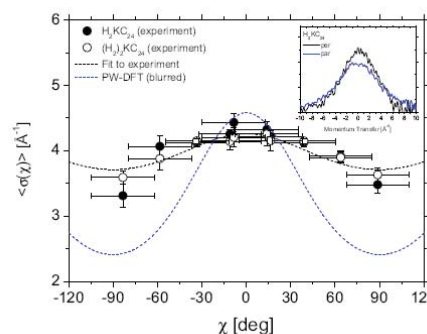
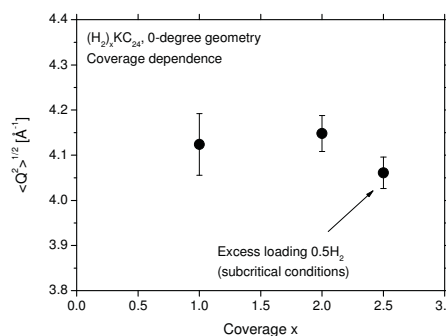
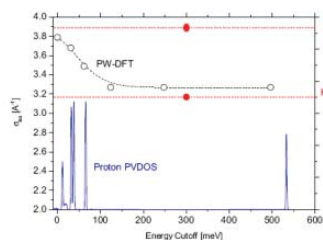
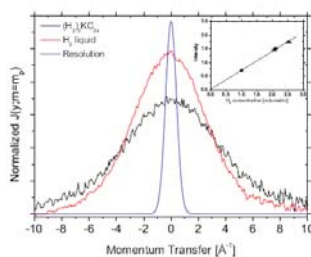
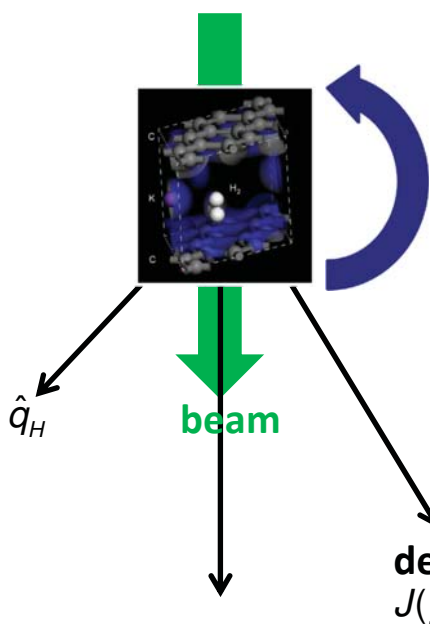
Phys Rev Lett **89** 135505 (2002)



This journal is © The Royal Society of Chemistry 2011 Faraday Discuss., 2011, 151, 171–197

Probing the binding and spatial arrangement of molecular hydrogen in porous hosts *via* neutron Compton scattering

Maciej Krzystyniak,^{ab} Mark A. Adams,^a Arthur Lovell,^{ac} Neal T. Skipper,^c Stephen M. Bennington,^{ac} Jerry Mayers^a and Felix Fernandez-Alonso^{abc}



- Calculations to dissect recoil profiles.
- Access to adsorbate-adsorbate interactions.
- Direct probe of molecular alignment.



Other Merits of High-energy Neutrons

- Non-destructive (unlike conventional mass spectrometry), carries information not only on abundance but also on chemical forces.
- Li, B, etc: do not need costly isotopic enrichment protocols (negligible absorption at high neutron energies).
- Not restricted to low temperatures or solids: all information is in the spectral line shape and its integral must remain constant.
- Mass range: extendable to heavier masses (e.g., metals) via the use of neutron resonances – Dopplerimetry, under development.

MANSE (recoil)

Nuclear Resonances (Dopplerimetry)

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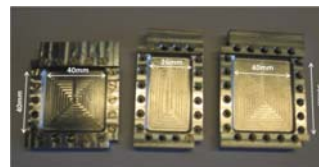
Some Practicalities

How Much Sample?

Always aiming for 'canonical 1/8' scattering: $\frac{I_T}{I_o} = e^{-n\sigma L}$ *Beer-Lambert Law*

Why?

- Keep multiple scattering to minimum.
- Important for both low and high energies.



Optimal thickness: $L \approx \frac{1}{n\sigma} \left(\frac{1}{8} \right)$



Number to remember: $L=0.25 \text{ mm}$ for H_2O ($0.25/\pi$ if annular)
Other cases can be estimated via scaling

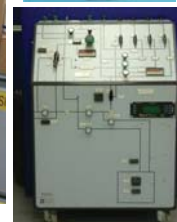
Sample quantities: from fractions of a gram to grams (not mg).



Bringing the Chemistry Lab to the Beamline

New Infrastructure

- Catalyst preparation rig.
- Dedicated residual-gas analysis.
- New cells to emulate operando industrial catalysis and gas adsorption (0-100 bar).
- Shared across instrument suite.



RCaH announced as location for EPSRC UK Catalysis Hub

RCaH announced as location for EPSRC UK Catalysis Hub

The Research Complex at Harwell (RCaH) is to become a research hub for catalytic science, following an announcement of £12.9 million of funding from EPSRC for the UK Catalysis Hub initiative. The RCaH is perfectly placed to become a hub - researchers work across the boundaries of traditional research disciplines and it's uniquely placed to benefit from the scientific facilities on the RAL campus. This initiative will coordinate and strengthen research efforts in catalytic science, allowing the UK to remain a world-leader in the field and tackle major global changes. There will be a strong emphasis on energy sustainability, environmental protection and innovative catalytic processes to support the UK chemical industry (for more information click [here](#)).



Gas Adsorption

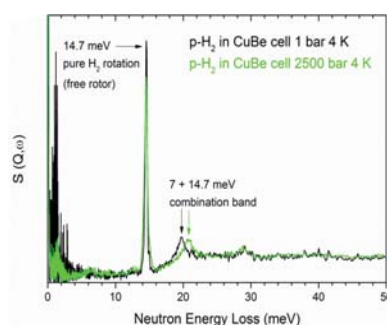
*In-situ Sieverts and
TPD manifolds*



p-H₂ generator



Gas cells up to 8 kbar, including H₂



***Emphasis on increased
automation and ease
of use***

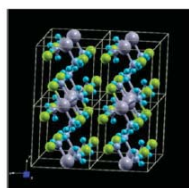


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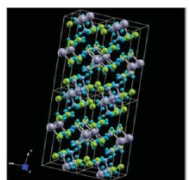
Simultaneous Neutron Scattering and Raman Scattering

Appl Spect. 63 2009 (2009)

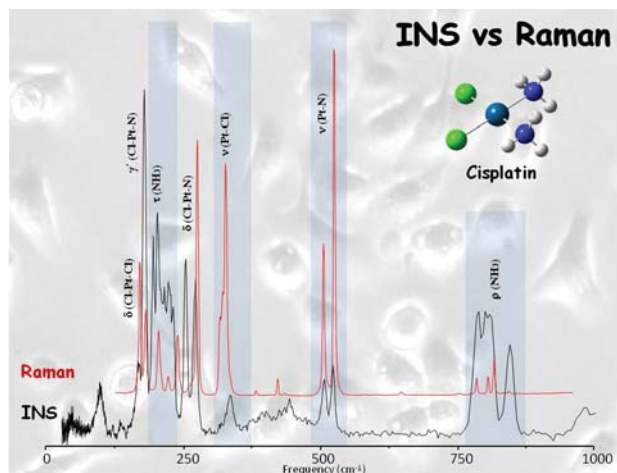
MARK A. ADAMS,* STEWART F. PARKER, FELIX FERNANDEZ-ALONSO,
DAVID J. CUTLER, CHRISTOPHER HODGES, and ANDREW KING
STFC, ISIS Pulsed Neutron Facility, Chilton, Didcot, Oxon, OX11 0QX (M.A.A., S.F.P., F.F.A.); and Renishaw PLC, Wotton-under-Edge,
Gloucestershire, GL12 8JR (D.J.C., C.H., A.K.)



alpha



beta



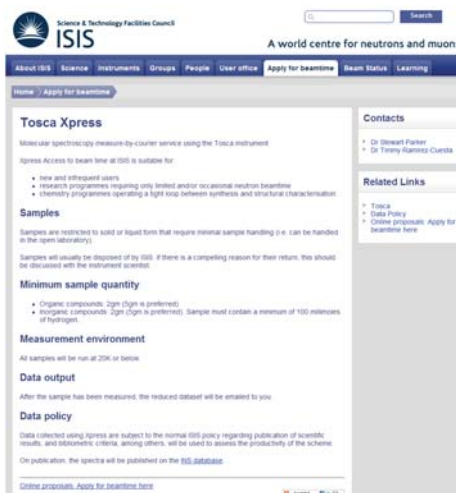
J Phys Chem B 117 6421 (2013)

***Also possible in gas-
handling experiments***



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Easy Access: Xpress

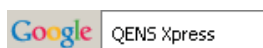
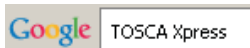


Successfully running since 2006

Builds on TOSCA experience

Aimed at new and infrequent users

Started Summer 2011



Get in Touch, Come Talk to Us



Molecular Spectroscopy

Welcome to the Molecular Spectroscopy Group. The group is responsible for four spectrometers: Isis, Osiris, Tosca and Vesuvio. The instruments are used for investigations of dynamics in condensed matter science including: chemistry, physics, biology, materials science and geology.

Team

Main Contact

• [Prof Felix Fernandez-Alonso](#)

Other Contacts

• [Dr Frans Demmel](#)
• [Dr Victoria Garcia Sakai](#)
• [Dr Sanghamitra Mukhopadhyay](#)
• [Dr Stewart Parker](#)
• [Dr Svenmir Rüdiger](#)
• [Dr Andrew Seal](#)

Instruments

► Isis
► Osiris
► Tosca
► Vesuvio
► Fires
► Maps

Related Articles

► Dynamics in lipid vesicles
► Protein motion in red blood cells
► Polymers in prison
► Understanding a catalyst from formula to mechanism
► Neutron Compton scattering in moderate-mass systems

Scientific Areas

► Advanced Materials
► Bioscience
► Chemistry
► Natural World
► Energy
► Magnetism research at ISIS
► Nanostructured Hydrogen Storage Materials
► Physics
► Soft Matter

Related Links

► Good Vibrations Newsletter Vol 4 Iss 1 (Mar'13)
► Good Vibrations Newsletter Vol 3 Iss 2 (Sep'12)
► Good Vibrations Newsletter Vol 3 Iss 1 (Mar'12)

Xpress and Rapid-access proposals encouraged any time

**Next proposal round
16 April 2015**

www.isis.stfc.ac.uk/groups/molecular-spectroscopy



What to Remember A Year From Now

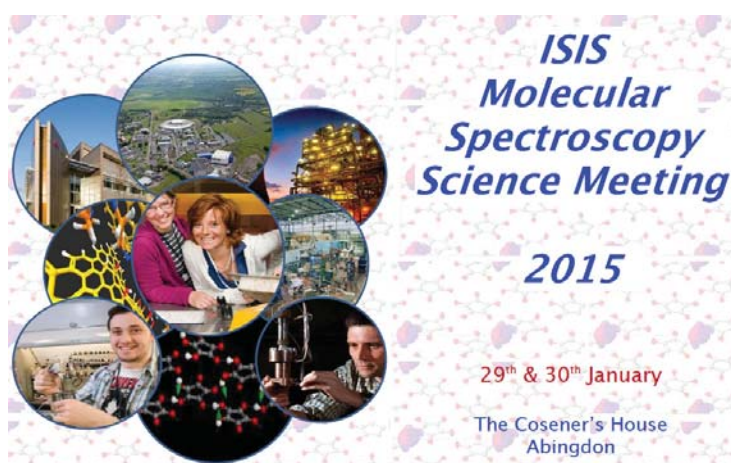
- **Neutron spectroscopy:** plenty of opportunities below and above molecular vibrations.
 - Supramolecular motions, molecular tunnelling, energetics (barriers), molecular transport (diffusion coeffs), element-specific quantum thermometry, and nuclear quantum effects.
 - In most of these cases, can't do it without neutrons.
- **In-silico spectroscopy:** can't do without it – computational modelling and neutron spectroscopy go hand-in-hand; **more later by Keith Refson.**
- **Increasing complexity:** sample environment for in-situ and operando studies, other techniques (simultaneous diffraction or Raman) – **if we can't do it yet, talk to us.**



Science & Technology Facilities Council

ISIS

Come Join Us This January



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
Joaquín Silvestre-Albero, Universidad de Alicante
Maths Karlsson, Chalmers University
Maria Paula Marques, Universidade de Coimbra
Christoph Saizmann, University College London
Roberto Senesi, Università di Roma - Tor Vergata

Thank you



Science & Technology Facilities Council

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Quasi-elastic neutron scattering study of diffusion inside porous materials

Hervé Jobic

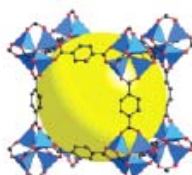
IRCELYON
2 avenue Albert Einstein, Villeurbanne, France



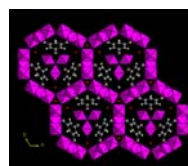
Institut de recherches sur la catalyse et l'environnement de Lyon



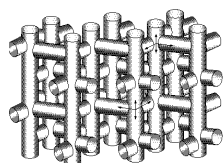
Zeolite A (LTA)



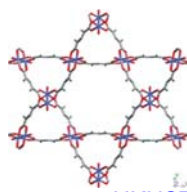
MOF-5



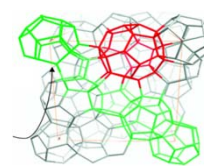
MIL-96(Al)



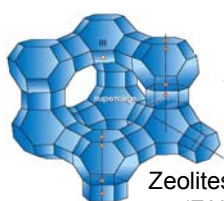
silicalite / ZSM-5 (MFI)



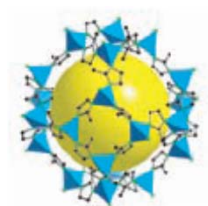
HKUST



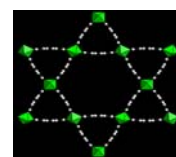
MIL-100(Al)



Zeolites X & Y
(FAU)

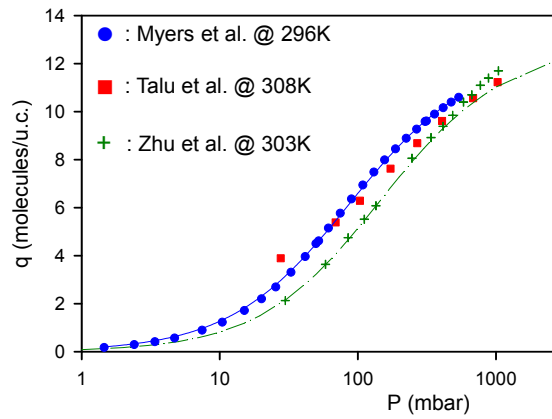
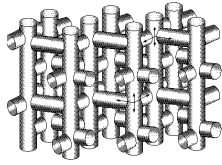


ZIF-8



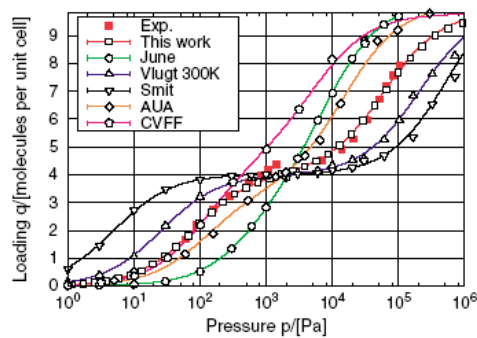
MIL-68(Al, Fe)_X

ethane in silicalite



$$\text{Langmuir: } q = \frac{q_s KP}{1 + KP}$$

$$\text{Van't Hoff: } K = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right)$$

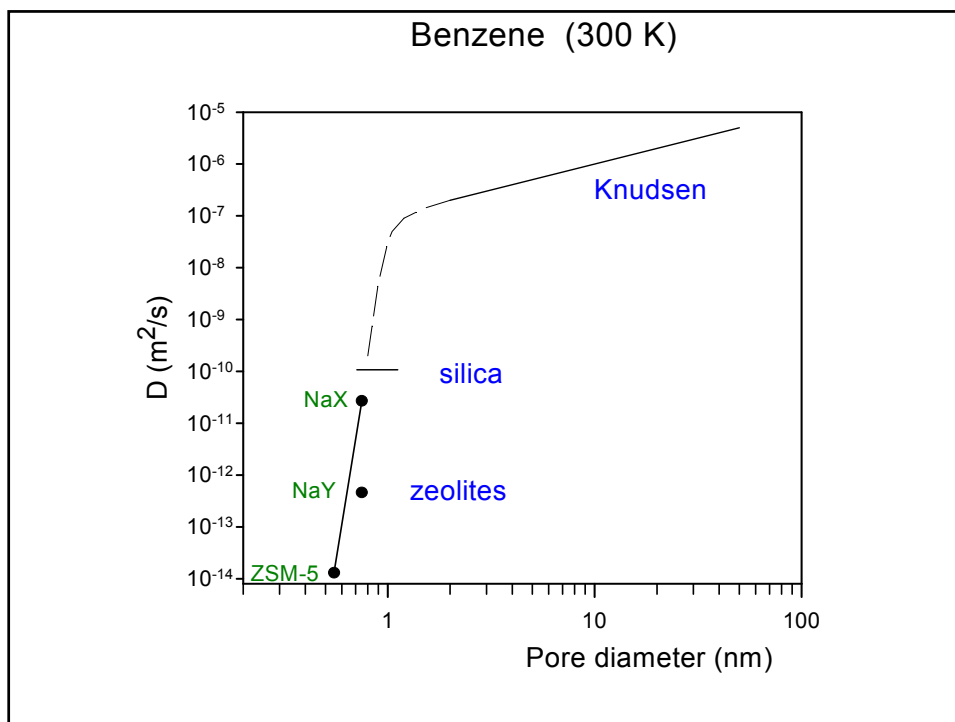


Isotherms of 2-methylpropane at 308 K in silicalite-1 compared to various computational models.

PRL 93 (2004) 88302

FF

CBMC technique



J. Kärger and D. M. Ruthven: Diffusion in Zeolites (1992)

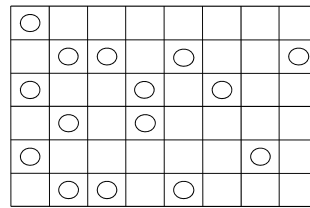
\mathcal{D}	self-diffusivity (defined by Eq. 1.11 or 1.12)
\mathcal{D}_∞	pre-exponential factor in Arrhenius expression for temperature dependence of \mathcal{D} (Eq. 4.70)
$\mathcal{D}_{\text{inter}}$	self-diffusivity in inter-crystalline space
$\mathcal{D}_{\text{intra}}$	intracrystalline self-diffusivity
$\mathcal{D}_{\text{l.r.}}$	long range self-diffusivity (through a bed of microporous crystals)
D	transport diffusivity (defined by Eq. 1.1)
D_0	corrected transport diffusivity (defined by Eq. 1.29)
D_c	intracrystalline diffusivity
D_e	effective diffusivity
D_K	Knudsen diffusivity
D_L	axial dispersion coefficient
D_m	molecular diffusivity
D_p	pore diffusivity
D_p^*	micropore diffusivity (Eq. 11.3)
D_s	surface diffusivity
D_{AB}	molecular diffusivity in binary A - B mixture
D_{des}	diffusivity calculated from desorption rate
D_{micro}	diffusivity in micropores
D_{macro}	diffusivity in macropores
$D_{\text{Poiseuille}}$	equivalent diffusivity for Poiseuille flow
\bar{D}	integral diffusivity (derived from uptake rate measurement over a large concentration step)
\bar{D}	average diffusivity (over a defined concentration range)

Techniques for measuring diffusion coefficients

Out of equilibrium

- gravimetry
- chromatography
- frequency response
- infrared (FT & surface)
- permeability

...



$$J = -D_T \frac{dc}{dx}$$

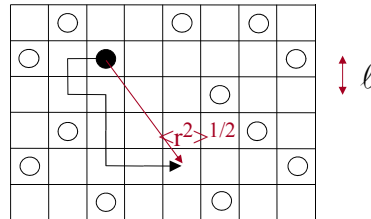
At equilibrium

- PFG NMR , QENS (inc. scattering)

$$D_S = \frac{1}{6} \frac{\langle r^2(t) \rangle}{t} = \frac{\ell^2}{6\tau}$$

- QENS, NSE (coh. scattering):

$$D_T$$



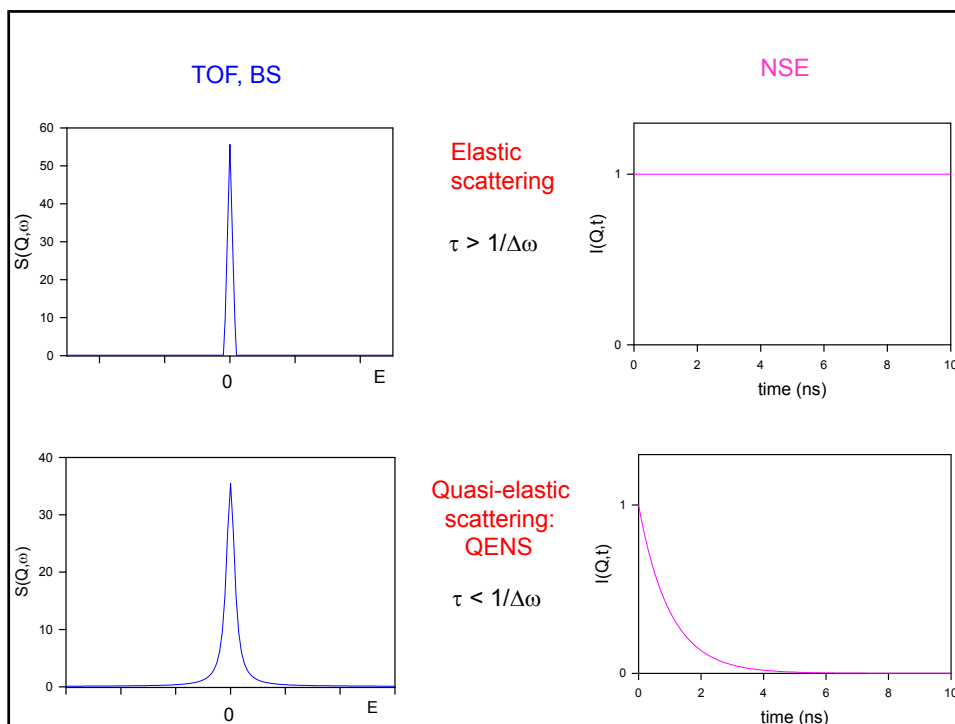
Zero length column (ZLC) chromatography



pulsed-field gradient NMR
PFG NMR



quasi-elastic neutron scattering
QENS



Separation of paraxylene from the C₈ aromatic cut

ELUXYL Process IFP

Liquid phase (> 100°C)

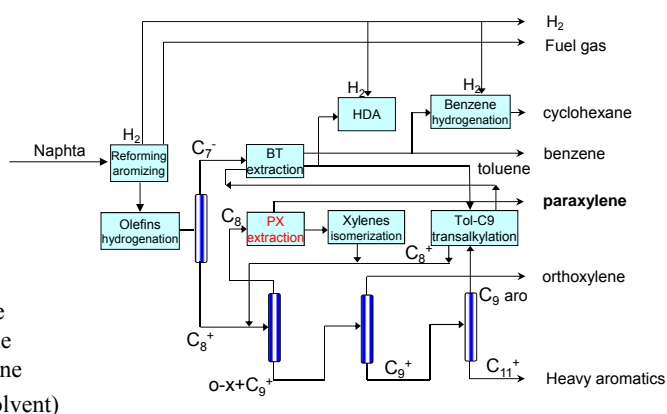
Faujasite zeolite (BaX)

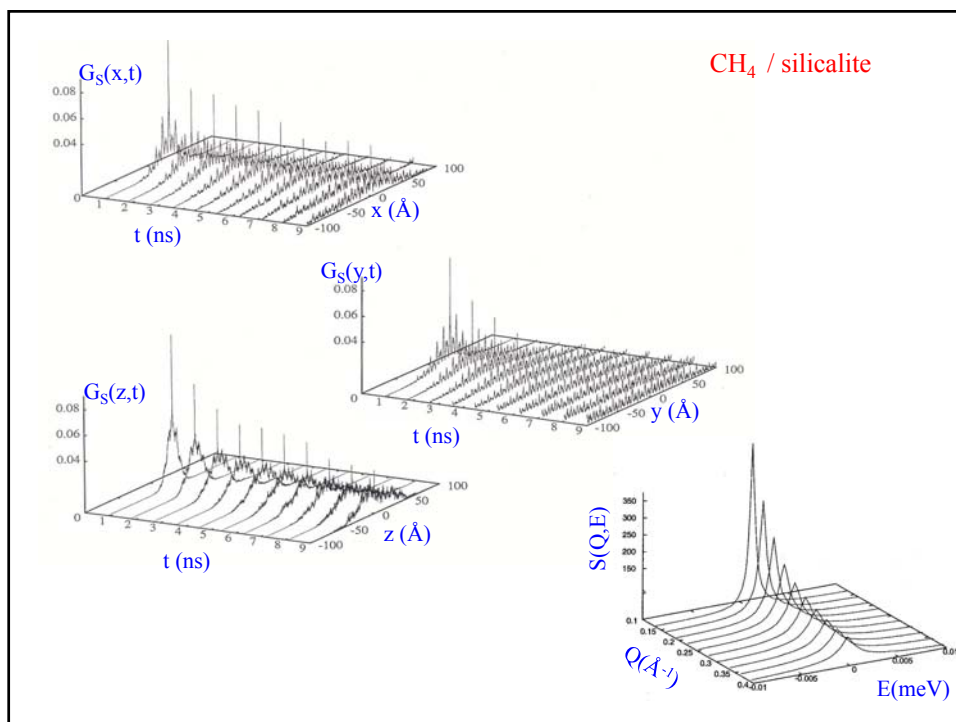
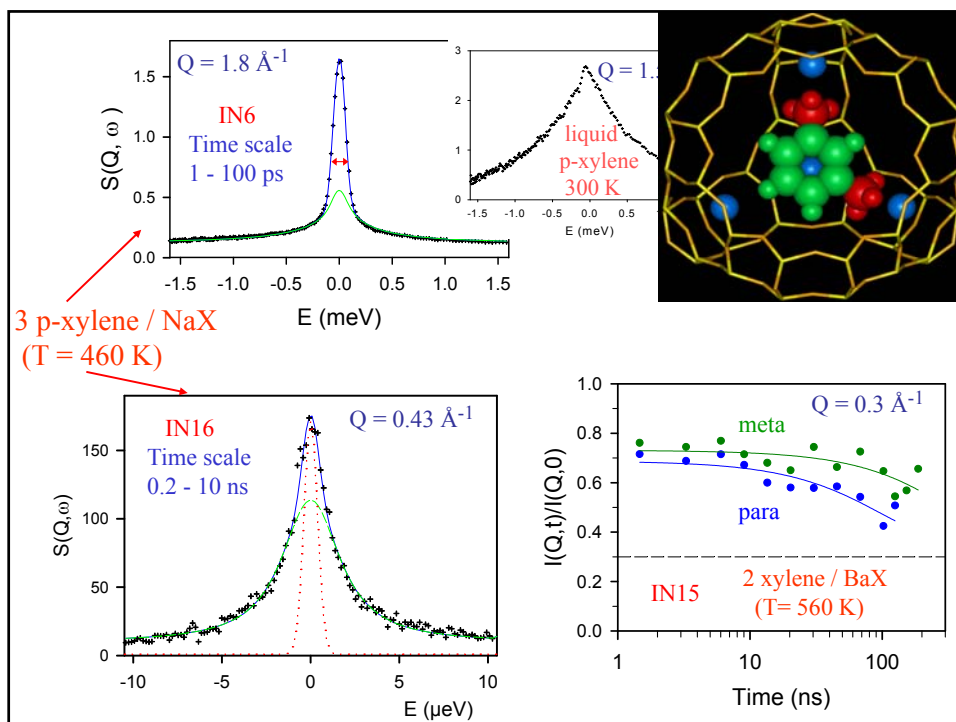
Charge: C₈ : - Paraxylene
 - Metaxylene
 - Orthoxylene
 - Ethylbenzene
 +Toluene (solvent)

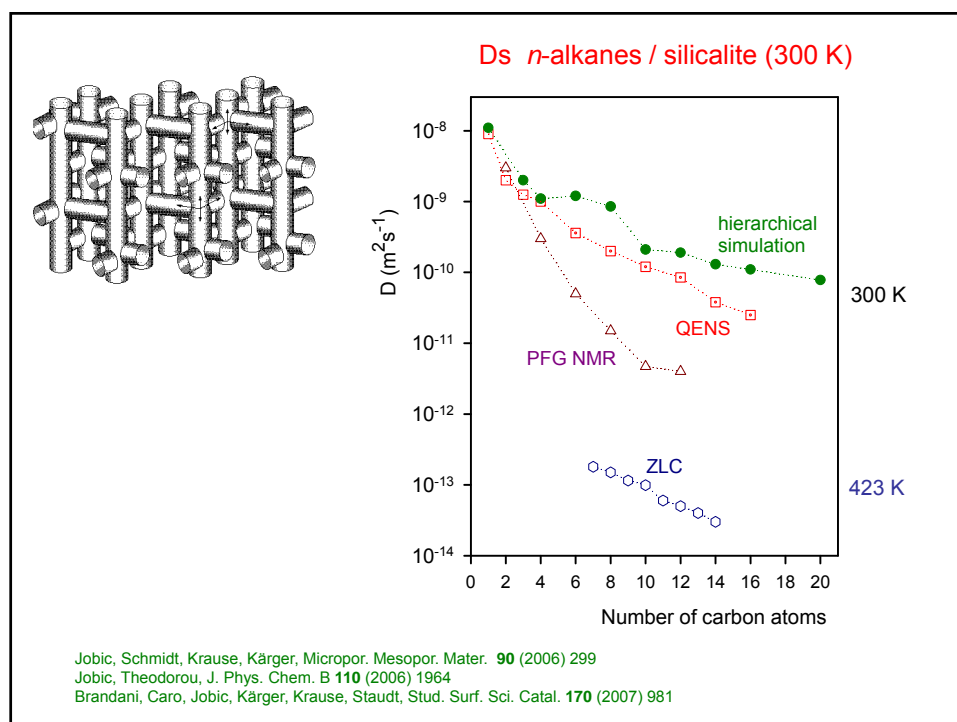
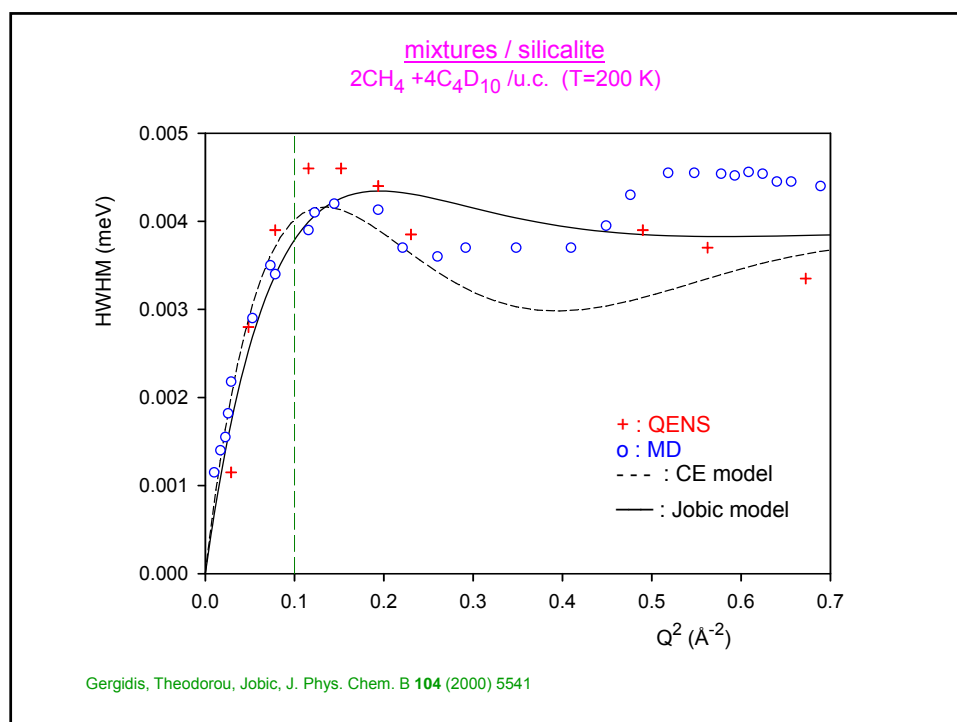
High Purity of the extract (Px): 99.8%

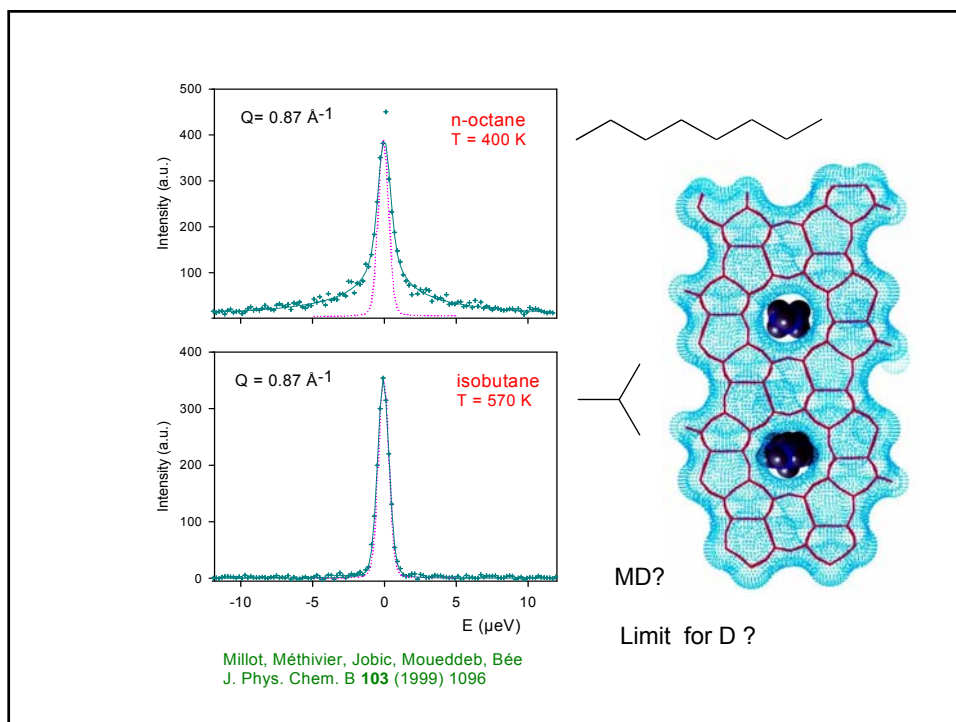
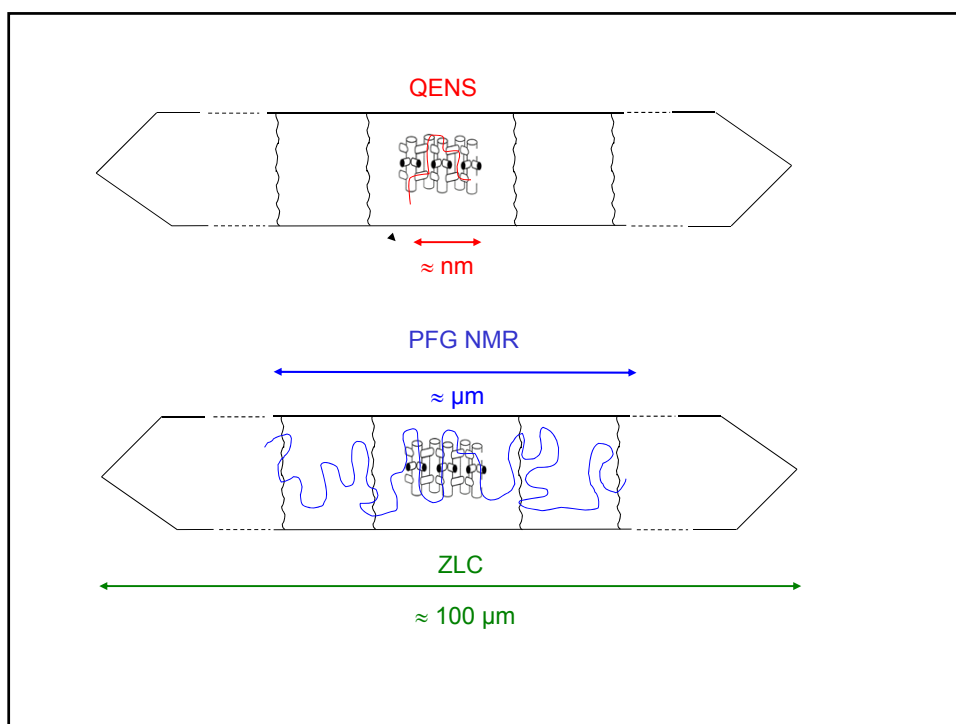
Order of magnitude:

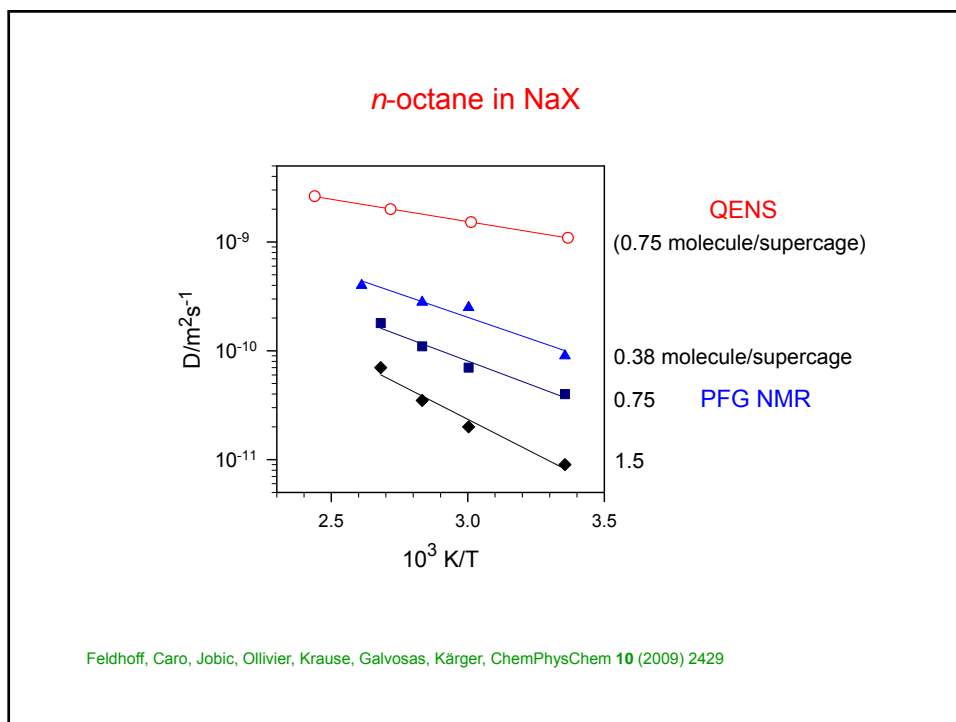
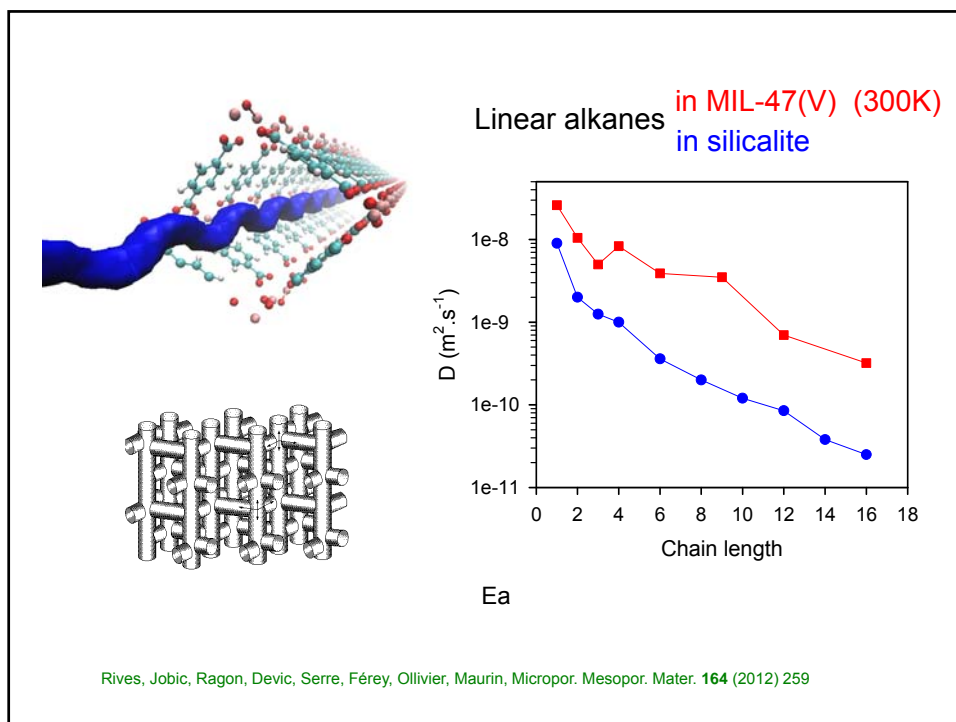
- Molecular sieve: 1000 Tons
- Px produced: 700 000 Tons/year

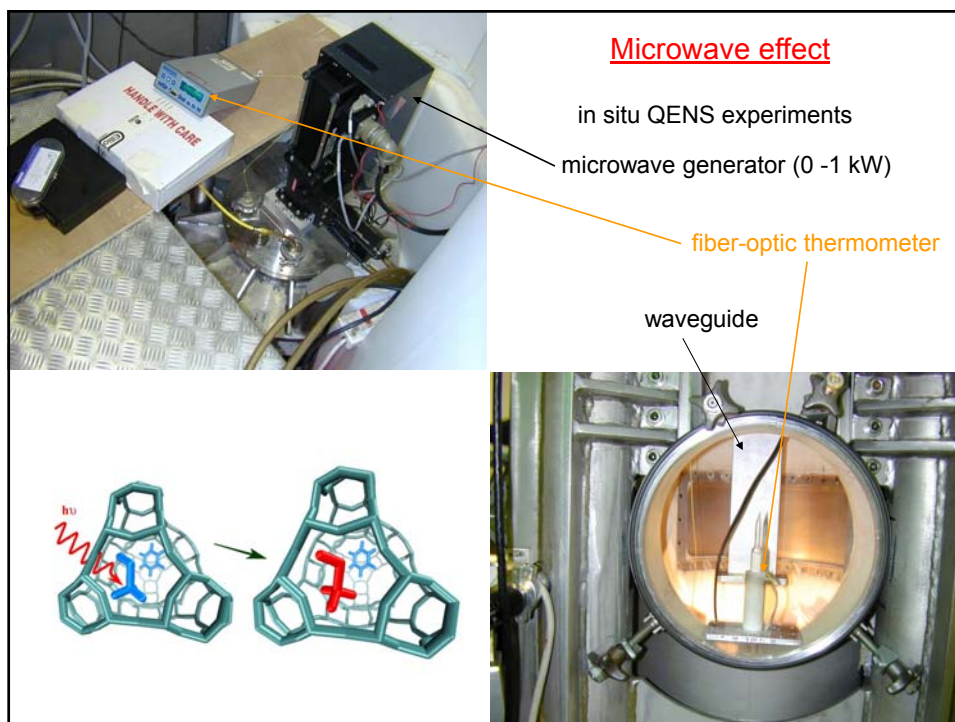
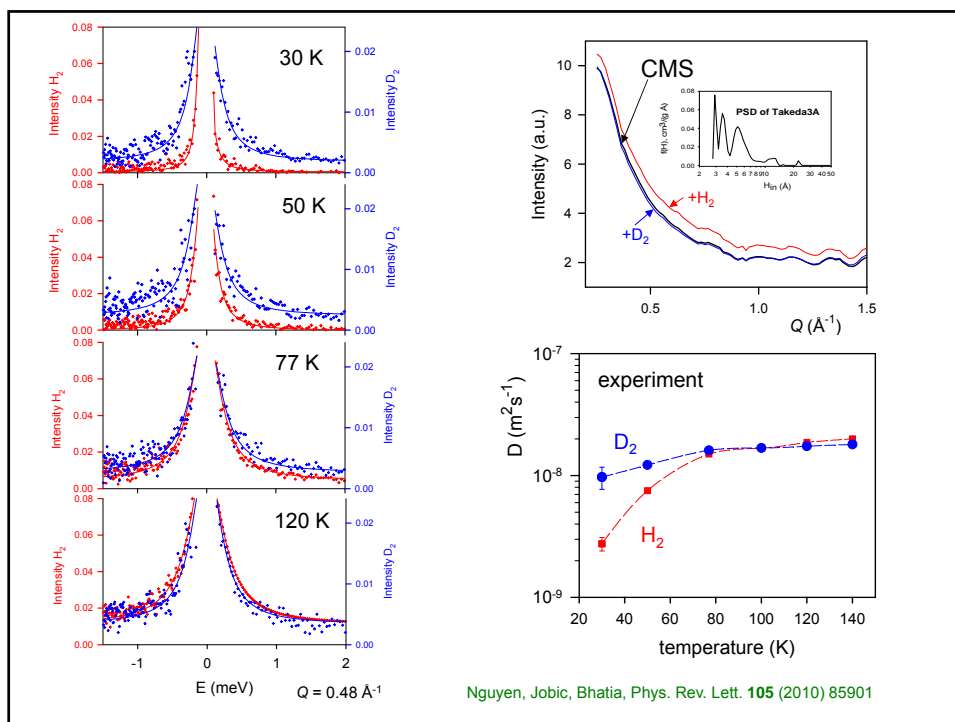


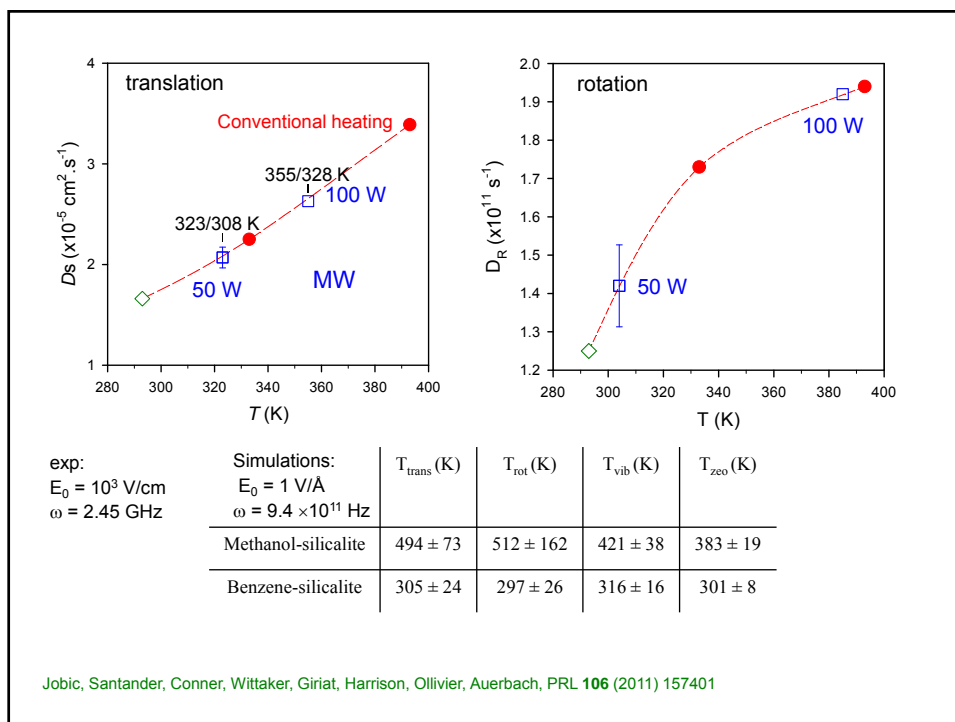
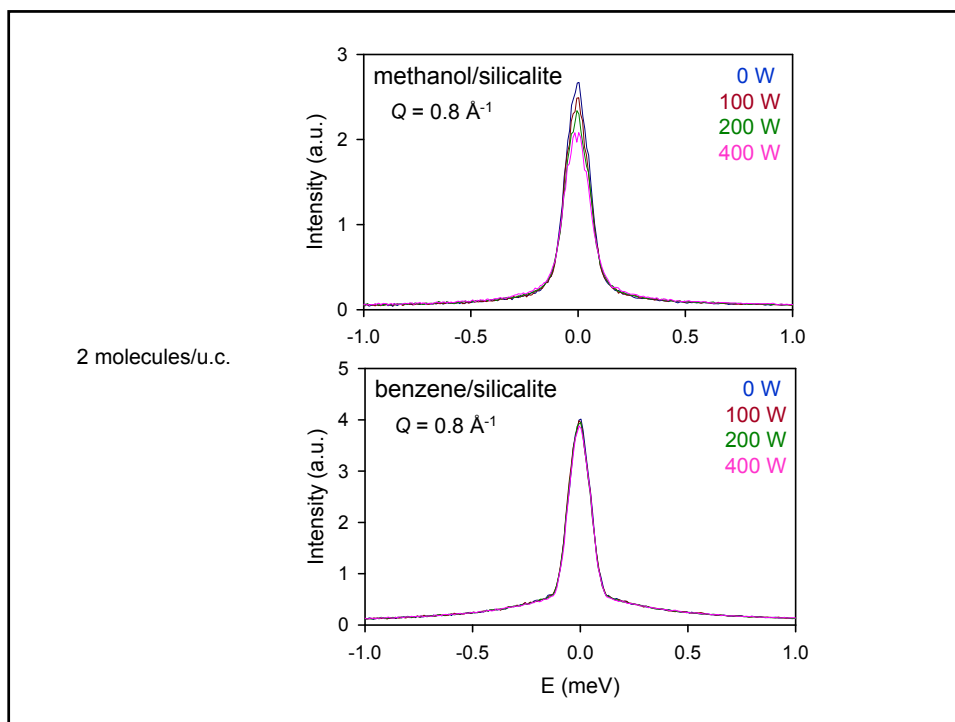


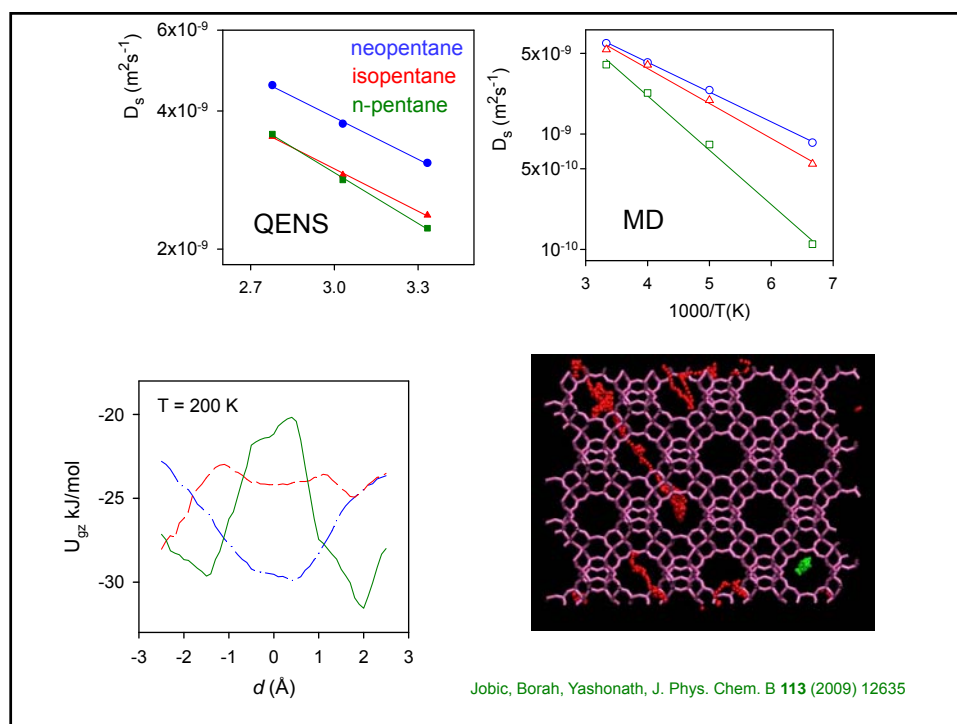
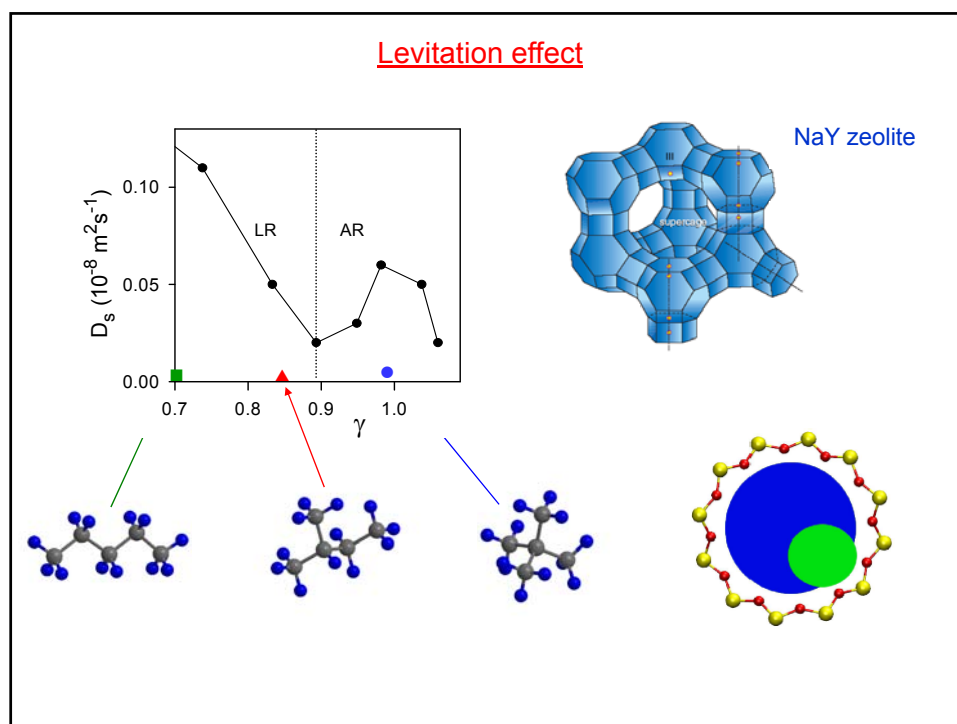




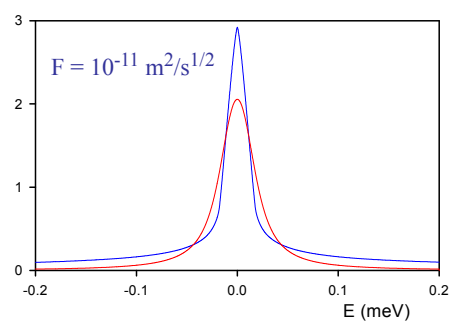
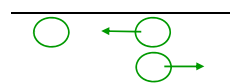
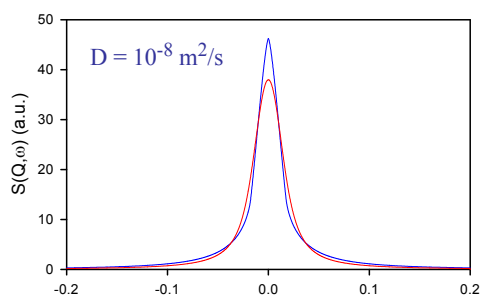




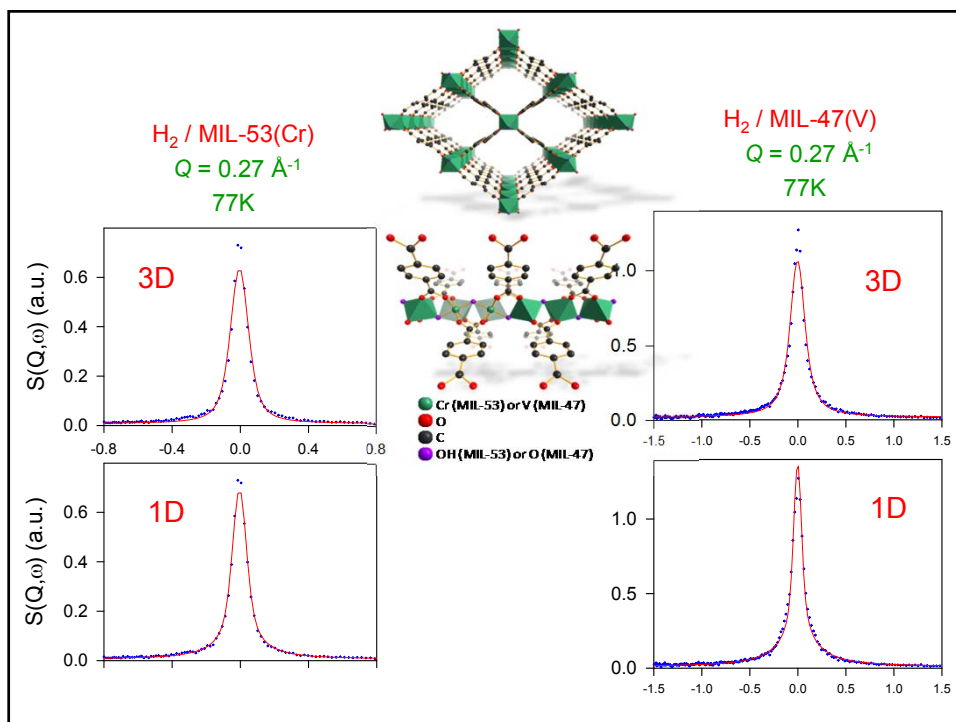


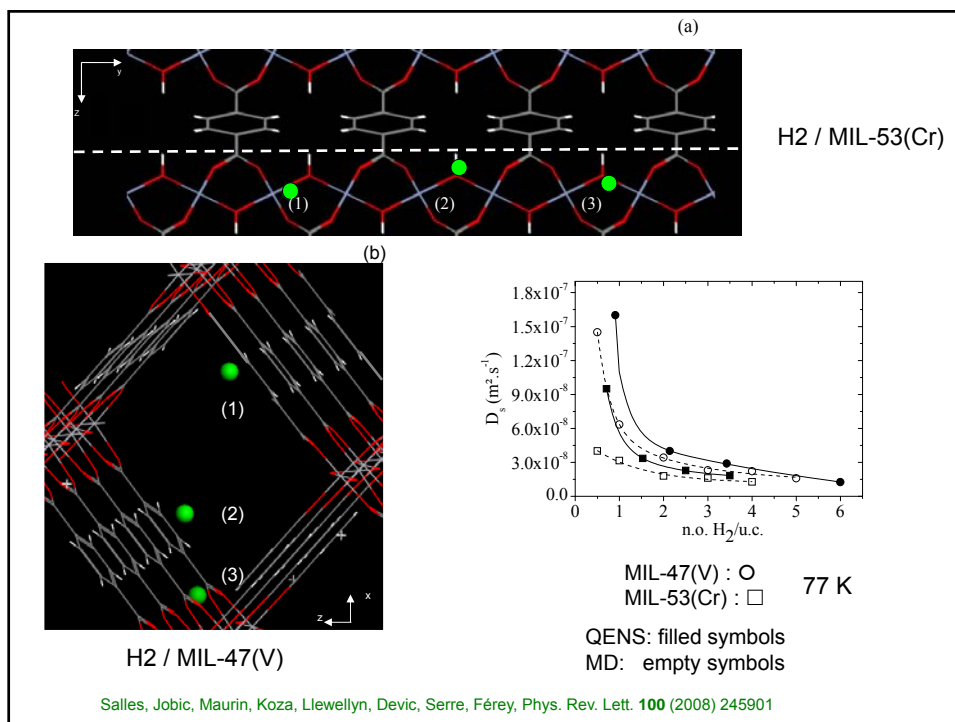
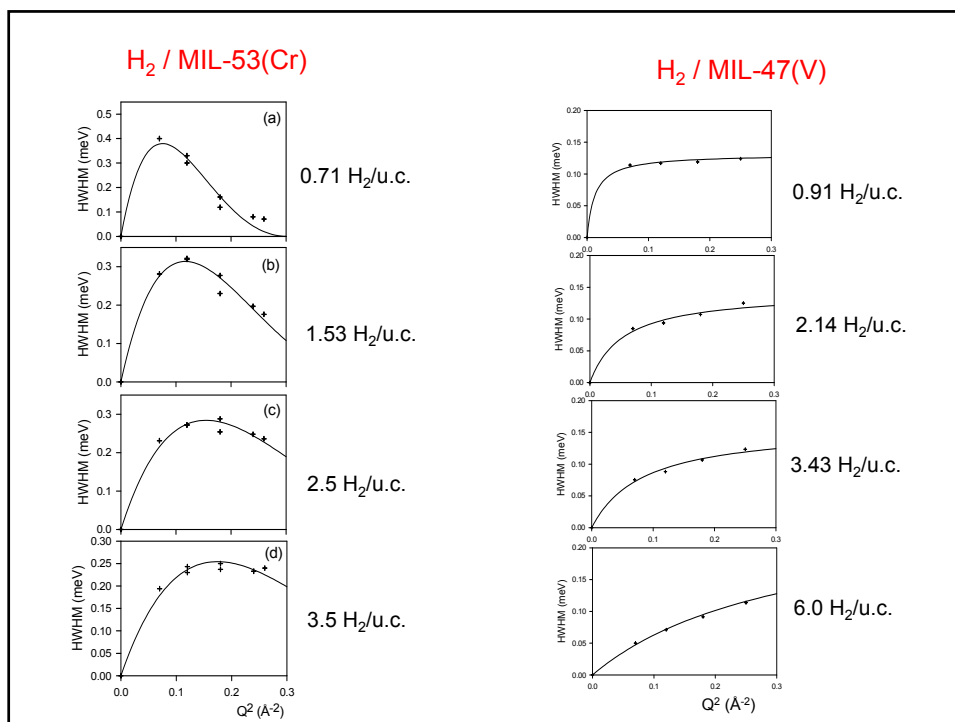


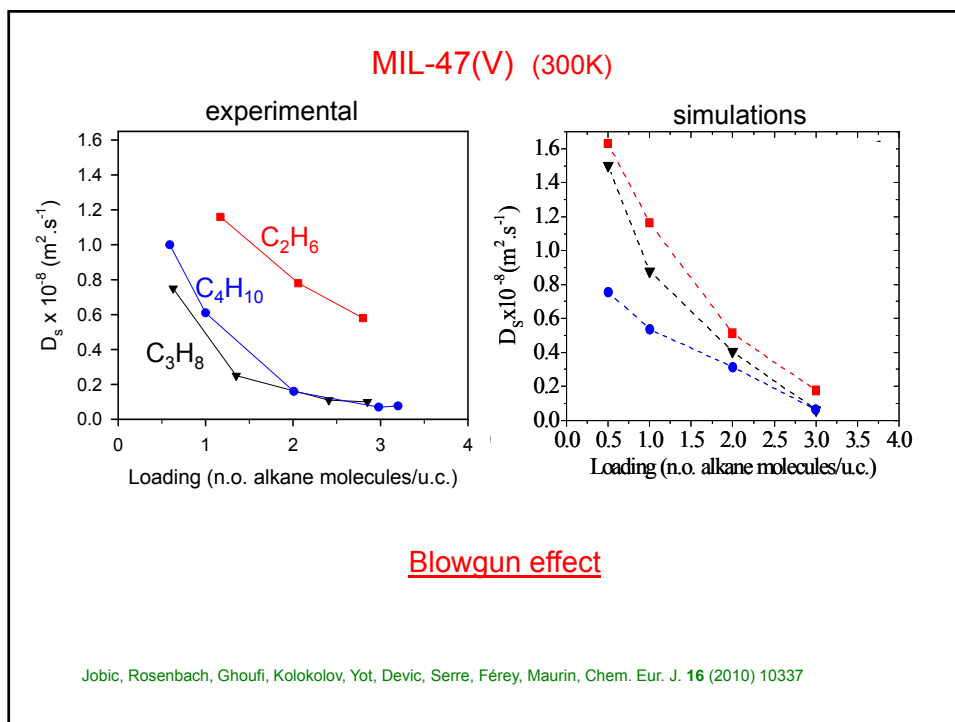
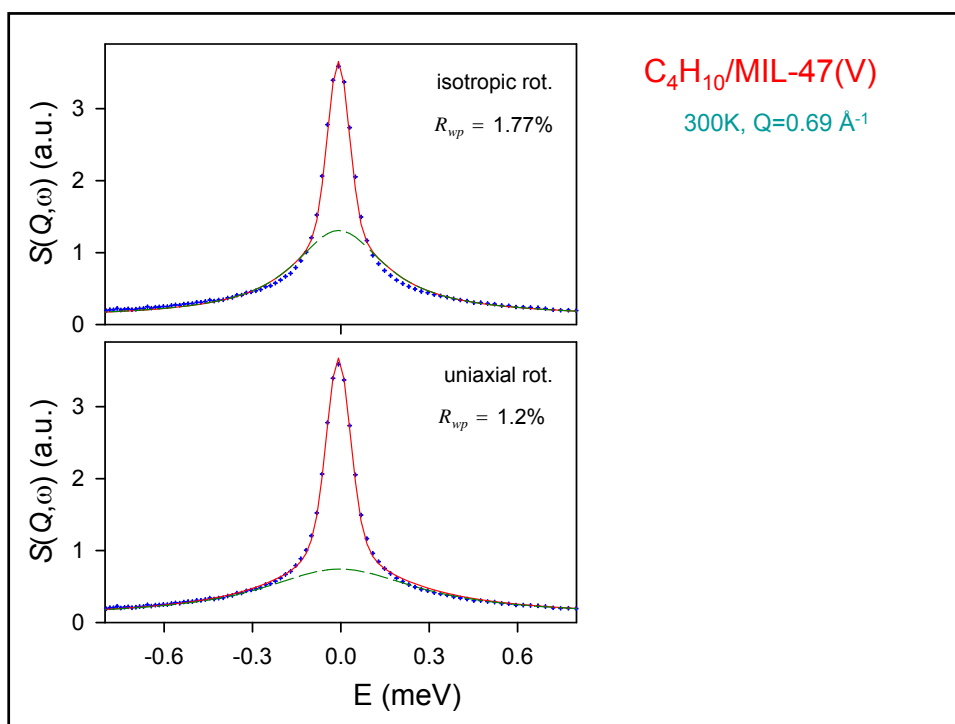
Diffusion in 1D channel systems

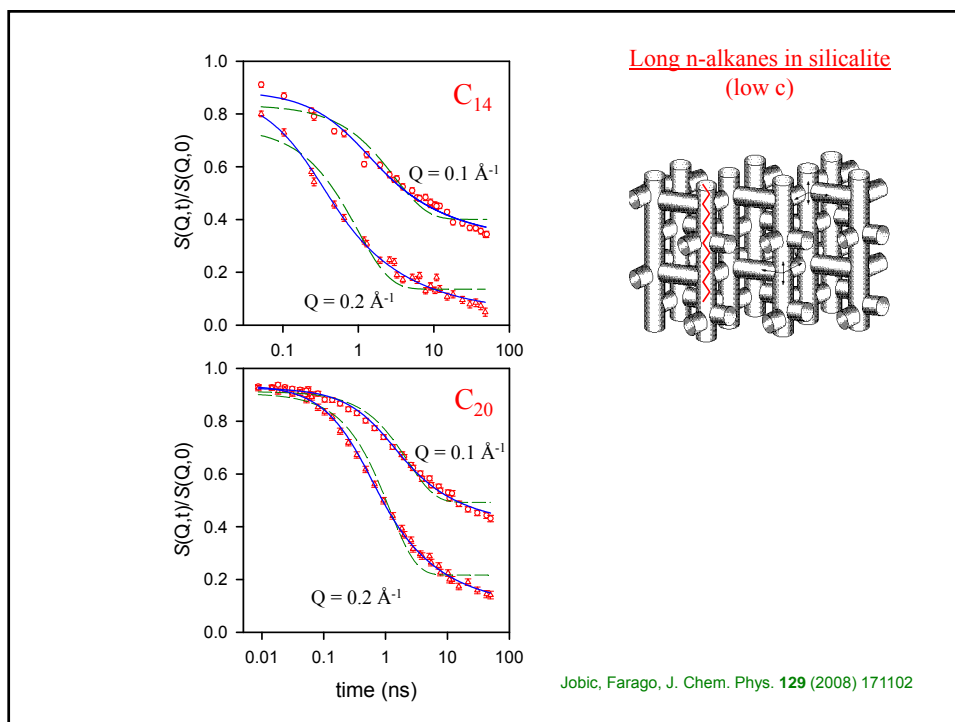
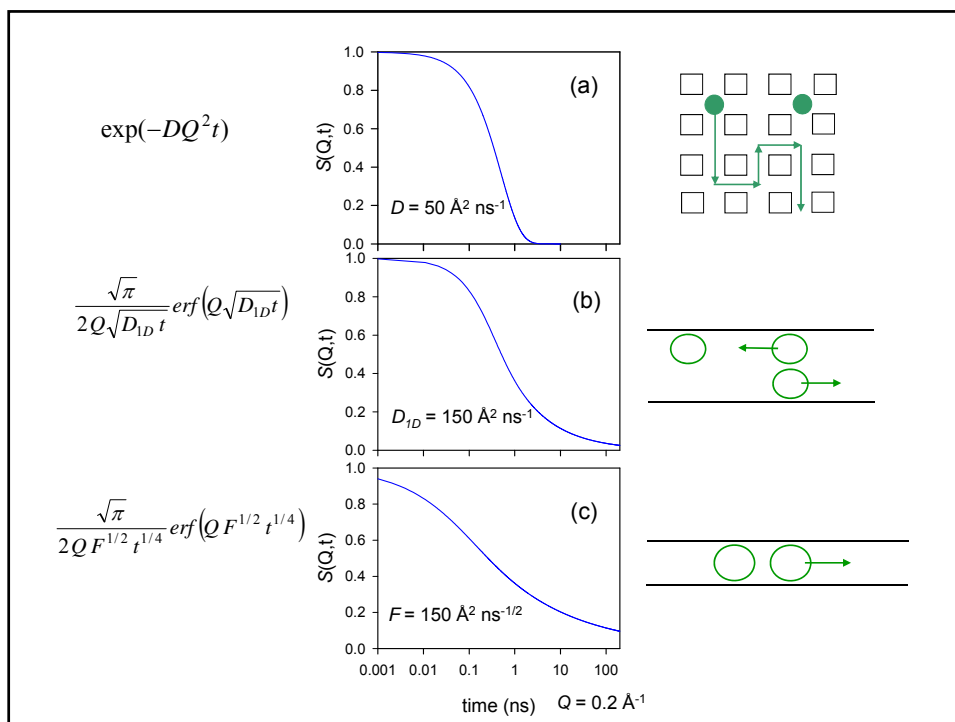


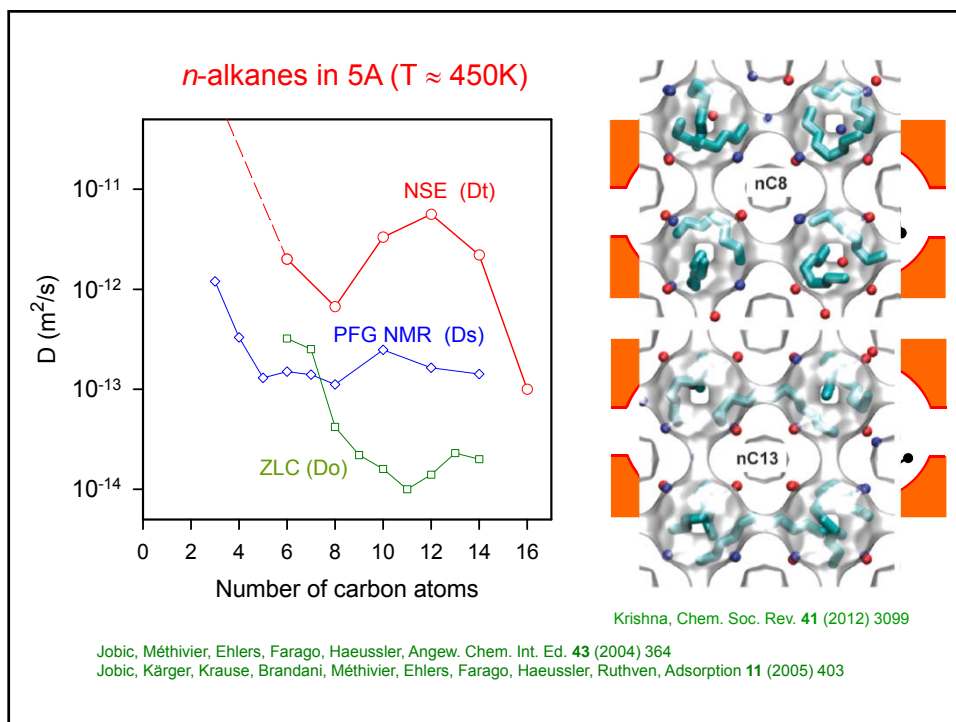
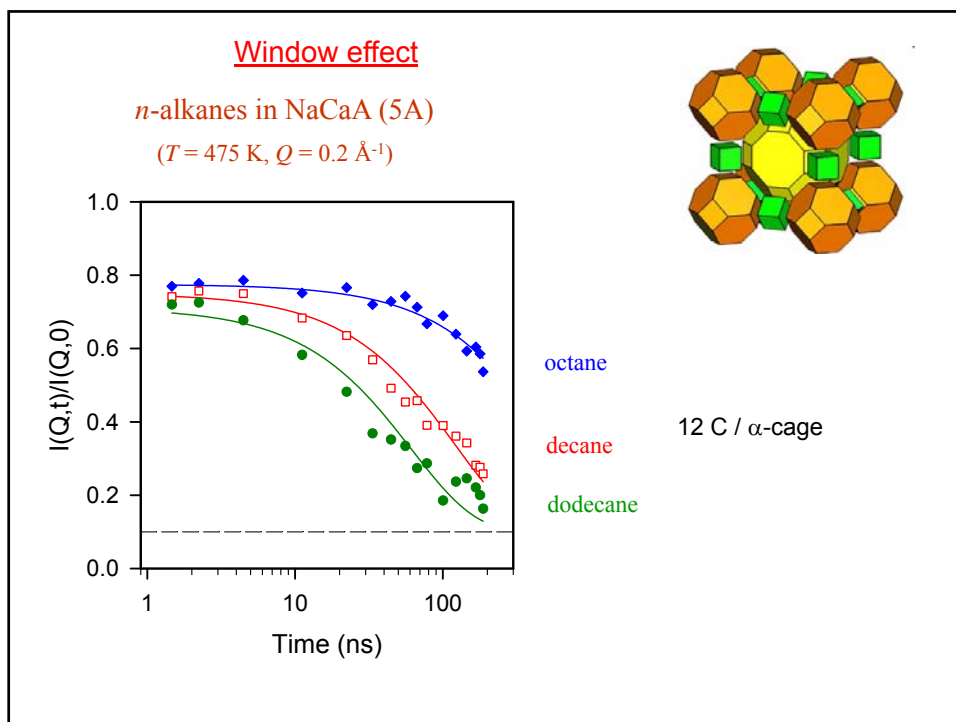
Jobic, Hahn, Kärger, Bée, Tuel, Noack, Kearley
 J. Phys. Chem. B **101** (1997) 5834

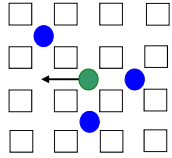




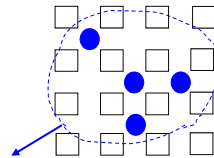








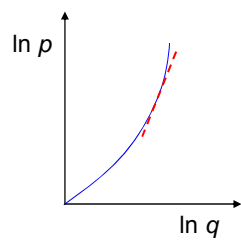
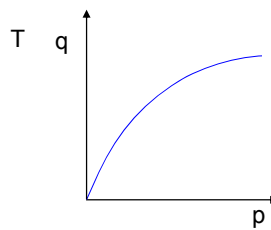
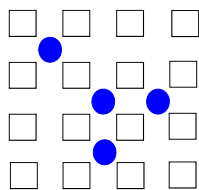
$$\frac{\partial G_S(\mathbf{r}, t)}{\partial t} = \mathbf{D}_s \nabla^2 G_S(\mathbf{r}, t)$$



$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \mathbf{D}_t \nabla^2 \rho(\mathbf{r}, t)$$

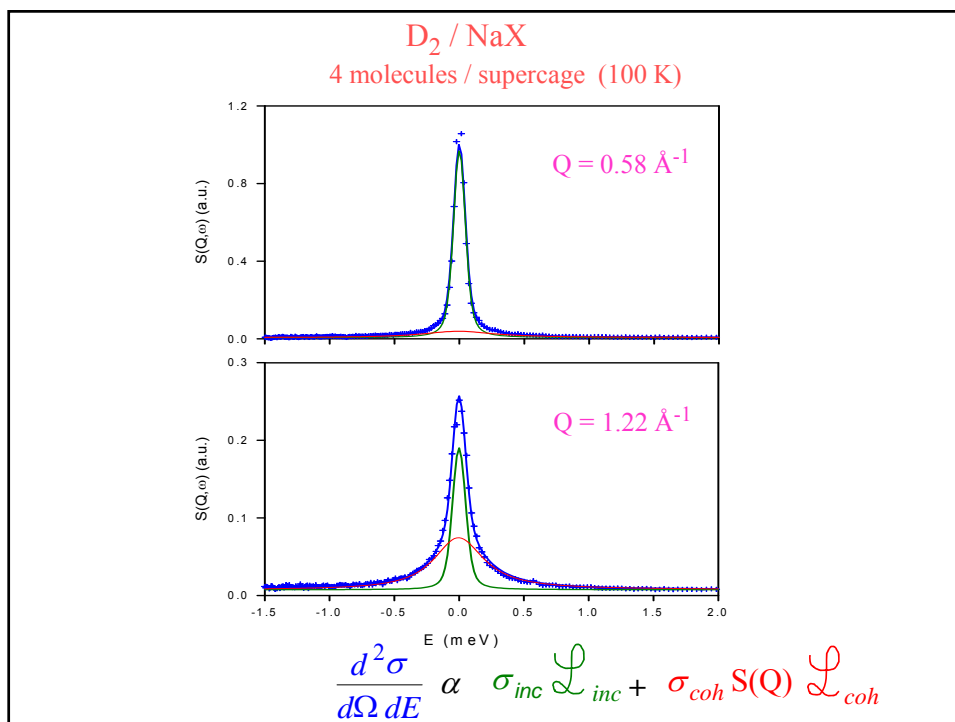
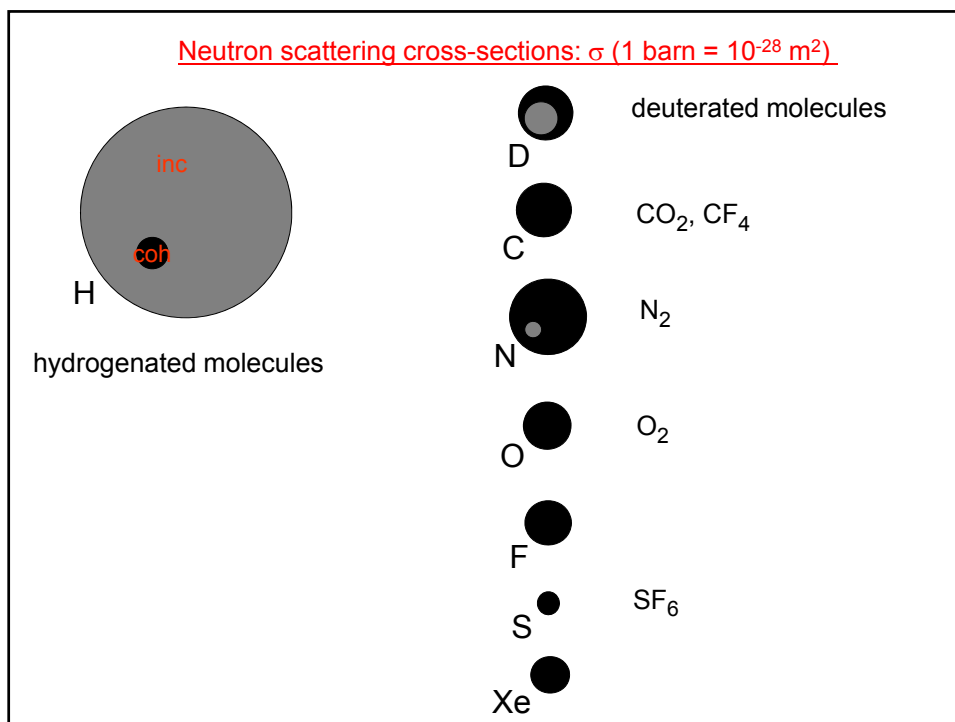
$$D_t = D_0 \frac{d \ln p}{d \ln c} = D_0 \Gamma$$

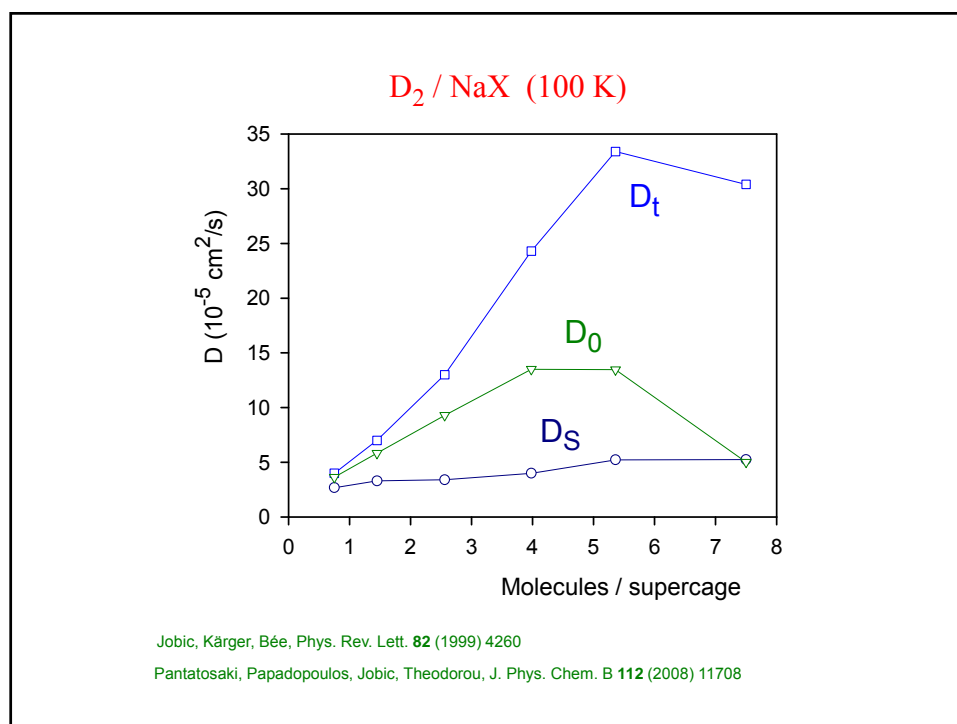
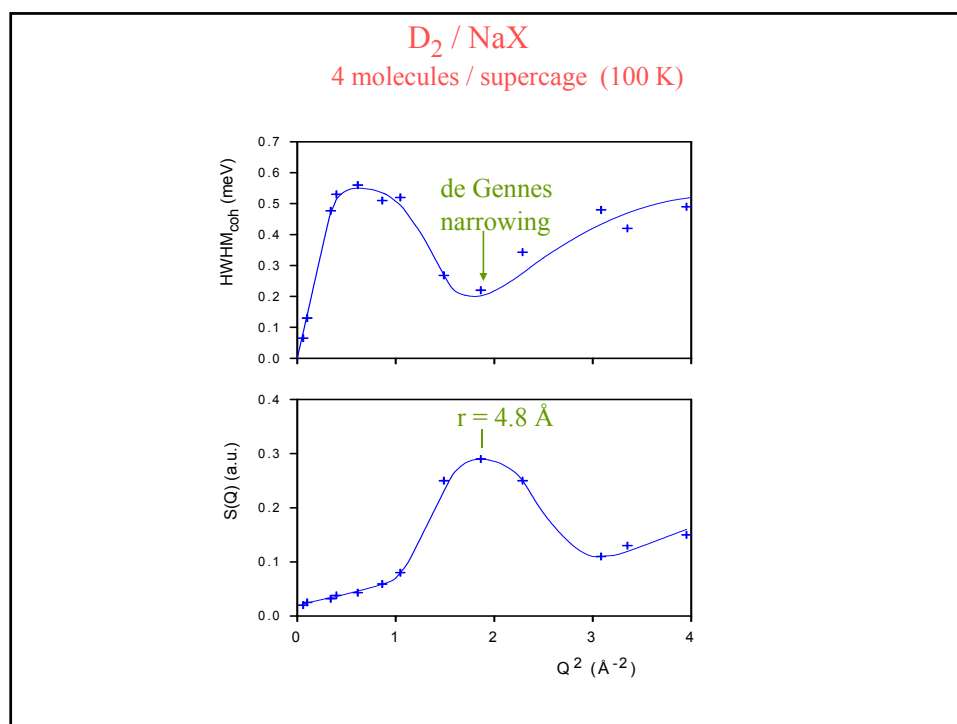
Thermodynamic correction factor

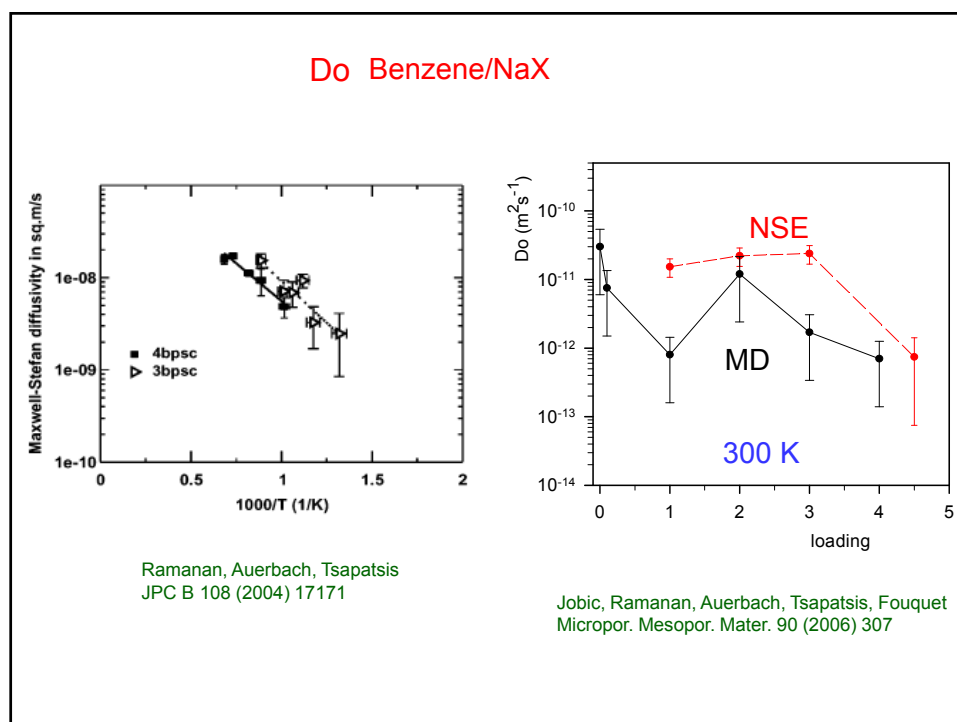
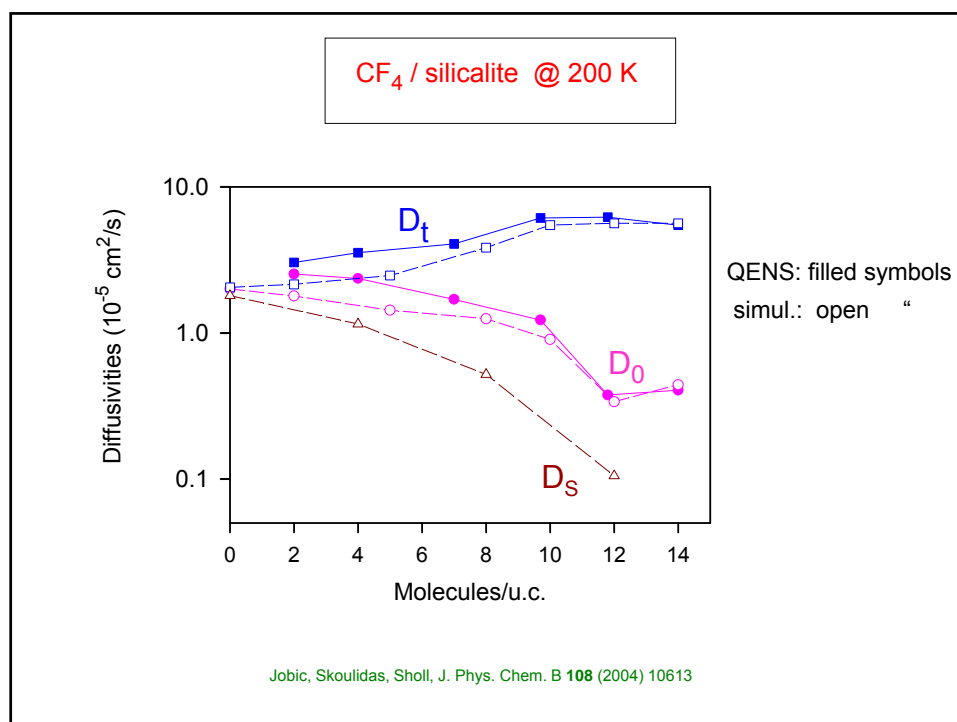


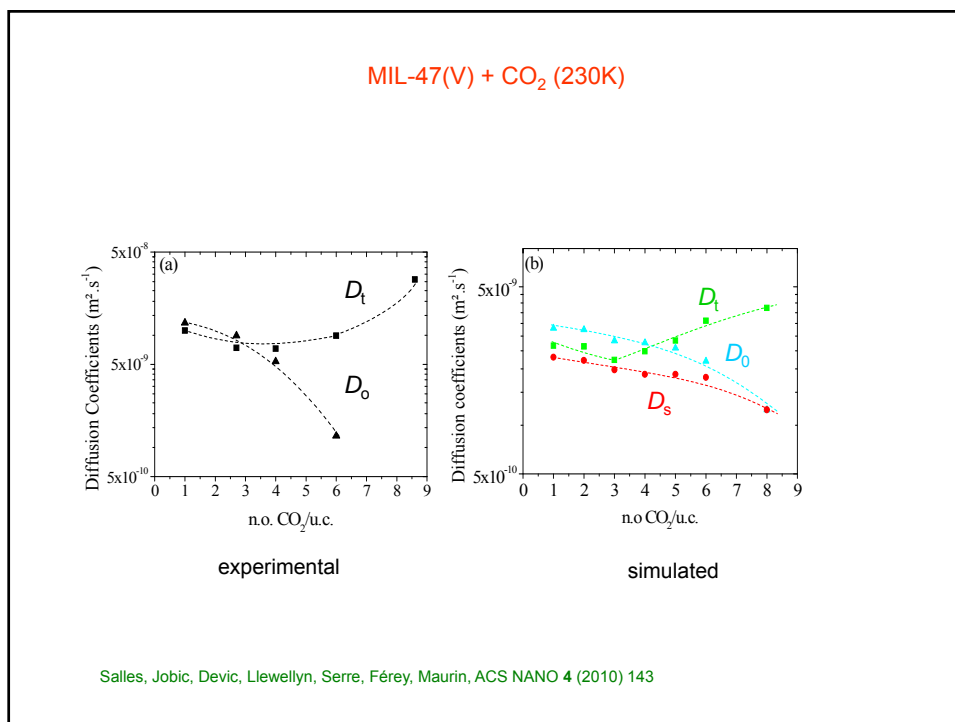
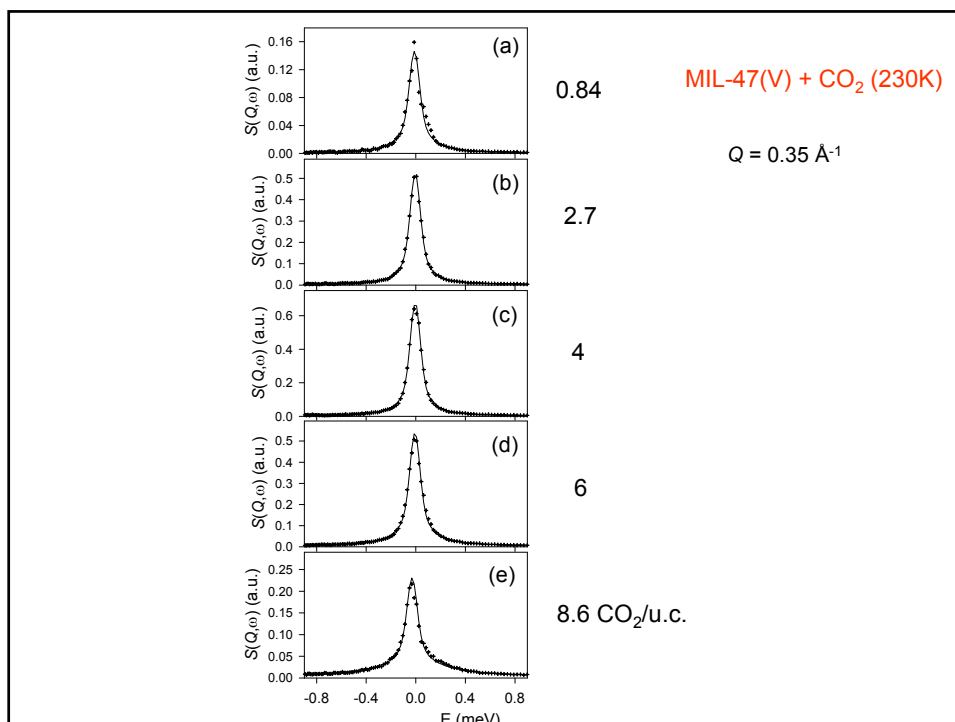
$$\Gamma = \frac{d \ln p}{d \ln q}$$

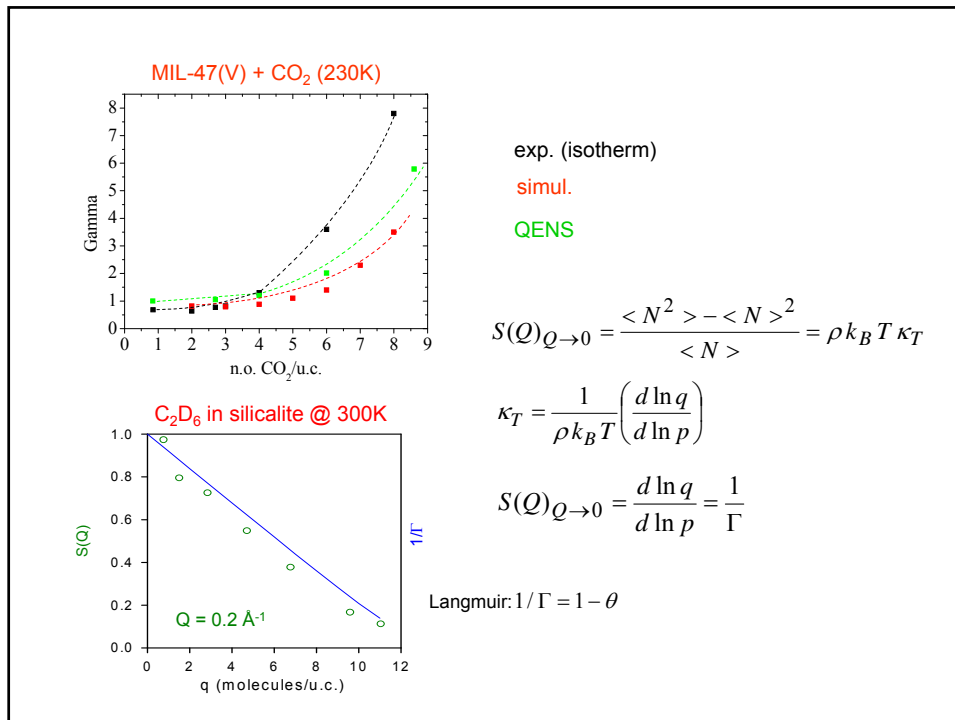
$$\text{Langmuir: } \Gamma = \frac{1}{1 - \theta}$$











CONCLUSIONS

Neutrons: structure and dynamics

Differences between D in zeolites : defects

QENS – simulations: same length and time scales

Diffusion is a sensitive test of the potential

Flexibility of the framework ?

Acknowledgements

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FP7-NMP-2008-LARGE-2, FP7-NMP-2008-EU-India-2

A Practical Introduction to Total Scattering

Dr Tristan Youngs

NIMROD Instrument Scientist, Disordered Materials Group

*ISIS Facility, STFC Rutherford Appleton Laboratory
Harwell Oxford, Didcot, Oxon, OX11 0QX*

3rd November 2014



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Overview

1. What is total scattering?
 - What's in the data?
 - Instrument requirements
 - Total scattering of MCM-41
2. What can total scattering offer catalysis?
 - Current unknowns
 - Basic total scattering experiment
 - Isotopic substitution
 - Examples
 - Solvation
 - Aggregation
 - Large structure collapse
3. Rules & Practical considerations
 - Experimental concerns
 - Sample size / composition
 - Isotopic substitution
 - Sample environment
 - Complexity
4. Summary



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1

What is total scattering?



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Neutron Scattering and Spectroscopy

Principal Types

Inelastic

Excitations: vibrational modes, phonons etc.

Quasielastic

Diffusion in liquids and solids, low energy crystal modes

Reflectometry

Composition / density of surfaces, layers, bilayers

Magnetic

Magnetic correlations / structure

Imaging

Material radiography, tomography and imaging

Crystallography

Bragg scattering: crystal structures, strain etc.

Diffuse Scattering

Structure of disordered liquids and solids (e.g. glasses)

Small-Angle Scattering

Surface scattering, micelles, surfactants, solid particles etc.



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Total Scattering

“A scattering experiment that does not distinguish between Bragg, diffuse, and small-angle scattering”

...or...

“A scattering experiment that involves or requires analysis of a combination of Bragg, diffuse, and small-angle scattering”

- Scattering from one type cannot be prevented:
 - If instrument design allows it
 - If sample contains it

Crystallography

Bragg scattering: crystal structures, strain etc.

Diffuse Scattering

Structure of disordered liquids and solids (e.g. glasses)

Small-Angle Scattering

Surface scattering, micelles, surfactants, solid particles etc.



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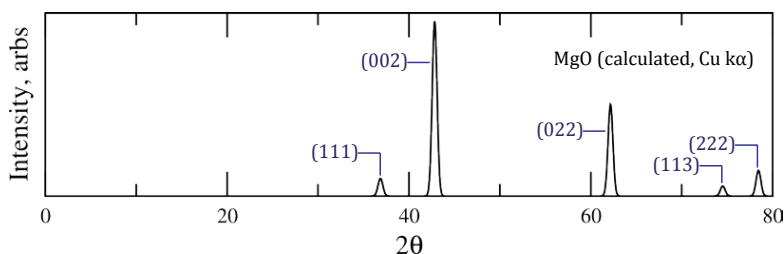
Total Scattering

1. Bragg Scattering

“Constructive scattering from planes of a crystalline solid”

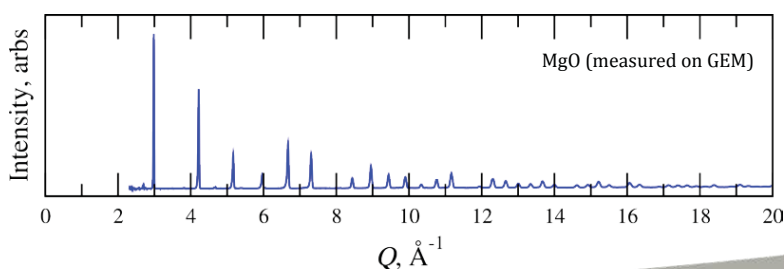
$$n\lambda = 2d \sin \theta \quad d_{cubic} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Peaks correspond to reflections between Miller planes



$$h^2 + k^2 + l^2 = \left(\frac{2a \sin \theta}{\lambda} \right)^2$$

Or, in Q ...



$$h^2 + k^2 + l^2 = \left(\frac{aQ}{2\pi} \right)^2$$



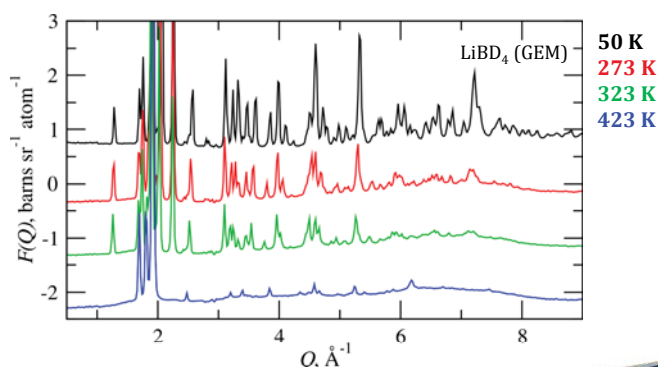
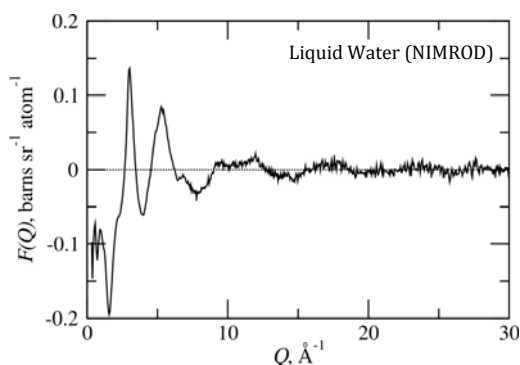
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Total Scattering

2. Diffuse Scattering

- Scattering from disorder in crystals
 - Bragg scattering represents time- and unit cell-averaged positions
 - Diffuse “background” represents occupational and positional disorder
- Scattering from irregular, disordered materials – e.g. liquids, melts, and glasses
 - No long range ordering = no sharp features
 - Local correlations between species



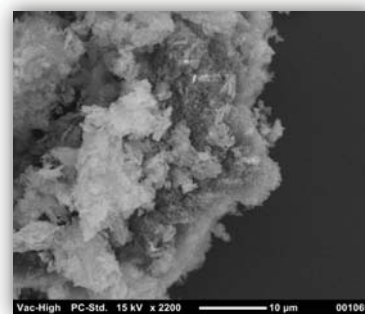
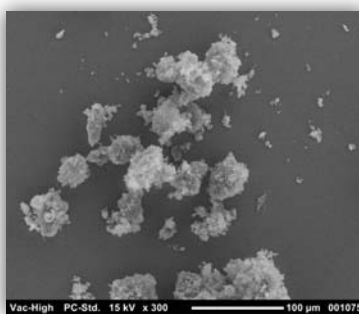
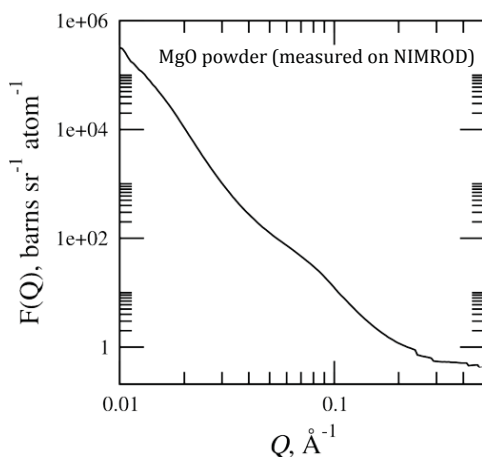
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3. Small Angle Scattering

- Probes length scales much larger than interatomic spacing in materials
- Scattering arising from differences in neutron contrast between domains, regions, or aggregate structures in the underlying system
- Can provide information on
 - Size, shape (geometry) of scattering objects
 - Surface roughness (sharpness)



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Total Scattering

In a perfect world...

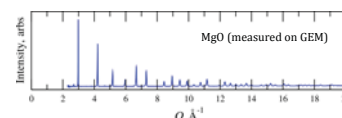
No fundamental difference between small-angle, Bragg, and diffuse scattering

- Only the length scales and ordering of the scattering objects differ

Total scattering permits **single measurements** that, in principle, contain complete information on the structure of a given system...

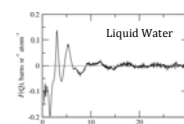
Bragg Scattering (*single body correlation function*)

- Characterisation of ordered, crystalline components of sample



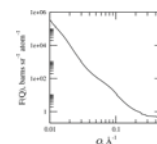
Diffuse Scattering (*pair correlation function*)

- Characterisation of disordered parts of the system
- Correlations between atoms / molecules



Small-Angle Scattering (*scattering length density variations*)

- Characterisation of “particle” size, shape, and distribution
- Correlations between “particles”



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Total Scattering

However...

Instruments are optimised to give best results for one specific type of scattering

- SANS
 - Only longer wavelength neutrons required
 - Low Q region is the target, don't really care about $Q > 0.5 \text{ \AA}^{-1}$
- Bragg scattering
 - Good Q resolution (dQ/Q) necessary to resolve closely-spaced reflections
- Diffuse scattering
 - Q resolution not so important, as all features are broader anyway
 - High Q limit necessary to accurately resolve atomic pair distance correlations

Is it possible for a single instrument to access the necessary Q -range?

Is it possible for a single instrument to resolve all three types of features?



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Total Scattering

In the real world...

NIMROD – the “Near and InterMediate Range-Order Diffractometer”

Q range : $0.01 < Q < 50 \text{ \AA}^{-1}$

r (correlation) range : $0.1 < r < 300 \text{ \AA}$

θ coverage : $0.4 < \theta < 40^\circ$



- Perfectly suited to study of disordered materials
- Modest resolution of Bragg features
 - Liquid↔solid transition: freezing / melting
 - Formation of crystalline component
 - Principal Bragg reflections permit some characterisation of crystalline components
- Lower Q limit permits reasonable coverage of small-angle region

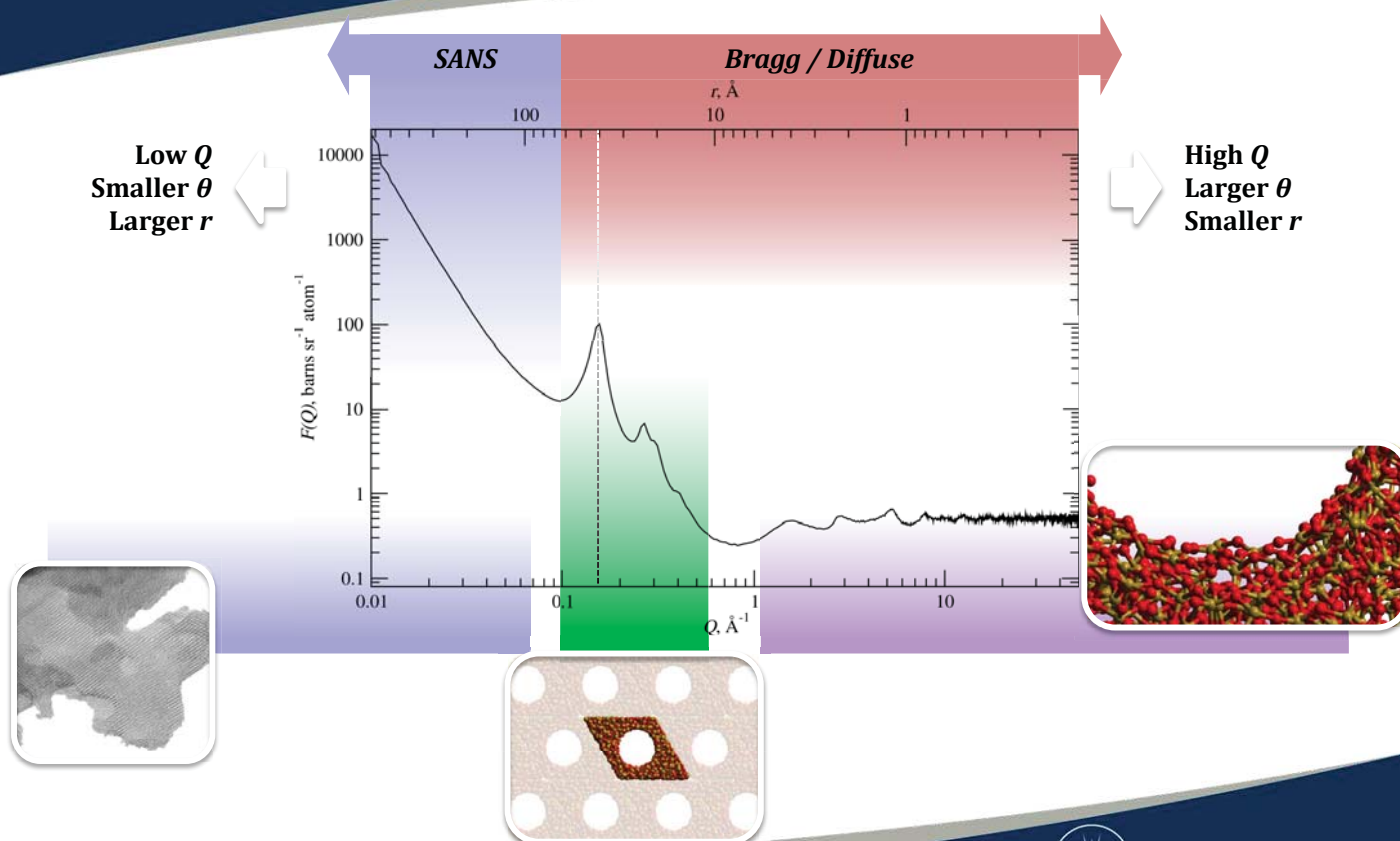


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Total Scattering $F(Q)$

MCM-41



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What Can Total Scattering Offer Catalysis?



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Catalysis...

- ...is used at some point in the manufacture of 80% of all man-made materials
- ...employs 20 million people worldwide
- ...is used in 90% of all chemical processes[†]
- ...is worth...

\$3, 120, 000, 000, 000[‡]

- ...equivalent to 5% of the World Gross National Product...
- ...or roughly equivalent to the Gross National Index of...



France
(\$2.75×10¹²)



Germany
(\$3.54×10¹²)

[†]G. Ertle, H. Knozinger, F. Schuth, J. Weitkamp, ed. Handbook of Heterogeneous Catalysis, Weinheim, 2nd Edition, 2008

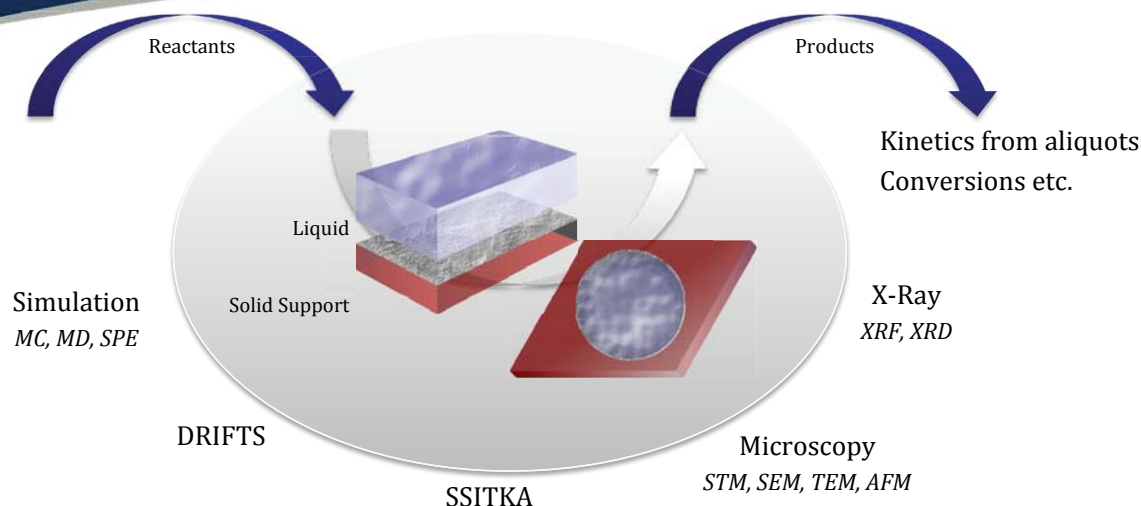
[‡]Estimated Industry Turnover in 2010, International Council of Chemical Associations



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Understanding Catalysts

Liquid Phase / Solid Support



What don't we know?

- What's really happening in the liquid phase? In the pores?
- How are the reactants / products distributed? Intermediates?
- Can we get this information, and at what resolution?



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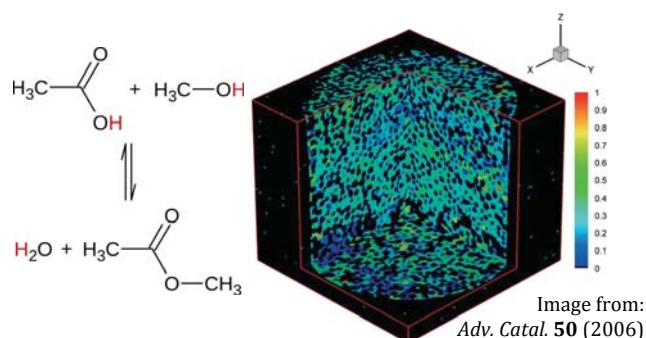
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MRI / APT

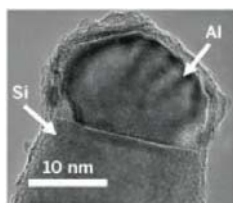
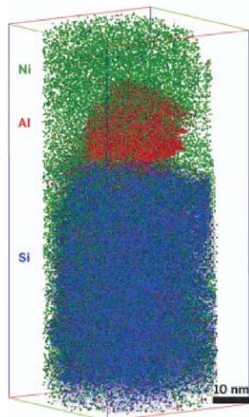
Magnetic Resonance Imaging (MRI)

Spatially-resolved NMR

- Flow and conversion maps of real systems
- Non-invasive
- Sensitive to chemical composition
- μm resolution



Atom-Probe Tomography (APT)



Images from C&EN,
13th October 2014

"...determine, with sub-nm resolution, the 3D atomic structure of internal or buried interfaces"

- Literal 'atomic resolution'
- Destructive
- Not for molecular or organic systems

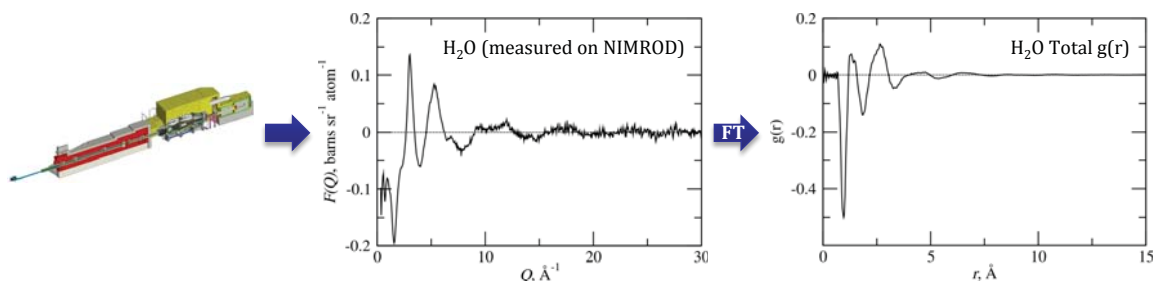


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For a given sample we obtain the total $F(Q)$, which contains information on the correlations of all **objects** in the system arising from Bragg, diffuse, and small-angle scattering

⇒ **Structure Factor**



Total and **partial** structure factors related to the relevant **radial distribution functions**

$$F(Q) = \sum_{i,j} (2 - \delta_{ij}) c_i c_j b_i b_j S_{ij}(Q)$$

$$S_{ij}(Q) = 4\pi\rho \int r^2 (g_{ij}(r) - 1) \frac{\sin Qr}{Qr} dr$$

Three partials ($S_{ij}(Q)$) for water: $S_{OO}(Q)$, $S_{HH}(Q)$, and $S_{OH}(Q)$



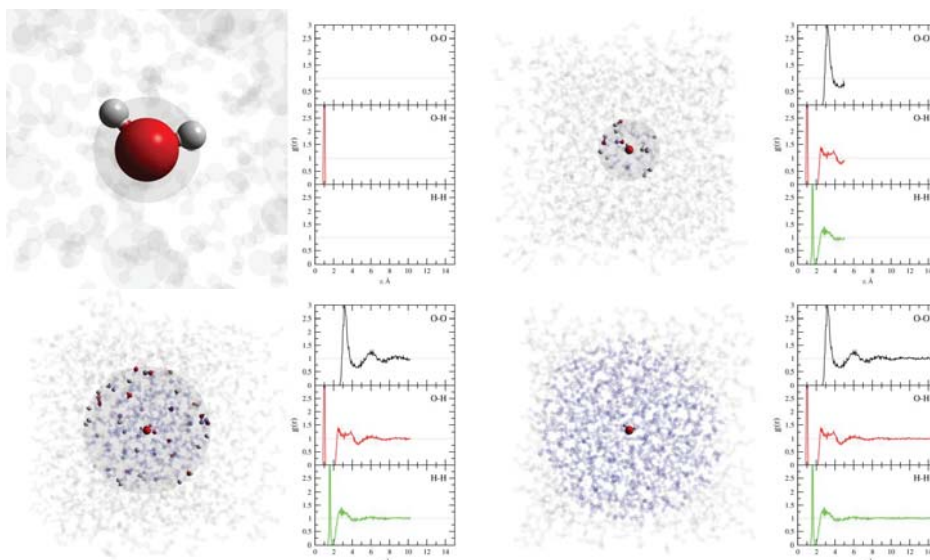
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Radial Distribution Functions

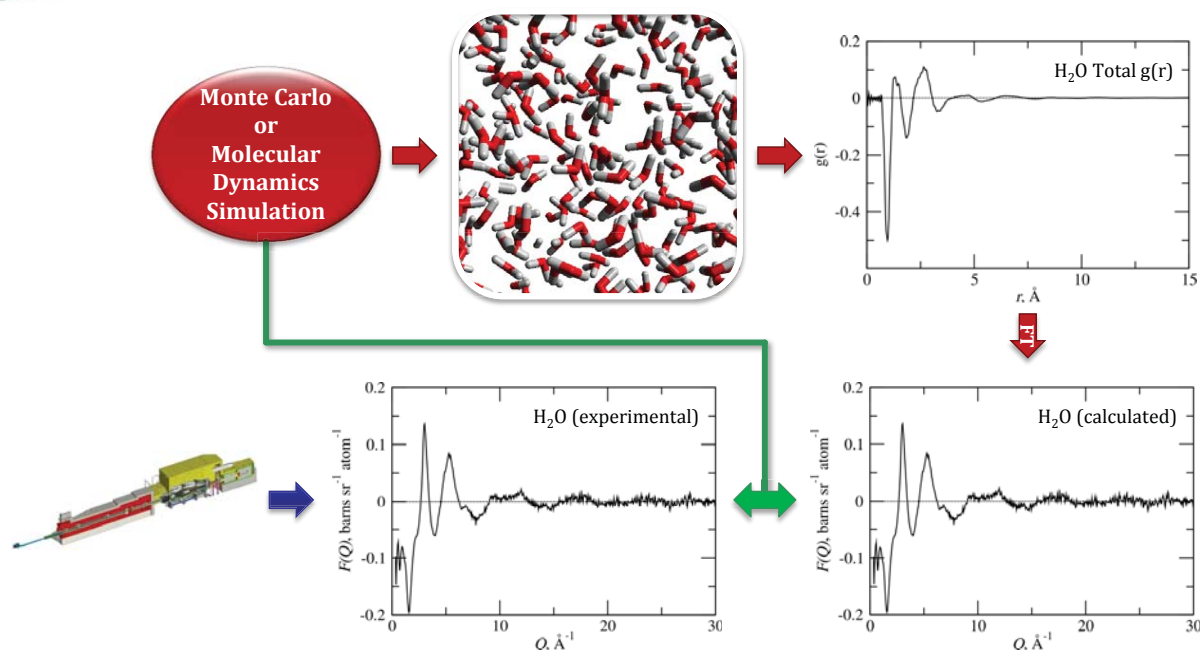
Radial distribution function (RDF) or pair distribution function (PDF) critical to diffraction

- Total RDF – correlations between all atoms / objects in the system
- Partial RDF – correlations between all atoms / objects of a given type (e.g. elements, isotopes etc.)
- RDFs **directly related** to $F(Q)$ via Fourier transform



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Isotopic Substitution

Allows multiple measurements on the same system, each resulting in different $F(Q)$

Most common example is switching Hydrogen (^1H) for Deuterium (^2H)

Key assumption is that **changing isotopes does not change structure**

b_v fm	H	D (^2H)	C	Al	Fe
	-3.74	6.67	6.65	3.45	9.45

Different b values affect weighting of partials in total $F(Q)$...

$$F(Q) = \sum_{i,j} (2 - \delta_{ij}) c_i c_j b_i b_j S_{ij}(Q)$$

$$S_{ij}(Q) = 4\pi\rho \int r^2 (g_{ij}(r) - 1) \frac{\sin Qr}{Qr} dr$$

	O	H	D
O	$1/9 \times 5.805^2$	$-2/9 \times 5.805 \times 3.74$	$2/9 \times 5.805 \times 6.67$
H	--	$4/9 \times 3.74^2$	$-4/9 \times 3.74 \times 6.67$
D	--	--	$4/9 \times 6.67^2$

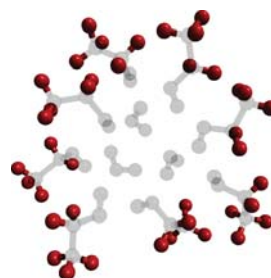
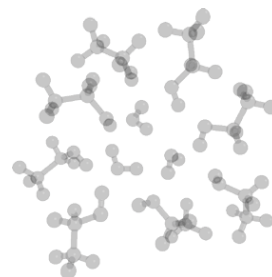
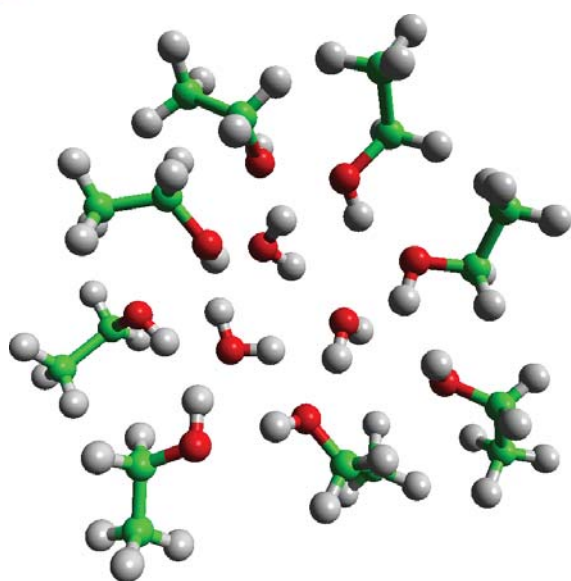
Weighting factors for water



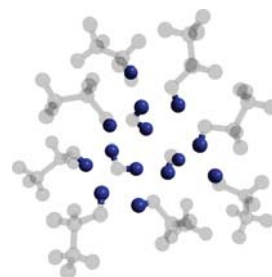
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Isotopic Substitution



Focus on ethanol CH



Focus on OH

Perform isotopic measurements on all sites of a given type to highlight associated interactions
For hydrogen sites, H, D, and a 50:50 H/D mix are the important trio of measurements



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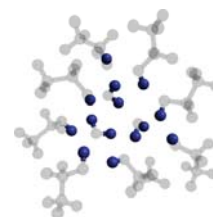
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Isotopic Substitution 2

Scattering length density

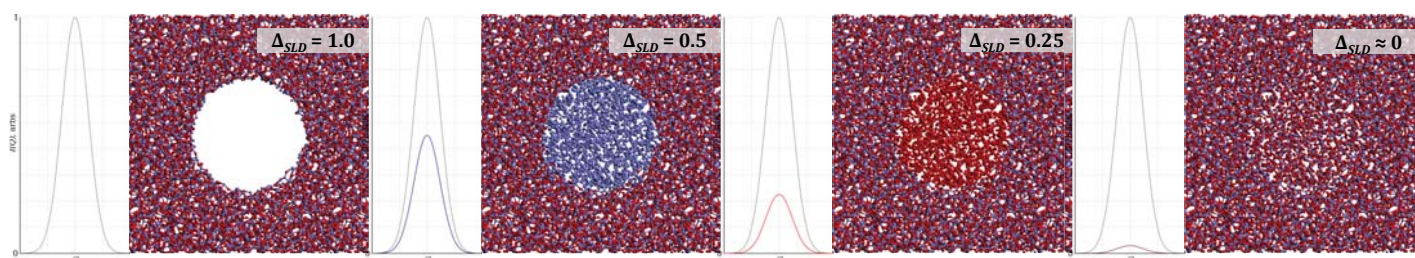
No longer thinking about contrast from the **atomic** perspective...

	H	D (^2H)	C	Al	Fe
b_c , fm					
	-3.74	6.67	6.65	3.45	9.45



Scattering Length Density (SLD)

"Average scattering length of atoms **per unit volume**"

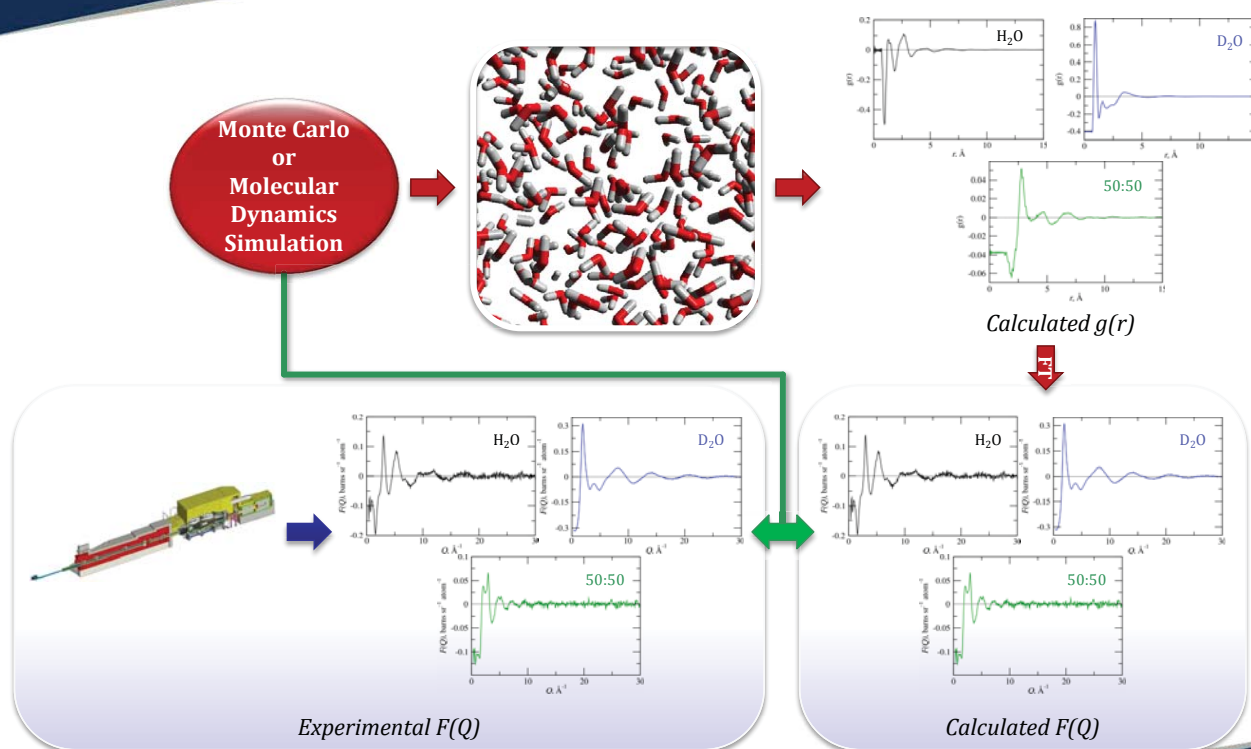


- Depends on isotopic substitution and local density of material



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Example: Solvation in Ionic Liquids

Glucose in 1-ethyl-3-methylimidazolium acetate

Multi-technique:

- Neutron
- Molecular dynamics
- 2D NOESY NMR

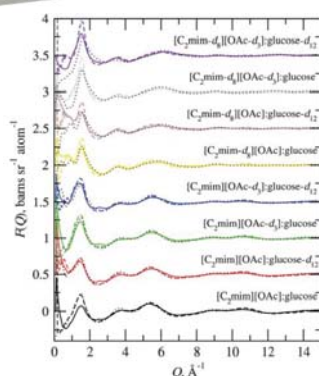


Fig. 1 Experimental (solid lines), EPSR refined (dotted lines) and MD simulated (dashed lines) distinct scattering profiles of all isotopically substituted 6:1 [C₂mim][OAc]:glucose mixtures examined.

Correlations between ionic liquid ions, glucose-ionic liquid, and glucose-glucose

Spatial orientations of ionic liquid ions around sugar molecules

Proved that ionic liquid H₂ proton did not significantly interact with glucose OH

Chemical Science

Dynamic Article Links

Cite this: *Chem. Sci.*, 2011, **2**, 1594

www.rsc.org/chemicalscience

EDGE ARTICLE

Neutron diffraction, NMR and molecular dynamics study of glucose dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate†

Tristan G. A. Youngs,^a John D. Holbrey,^b Claire L. Mullan,^b Sarah E. Norman,^b M. Cristina Lagunas,^b Carmine D'Agostino,^c Mick D. Mantle,^c Lynn F. Gladden,^c Daniel T. Bowron^d and Christopher Hardacre^{ab}

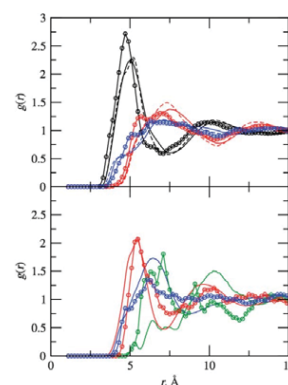


Fig. 2 Centre-of-mass radial distribution functions for a 6:1 [C₂mim][OAc]:glucose system, as determined by EPSR fitting of experimental neutron diffraction data (solid lines with symbols) and MD simulation (solid line). MD data for the neat ionic liquid is also shown for comparison (dashed line). Top panel shows ionic liquid cation-anion (black), cation-cation (blue) and anion-anion (red) distributions. Bottom panel shows glucose-glucose (green), glucose-cation (blue) and glucose-anion (red) correlations.

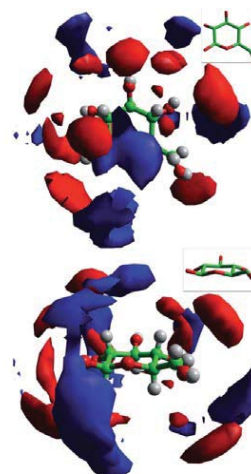


Fig. 3 Spatial probability distributions of anions (red) and cations (blue) around a central glucose derived from the MD model. The surfaces are drawn to encompass regions containing greater than six anions or four cations times the bulk density of ions in the system. Insets show the orientation of the central glucose molecule in each case, plan view (top) and side view (bottom).



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Example: Micelle structure

$C_{10}TAB$ in water

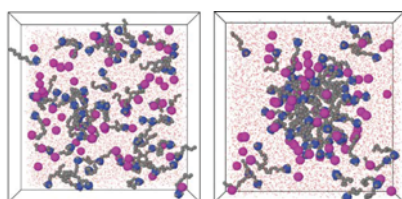


Figure 2. Snapshot of the starting configuration of a 64 $C_{10}TAB$ EPSR simulation (left) and a snapshot once a micelle of 43 surfactant molecules has formed (right). Color scheme: small red spheres are the water molecules' oxygen atoms, the gray spheres are the carbon atoms in $C_{10}TAB$ molecules, the large blue sphere is the nitrogen atom in the headgroup of the $C_{10}TAB$ molecule, and the magenta spheres are the bromide ions. These images were created using the Jmol program.⁴⁶

Resolution of local molecular arrangement and micelle size / shape

Largest (published) EPSR simulation to date

- ~ 30k atoms
- 64 Å cubic box

Atomistic Structure of a Micelle in Solution Determined by Wide Q-Range Neutron Diffraction

Rowan Hargreaves,^{*,†} Daniel T. Bowron,[†] and Karen Edler[‡]

[†]STFC—ISIS Neutron Scattering Facility, Didcot, United Kingdom

[‡]Department of Chemistry, University of Bath, Bath, United Kingdom

Supporting Information

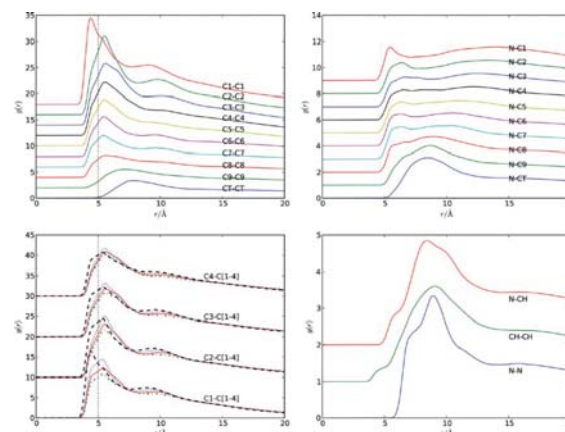


Figure 3. Surfactant-surfactant RDFs: the top left-hand plot shows the RDFs between the carbon atoms in the surfactant tail along the length of the tail, the bottom left-hand plot shows the RDFs of the 16 permutations of pair correlations of the last four carbon atoms in the tail (color scheme: the black dashed line is the C^{*}-C^{*} RDF, the blue dotted line is the C^{*}-C^{*} RDF, the red solid line is the C^{*}-C^{*} RDF, and the green dashed-dotted line is the C^{*}-C^{*} RDF). The top right-hand plot shows the RDFs between the nitrogen atom and the carbon atoms down the surfactant tail, and the bottom right-hand plot shows the headgroup-headgroup RDFs. For clarity the RDFs are offset by 1.0 up the ordinate. Also shown in the tail-tail plots is a dashed vertical line corresponding to the cutoff used in the cluster criteria.



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Example: Micropore collapse

Amorphous solid water

PCCP

PAPER

Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 16013

Small-angle neutron scattering study of micropore collapse in amorphous solid water[†]

Christian Mitterdorfer,^a Marion Bauer,^b Tristan G. A. Youngs,^c Daniel T. Bowron,^c Catherine R. Hill,^d Helen J. Fraser,^d John L. Finney^c and Thomas Loerting^{a*}

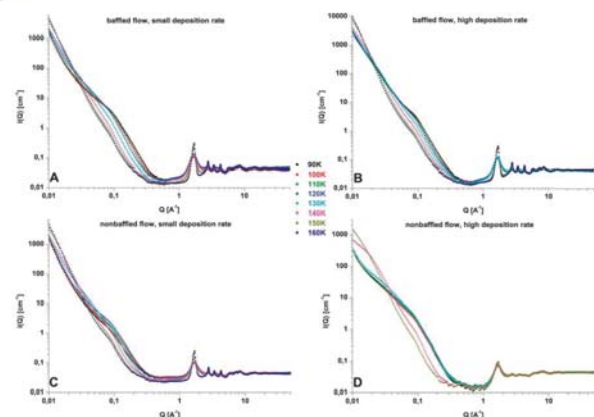


Fig. 1 Temperature evolution between 90 and 160 K of the scattered intensity for the whole available Q-range (0.01–50 Å⁻¹) for different deposition conditions: (A) buffered flow, small deposition rate, (B) buffered flow, high deposition rate, (C) non-buffered flow, small deposition rate and (D) non-buffered flow, high deposition rate. Error bars on the data points are about the symbol size.

Simultaneous observation of Q scales corresponding to molecular water, local ice-like structure, and SANS-active superstructures

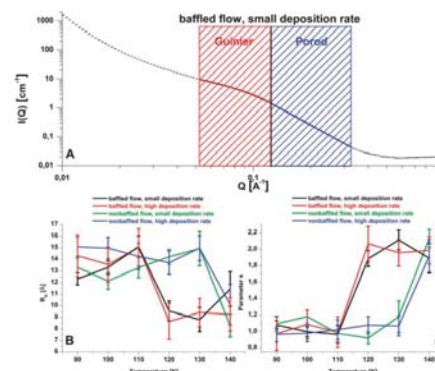
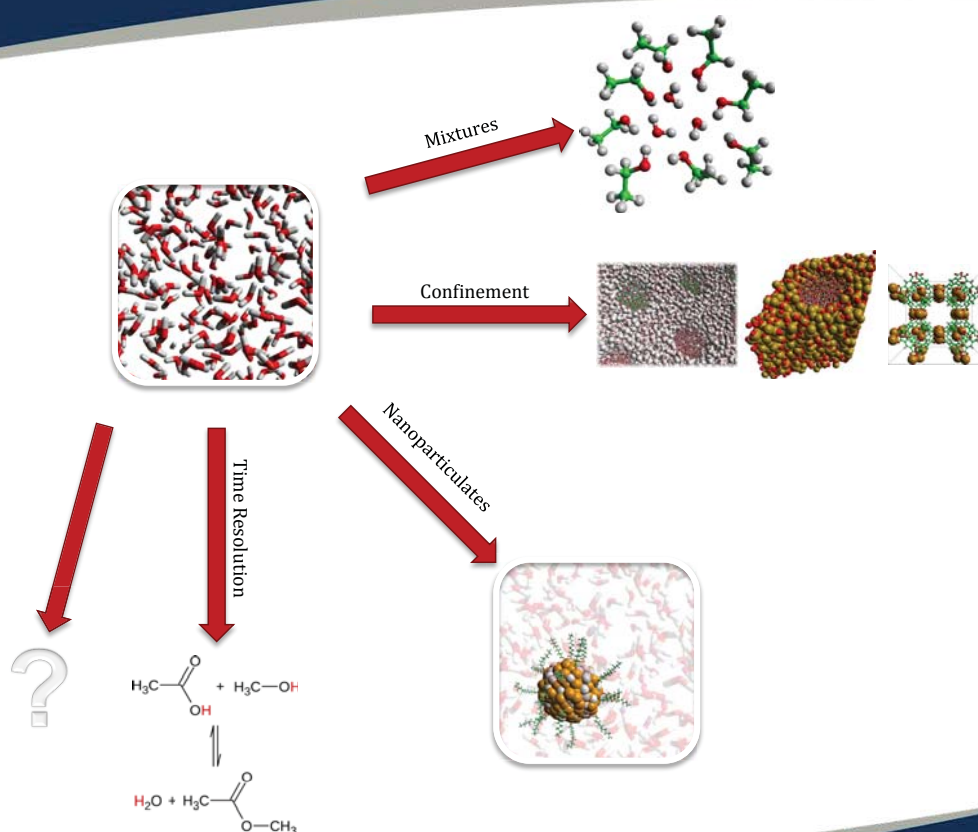


Fig. 5 Data evaluation by a new Guinier-Porod model in the low Q-range. (A) Scattered intensity in the low Q-region (0.01–1 Å⁻¹) including the Guinier and Porod region. Error bars on the data points themselves are indicated. (B) Temperature development of the radius of gyration between 90 and 140 K for all four specimens. (C) Temperature evolution of the Porod index s between 90 and 140 K for all four specimens.



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Rules & Practical Considerations



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We measure correlations from the structural scattering of **anything** and **everything** in the path of the beam

- Sample
- Sample impurities
- Stabilisers in liquids (e.g. antioxidants, free radical scavengers)
- Substrates (silicon mounts, Sellotape, etc.)
- Containers
 - Preferred containers are null scattering or have only weak structural signal
 - TiZr, silica, vanadium
 - Other metallic containers possible, but Bragg scattering can be a problem
 - Al, steel
- Some elements activate in the beam
 - e.g. Pt, Pd, Cu
 - Prevents re-use or refilling (generally, any handling) of sample in the experiment
- Some elements are strong neutron absorbers
 - e.g. B, Ag, Au
 - Subsequent analysis may be difficult or highly unreliable



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Sample Size / Containment



Gram quantities of material are typically required

Preferred sample geometry is usually flat-plate or cylindrical



Flat Plate

- 1 or 2 mm slot
- Volumes from 1.5 to 6 cc



Cylindrical

- Length up to 100 mm
- Diameter up to 10 mm

Solid samples take typically 0.8 – 1 g to pack a flat plate can with 2 mm slot

- Doesn't have to run in powder form, can be pelletised
- 2 hours measurement time

Liquid samples typically require 2 ml per isotopic substitution (flat plate can with 1 mm slot)

- 3 – 4 hours measurement time



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Isotopic Substitution



Isotopic substitution is often key to a successful experiment

Even simple liquids can't be probed **confidently** without using isotopic substitution

- Multiple isotopic samples needed for a full analysis

Careful selection allows specific interactions to be highlighted or suppressed

- Study structure "from the point of view of" specific atoms
- Focus on specific contacts in the liquid

Spatial information on location of species in porous systems

Dependent on concentration ($c_i c_j b_i b_j$) so component must be present in system in a suitable amount

- Between 5 and 10 atom% exchangeable atoms required

Deuteriated versions of 'speciality' chemicals are usually expensive



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Sample Environment



Generally speaking, we can provide whatever conditions your experiment requires

Temperature control

- Circulating water/oil baths
- High temperature furnaces
- Low temperature cryostats, CCRs, dilution fridges

Gas handling

- High pressure gas dosing
- Gases / vapours can be delivered to the sample *in situ*

Liquid handling

- Flow cells etc.

Something else?

- Within reason, can accommodate custom requests



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Measurement is easy.
Analysis is hard.

We measure everything – this does not mean we can analyse it!

Some information readily available from raw data

- Appearance / shift / intensity change of Bragg features
- Small angle regime can offer some immediate information

Diffuse scattering does not readily yield answers

Atomistic simulation / modelling almost always required

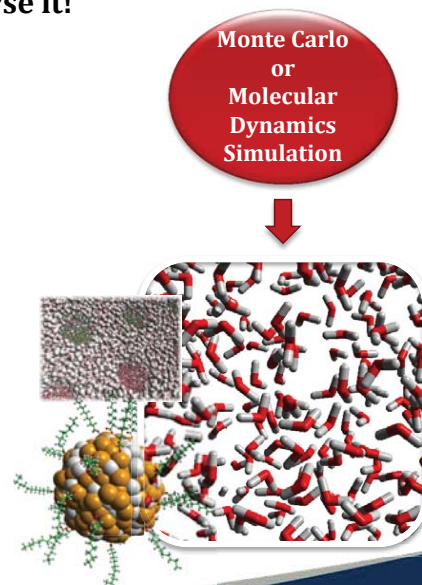
System size usually limiting factor

Time-resolved studies are possible

Acquisition times can be pushed down to minutes

Slowing down the dynamic process is a must

- Temperature control
- Reduced concentration / flow of reactant / initiator



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Summary

1



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Why Use Neutron Total Scattering?

General

- Non-destructive
- Can probe material interior (i.e. pores)
- Sensitive to hydrogen

Complete structural perspective

- Liquid correlations (pure, mixtures, confined)
- Bragg scattering (including occupational and positional disorder)
- SANS give information on particle form
- Some degree of modelling usually required

Isotopic substitution

- Use to give confidence in analysis
- Use to highlight specific interactions or 'domains' of interest

If you have structural questions about your material, total scattering can (given the caveats discussed) provide you with an answer



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Acknowledgements

Dr D. T. Bowron (ISIS, DM)

Dr S. Callear (ISIS, DM)

Your Experiment

Talk to us!

We are always happy to discuss experiment feasibility etc.



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Steps in heterogeneously catalysing a liquid phase reaction

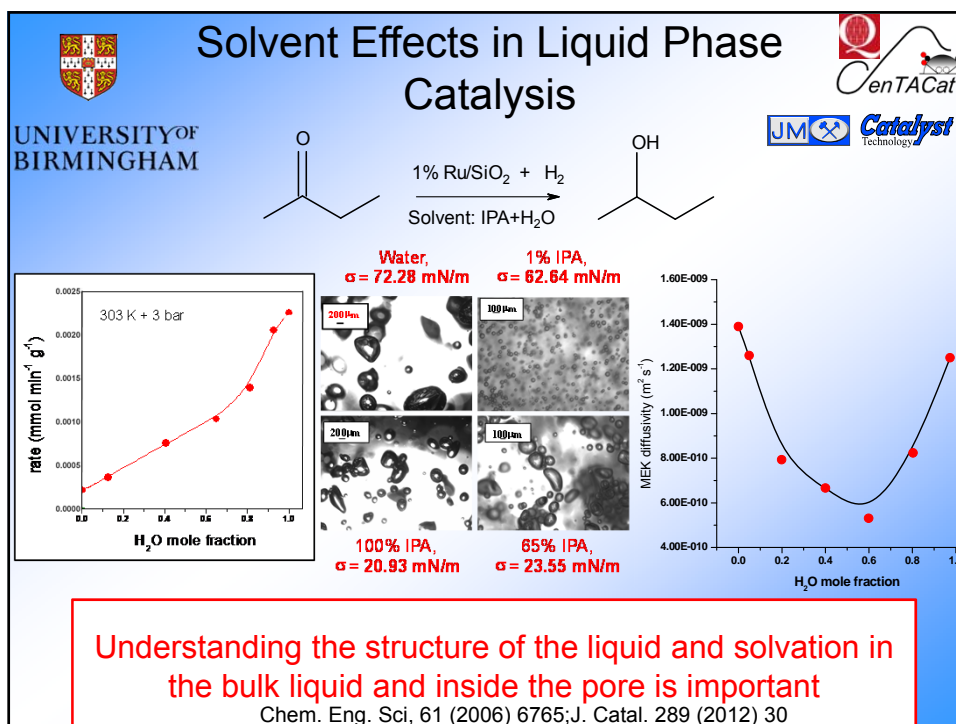
Reaction steps

1. Reacting molecules are transported from the bulk fluid to the catalyst site.
2. Molecules adsorb on the surface and react.
3. Molecules desorb from the surface.
4. Products are transported out into the bulk fluid.

Steps 2, 3 relate to the chemical interactions between catalyst and reagent/product.
Steps 1, 4 relate to the transport of materials to and from the reactive sites.

What is the role of the solvent versus the catalyst surface?

Thanks to D. Rooney



Bulk Liquid Structure & Solvation

Ionic Liquids

Liquids comprised solely of ions which are liquid at room temperature.

Bulky cations which are normally asymmetric.
Increased anion and cation charge delocalisation.

$[\text{NRR}'\text{R}''\text{R}''']^+$

$[\text{PF}_6]^-$

$[\text{SO}_3\text{CF}_3]^- = [\text{OTf}]^-$

$[\text{BF}_4]^-$

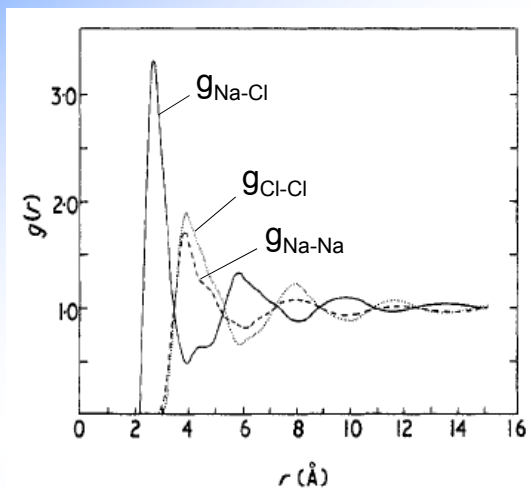
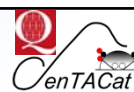
$[\text{N}(\text{SO}_2\text{CF}_3)]^- = [\text{NTf}_2]^-$

$[\text{PRR}'\text{R}''\text{R}''']^+$

$[\text{EtSO}_4]^-$

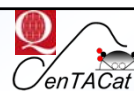
$[\text{CF}_3\text{COO}]^-$

Neutron Diffraction of molten NaCl

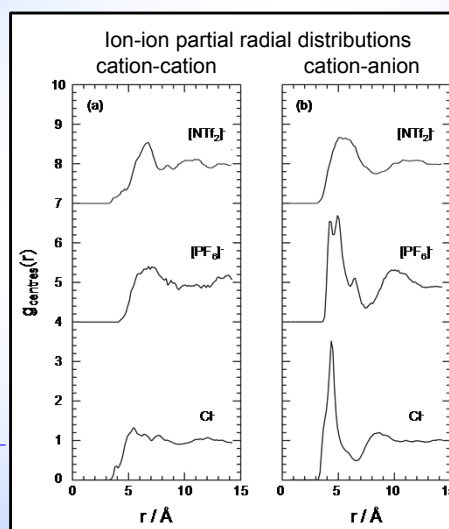
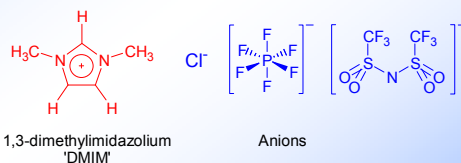


Edwards *et al.* J. Phys. C: Solid State Phys. **8** (1975) 3483

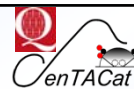
Ionic liquid structure from neutron scattering



- Approach
 - Selective H/D isotopic substitution on cation (and anion if possible)
 - Collect experimental liquid structure data from neutron scattering experiments
 - Analyse using EPSR (empirical structure refinement)
 - Use this data to compare and validate force fields for molecular dynamics simulations of ionic liquids
- [DMIM]⁺ based IL structure
 - Anion effects
 - IL-solute interactions

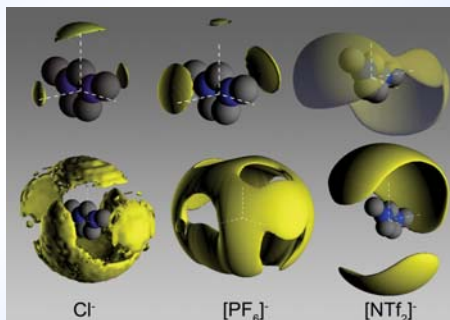


Ionic liquid structure from neutron scattering

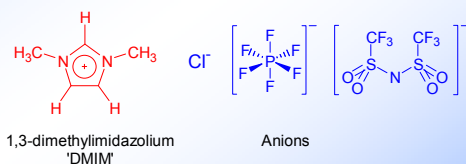


- Approach
 - Selective H/D isotopic substitution on cation (and anion if possible)
 - Collect experimental liquid structure data from neutron scattering experiments
 - Analyse using EPSR (empirical structure refinement)
 - Use this data to compare and validate force fields for molecular dynamics simulations of ionic liquids

Ion-ion spatial probability distributions

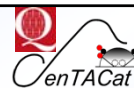


- [DMIM]⁺ based IL structure
 - Anion effects
 - IL-solute interactions

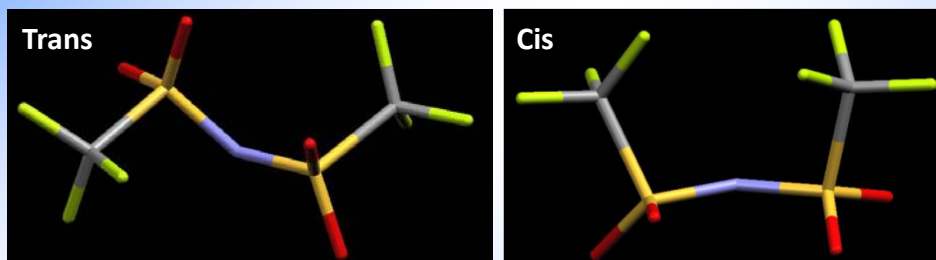


Decreasing ion-ion bonding character

Conformers - example of Bis{(trifluoromethane)sulfonyl}imide

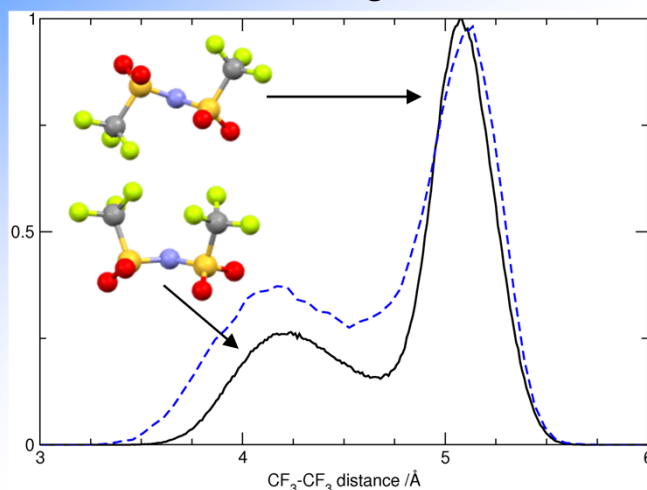
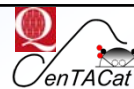


Structure or configuration of atoms for the same molecule



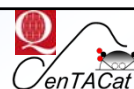
Similarly for the cation

Anion Configuration



Distribution of the anion $\text{CF}_3\cdots\text{CF}_3$ distance in liquid from the EPSR model (dashed line) and the MD simulations (solid line) showing the populations of the *cis* and *trans* conformers

What do we get from the liquid structure?



Anion-cation structure

Near neighbours

Information on local, or bulk, correlations

Solute-solvent interactions

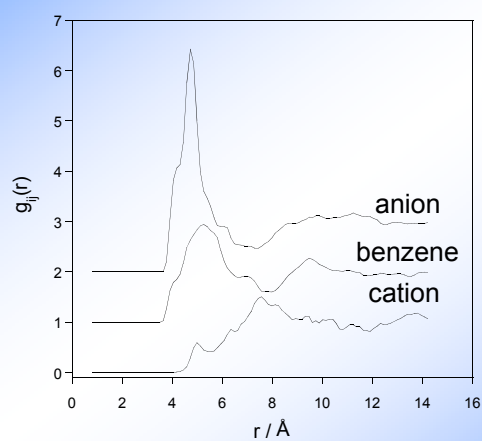
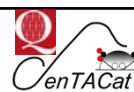
Understanding the structure is needed if we are to design ionic liquids for a given process

Case studies:

Benzene dissolution in ILs

Large IL structures

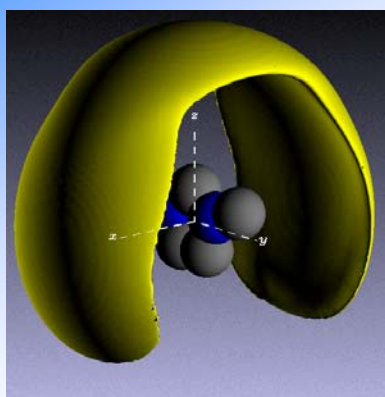
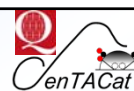
Benzene dissolved in [C₁mim][PF₆]



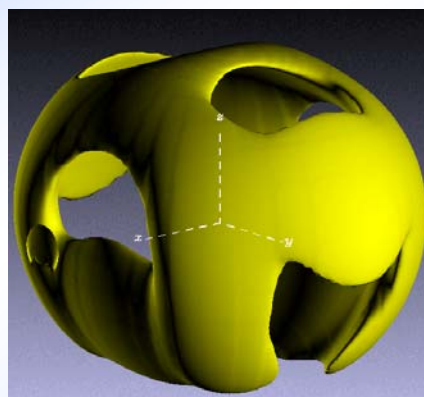
Radial distribution around [C₁mim]⁺

Benzene does not disrupt long range order

Cation distribution around cation



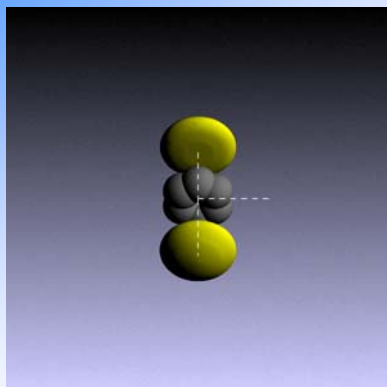
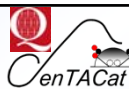
With benzene



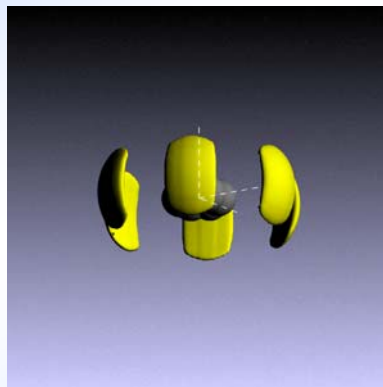
Without benzene

Anion distribution around cation
remains unchanged

Ion distribution around benzene



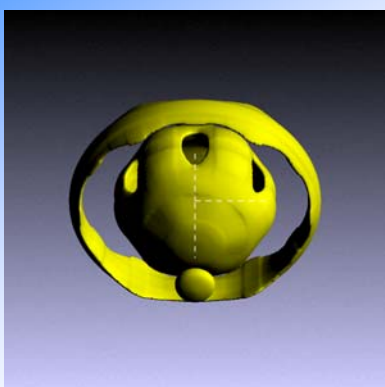
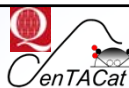
Cations



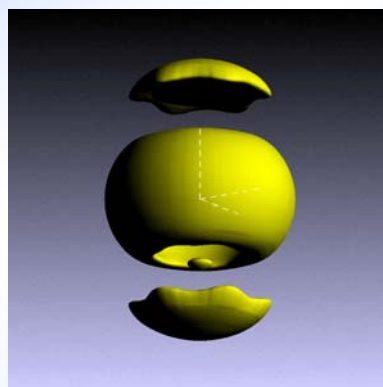
Anions

1st Shell

Ion distribution around benzene



Cations

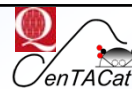


Anions

2nd Shell

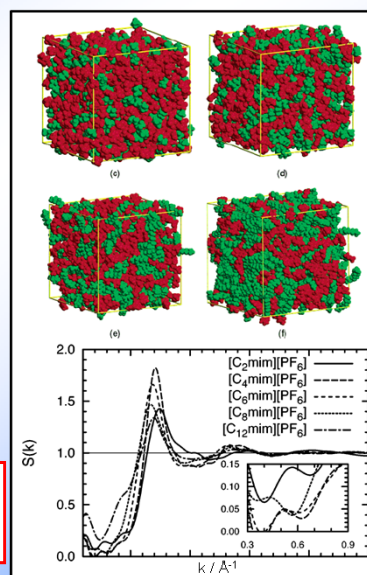
Nanostructural organization in ionic liquids

Canongia Lopes and Pádua,
J. Phys. Chem. B 110 (2006) 3330



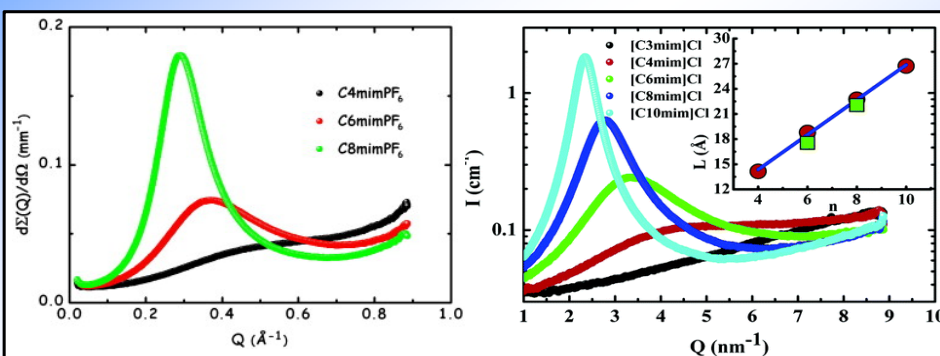
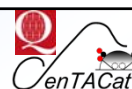
- Nanometre-scale structuring...with aggregation of the alkyl chains in nonpolar domains
- Domains permeate a tridimensional network of ionic channels
- As the length of the alkyl chain increases, the nonpolar domains become larger and more connected
- Domain length scales estimated from 'peak' in $Q = 0.3\text{--}0.6 \text{ \AA}^{-1}$ region

Is there experimental evidence at the molecular level?

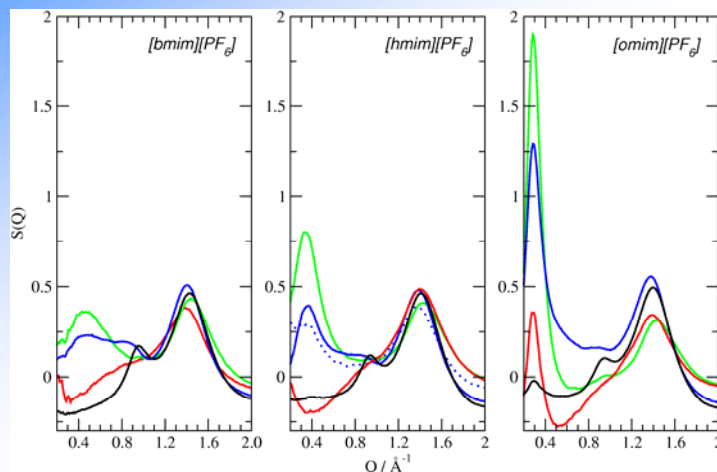
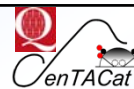


X-Ray Data – $[\text{C}_n\text{mim}][\text{PF}_6]/\text{Cl}$ ILs

Triolo *et al.*, *J. Phys. Chem. B*, **2007**, 111, 4641;
Chem. Phys. Lett. **2008**, 457, 362



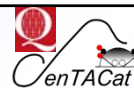
Neutron Data – $[C_n\text{mim}][\text{PF}_6]$ ILs



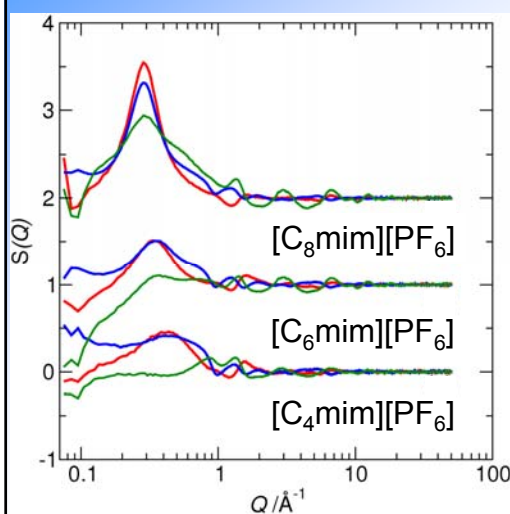
Protiated
Alkyl-deuterated
CH₃-deuterated
Deuterated

JCP 133 (2010) 074510

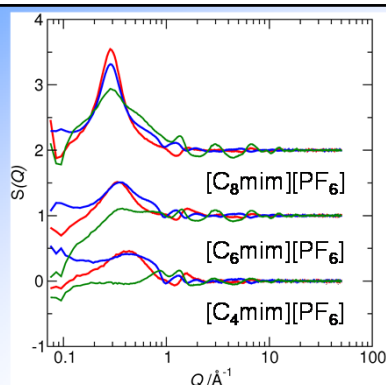
Data reduction



Difference $S(Q)$ diffraction spectra



All-H – methyl-D
 (methyl H contribution)
 All-D - alkyl-D
 (imidazolium ring+methyl H contribution)
 Alkyl-D – all-H
 (alkyl-alkyl contribution)

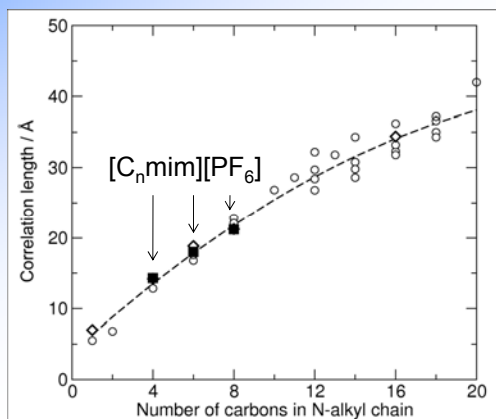


Substantial contribution to the low- Q peak arises from spatial correlations between imidazolium head groups.

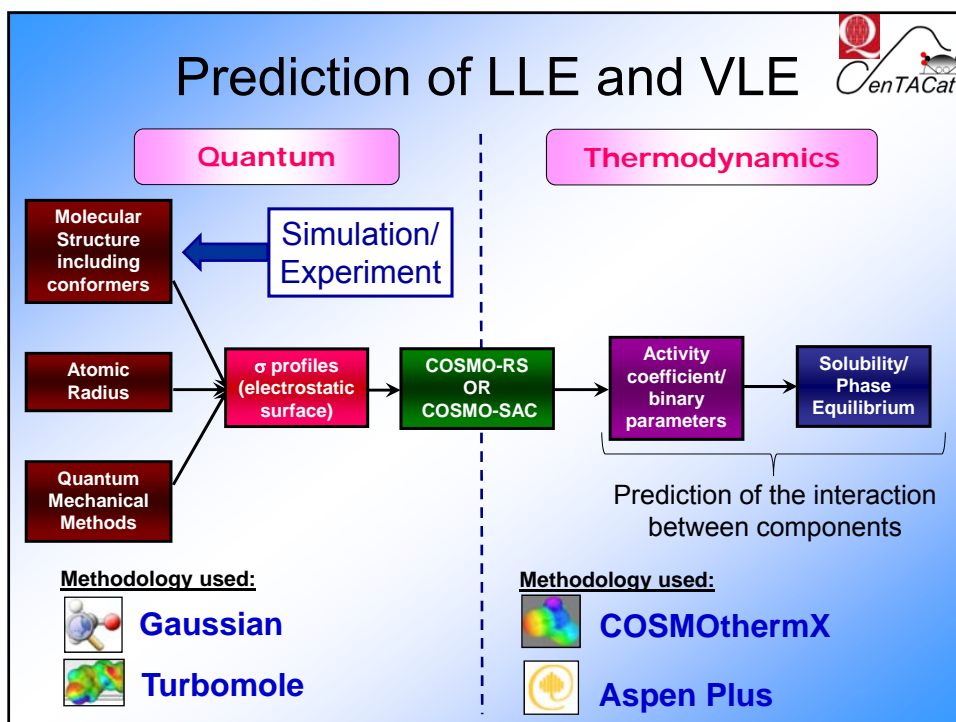
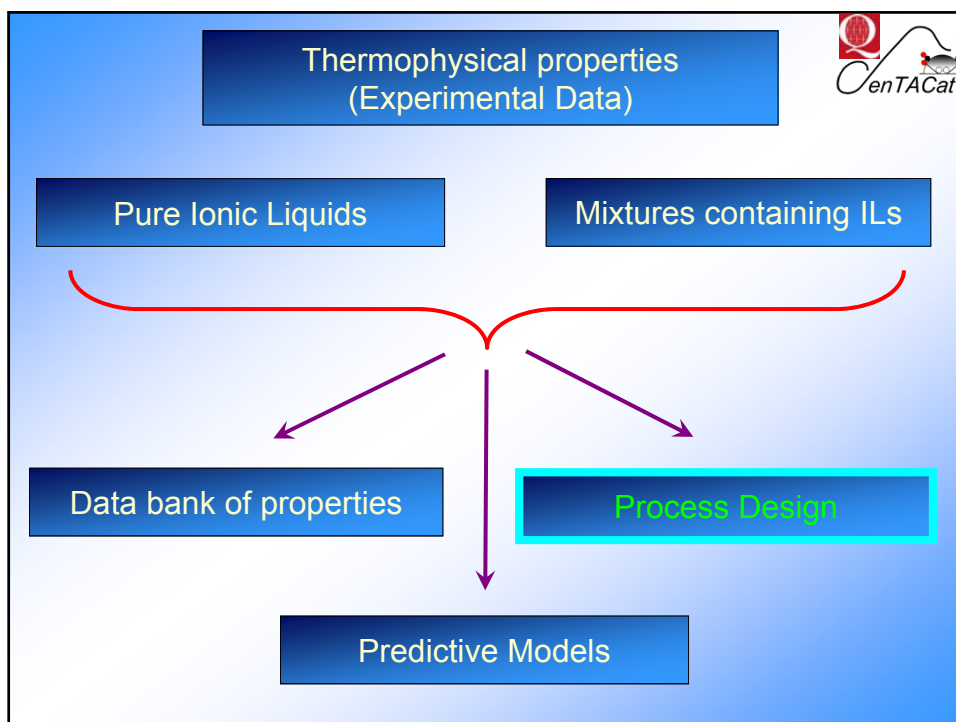
This is at separations larger than the second shell cation-cation separation in the case of $[\text{C}_1\text{mim}][\text{PF}_6]$.

Alkyl-alkyl van der Waals interactions, shows a much smaller contribution to the scattering in the low- Q region.

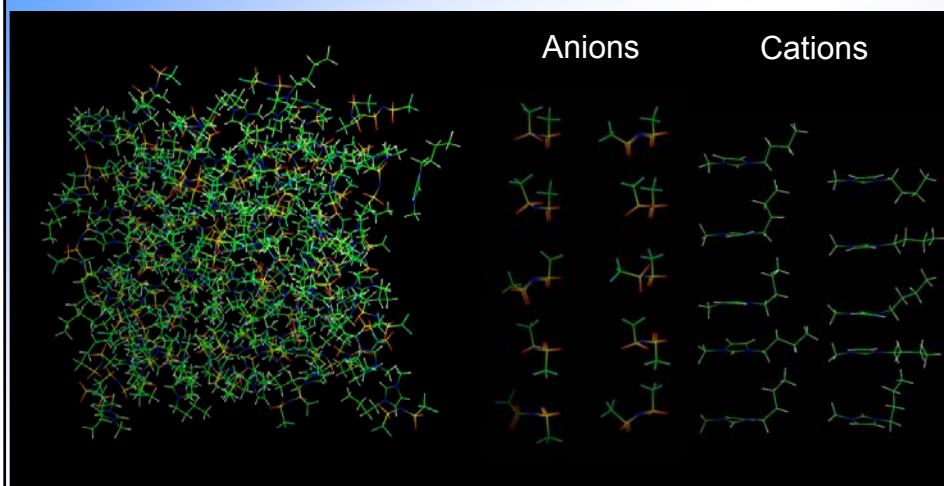
Correlation length vs alkyl chain length



The length-scale of the observed low- Q correlation in these structures expands linearly with increasing alkyl-chain length, from the small, rigid $[\text{C}_1\text{mim}][\text{PF}_6]$ to the long-chain liquid systems.



Snap shot of ions in [C₄mim][NTf₂]



Boltzmann Distribution Comparison of energies of the ion pair conformers in [C₂mim][NTf₂]

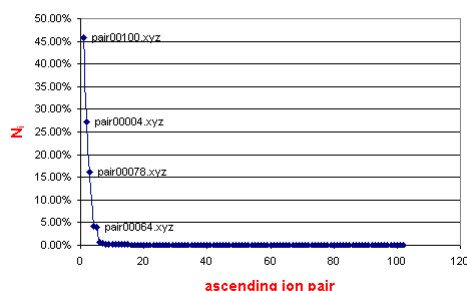


# Pair	Energy With charges / kJ.mol ⁻¹	Difference in energy (ε _j - ε ₀) / J.mol ⁻¹	exp(ε _j /kT)	N _j / fraction
pair00100.xyz	136.77900	0.0000	1.0000	45.69%
pair00004.xyz	138.07040	1291.4000	0.5959	27.22%
pair00078.xyz	139.39740	2608.4000	0.3514	16.06%
pair00017.xyz	142.71250	5933.5000	0.0927	4.23%
pair00064.xyz	142.87970	6100.7000	0.0867	3.96%
pair00049.xyz	147.23070	10451.7000	0.0151	0.69%
pair00065.xyz	149.04070	12261.7000	0.0073	0.33%
pair00092.xyz	149.53190	12752.9000	0.0060	0.28%
pair00035.xyz	149.62780	12848.8000	0.0058	0.26%
pair00095.xyz	149.76040	12981.4000	0.0055	0.25%
pair00087.xyz	150.55570	13776.7000	0.0040	0.18%
pair00066.xyz	150.56770	13788.7000	0.0040	0.18%
pair00077.xyz	150.84900	14070.0000	0.0036	0.16%
pair00038.xyz	150.94910	14170.1000	0.0034	0.16%
pair00085.xyz	151.12980	14350.8000	0.0032	0.14%
pair00086.xyz	153.35570	16576.7000	0.0013	0.06%
pair00041.xyz	154.69660	17917.6000	0.0008	0.03%
pair00093.xyz	155.24300	18464.0000	0.0006	0.03%
pair00089.xyz	155.30190	18522.9000	0.0006	0.03%
pair00076.xyz	157.49440	20715.4000	0.0002	0.01%
pair00090.xyz	157.89050	21111.5000	0.0002	0.01%
pair00007.xyz	159.01440	22235.4000	0.0001	0.01%
pair00006.xyz	159.57100	22792.0000	0.0001	0.00%
pair00061.xyz	160.32440	23545.4000	0.0001	0.00%
pair00002.xyz	160.55880	23776.8000	0.0001	0.00%

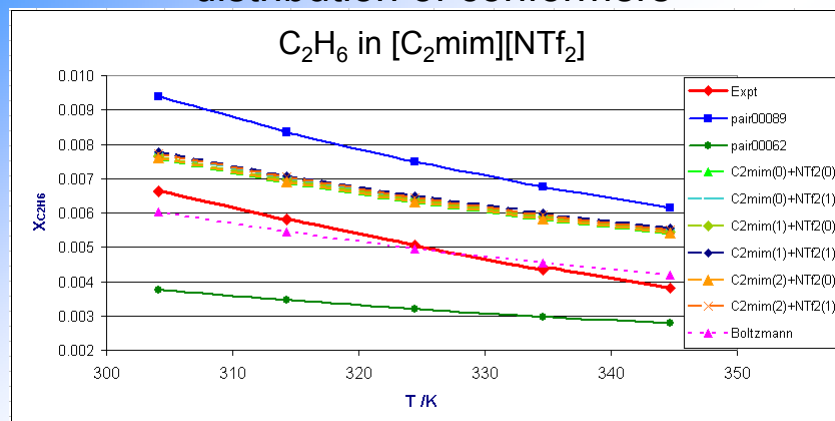
$$\frac{N_j}{N} = \frac{e^{-\varepsilon_j/kT}}{\sum_i e^{-\varepsilon_i/kT}}$$

ε = Difference in molecular energy level
k = Boltzmann constant
T = Temperature (K)
N_j = Molecule in the jth state
N = Total molecules

pair vs. % weighted



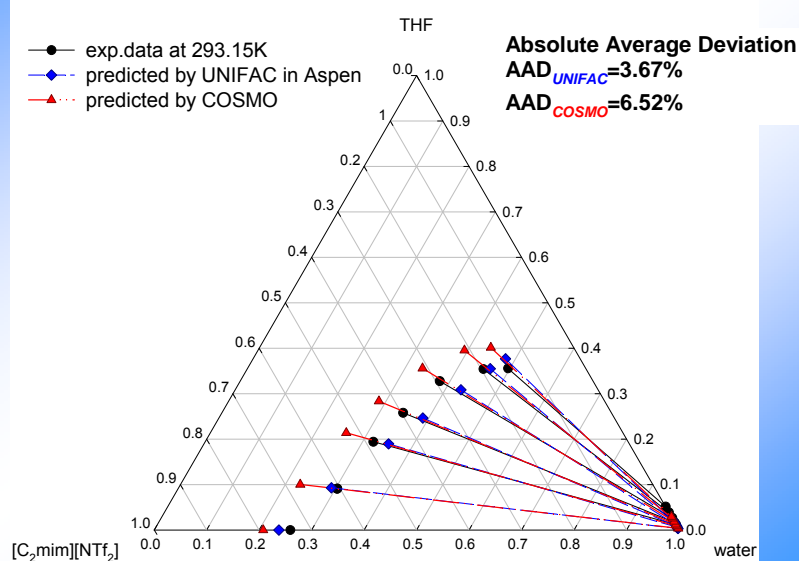
Calculation using Boltzmann distribution of conformers



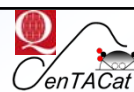
Experimental/theoretical derived structures
can assist in prediction of physical properties

J. Chem. Eng. Data 54 (2009) 2005

Phase behaviour of ($[C_2mim][NTf_2]$ + water + THF)

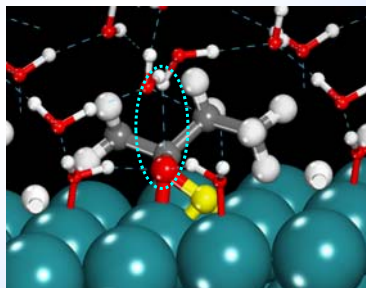


The Role of Solvents



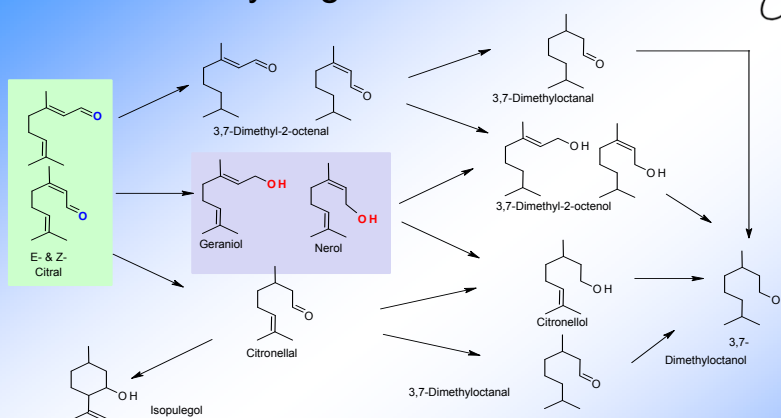
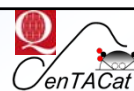
In liquid phase reactions the role of solvents is **not limited** to simple dissolution and/or dilution of substrates but it is **a key design parameter** significantly influencing the:

Reaction Mechanism
Substrate adsorption
geometry/strength
Product Selectivity
Catalyst deactivation
Interfacial Tension (wetting)
Viscosity, P_{vap} , mpt
Distribution Coefficient



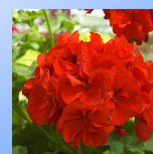
In heterogeneous catalysis, understanding the **liquid structure**, **H-bond networking and dynamics** are key parameters in process design but it is often overlooked!!

Hydrogenation of Citral



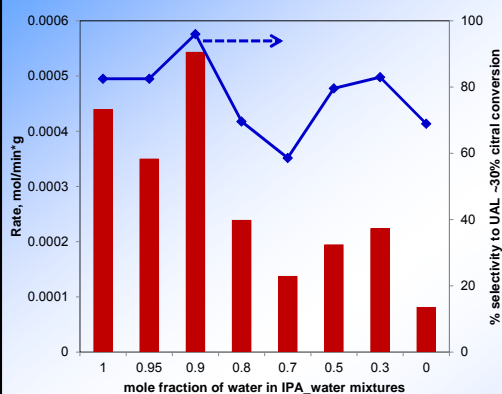
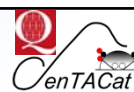
Influence of solvent effects on the reaction rate and selectivity towards unsaturated alcohols (Geraniol & Nerol)

Influence of the competitive adsorption of citral, citronellal and citronellol on the selectivity



Geranium,
smell comes from geraniol

Reaction rates for Citral hydrogenation using 5% Pt/SiO₂ in different IPA-water mixtures

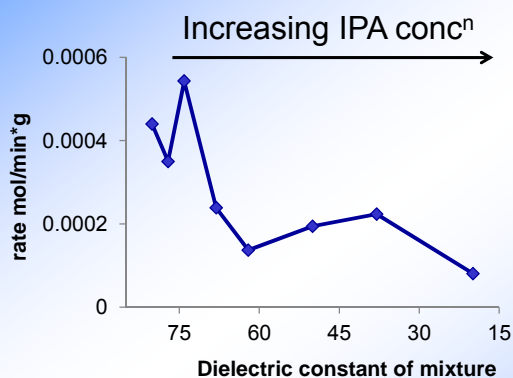
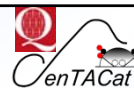


Water mole fraction	%Geraniol + Nerol Selectivity
1	87.8
	88.6
0.95	82.5
	91.5
0.9	78.3
	97
0.8	69.6
	91.8
0.7	58.6
	89.8
0	68.9
	95.6

Significant variation of rate and selectivity with solvent composition

Initial selectivity
Selectivity at 99% conv.

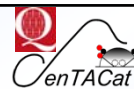
Liquid structure and Dynamics



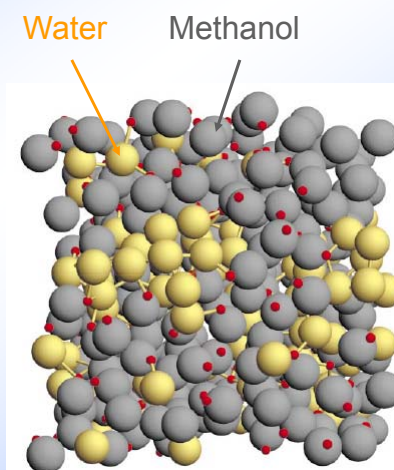
High reaction rate and selectivity in 90mol% water **cannot be explained by simple solvent parameters** such as dipole moment or Lewis acidity/basicity of solvent mixture.

How does the structure of the solvent change?

Non-ideal mixing at the molecular level

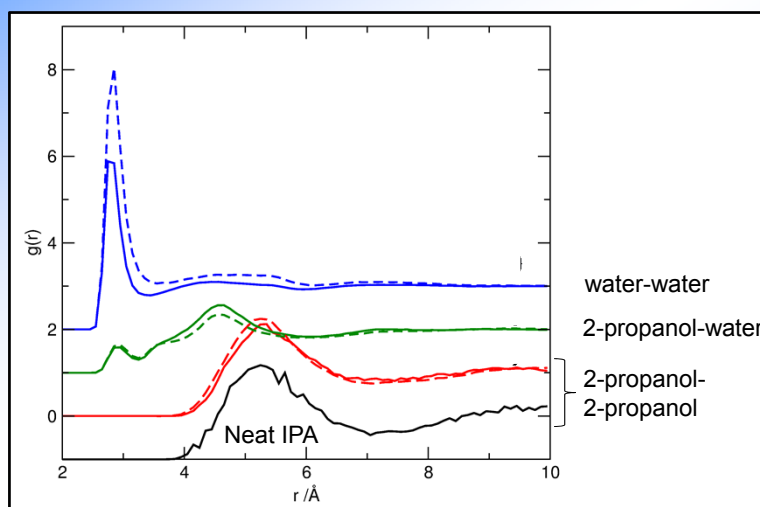
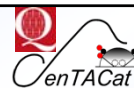


- Neutron diffraction studies of water – methanol mixtures
 - Methyl head groups cluster to form hydrophobic regions that inhibit proton transport.
 - Formation of small water clusters or strings comprised of 2-20 water molecules.
- so what does H₂O-IPA look like at this resolution?

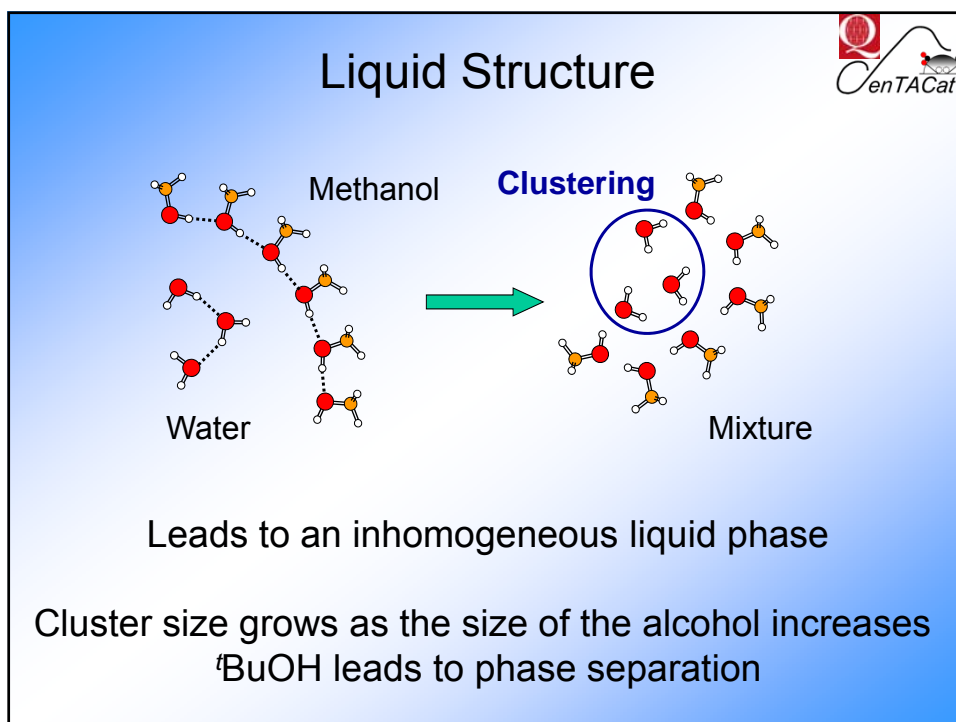
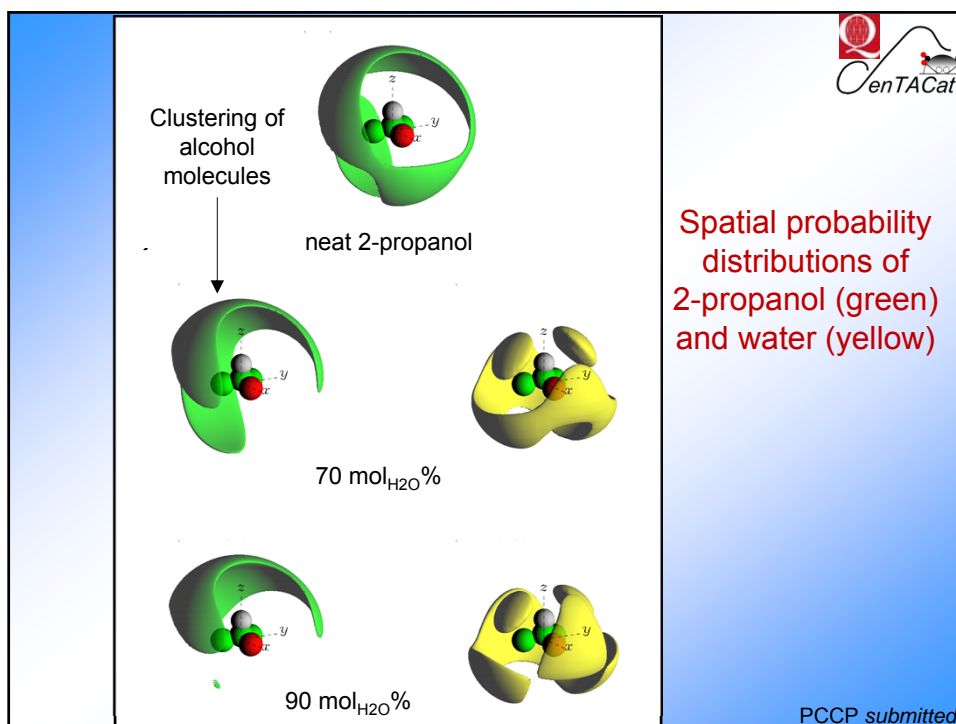


S. Dixit (2002) Nature

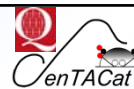
Centre of mass molecule-molecule radial distribution functions



70 mol_{H₂O} % (dashed lines) and 90 mol_{H₂O} % (solid lines)

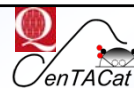


Can we use neutrons to probe reactions in solids



- Ideally, for a given reaction we want to know:
 - Chemical distribution as a function of time
 - Kinetics, selectivities, conversions
 - Chemical distribution as a function of position
 - Diffusion rates, physical location of products / reactants in system
 - Both simultaneously on an atomic/molecular scale

In-situ techniques to examine liquid phase heterogeneously catalysed reactions

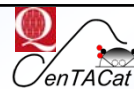


Neutron Scattering to probe reactions inside a catalyst pore

Benzene Hydrogenation over Pt/MCM-41

Chem. Sci. 4 (2013) 3484

NIMROD

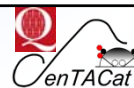


- **N**ear and **I**nter**M**ediate **R**ange **O**rd**E**r Diffractometer
- Target Station 2 at ISIS



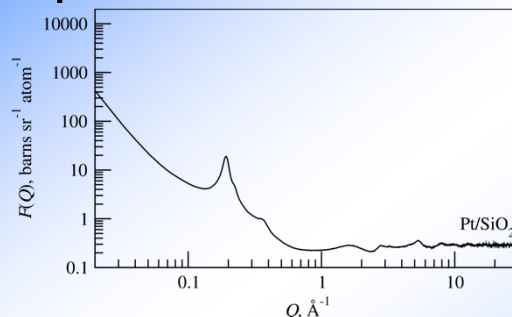
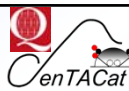
- Accesses the Q-range of a traditional wide-angle instrument combined with a small-angle instrument ($0.01 < Q < 50 \text{ \AA}^{-1}$) giving a real-space range of $0.125 < r < 300 \text{ \AA}$

Experimental Setup



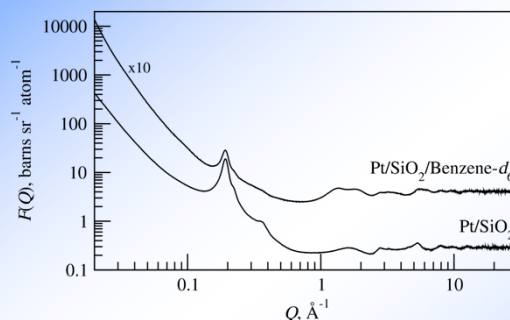
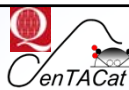
Capillary condensation of reactants
and products into the pores
– *no bulk liquid present*

Endpoint Characterisation



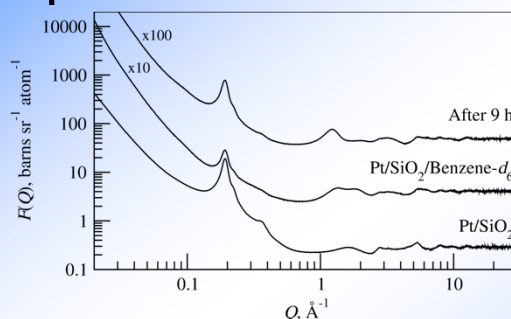
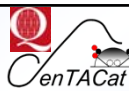
- Empty Pt/SiO₂ shows a characteristic 'mesopore' peak at 0.19 Å⁻¹
 - Corresponding real-space distance of 33 Å
- Direct characterisation of pore spacing (c.f. BET)

Endpoint Characterisation



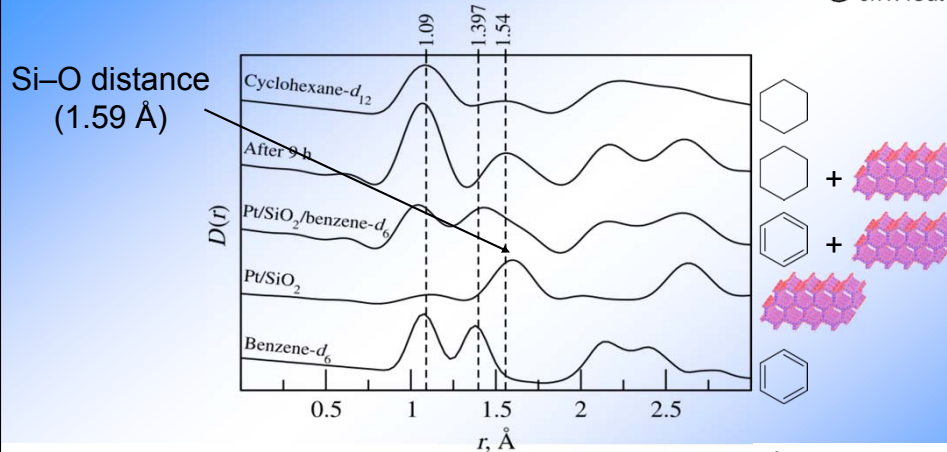
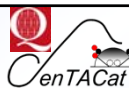
- Introduction of benzene-*d*₆ reduces intensity of FDP – contrast matching of condensate to bulk SiO₂
- Confirms material has entered pores
- Change in higher- Q region consistent with introduction of 'chemical' species

Endpoint Characterisation



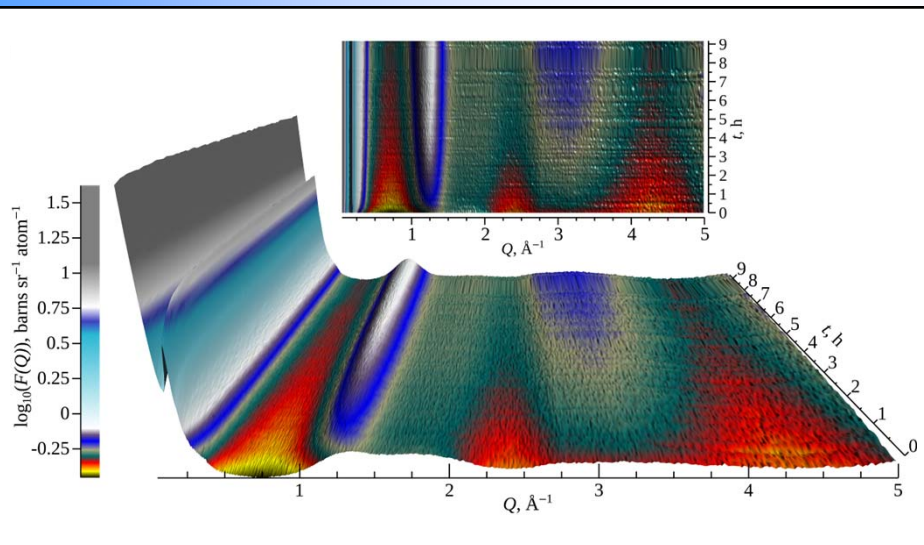
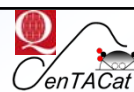
- Expose loaded benzene-*d*₆ system to 250 mBar D₂ at 25°C
- After 9 hours, steady-state conditions reached, i.e. no further changes in measured $F(Q)$
- Re-emergence of FDP (increased material/pore contrast c.f. benzene-*d*₆)
- Differences in intramolecular Q -region ($1 - 5 \text{ \AA}^{-1}$)

Radial Distribution Functions

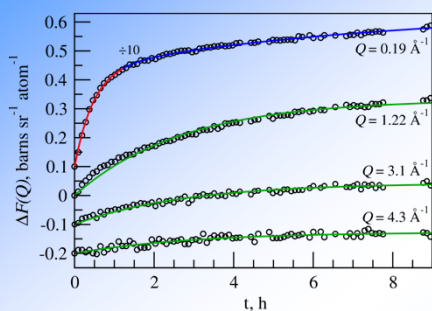
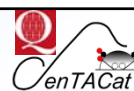


- Derived RDFs show presence of C-D bonds (1.09 \AA) throughout, with increased intensity after 9 h reaction time
- Benzene C-C distance (1.397 \AA) not present after reaction
- Peak at cyclohexane C-C distance (1.54 \AA) clearly visible

Time-Resolved $F(Q)$



Kinetics

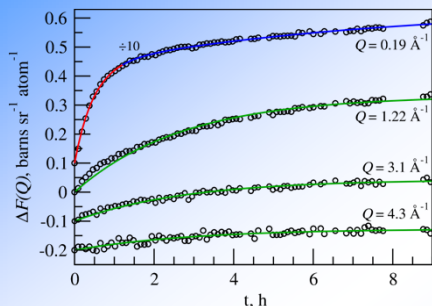
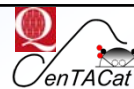


$$\Delta F(Q) = (a_0 + a_1) - a_0 e^{-\frac{t}{t_0}} - a_1 e^{-\frac{t}{t_1}}$$

$Q, \text{\AA}^{-1}$	a_0	t_0	a_1	t_1
0.19	3.584	0.466	2.234	7.343
1.22	0.332	2.714	--	--
3.1	0.143	2.773	--	--
4.3	0.074	2.999	--	--

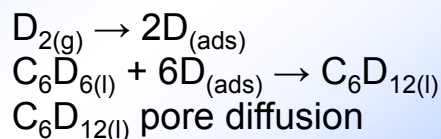
- FDP at $Q = 0.19 \text{ \AA}^{-1}$ only affected by inter-species correlations
 - Two corresponding timescales – one fast (D_2 dissociation and surface restructuring) and one slow (mass transport of products)
- All other values of $F(Q)$ evolve with similar, moderate timescale
 - Related to chemical changes in the system (i.e. conversion of benzene to cyclohexane)

Kinetics



$$\Delta F(Q) = (a_0 + a_1) - a_0 e^{-\frac{t}{t_0}} - a_1 e^{-\frac{t}{t_1}}$$

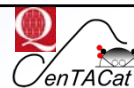
Q, Å ⁻¹	a ₀	t ₀	a ₁	t ₁
0.19	3.584	0.466	2.234	7.343
1.22	0.332	2.714	--	--
3.1	0.143	2.773	--	--
4.3	0.074	2.999	--	--



$$\begin{aligned} k_0 &= 2.146 \text{ h}^{-1} \\ k_{2,3,4} &\approx 0.35 \text{ h}^{-1} \\ k_1 &= 0.136 \text{ h}^{-1} \end{aligned}$$

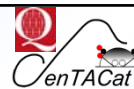
Pore diffusion is the slowest step

Rate Determining Step



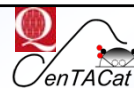
- In the present case, the fact that pore liquid diffusion is critical in determining the rate of reaction is important in understanding how the catalyst design may be developed.
- Improvements in the surface reaction process, i.e. increasing the number or reactivity of the active sites, will have little influence on the catalyst performance
- Addition of a solvent, to increase the rate of diffusion, is likely to have a significant promoting effect.

Summary



- NIMROD is able to completely characterise the atomic, molecular and mesoporous length scales in the system simultaneously and monitor the reaction ***in a time-resolved manner***
- Able to elucidate several different processes with distinct timescales present in the reacting system
- In principle, complete structural and kinetic picture of system obtained
 - Difficulty is in analysis!
- First time that neutron diffraction has been used in this manner

Acknowledgements



John Holbrey
Mark Nieuwenhuyzen
Jane McMath
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Maggel Deetlefs

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Lynn Gladden
Haresh Manyar
Marta Falkowska
Sarayute Chansai

Tris Youngs
Daniel Bowron
Alan Soper



Inelastic Neutron Scattering

Ian Silverwood

3/11/14

Neutron Interactions with Matter: Inelastic Scattering (INS)

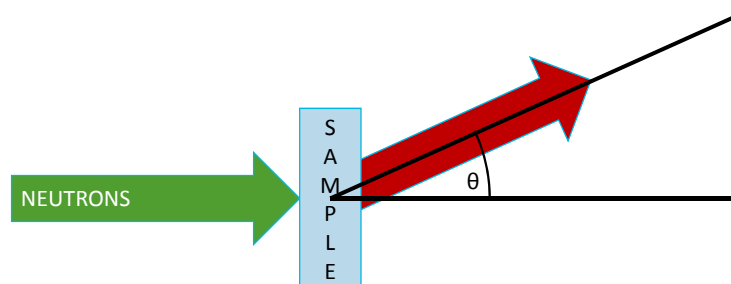
Neutrons can be scattered through an angle θ , and transfer energy to sample

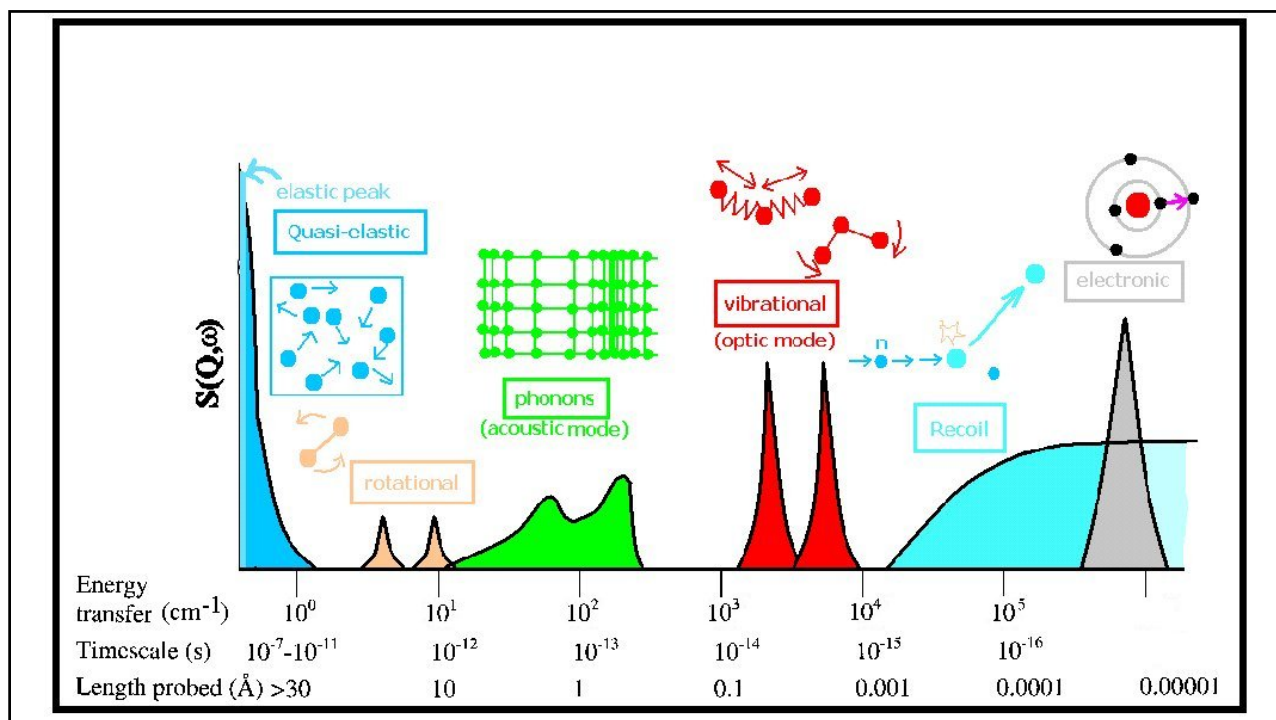
Also undergo change in momentum

Can provide vibrational information

INS is a minority effect

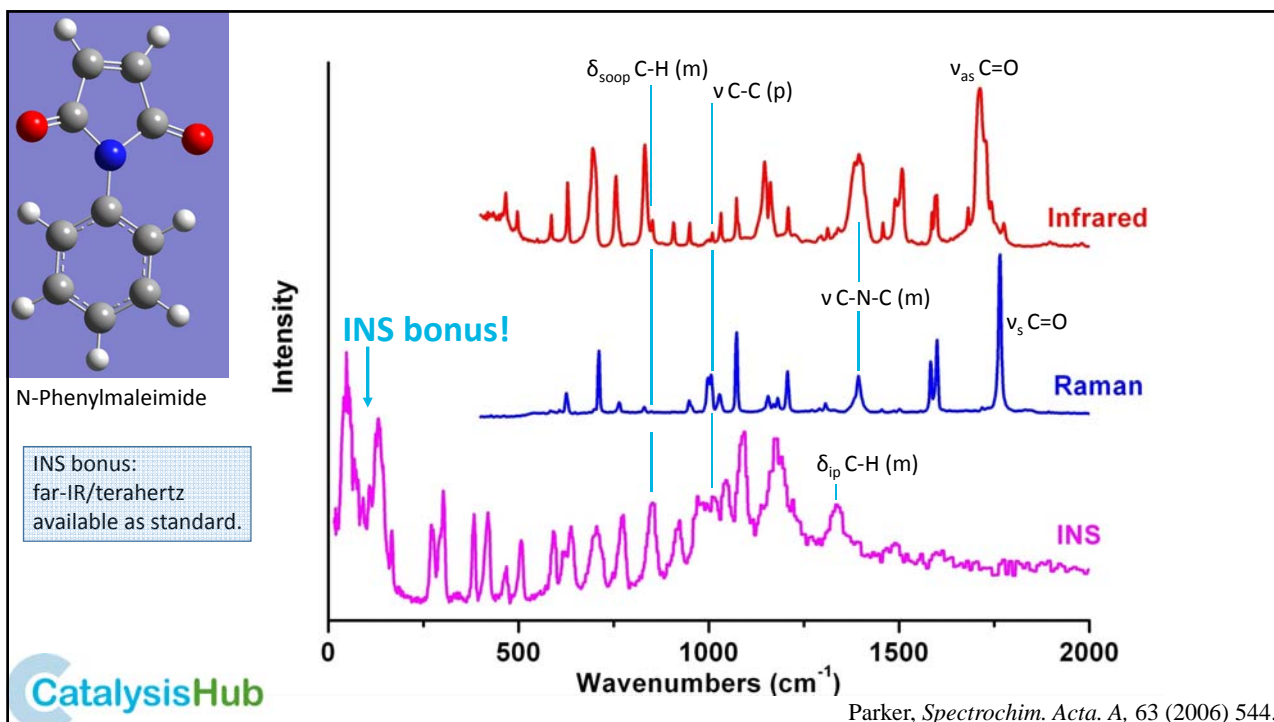
most neutrons do not scatter





Vibrational spectroscopy with INS

- For INS, easy approximation is neutrons only interact with hydrogen
 - Metal cells fine – in situ reactions
 - Metals + supports effectively transparent
- All modes allowed – can gain unique/complementary information
- Access wide spectral range
- Physical scattering – black samples OK
- Easy modelling – comparison with theory

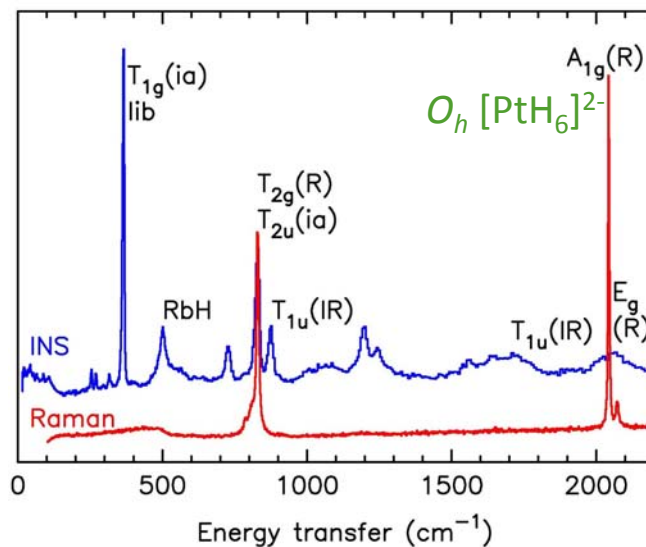


Vibrational spectroscopy with INS - drawbacks

- Low sensitivity
 - Large samples
 - High surface area
- Resolution can be relatively low *cf.* IR/Raman (at high energy)
- Generally measure at low temperature (20 K)
 - Minimise scattering due to thermal motion (Debye-Waller Factor)
- Slow (~12 hrs)
- Expensive (but not to you!)

Good reasons to do INS – Sample selection

- Black
- Interfering modes
- Non-active modes
- Extreme conditions
- Hydrogenous – H/D



Hydrogen/Deuterium substitution

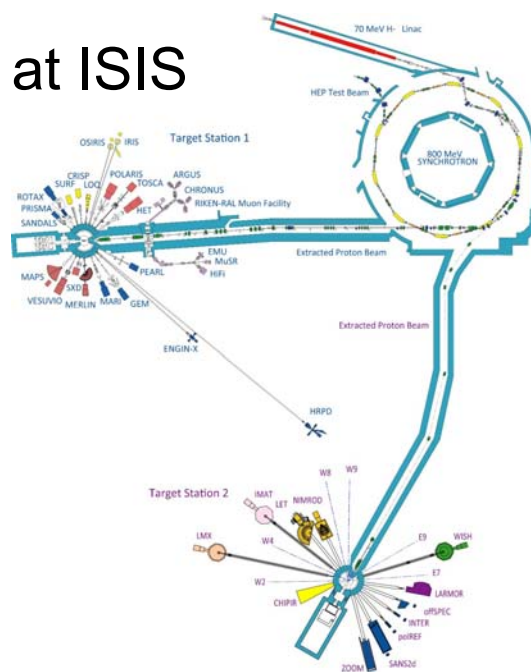
- Bands disappear/weaken – 7.6 vs 82.0 barn
- Bands shift $\sim\sqrt{2}$
- Needs to be well deuterated (99%)
 - other uses 90% deemed acceptable – INS will give approx. 50% signal due to H
- Can provide contrast or decrease unwanted signal from organic

Choosing a spectrometer

- Energy transfer/spectral range $1 \text{ meV} = 8.07 \text{ cm}^{-1}$
- Sensitivity
- Resolution
- Momentum transfer (more complex measurements)
 - detector angle/coverage dependant
 - decrease Debye Waller factor
 - resolve overtones
 - assist in peak assignment by mass distinction

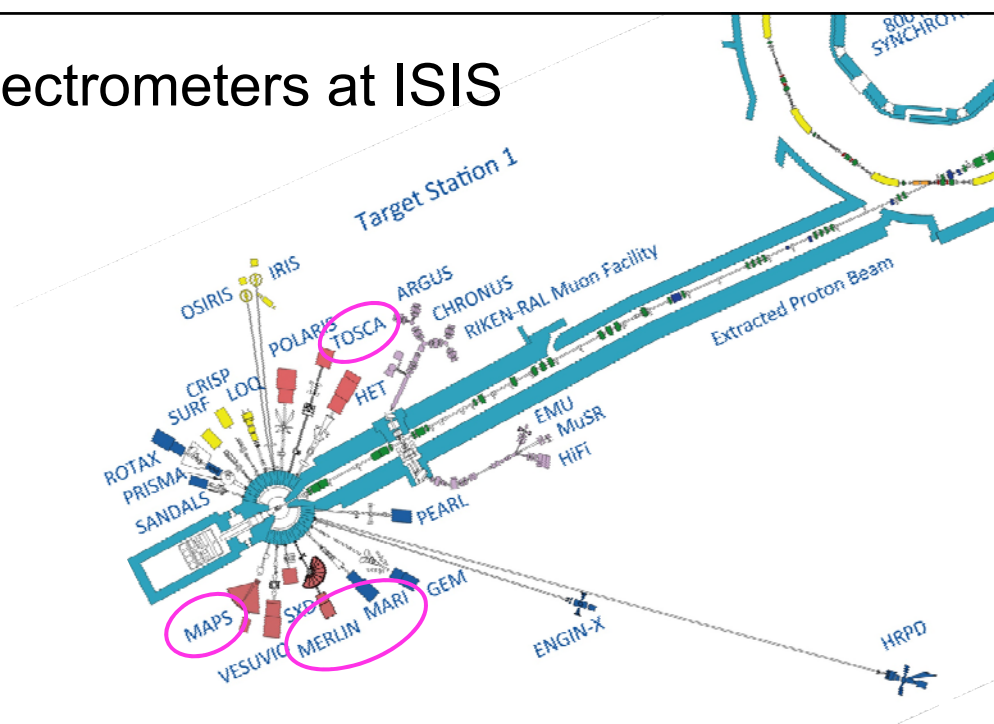


INS spectrometers at ISIS



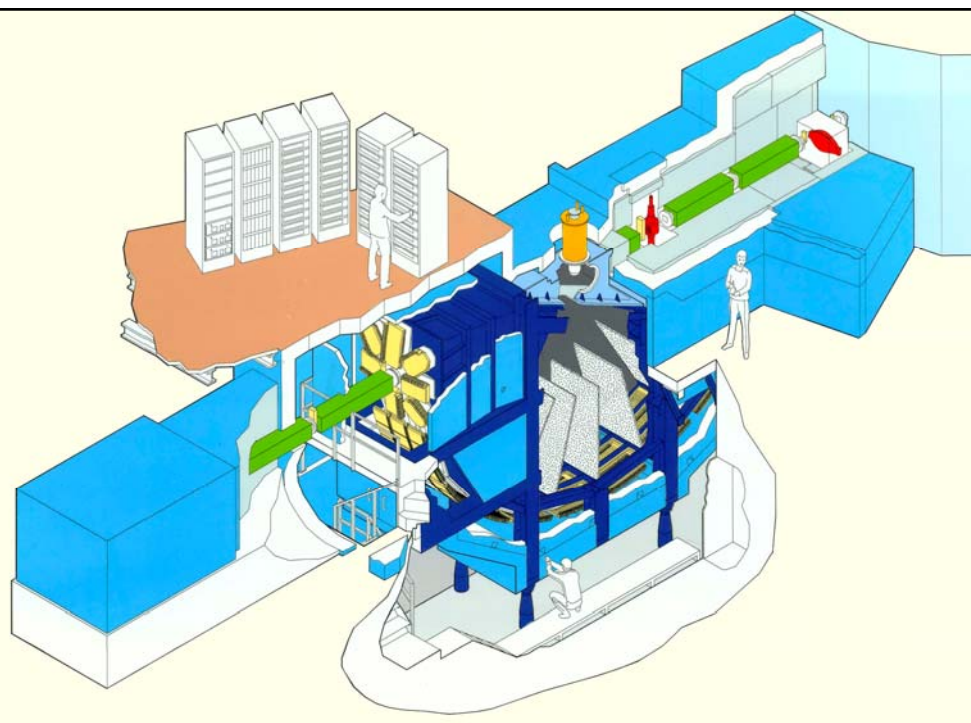
INS spectrometers at ISIS

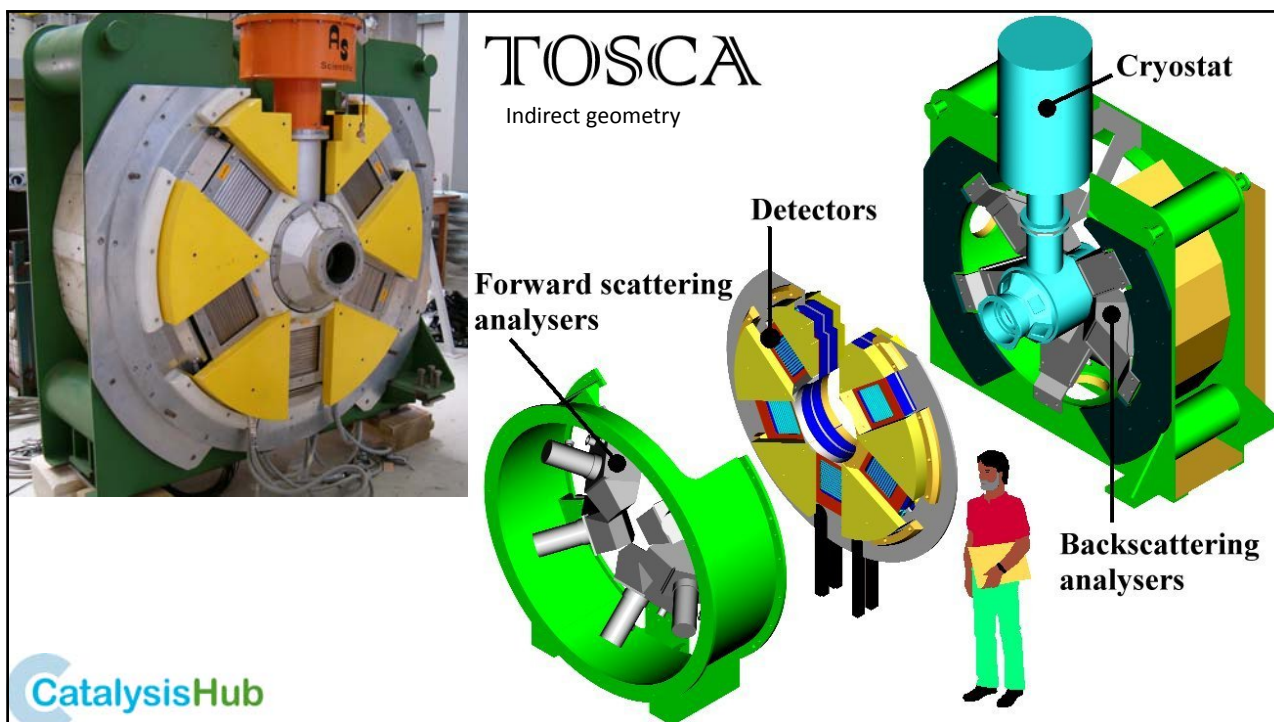
MARI
MAPS
MERLIN
TOSCA



MARI

Direct geometry





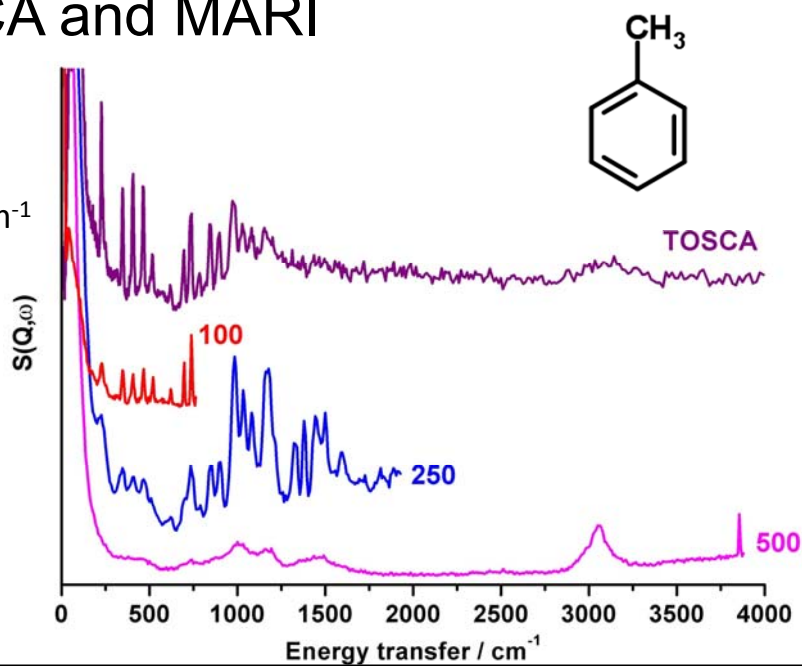
Toluene on TOSCA and MARI

Choose indirect geometry

- Excellent resolution and sensitivity below $\sim 2000 \text{ cm}^{-1}$

Choose direct geometry

- Higher energy features
- Degree of tuning



Summary:

- TOSCA Good for all samples with vibrational modes below 2000 cm^{-1}
- MARI has low background, good for higher energy modes with strong scatterers
- MAPS has large detector coverage – sensitive up to $\sim 5000\text{ cm}^{-1}$
- MERLIN most sensitive, lower resolution
- At ILL: IN1 / LAGRANGE spectrometer is pushing boundaries of sensitivity
- TOSCA/MAPS will have new guides (2016) – improved sensitivity



Sample loading

Avoid multiple scattering events

10-25 % scattered



Thin film or annulus for strong scatterers

Aim for $> 6 \times 10^{21}$ H atoms in beam (TOSCA)

Load in cryostat/CCR on centre stick

- 300 K difference between top and bottom
- Sharpens bands
- Decreases Debye-Waller factor



Sample loading



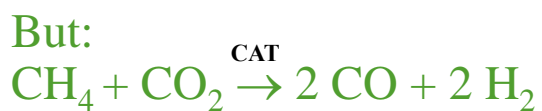
Simple samples – let someone else do it!

- TOSCA Xpress
 - Solid and liquid samples
 - Simple sample handling (open lab)
 - Sample changer run every cycle
 - 2 g organic (5 g preferred)
 - inorganic samples – discuss before submission
 - After 2 years data becomes public domain
- INS database
 - <http://www.isis.stfc.ac.uk/instruments/tosca/ins-database/>
 - Currently 680 samples and increasing!

Examples



Methane reforming



Both routes use a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst

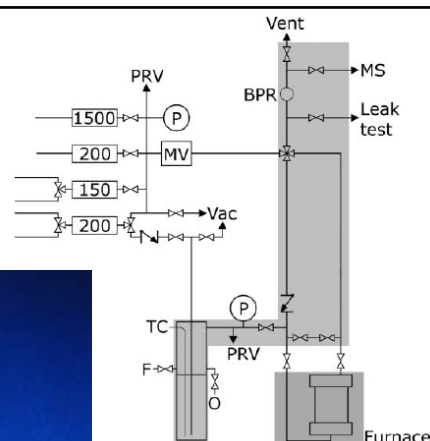
Deactivation by coking is a major problem



Ni/Al₂O₃ reforming



CatalysisHub

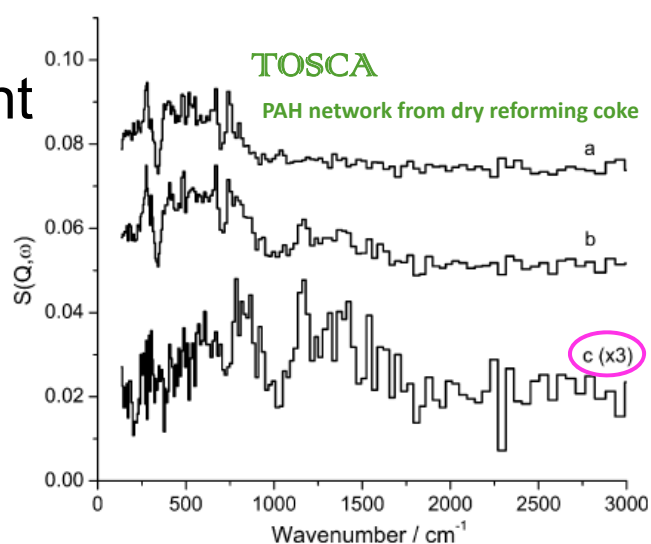


DN 40 CF flange
Inconel (avoids H embrittlement)
20 Bar
823 K

Silverwood, Parker, Lennon *et al*,
Rev. Sci. Inst. 82 (2011) 034101.

Typical measurement

- Activate catalyst in cell
- Background measurement
- Catalyst treatment – adsorption, reaction, etc.
- Sample measurement
- Data subtraction

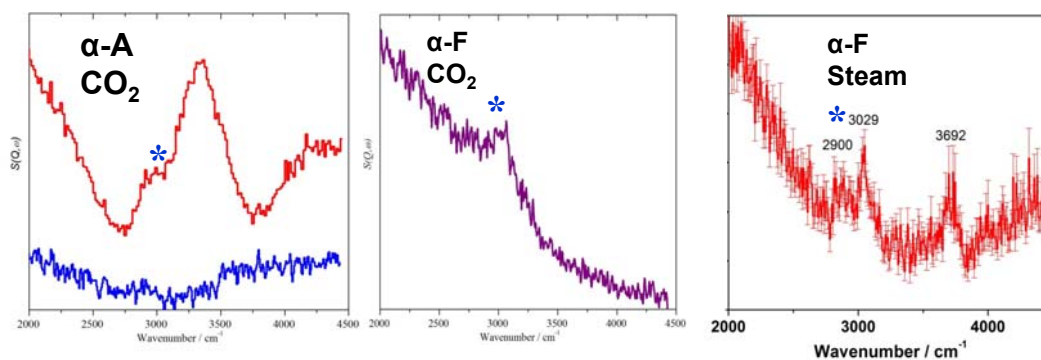
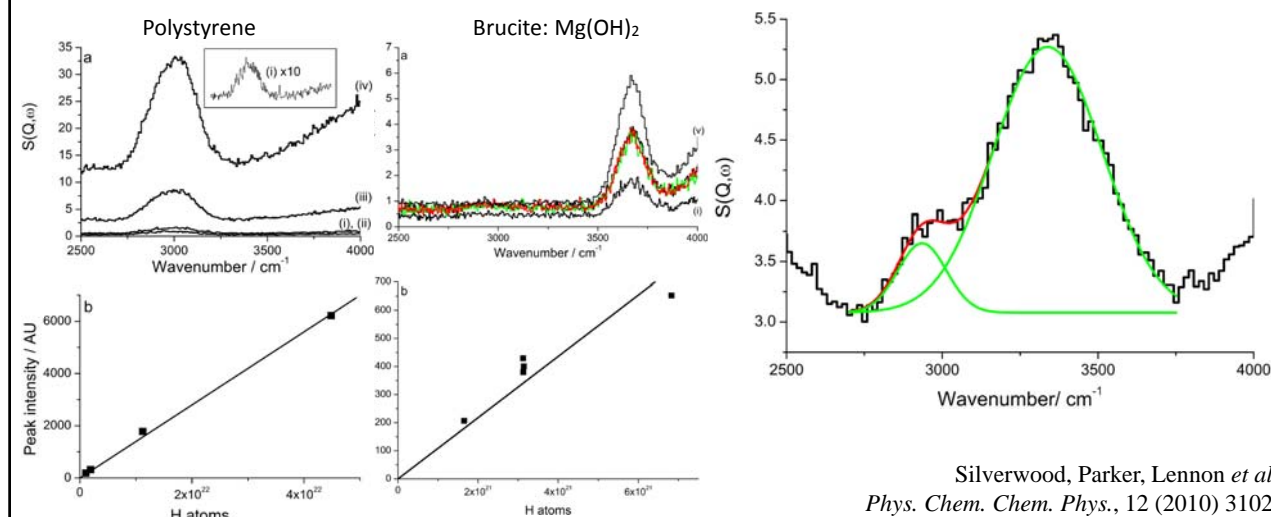


Efficient use of beam uses 2/3 samples: 1 in spectrometer, 1 in reactor (1 undergoing decay)

CatalysisHub

Silverwood, Parker, Lennon *et al*,
Catal. Today. 155 (2010) 319.

Hydrogen quantification and speciation



Nature of surface species dependent on catalyst preparation
and reaction conditions

Process	C:H
Dry reforming ($\alpha\text{-A}$)	160:1
Dry reforming ($\alpha\text{-F}$)	2550:1
Steam reforming ($\alpha\text{-F}$)	11689 : 1

Pd poisoning by methyl

Deactivated Pd catalyst from various industrial processes

Arom C=C → cyc HC-CH

Arom C=O → C-O-H

No evidence of coke, inorganic contaminants, poisons (CO, S)

H adsorption/desorption normal

No metal sintering/particle growth

IR/Raman not possible (black)



Science & Technology Facilities Council

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degussa.

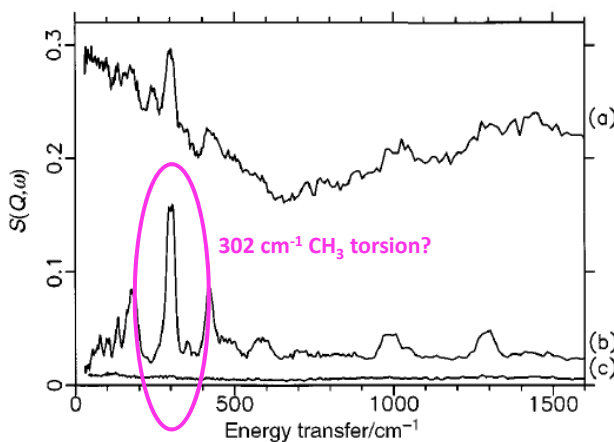


Fig. 1 INS spectra of palladium catalysts. Deactivated catalyst before (a) and after (b) extraction. Active catalyst after extraction (c).

Albers, Parker *et al*,
Chem. Commun., (1999) 1619.



Theory and experiment

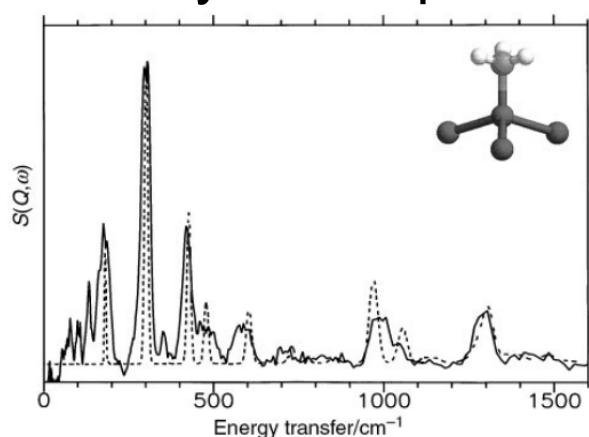


Fig. 2 Comparison of the INS spectrum of the deactivated catalyst (solid line) and the results from the CLIMAX analysis of the spectrum (dashed line).

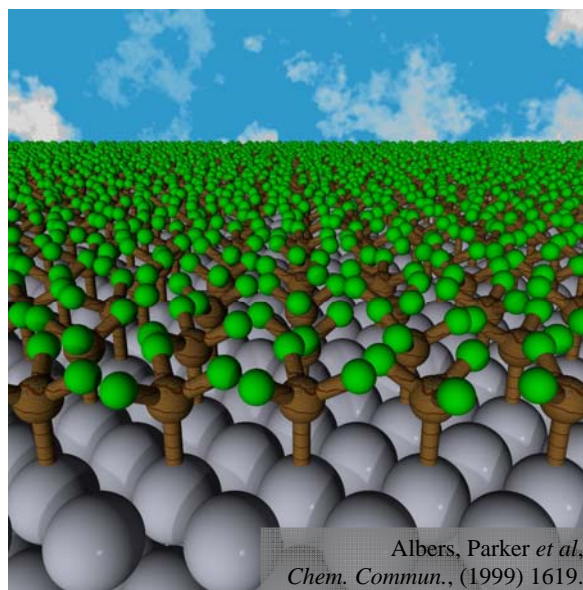


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Albers, Parker *et al*,
Chem. Commun., (1999) 1619.

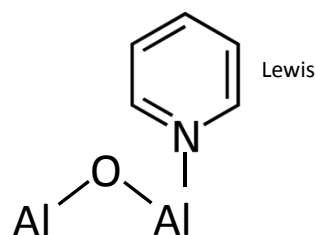
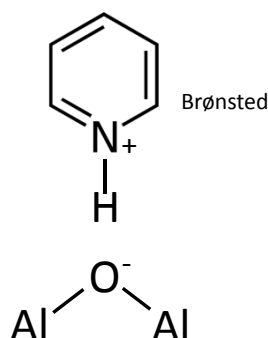
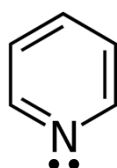


η -Alumina acidity by pyridine adsorption



UNIVERSITY
of
GLASGOW

- Solid acid catalysts important in petrochemicals
- Detailed understanding of acidity still lacking
- Generally investigated by probe adsorption IR
- Strong phonon absorption below 1100 cm^{-1} prevents IR

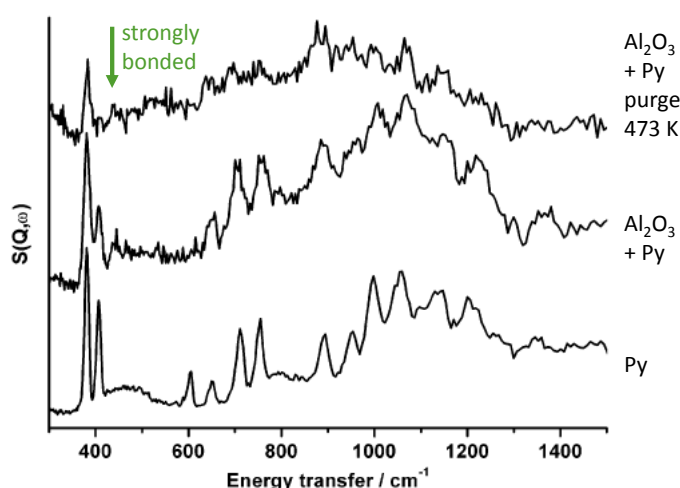


CatalysisHub

Lundie, Parker, Lennon *et al*,
J. Phys. Chem. B, 109 (2005) 11592.

η -Alumina acidity by pyridine adsorption

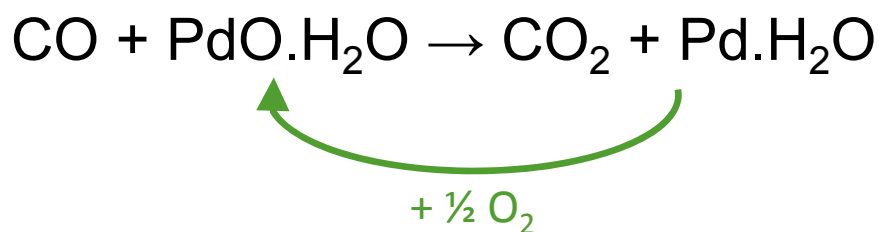
- Physisorbed, chemisorbed
+ pure pyridine show
similar vibrational
characteristics
- Previously unseen band @
 437 cm^{-1} diagnostic for
strong Lewis acid sites



CatalysisHub

Lundie, Parker, Lennon *et al*,
J. Phys. Chem. B, 109 (2005) 11592.

CO oxidation with hydrous palladium oxide



Reaction does not occur at low T with PdO

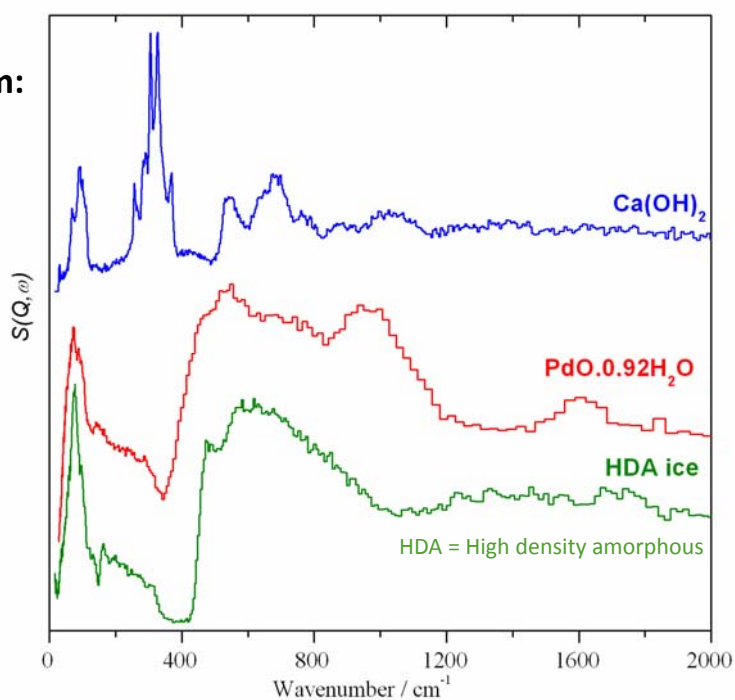
Deactivation seen – what is role/form of H₂O

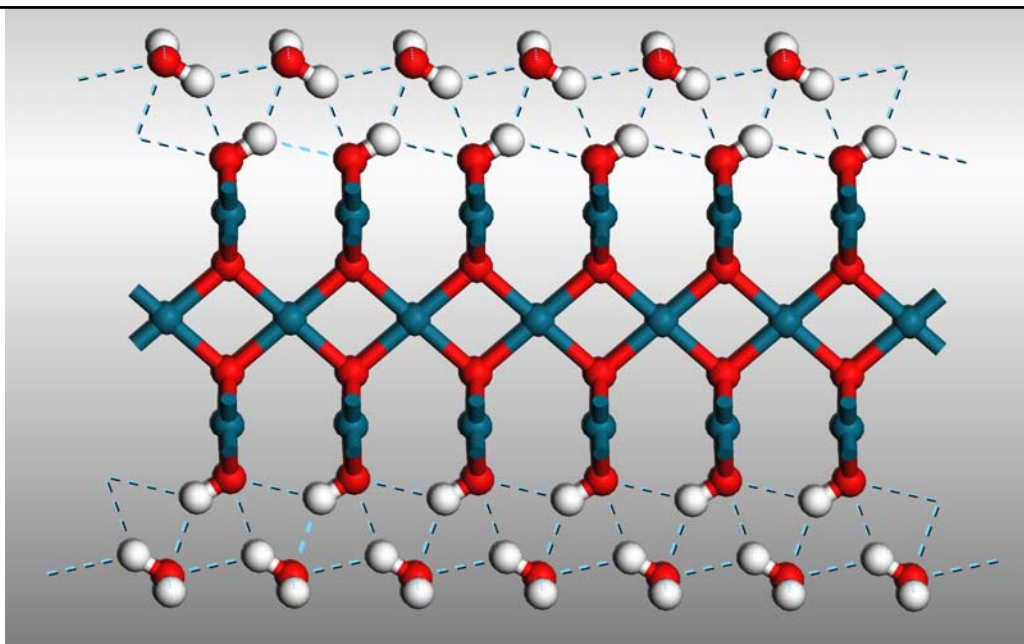


S.F. Parker, K. Refson, A.C. Hannon, E. Barney, S.J. Robertson and P. Albers,
J. Phys. Chem. C, 114 (2010) 14164.
S.F. Parker, *Chem. Comm.*, 47 (2011) 1998-1990

**Controversy about material form:
Pd(OH)₂/PdO or PdO.H₂O?**

Fingerprint comparison with
analogue



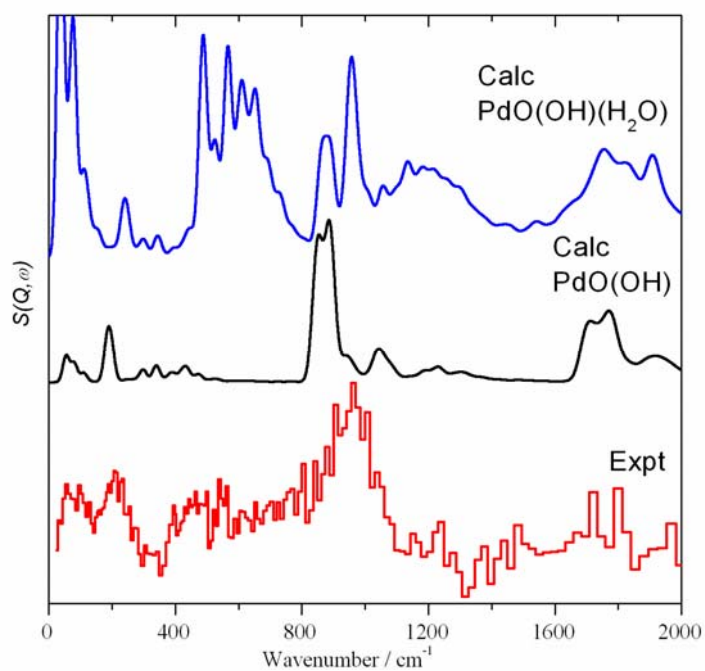


CatalysisHub

Model hydrous PdO as a slab capped by hydroxyls + with hydrogen-bonded water.

CO oxidation

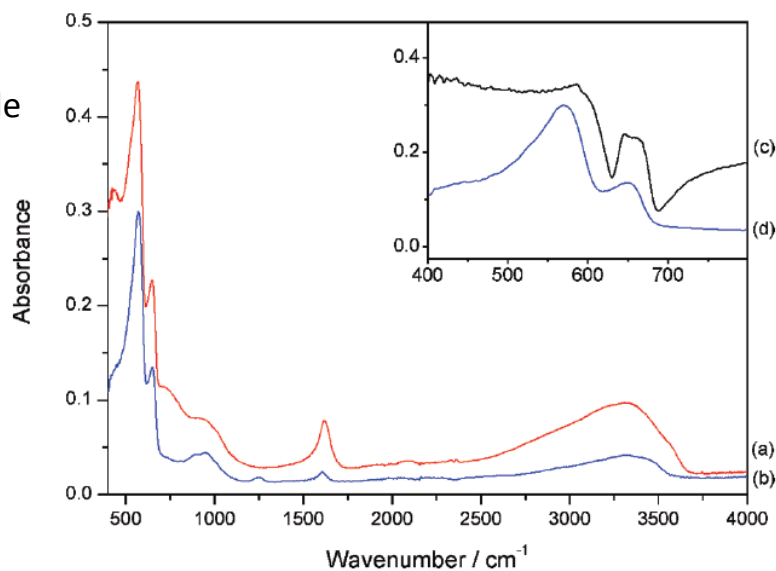
- INS of dehydrated sample supports model



CatalysisHub

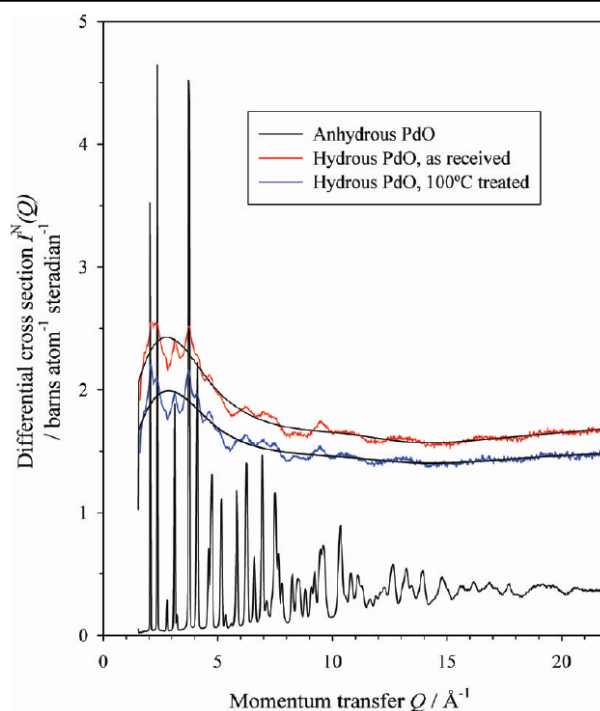
CO oxidation

- INS of dehydrated sample supports model
- And IR



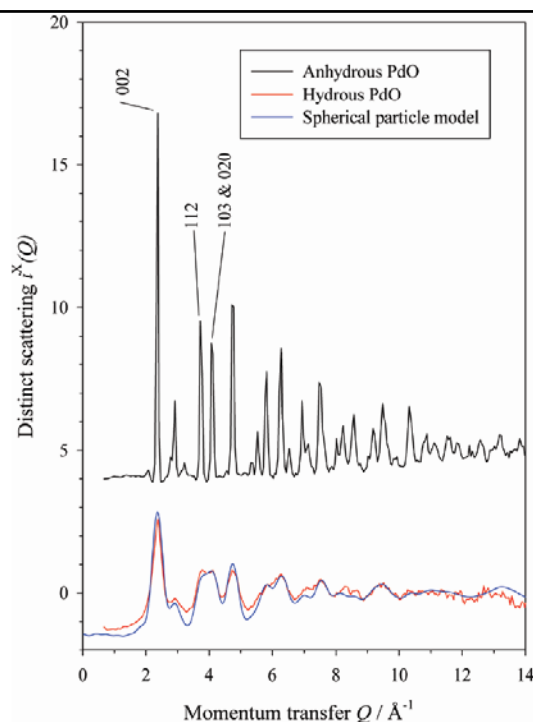
CO oxidation

- INS of dehydrated sample supports model
- And IR
- And neutron diffraction



CO oxidation

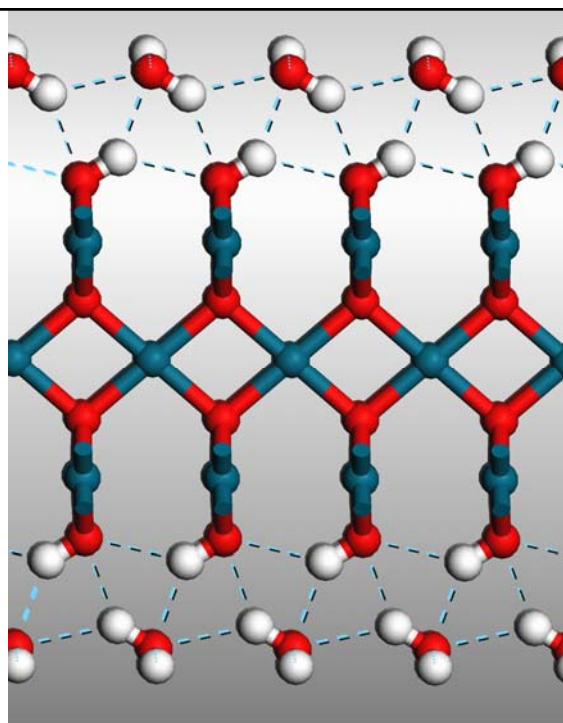
- INS of dehydrated sample supports model
- And IR
- And neutron diffraction
- And XRD



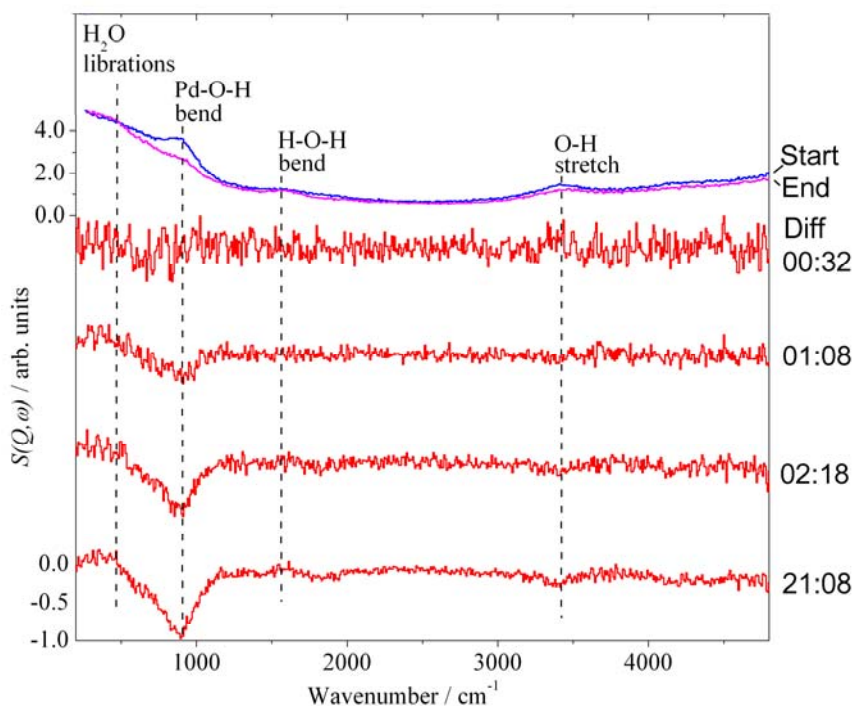
System benefits

- Bulk system (not supported metal)
- High surface area
- Lots of hydrogen
- Slow reaction rate

Try *operando*!

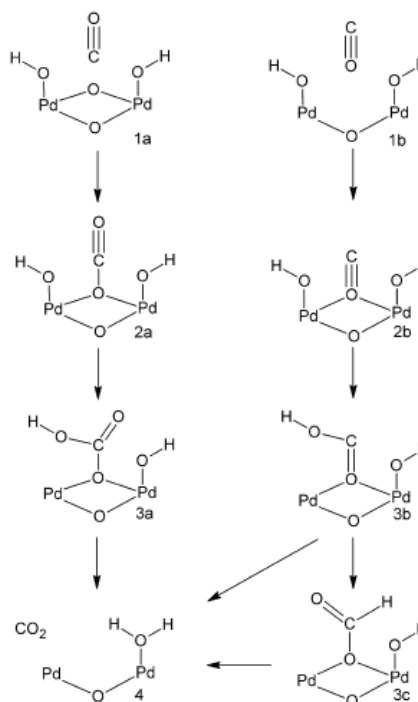


- MAPS
- 298 K
- First operando INS measurement



Not catalytic!

- Reaction stoichiometric in OH
- Demonstrates utility for catalytic reactions



Summary: 1

- Use neutrons if IR/Raman does not work
- Use neutrons with tough sample environment
- Use neutrons for hydrogenous vibrational modes
- Use TOSCA Xpress for simple samples without even visiting!
- Use TOSCA for low frequency modes
- Use MARI for higher frequency modes with lots of Hydrogen
- Use MAPS for higher frequency modes with little Hydrogen
 - MERLIN/LAGRANGE for very weak scatterers – more competition



Summary: 2

USE NEUTRONS



INS Studies of Porous Materials for Gas Adsorption and Catalysis

Sihai Yang

Sihai.Yang@nottingham.ac.uk

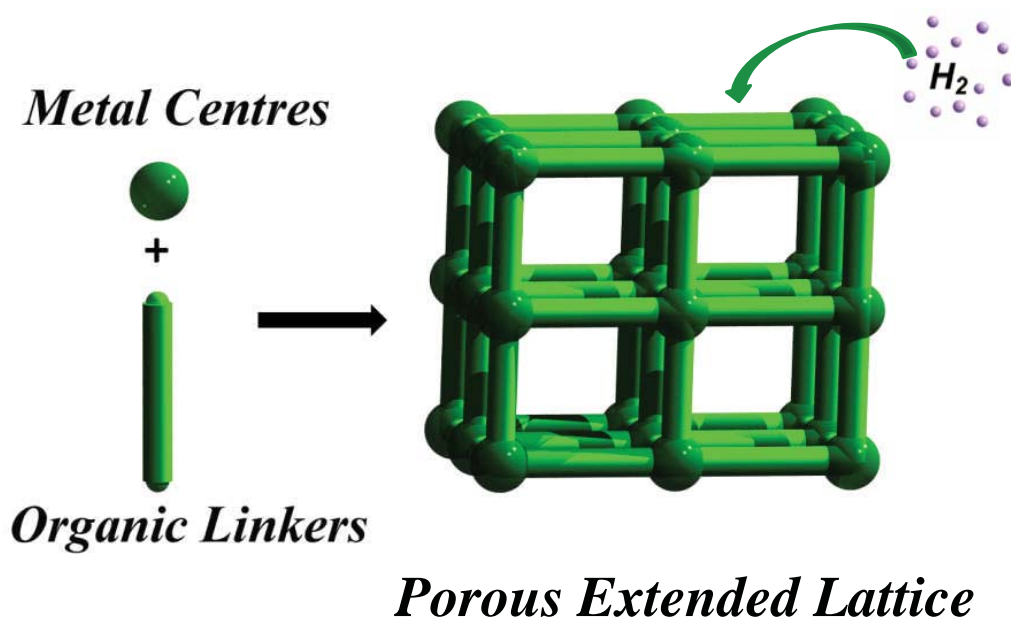
Porous Materials for Energy Applications

- H₂ Storage
- Carbon Capture
- Hydrocarbon Separations
- Biomass Conversion and Catalysis

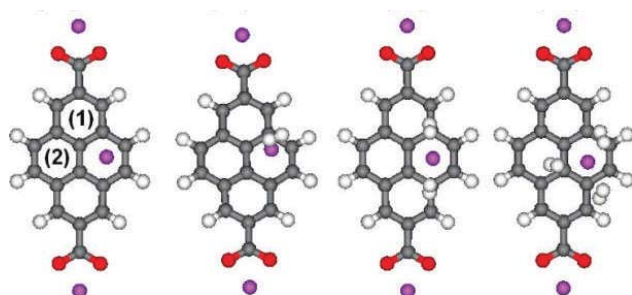
Research at National Facilities



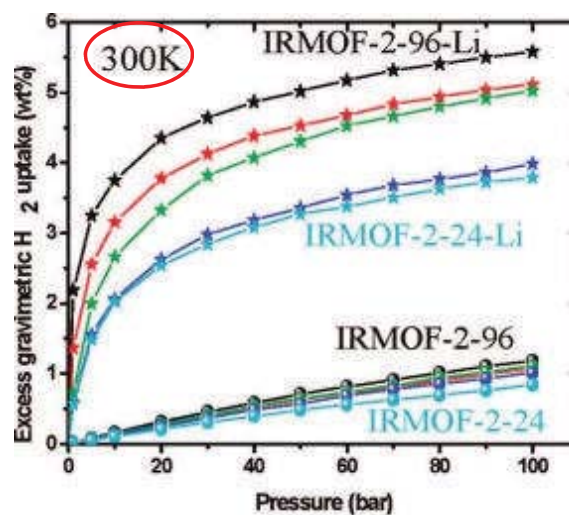
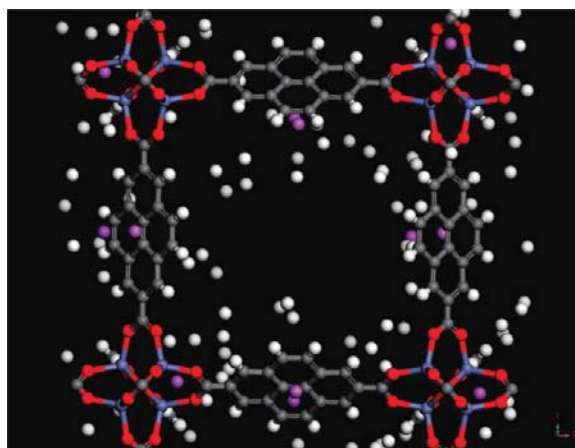
Metal-Organic Frameworks



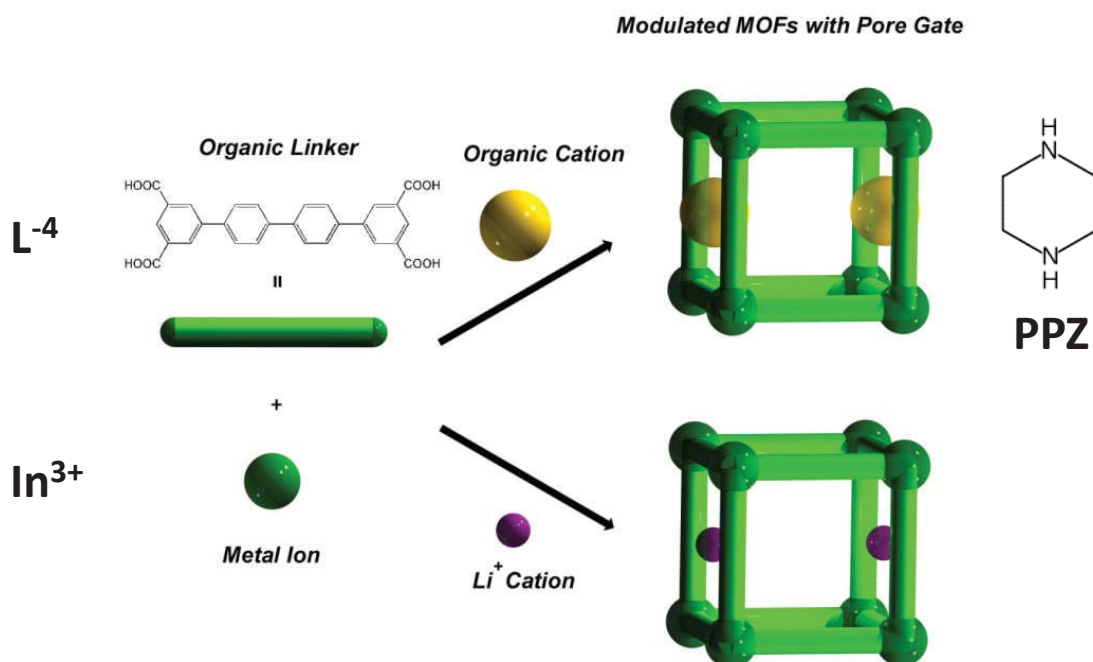
Theoretical Studies of Li-Doped MOFs



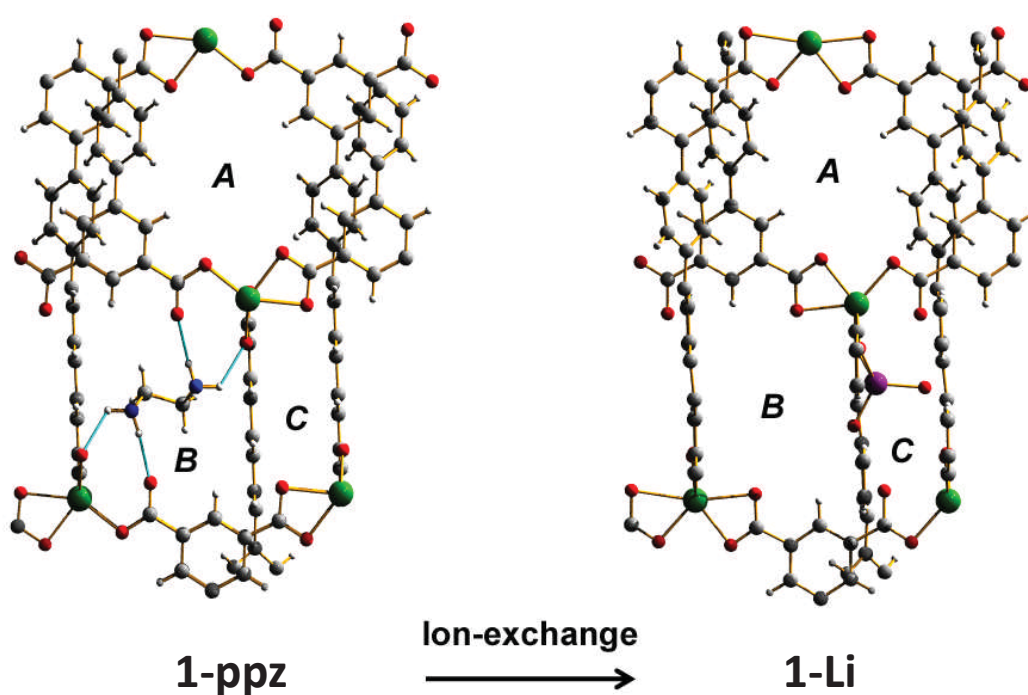
Room temperature H_2 Storage



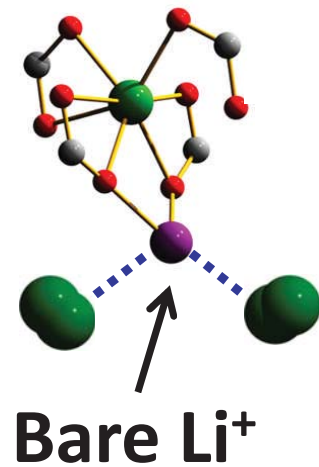
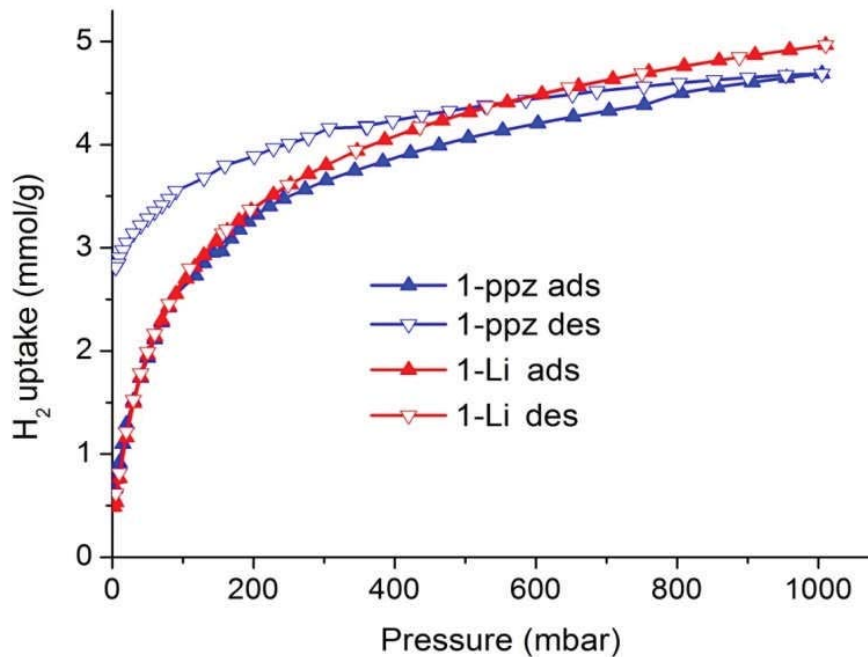
Anionic MOFs: Pore with Gate



Li⁺-Exchange in Anionic MOFs

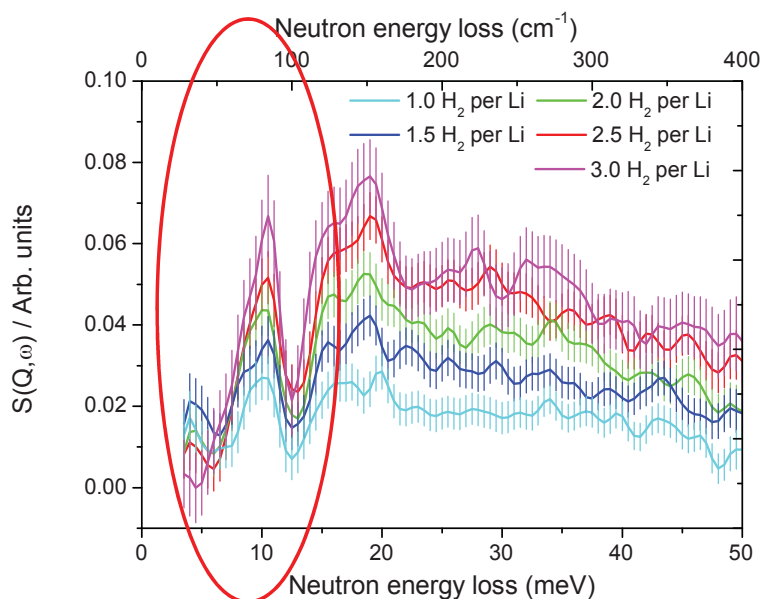


Controllable H₂ Adsorption



The heat of adsorption is also increased by ~1.5 kJ/mol.

Inelastic Neutron Scattering



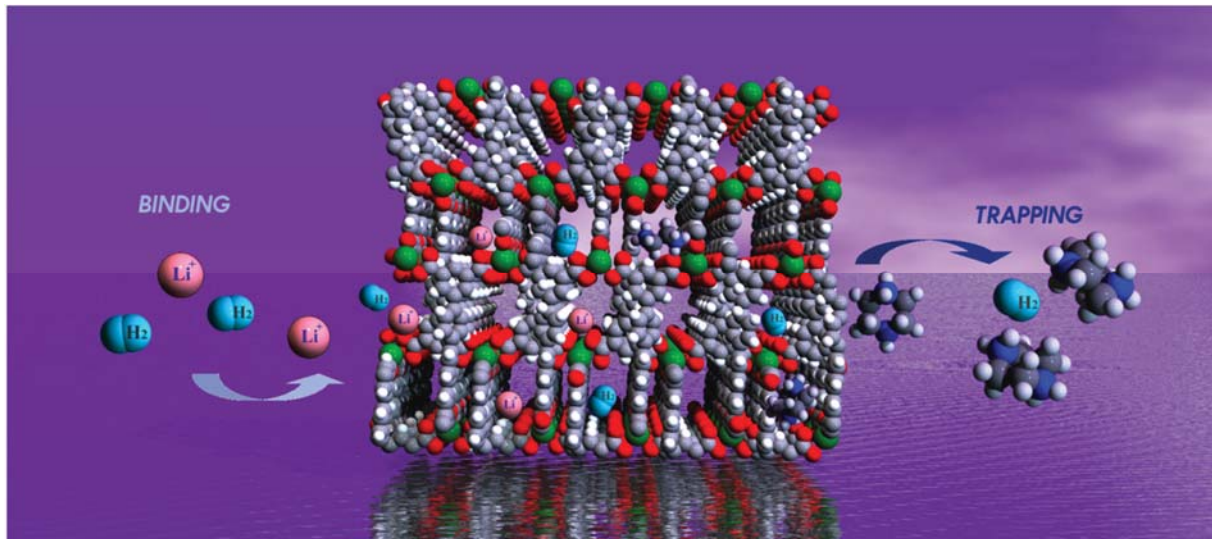
$$E_{JM} = J(J + 1)B_{rot}$$

B_{rot} for H₂: 7.35 meV

$J(1 \leftarrow 0)$

E_{JM} for H₂: 14.7 meV

Gated Pore for H₂ Storage



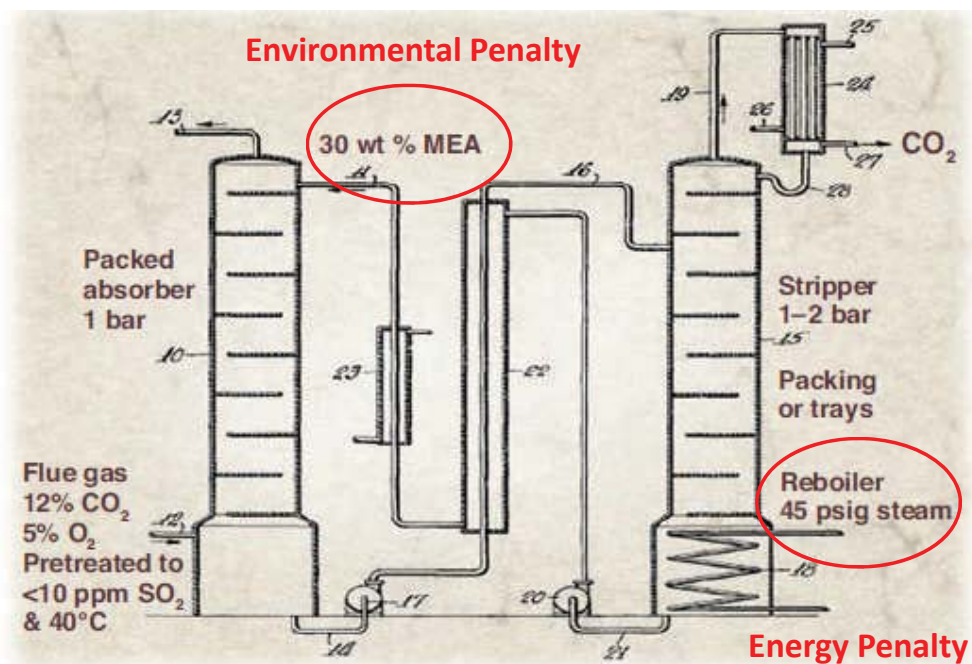
**Li⁺ Enhanced
Adsorption**



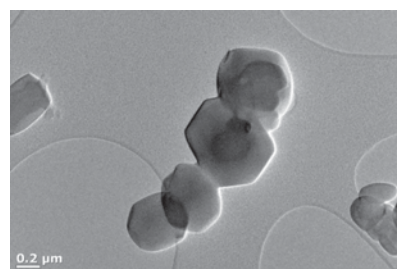
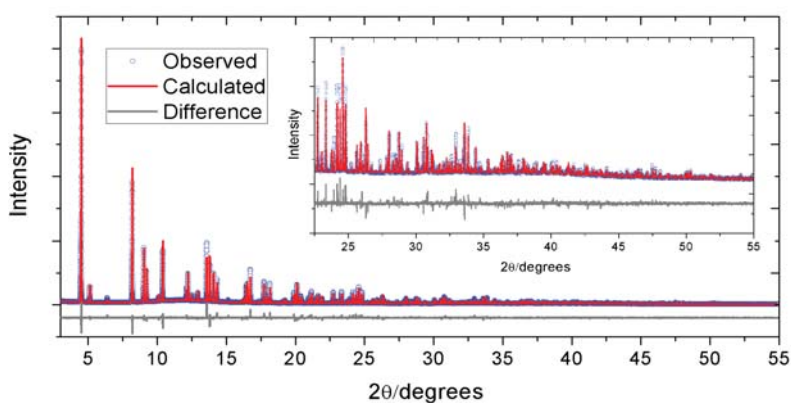
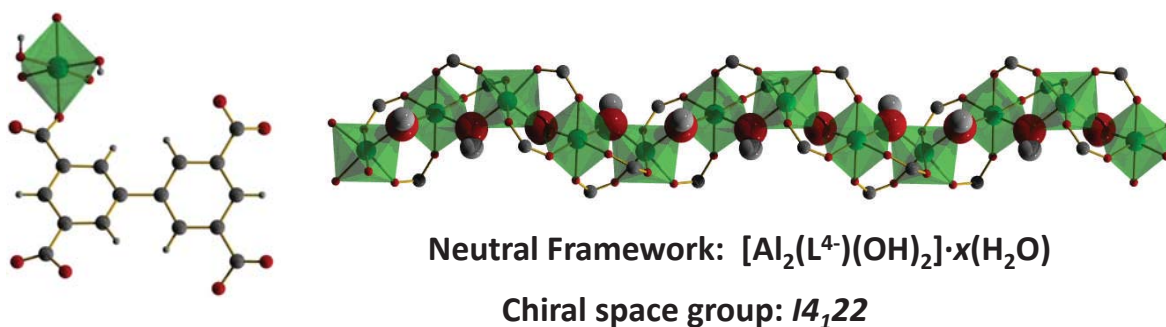
**Cation-Induced
Kinetic Trapping**

Chem. Commun., 2008, 6011; *Nature Chemistry*, 2009, 487;
Inorganic Chemistry, 2011, 9374; *Faraday Discussion*, 2011, 19.

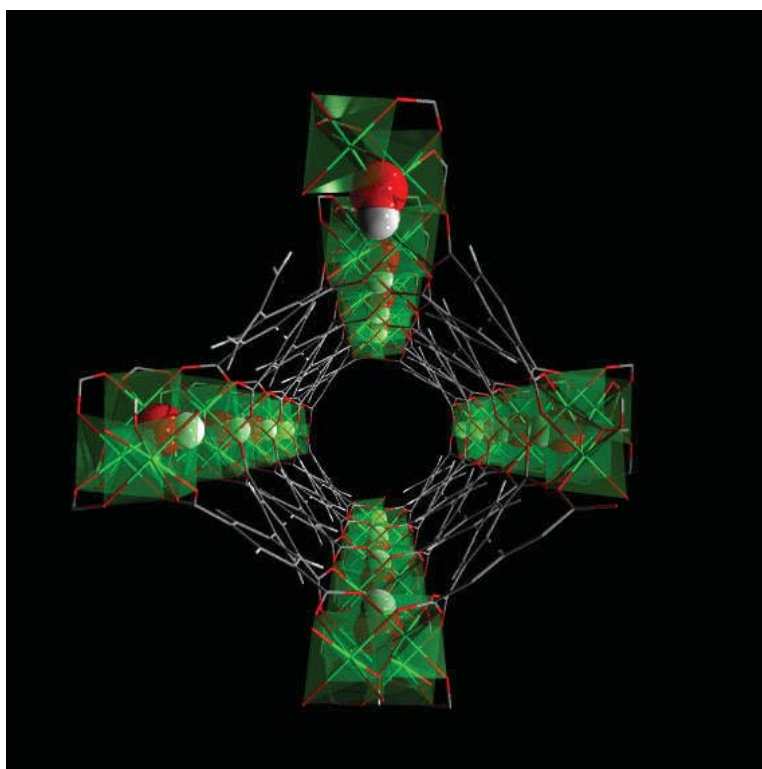
Carbon Capture—Amine Scrubbing



NOTT-300: A –OH Decorated MOF



Microporous Crystal Structure



1D helical pore channels

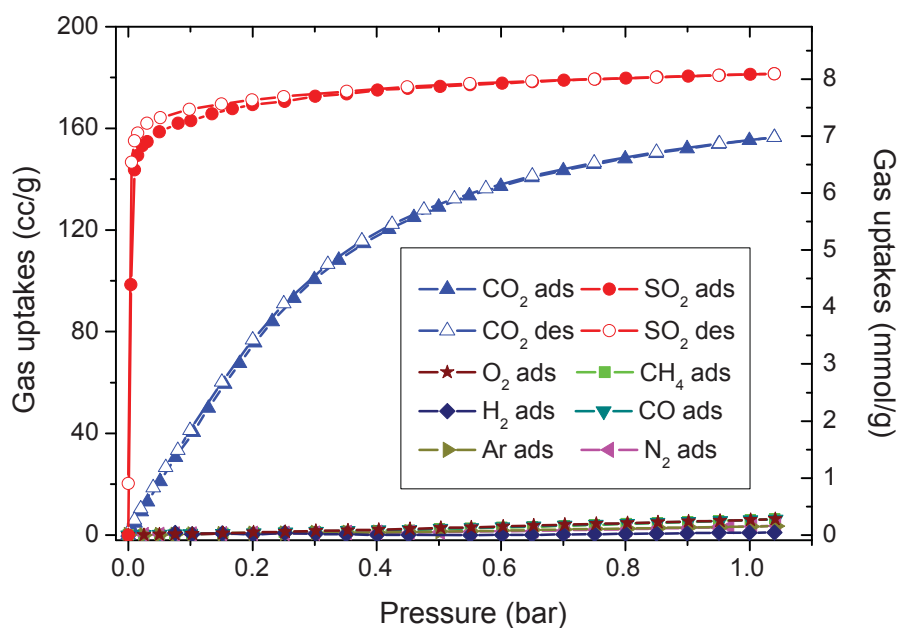
Pore size $6.5 \times 6.5 \text{ \AA}^2$

Pore volume 0.40 cc/g

Surface area $1370 \text{ m}^2/\text{g}$

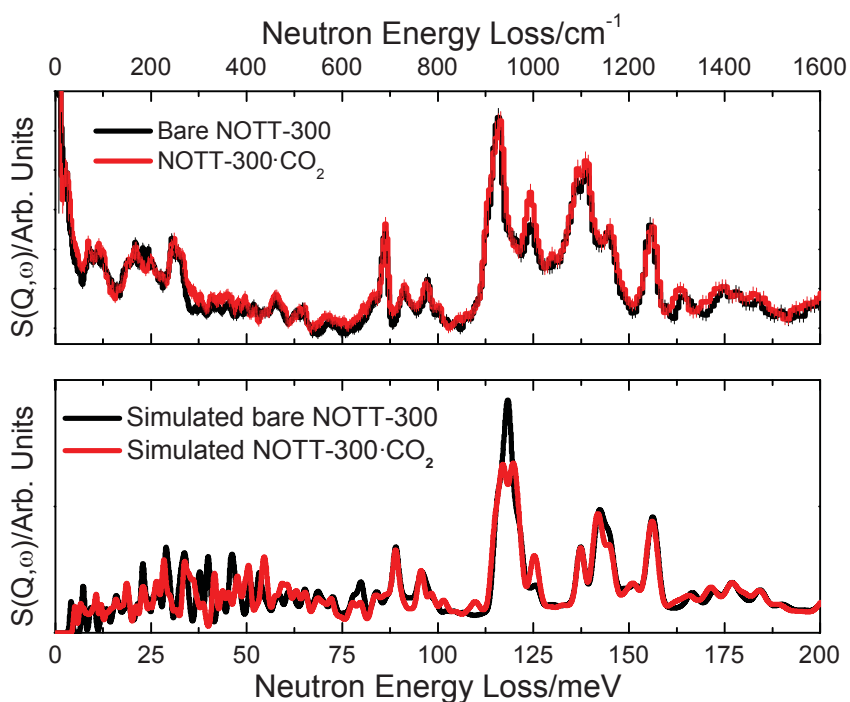
-OH decorated channels

Selective Gas Uptakes at 273 K

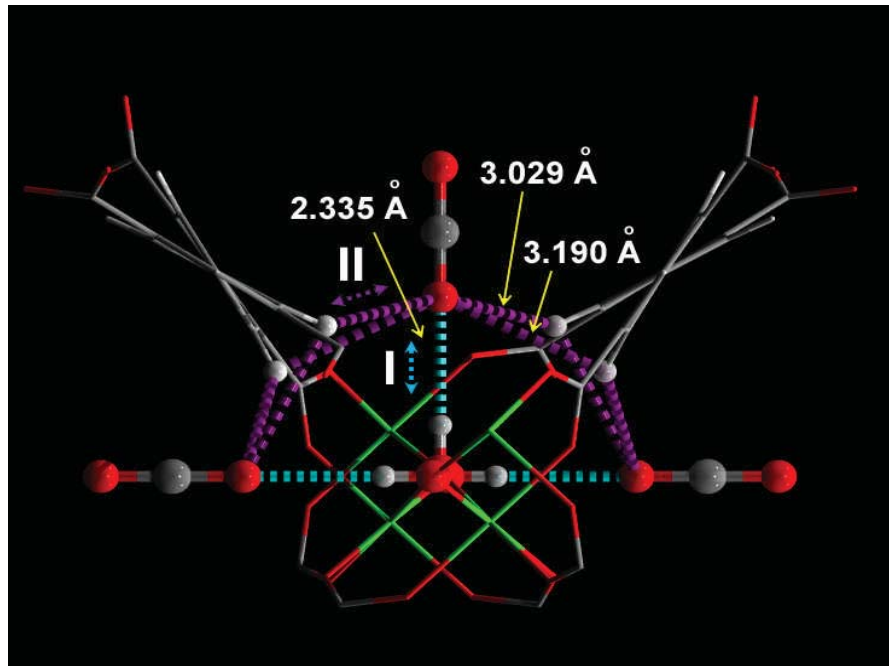


SO ₂	N ₂	CH ₄	CO	Ar	O ₂	CO ₂	H ₂
4.11Å	3.80Å	3.76Å	3.69Å	3.54Å	3.47Å	3.30Å	2.89Å

Inelastic Neutron Scattering (CO₂)

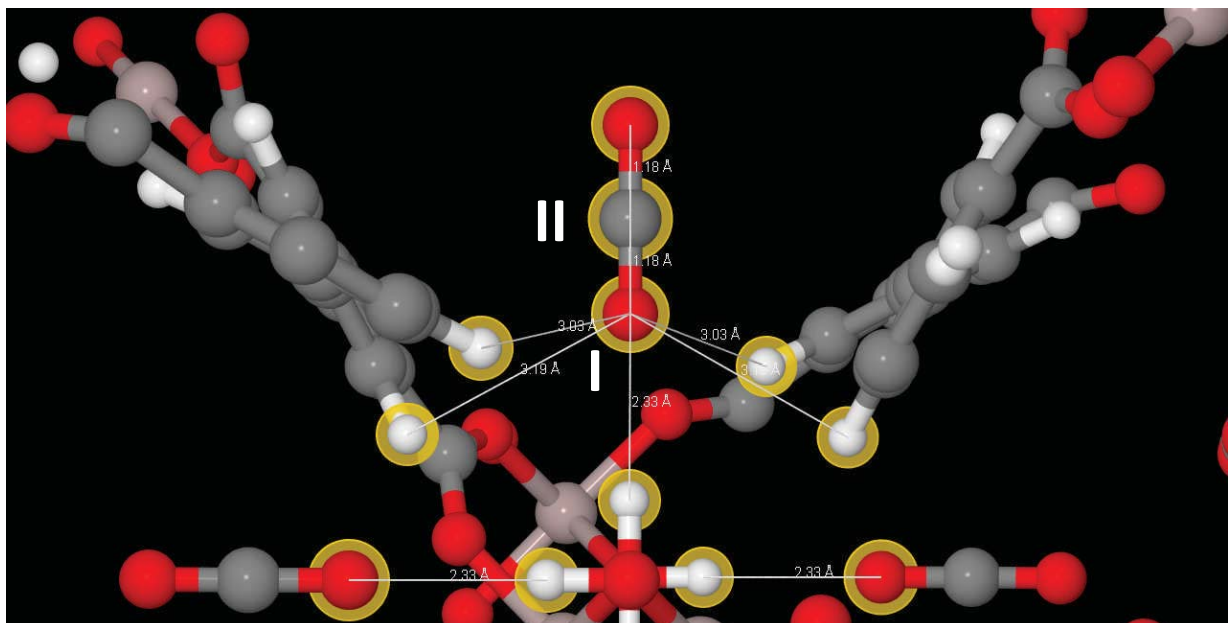


Inelastic Neutron Scattering (CO_2)

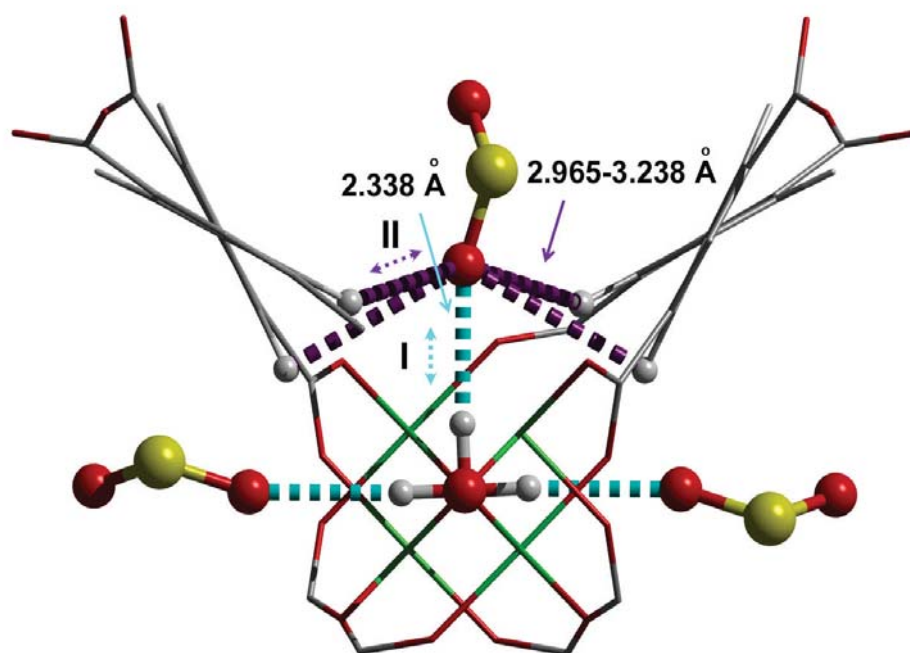


1D CO_2 helical molecular chain $\text{O}=\text{C}^{\delta+}=\text{O}^{\delta-}\cdots\text{H}^{\delta+}-\text{O}^{\delta-}$

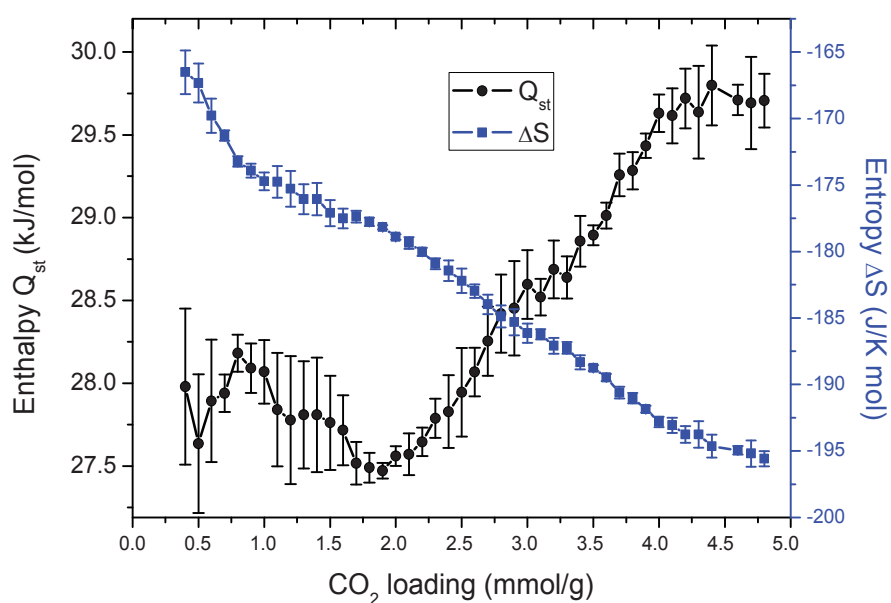
Dynamics for CO_2 Capture



Inelastic Neutron Scattering (SO_2)



Enthalpy of CO_2 Capture

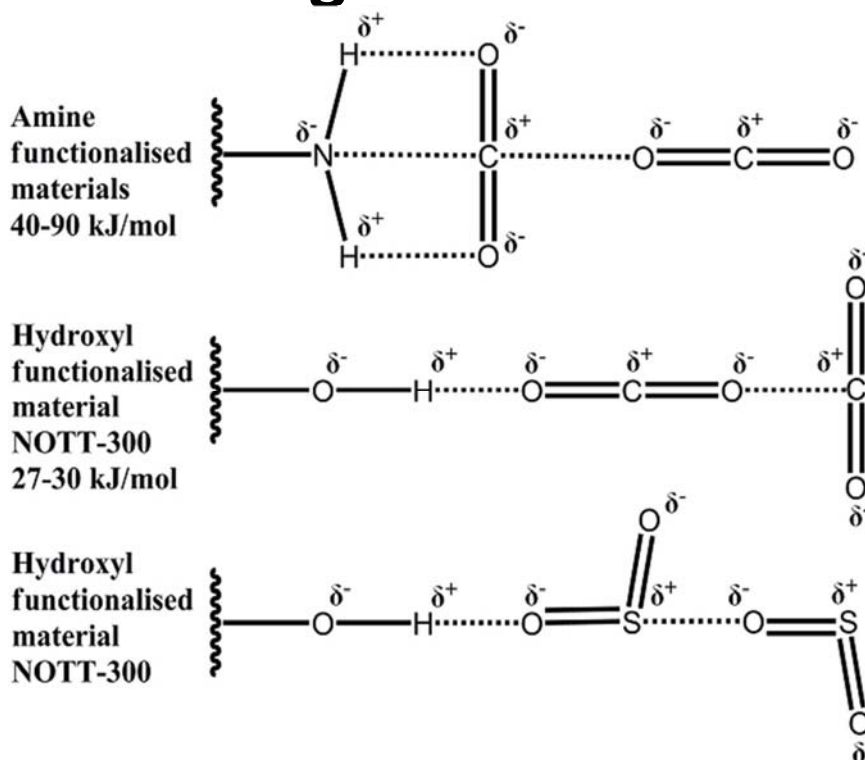


Chemical capture
Amine scrubbing
>100 kJ/mol

Physical capture
Amine-solids
45-90 kJ/mol

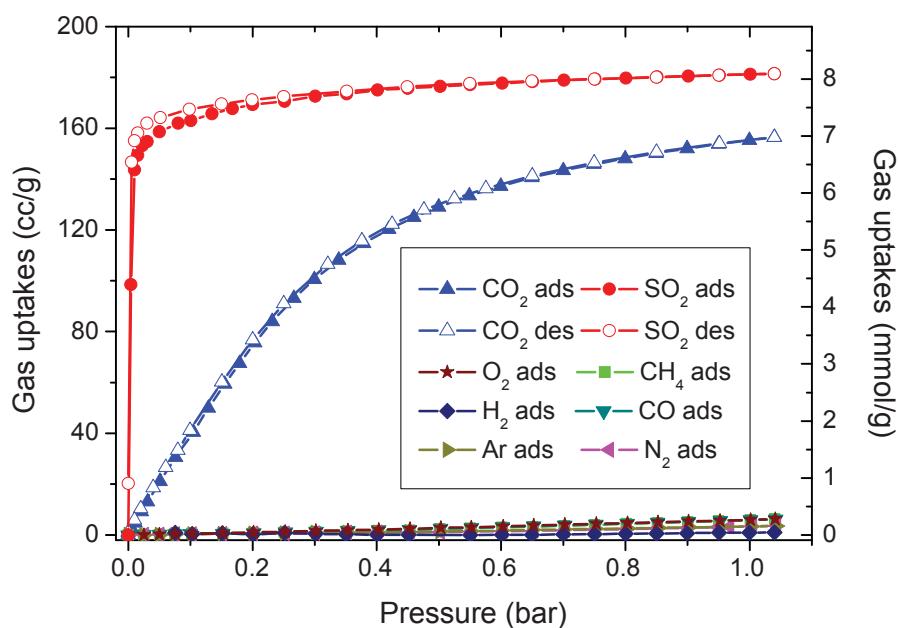
Less energy penalty!

Binding Mechanisms



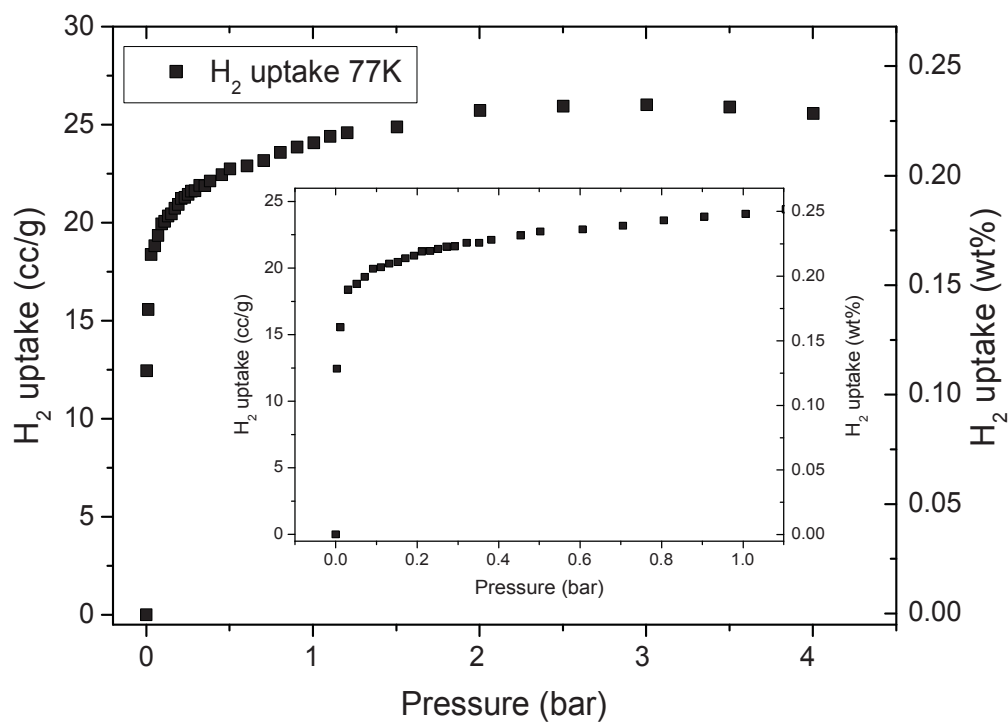
Nature Chemistry, 2012, 877-884.

Selective Gas Uptakes at 273 K

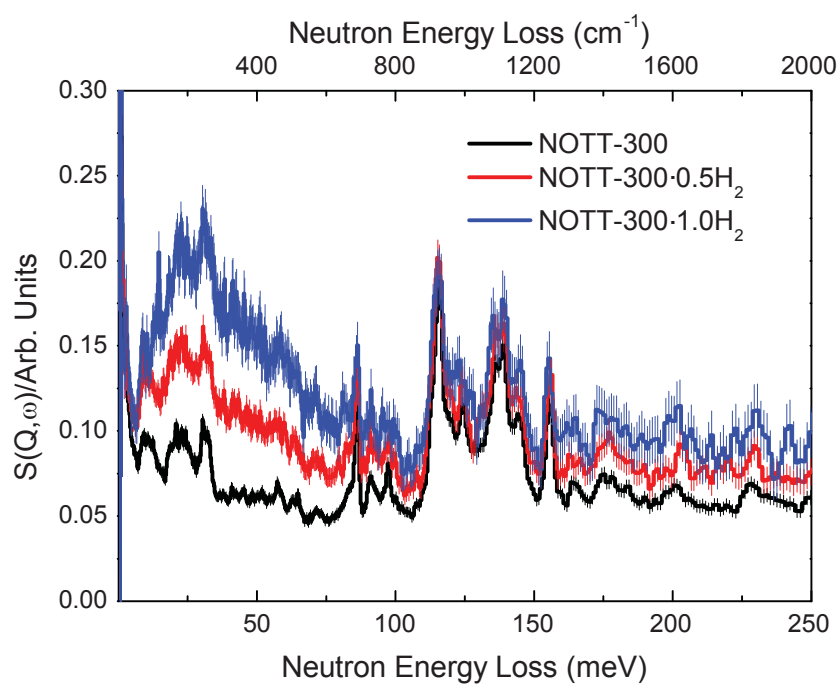


SO ₂	N ₂	CH ₄	CO	Ar	O ₂	CO ₂	H ₂
4.11Å	3.80Å	3.76Å	3.69Å	3.54Å	3.47Å	3.30Å	2.89Å

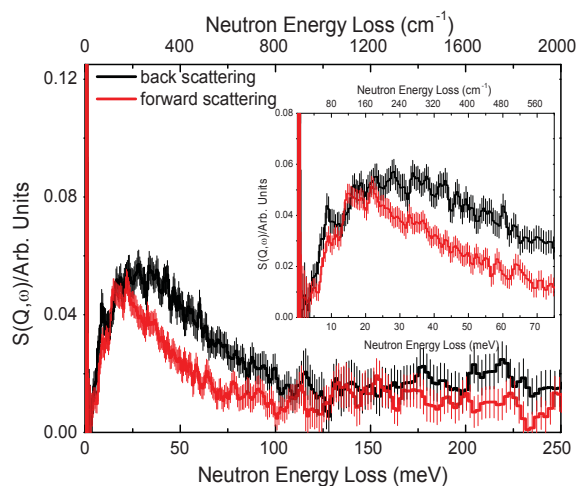
H₂ Uptake at 77 K



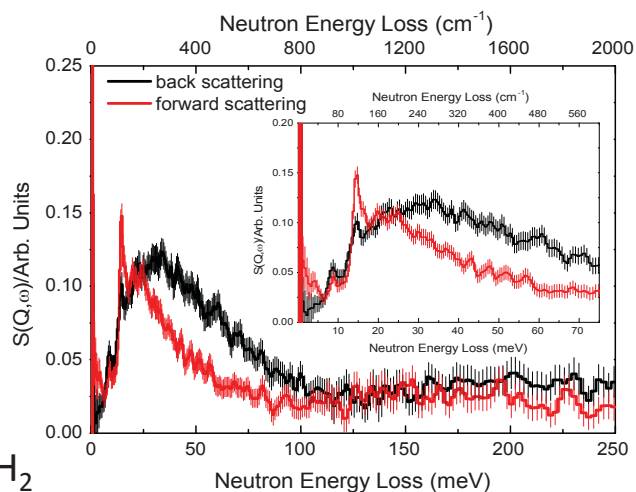
Inelastic Neutron Scattering (H₂)



Inelastic Neutron Scattering (H_2)

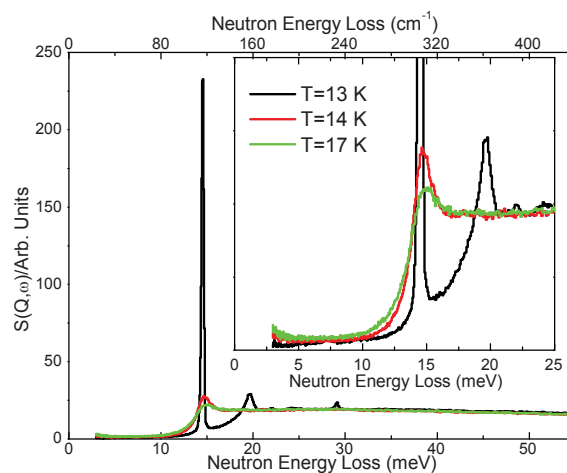
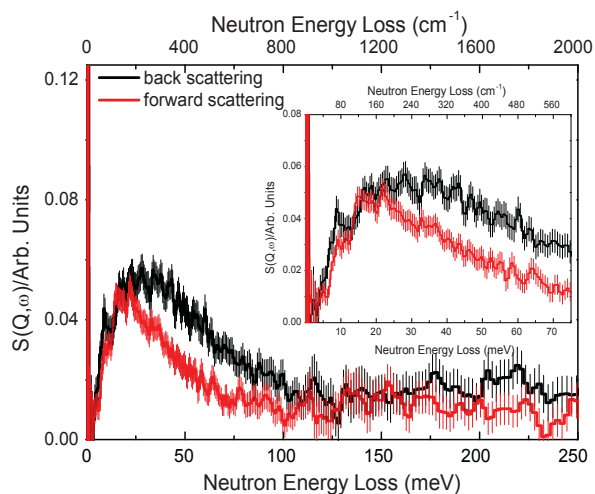


Difference spectra NOTT-300·0.5 H_2



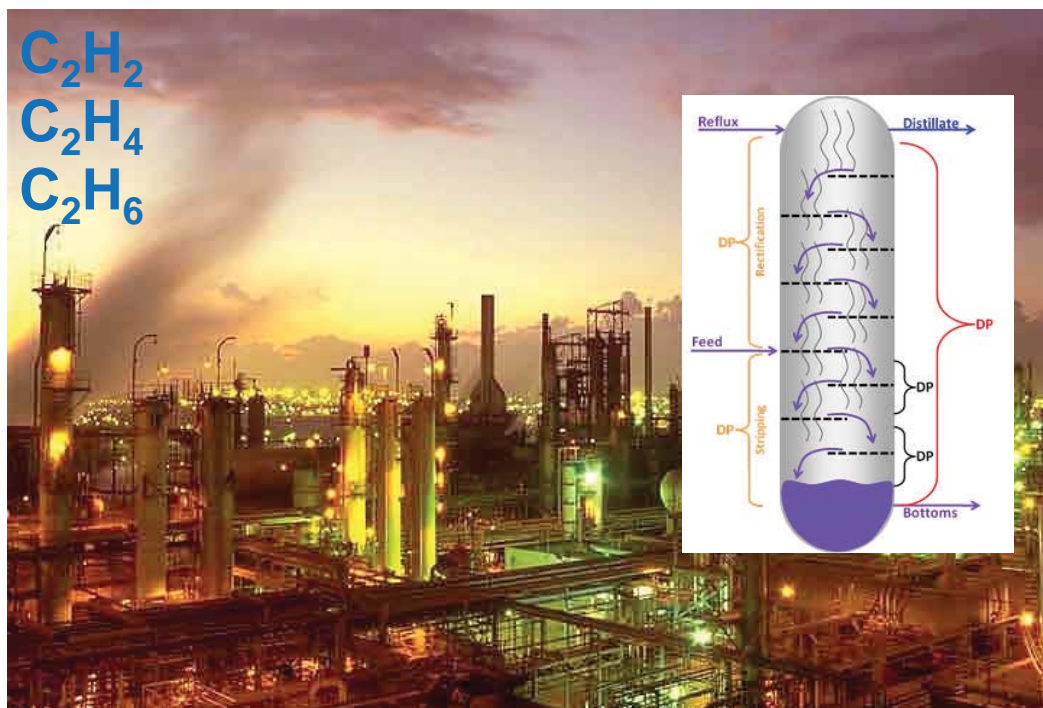
Difference spectra NOTT-300·1.0 H_2

Inelastic Neutron Scattering (H_2)



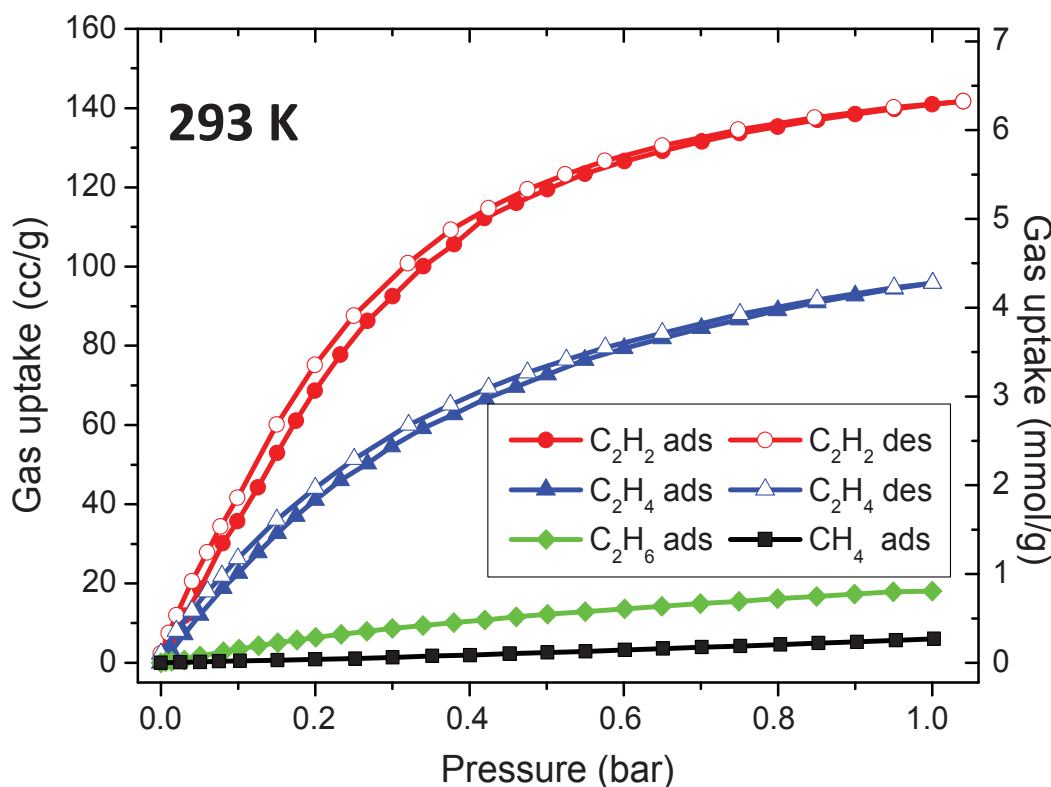
Liquid/recoil hydrogen motion in the pore— 7 K
Quantum mechanical reasons

Hydrocarbon Separations in Industry

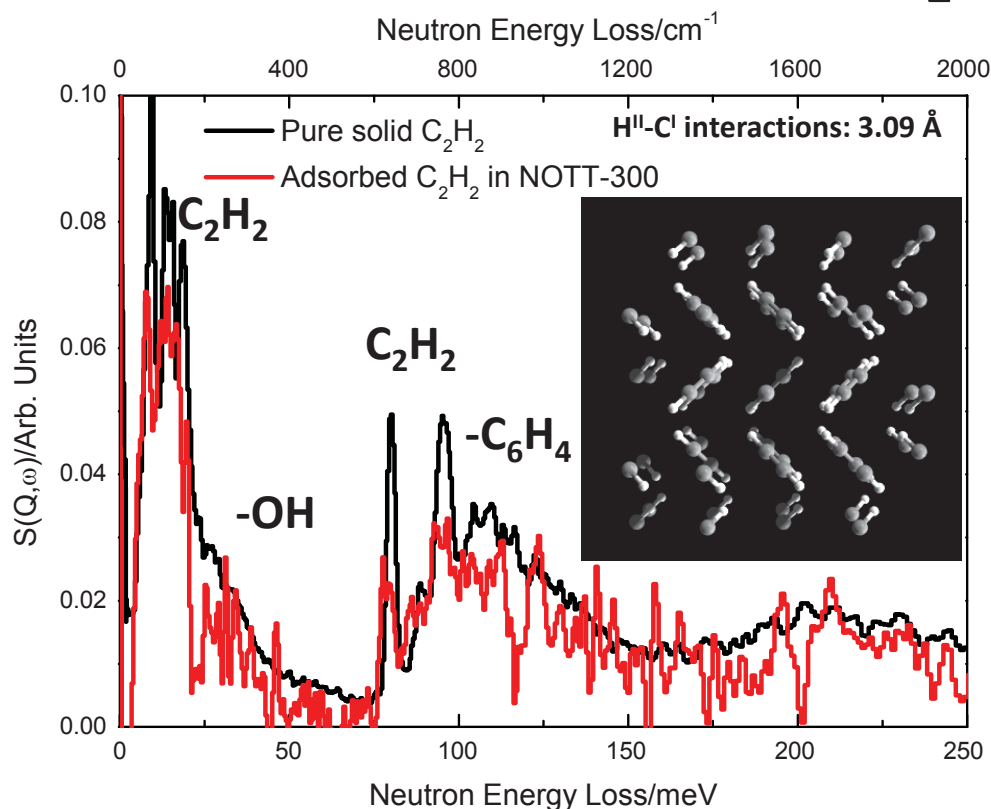


The energy consumption of distillation columns in USA is more than three times of the total energy consumption of Switzerland.

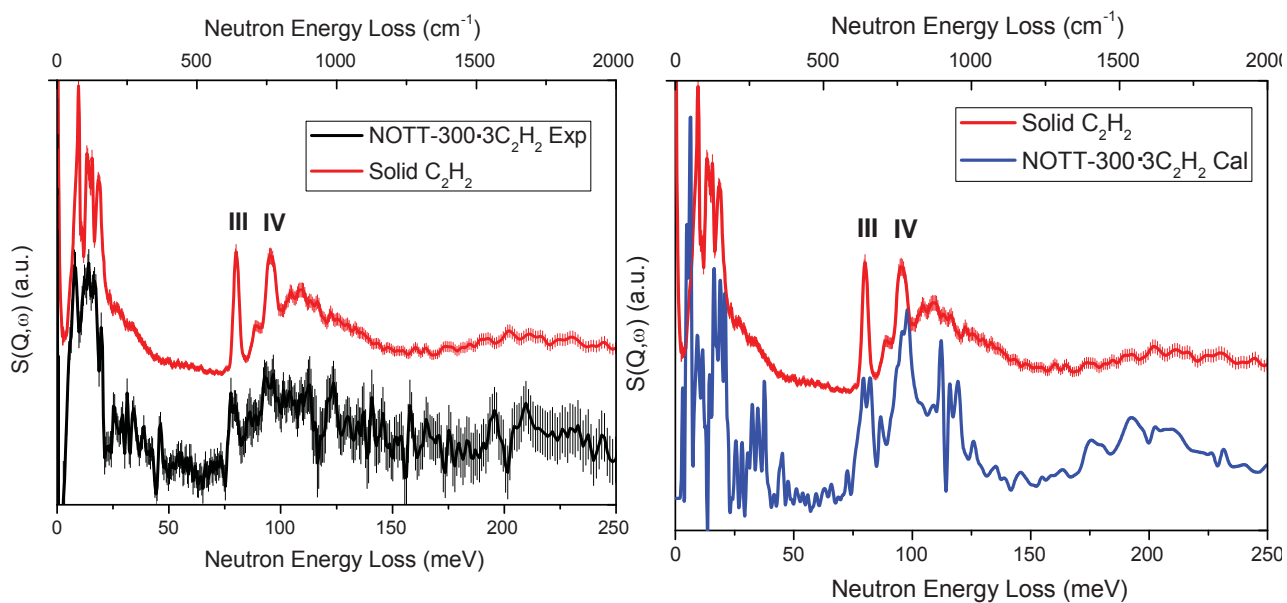
Hydrocarbon Uptakes in NOTT-300



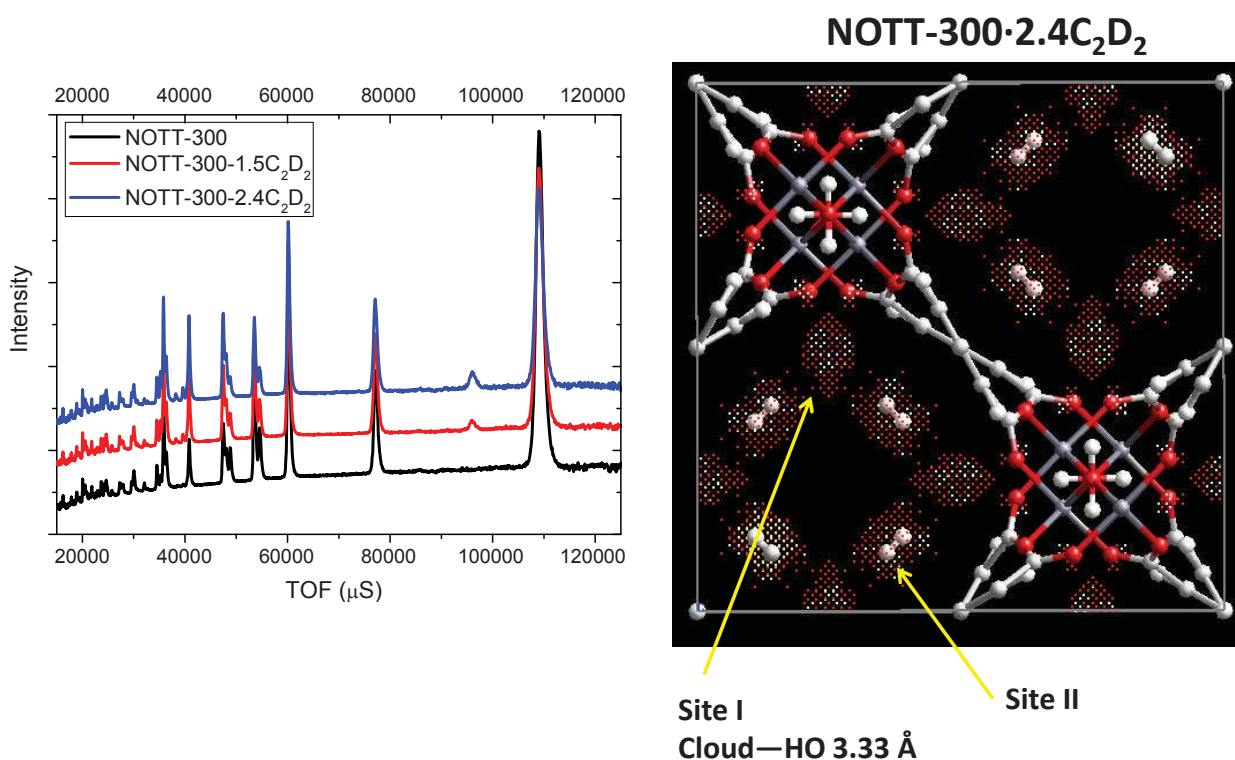
Inelastic Neutron Scattering (C_2H_2)



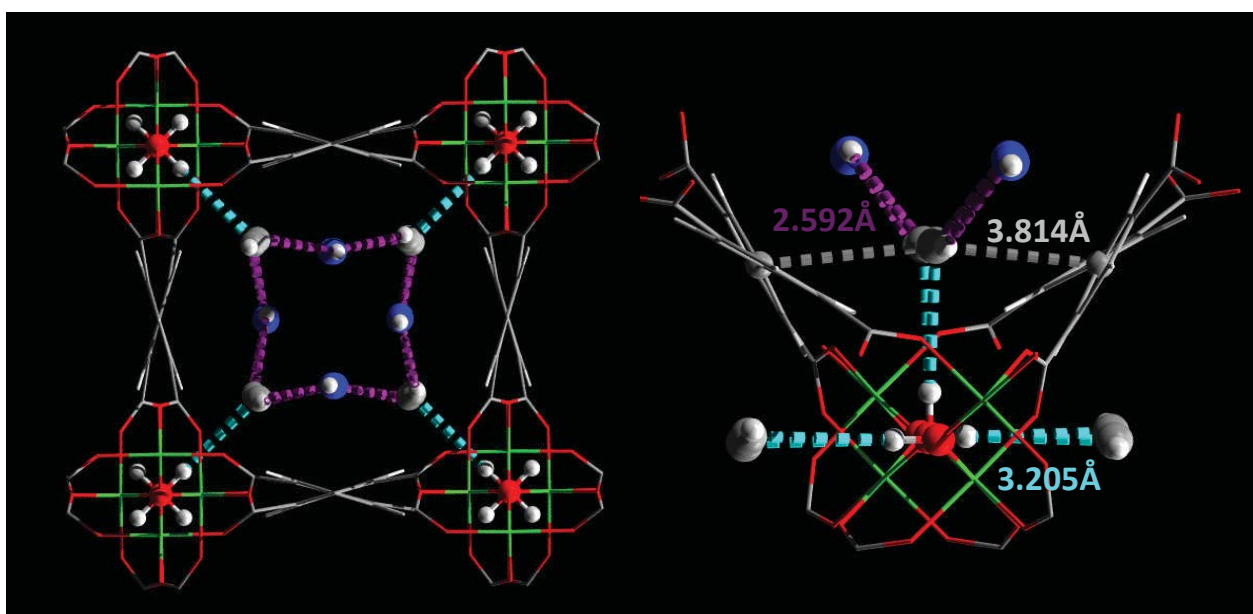
Experiment & Theory



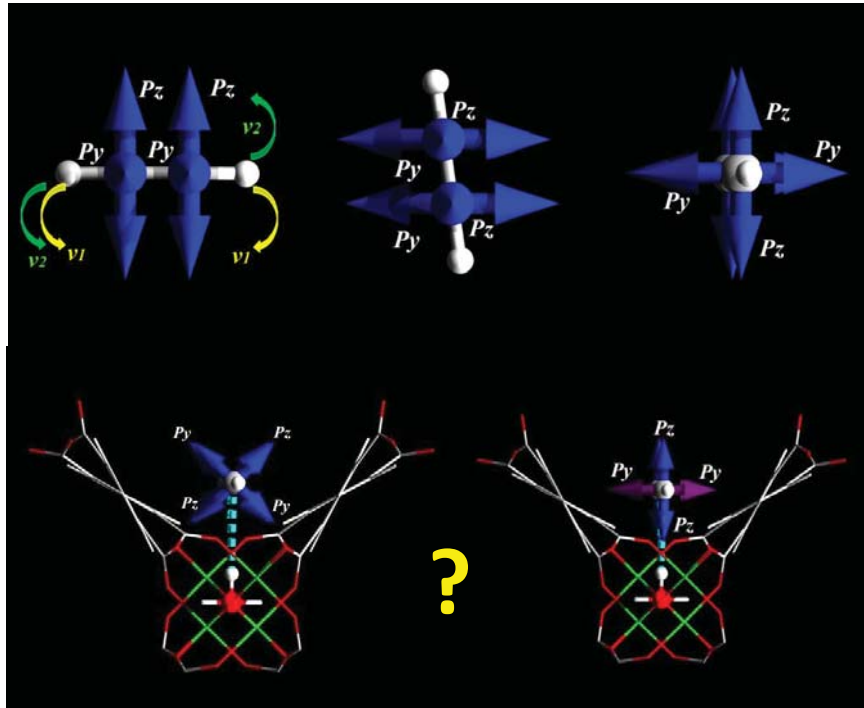
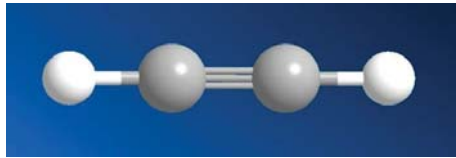
In situ Neutron Powder Diffraction Fourier Difference Map (Fobs-Fcalc)



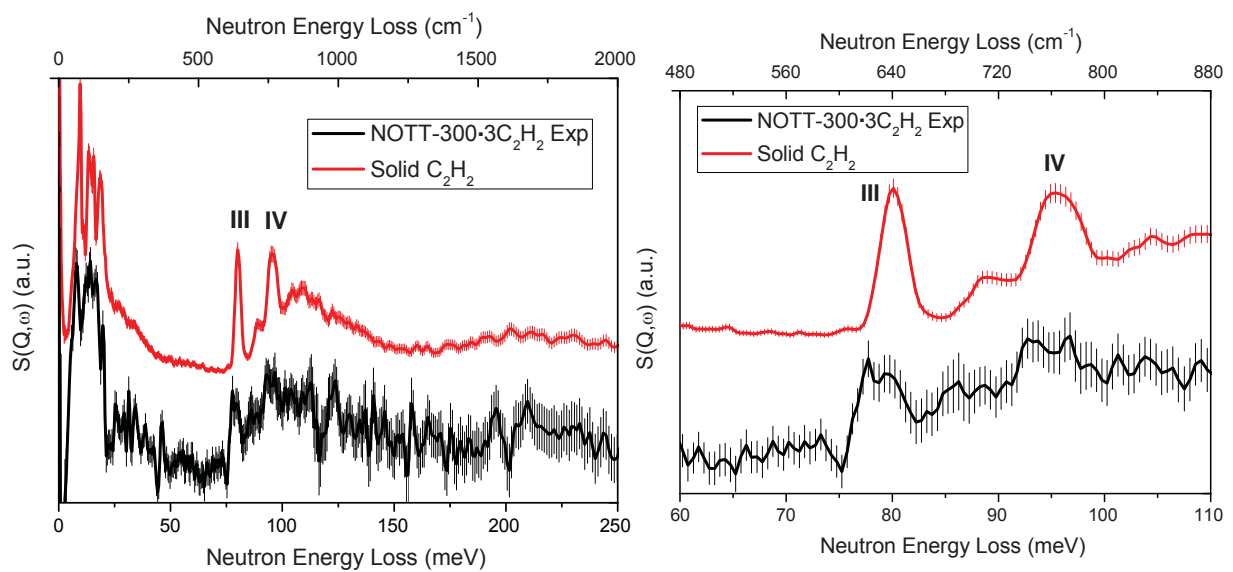
Structure of NOTT-300·3C₂H₂



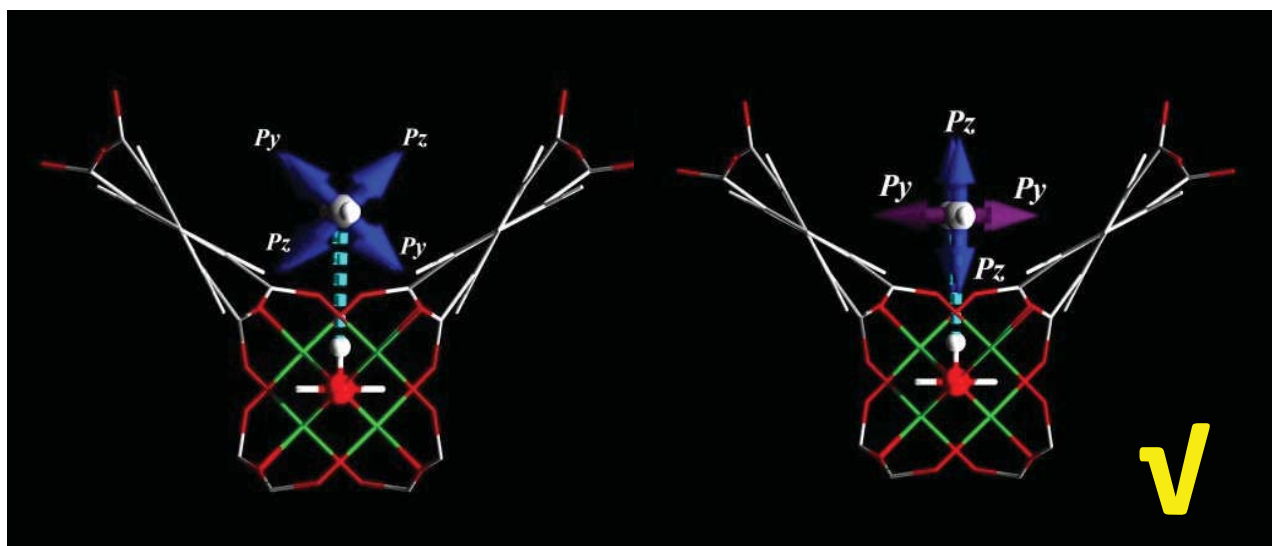
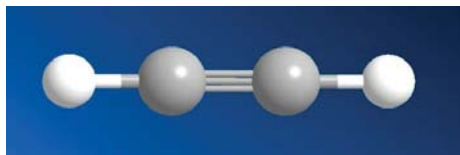
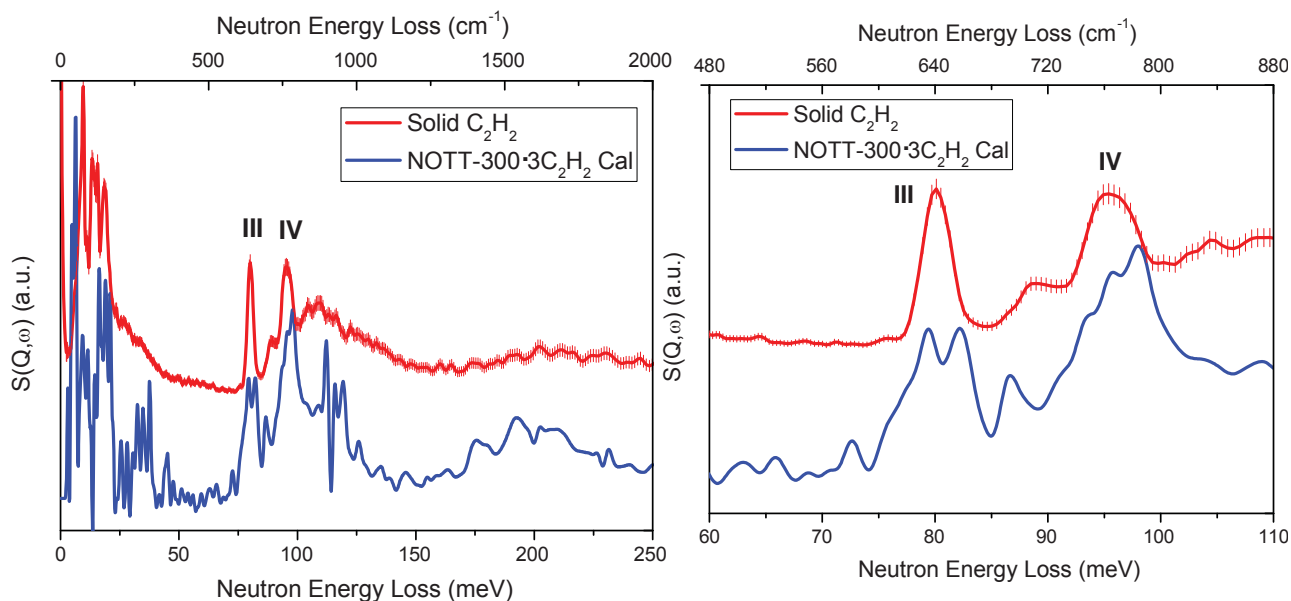
H^{II}...C^I interactions: 2.81 Å π ... π interactions: 3.81 Å π ...HO interactions: 3.21 Å



Inelastic Neutron Scattering (C_2H_2)



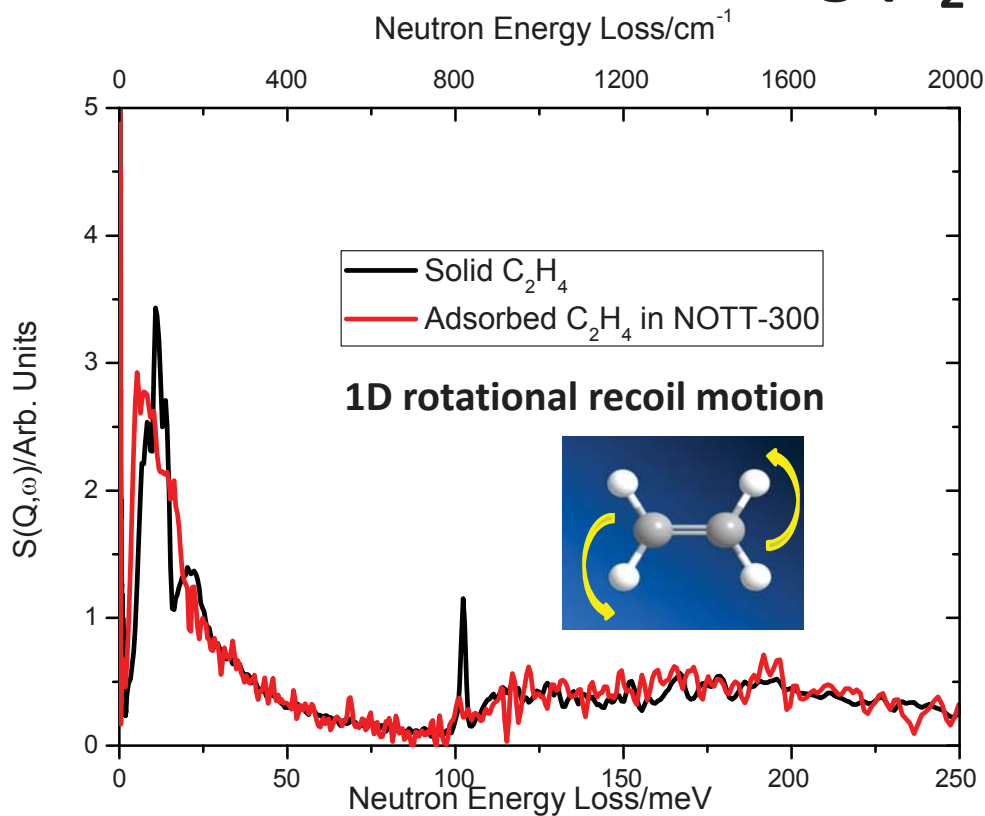
Inelastic Neutron Scattering (C_2H_2)



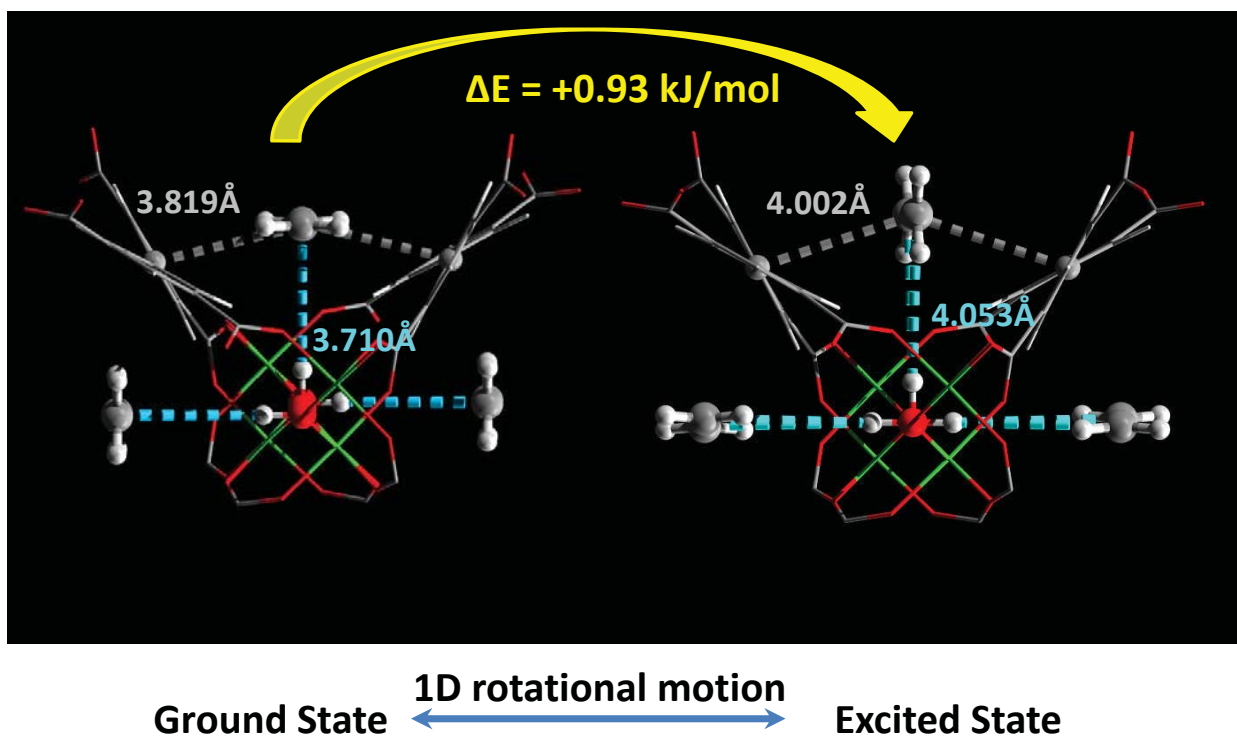
No change in degeneracy

Change in degeneracy

Inelastic Neutron Scattering (C_2H_4)



Transition of NOTT-300· C_2H_4

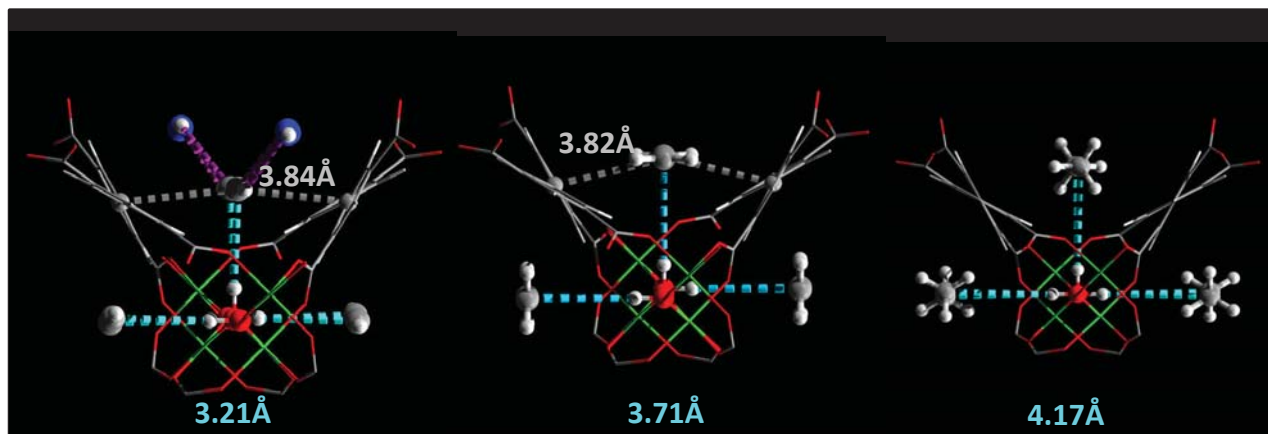


Structure of NOTT-300·xC₂H_{2,4,6}

Acetylene

Ethylene

Ethane

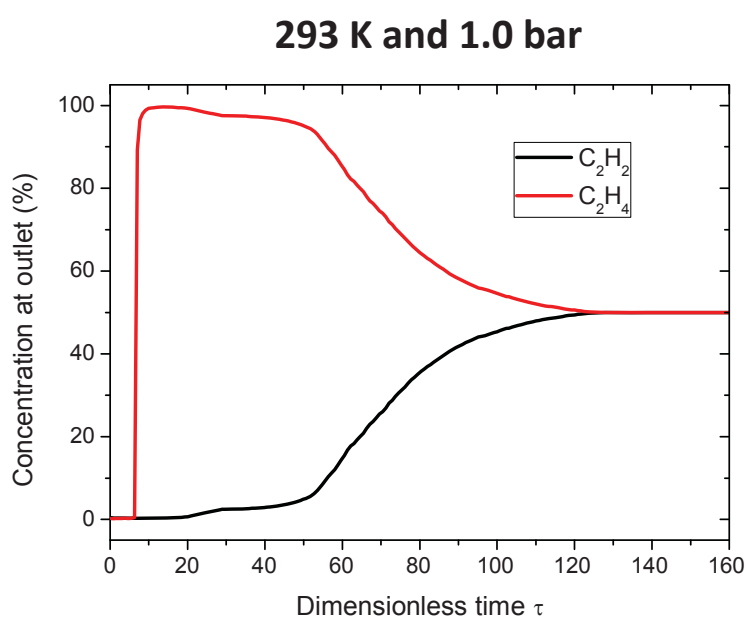
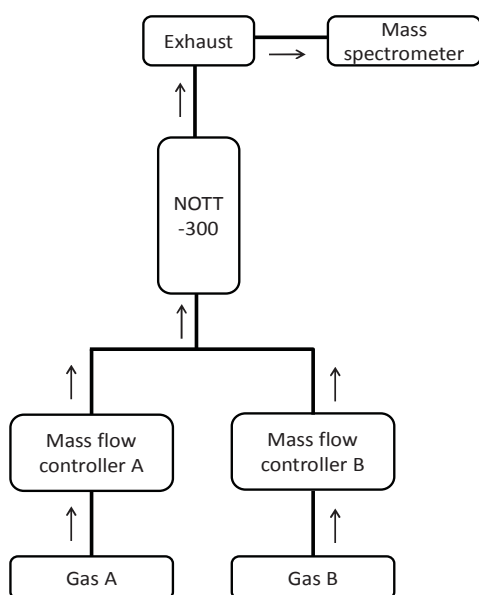


π-OH interactions: 3.21 Å

π-OH interactions: 3.71 Å

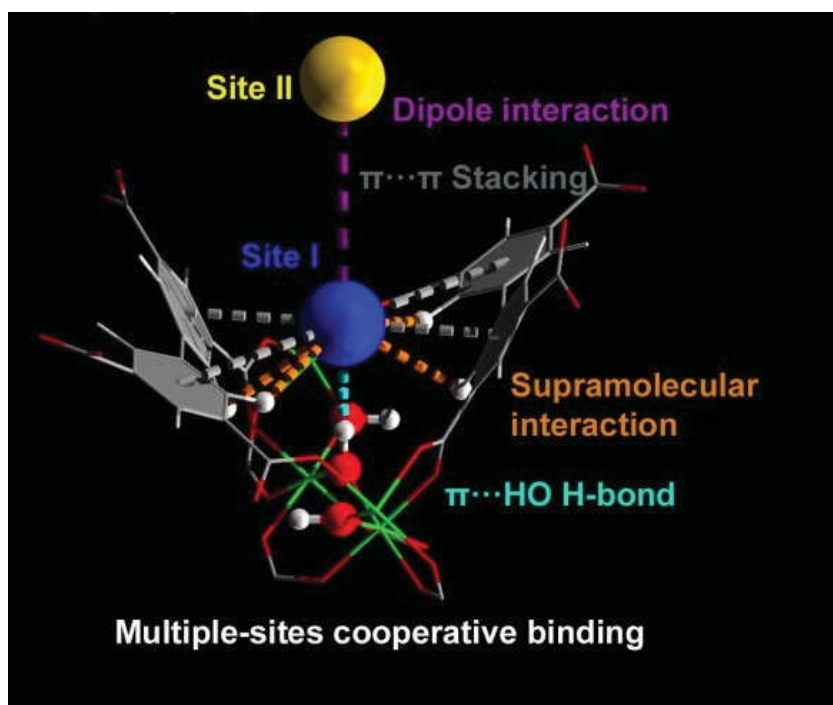
C-OH interactions: 4.17 Å

Breakthrough Separations



Equimolar mixture to 99.5%

Supramolecular Recognition and Binding



Nature Chemistry, 2014, 6, 10.1038/NCHEM.2114.

Deeper Understanding → Improved Materials

Crystallography
Dynamics
Thermodynamics
Diffusion
Kinetics
Modelling

Physical
Properties

Optimisation

New Material
Discovery

Acknowledgement

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Prof. Alexander Blake
Dr. Zhenzhong Lu
Daniel Anderson
Ruth Newby
Mathew Savage

ORNL:

Dr. Stuart Campbell

ISIS:

Dr. Timmy Ramirez-Cuesta
Dr. Stewart Parker
Dr. Svemir Rudic
Dr. Pascal Manuel
Dr. Victoria Garcia-Sakai
Prof. Bill David
Dr. Samantha Callear
Dr. Ivan da-Silva

Diamond:

Prof. Chiu Tang
Dr. Julia Parker
Prof. David Allen

ILL:

Dr. Mark Johnson

Stockholm:

Dr. Junliang Sun



The Leverhulme Trust





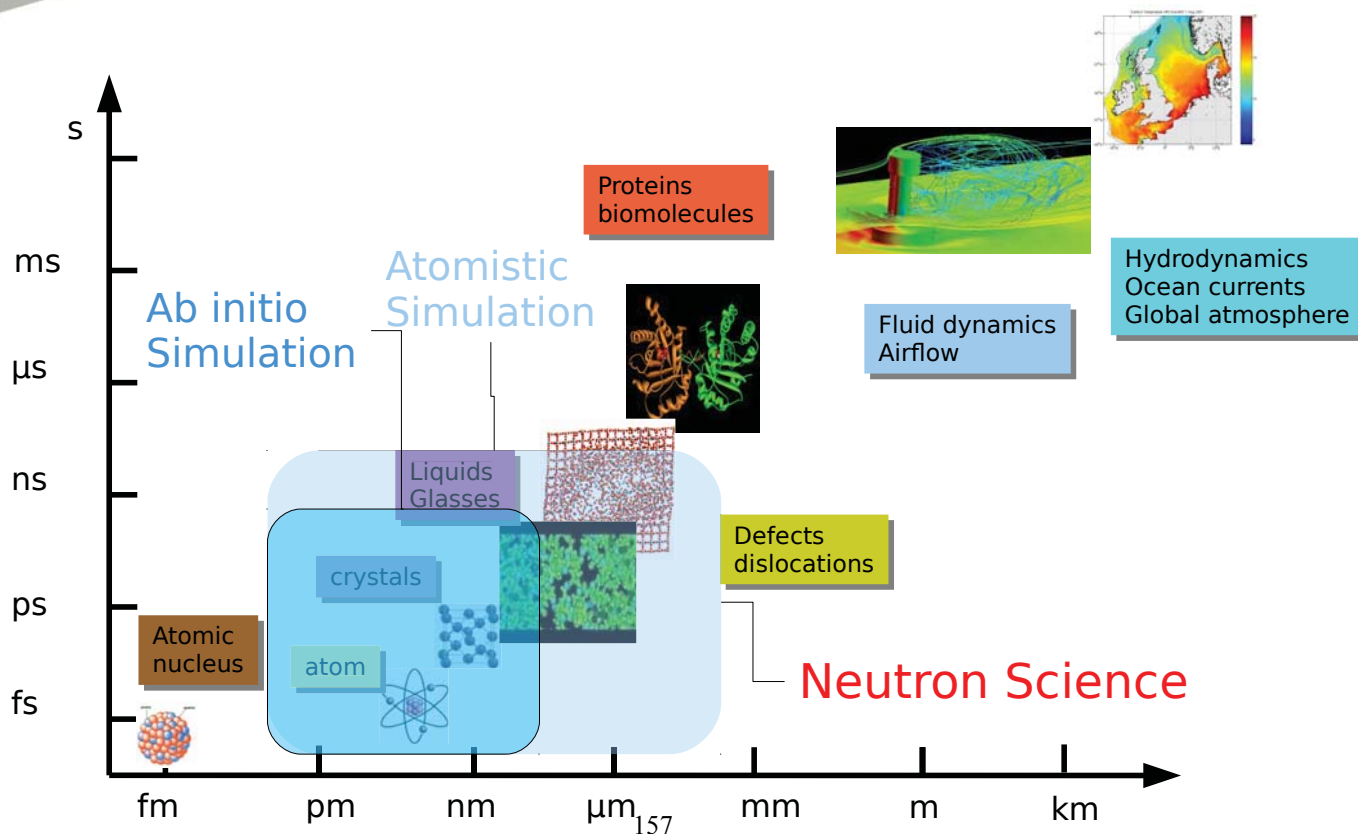
The Power of Density Functional Theory for materials simulation

Keith Refson

Royal Holloway University
& ISIS Facility, STFC

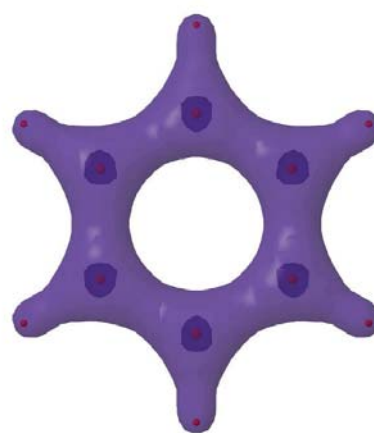
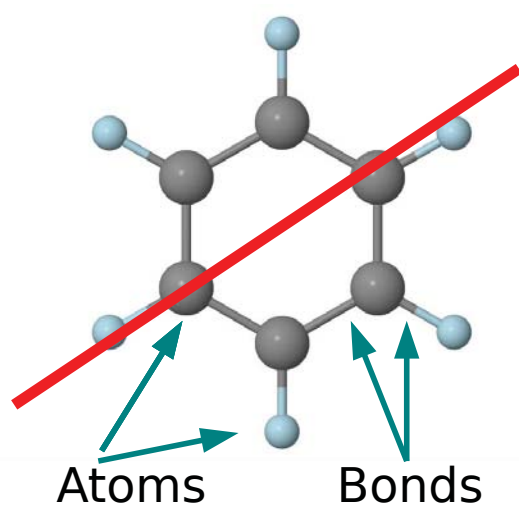


Simulation scales





The quantum Toolbox



Nuclei

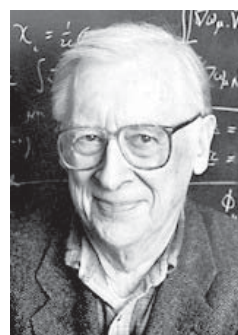
Electrons

$$\frac{-\hbar^2}{2m_e} \Psi + \hat{V} \Psi = E \Psi$$

3



Approximate quantum mechanics



The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the **density-functional theory**" and John A. Pople "for his development of computational methods in **quantum chemistry**".

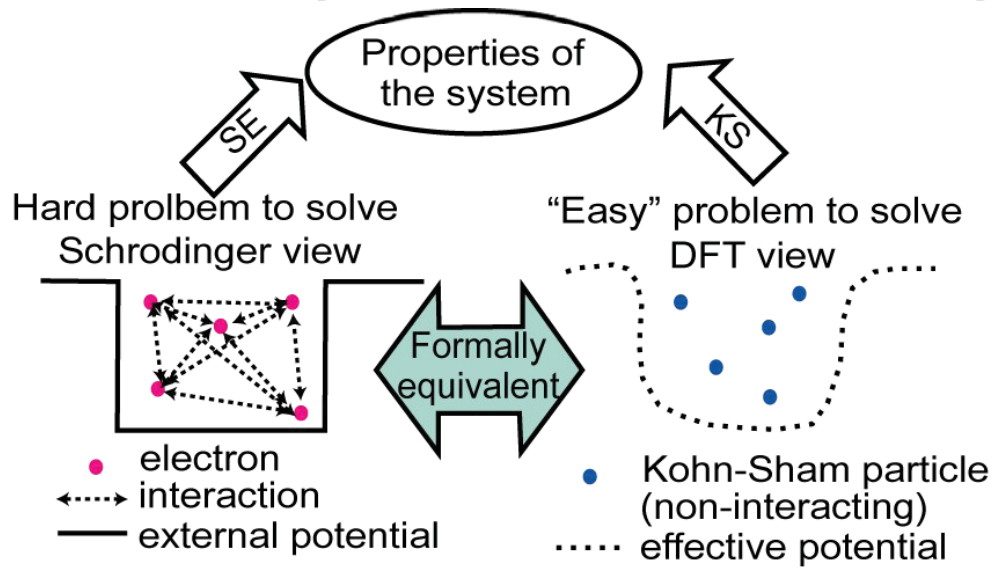
Key developments dating back to 1960s and 70s were approximate quantum theories which were nevertheless "good enough".

Density Functional Theory- Local Density Approximation

Hartree-Fock approximation, MP2, CI, CCSD(S,T)



Density Functional Theory



Approximate e-e interaction with

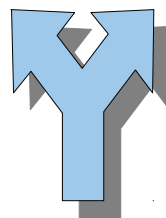
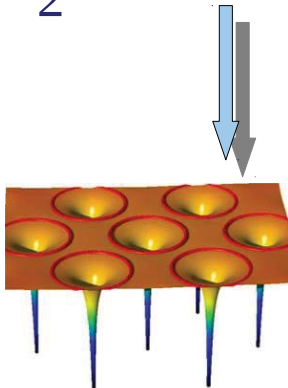
- local density approximation (LDA)
- generalized gradient approximation (GGA)
- Hybrids, DMFT, GW, ...

Modified from Mattsson et al.,
(2005) Modeling. Simul. Mater. Sci.
Eng. 13, R1.

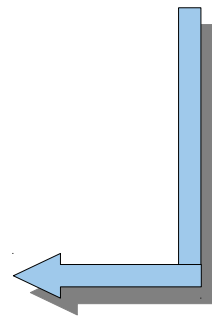


Kohn-Sham equations

$$\left\{ \frac{1}{2} \nabla^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + V_{\text{xc}}([n(\vec{r})]) \right\} \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$



$$n(\vec{r}) = \sum_i^{\text{occ}} |\varphi_i(\vec{r})|^2$$





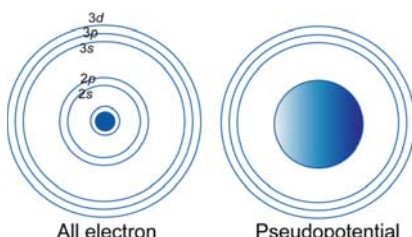
Plane-waves and pseudopotentials

Plane-wave basis set

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}},$$
$$u_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}}$$

- Well-adapted for crystalline and solid/liquid modelling
- Systematic control of basis set convergence

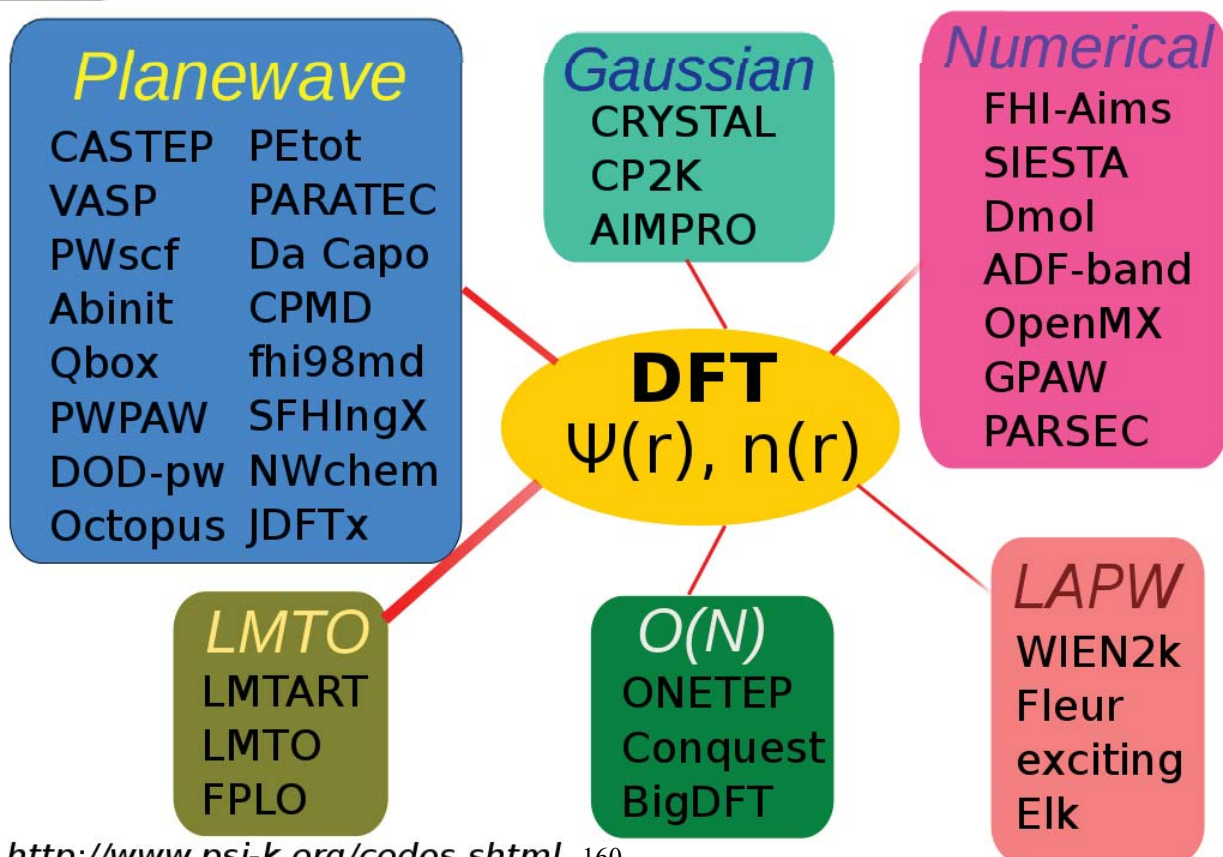
Pseudopotential for ionic interactions



- “All electron” method but frozen core.
- Retain chemically relevant valence electrons
- Good scaling/large systems



DFT Codes



Parallel Supercomputing

Parallel supercomputing enables large calculations and high throughput.



<http://www.hector.ac.uk>

<http://www.stfc.ac.uk/hartree>

<http://www.top500.org>

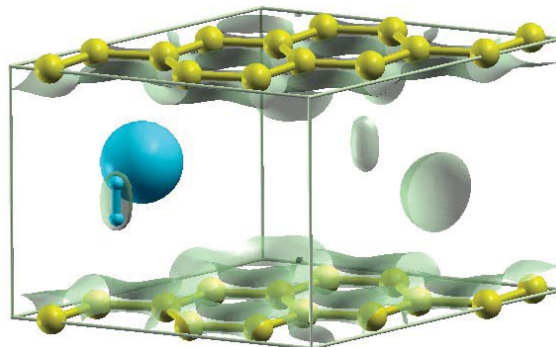


CASTEP

UK plane-wave materials simulation code

Emphasis on properties calculation

- **Electronic properties:** band structure, DOS, PDOS, Mulliken and Hirshfeld population analysis
ELF, Wannier Functions.
Core hole spectroscopy – EELS, XANES
EFG
- **Response properties**
NMR chemical shifts, J-coupling
- **Vibrational spectroscopy**
Density Functional perturbation for phonons
Quasi-harmonic thermodynamics.
Dielectric response and polarizability
Born effective charges
ir and Raman intensities.

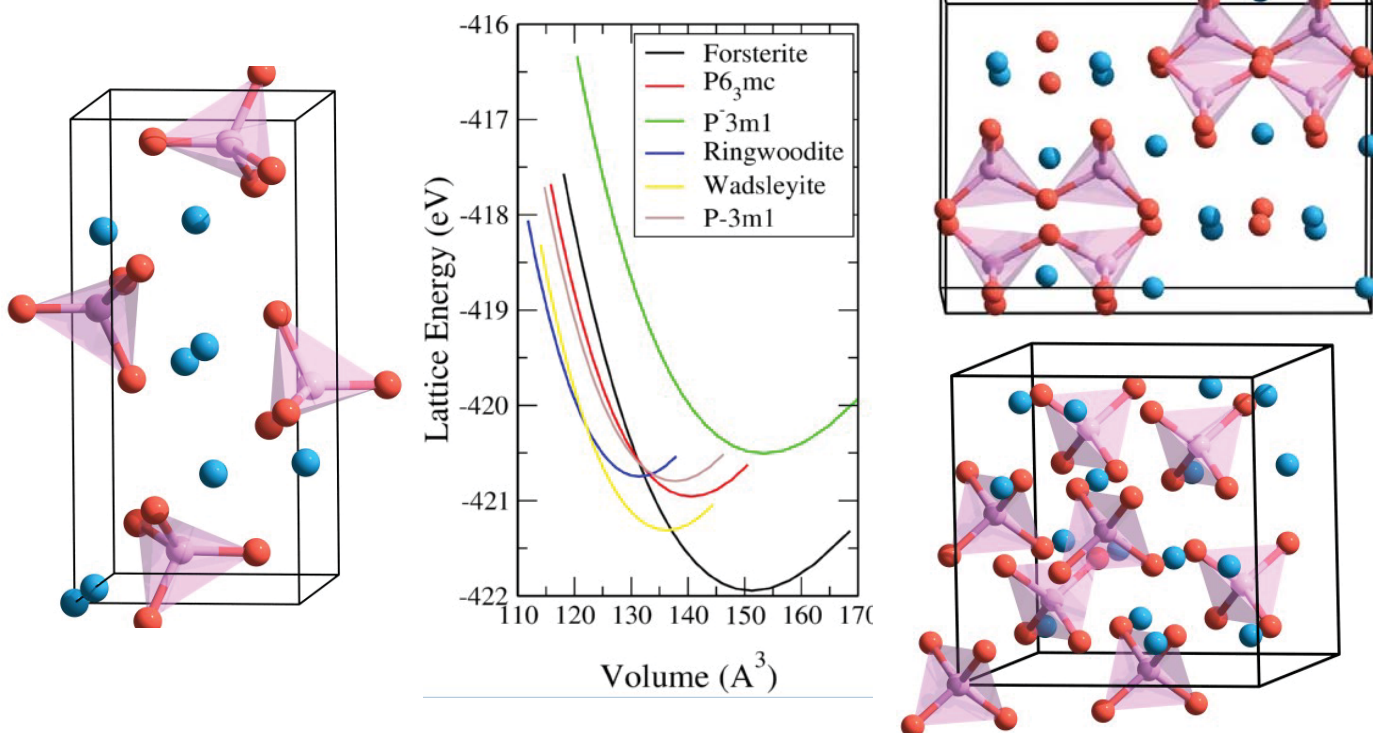


Roadmap

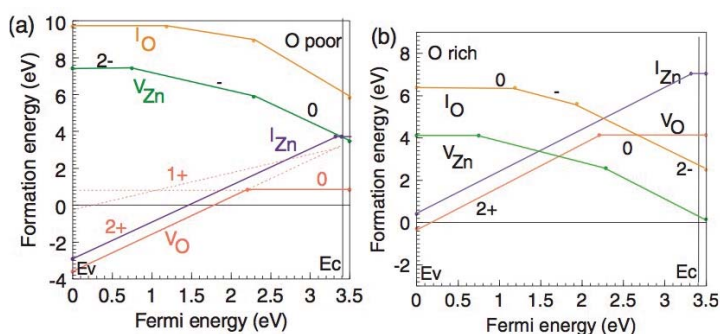
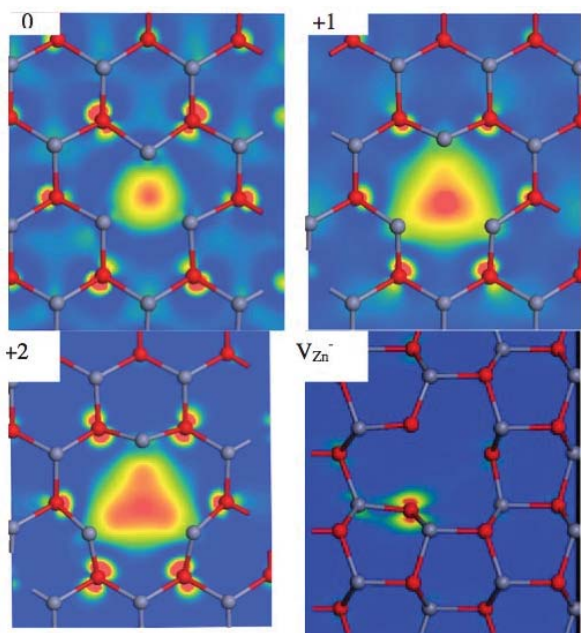
- Time-dependent DFT
- More efficient hybrid exchange functional approximations
- Spin-Orbit coupling
- Non-collinear magnetism
- GW

From electronic to crystal structure

Polymorphs of Mg_2SiO_4

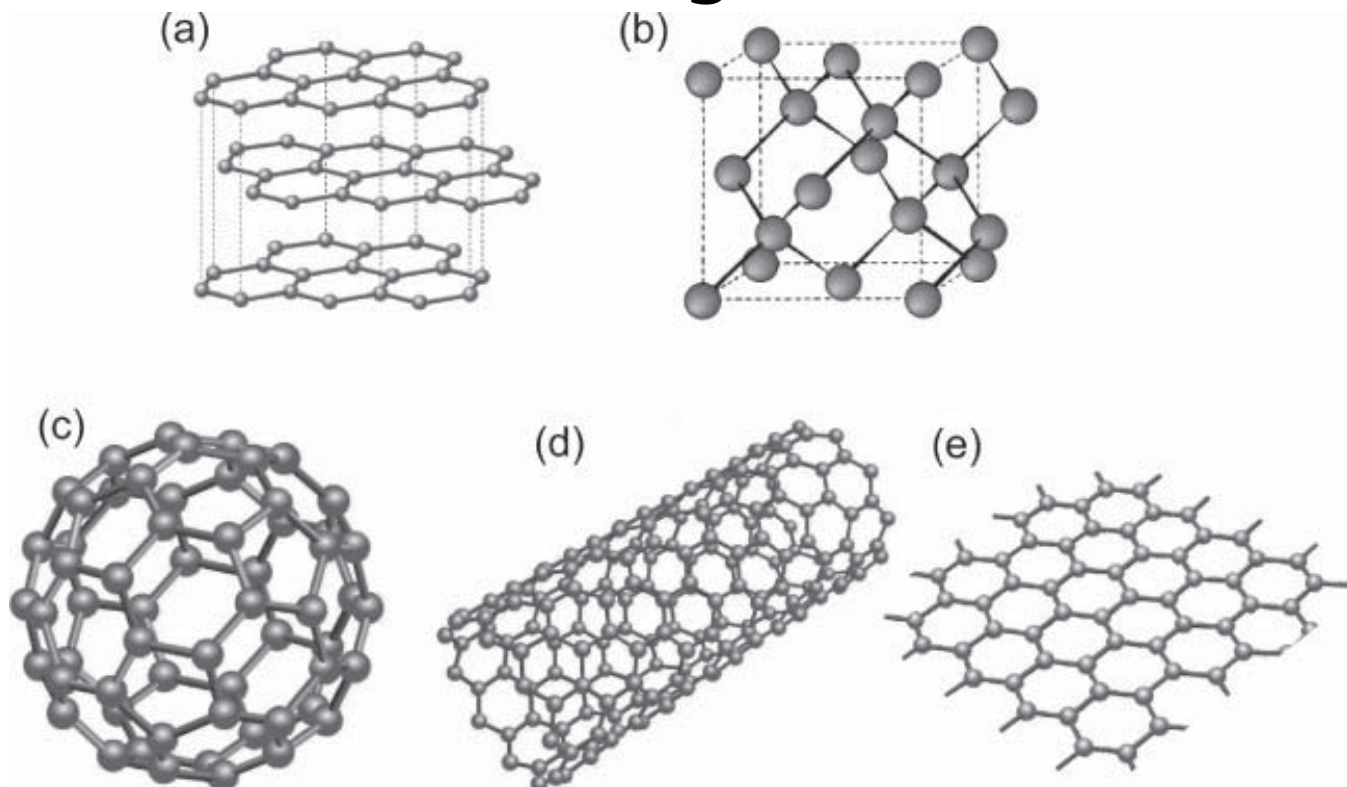


Charged Defects in ZnO





Predicting Structure



AIRSS

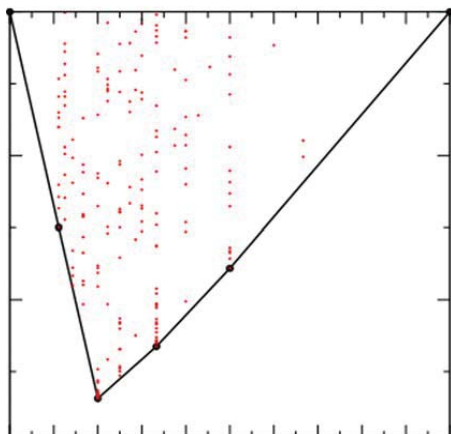
Ab initio random structure searching

Slide 3

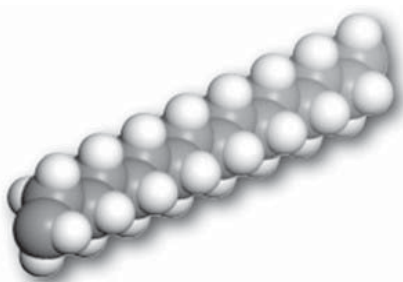
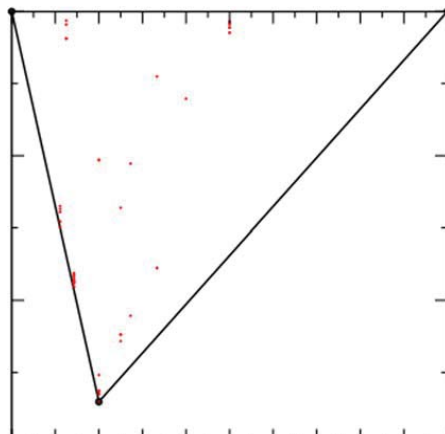




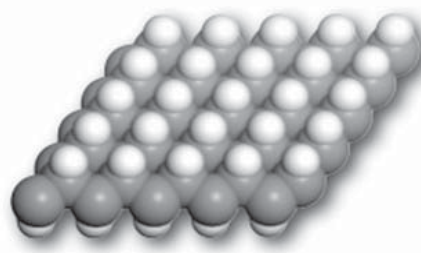
Prediction of Crystal Structures – AIRSS



methane



polyethane



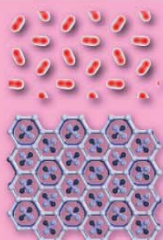
graphane



AIRSS - A tool for discovery

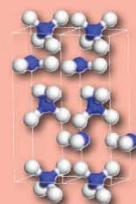
**Hydrogen is
polar and
“graphene”**

Nature Physics, 2007
Physical Review B, 2012



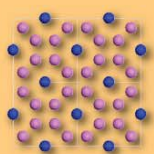
Ammonia is ionic

Nature Materials, 2008



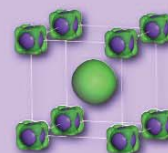
**Aluminium is
complicated**

Nature Materials, 2010



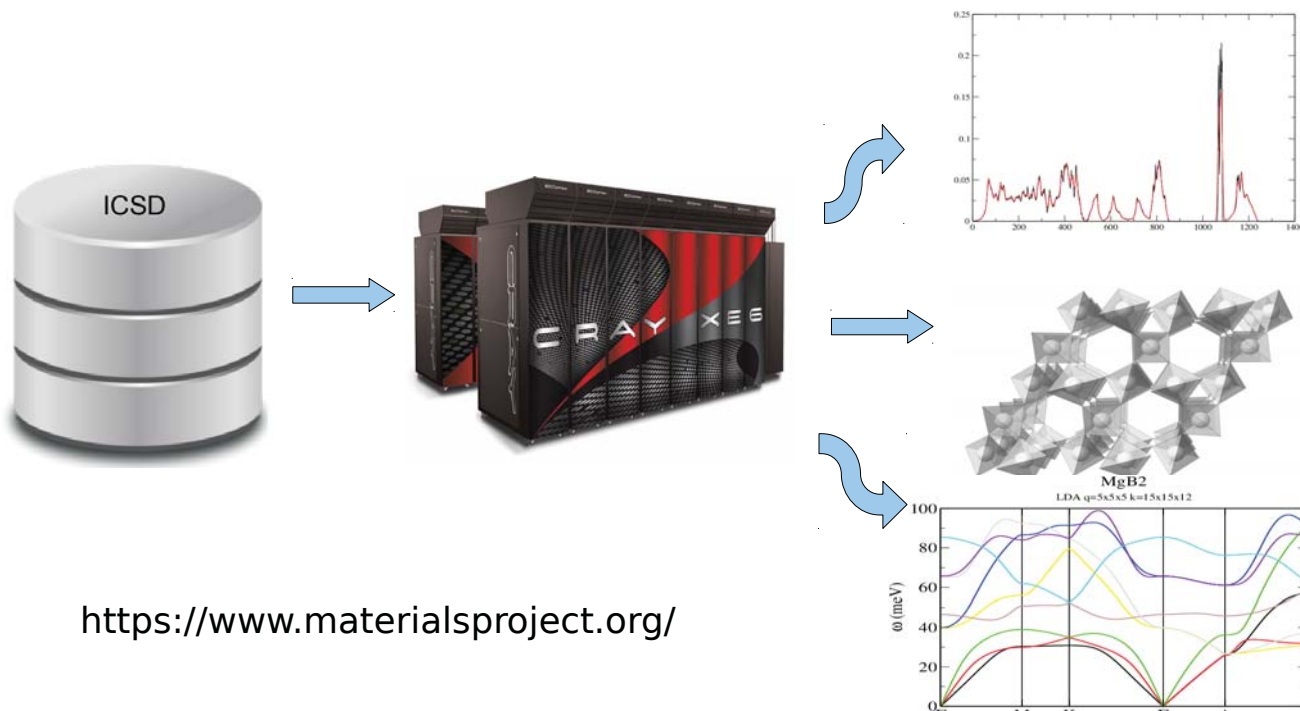
**Magnetic
potassium**

Physical Review Letters, 2011

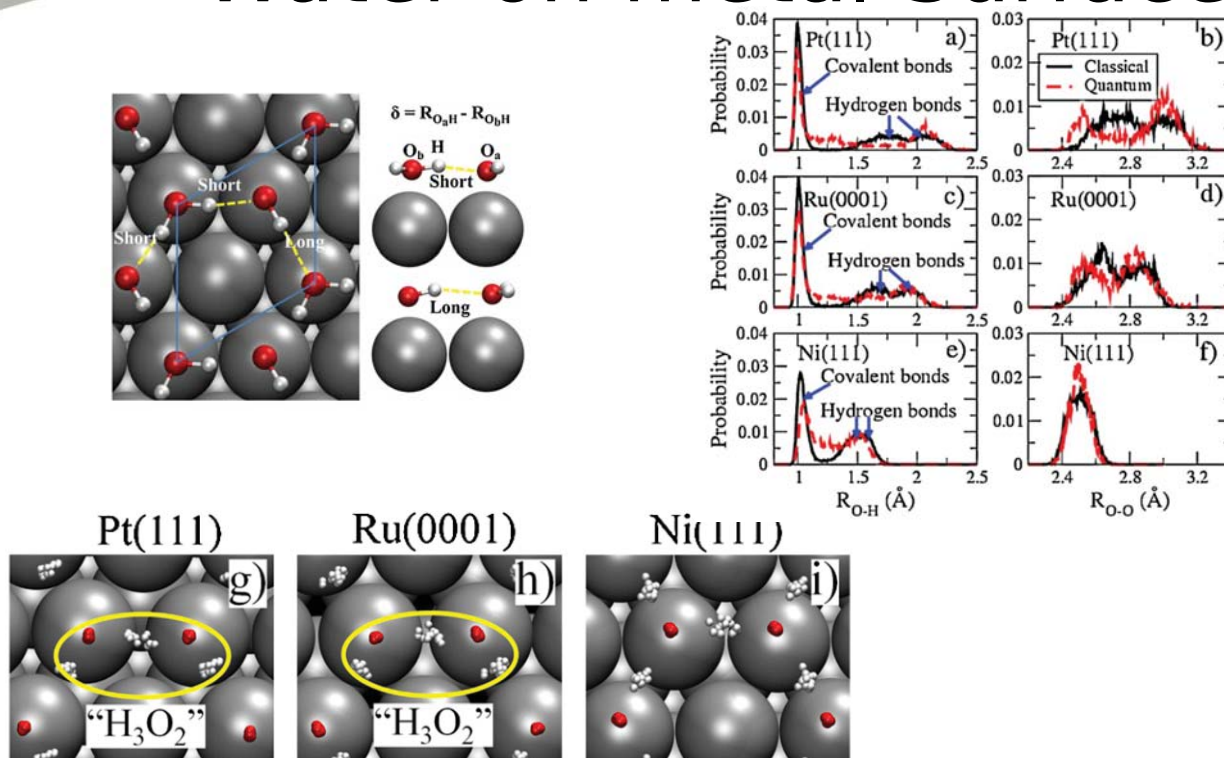




Materials Genome

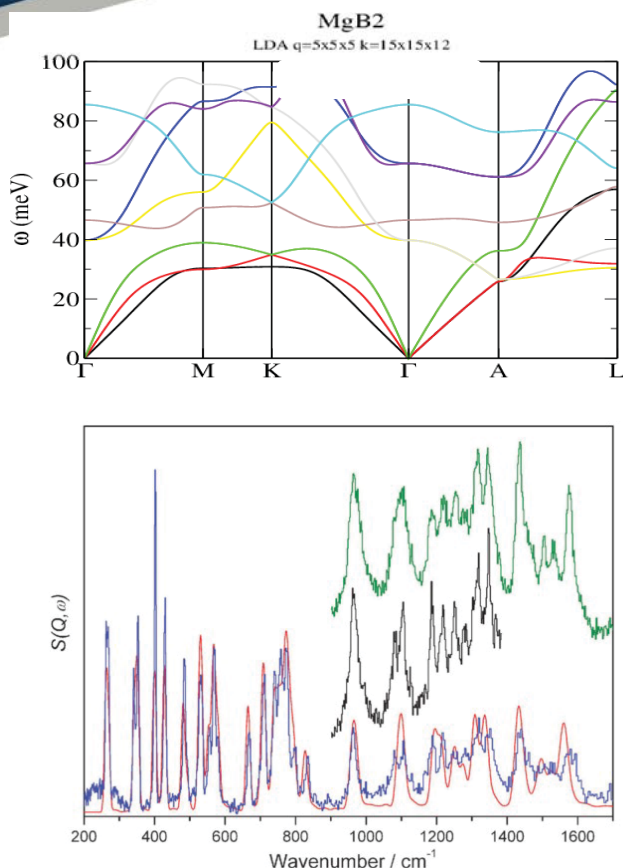


Water on metal Surfaces

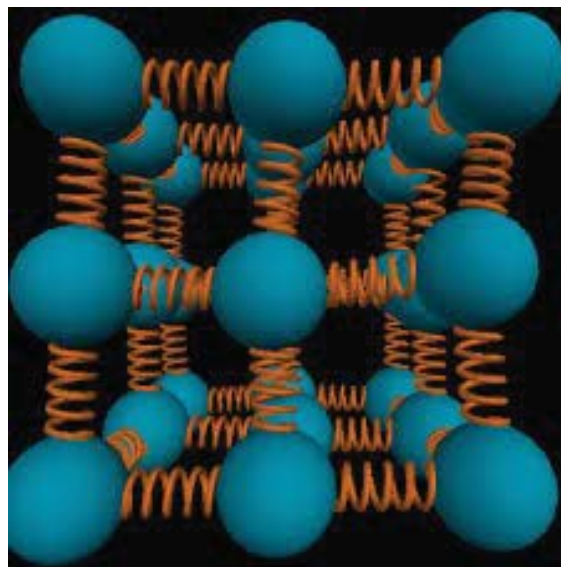




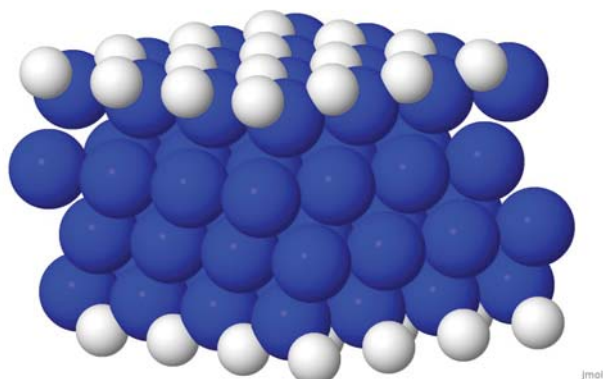
Vibrational Spectroscopy



$$\Phi_{\kappa'\alpha'}^{\kappa\alpha}(\mathbf{0}, \mathbf{R}) = \frac{\partial^2 E}{\partial r_{\kappa\alpha} \partial r_{\kappa'\alpha'}}$$



Raney(TM) Ni Catalyst



Ni-H distance

Neutron: 1.68 Å

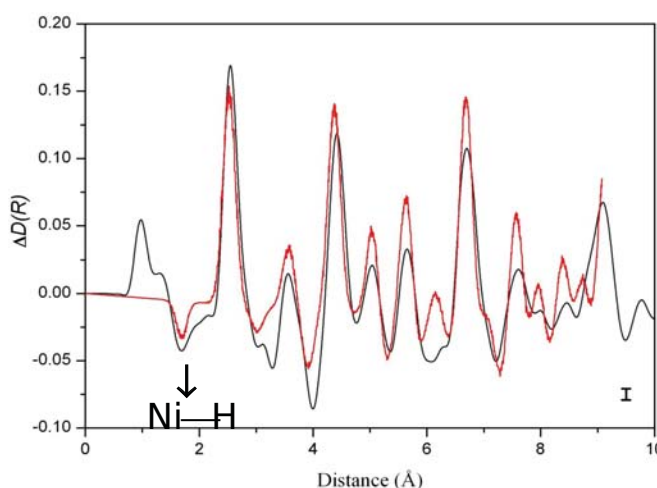
Ab initio: 1.68 Å

LEIS: 1.65 ± 0.05 Å

LEED: 1.84 ± 0.06 Å

Difference pair distribution $\Delta D(r)$ with and without H (SANDALS measurement)

Calculated $\Delta D(r)$ from simulation

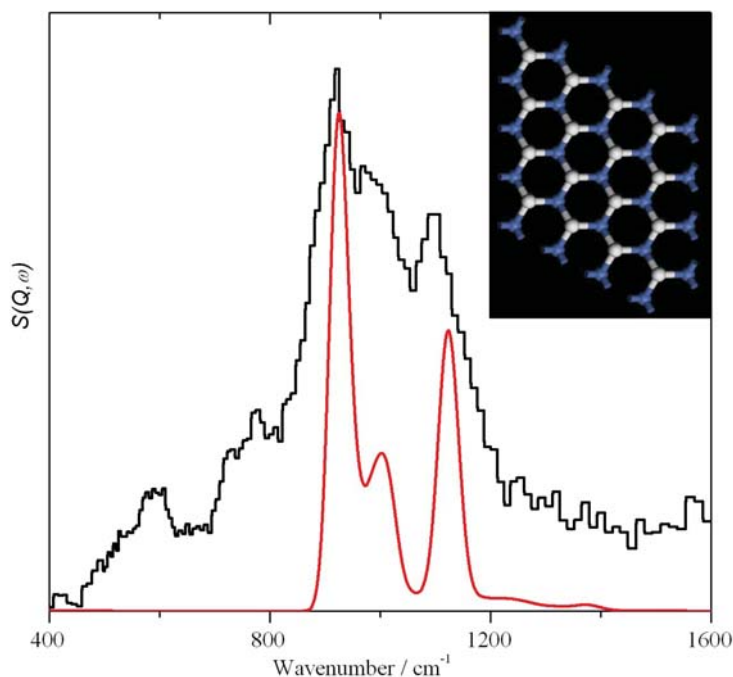


Raney(TM) Ni Catalyst

INS spectrum of hydrogen on Ni measured on TOSCA

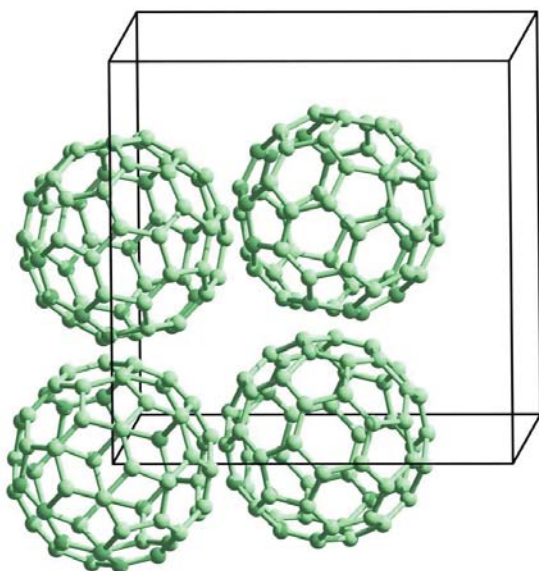
CASTEP calculation of Ni(111)/H (scaled by 0.93).

Agreement supports Structural model of H on threefold site with Ni-H 1.68Å



Stewart Parker, *et al* Chem. Comm. **46**, 2959-61 (2010).

Vibrational spectroscopy of C₆₀

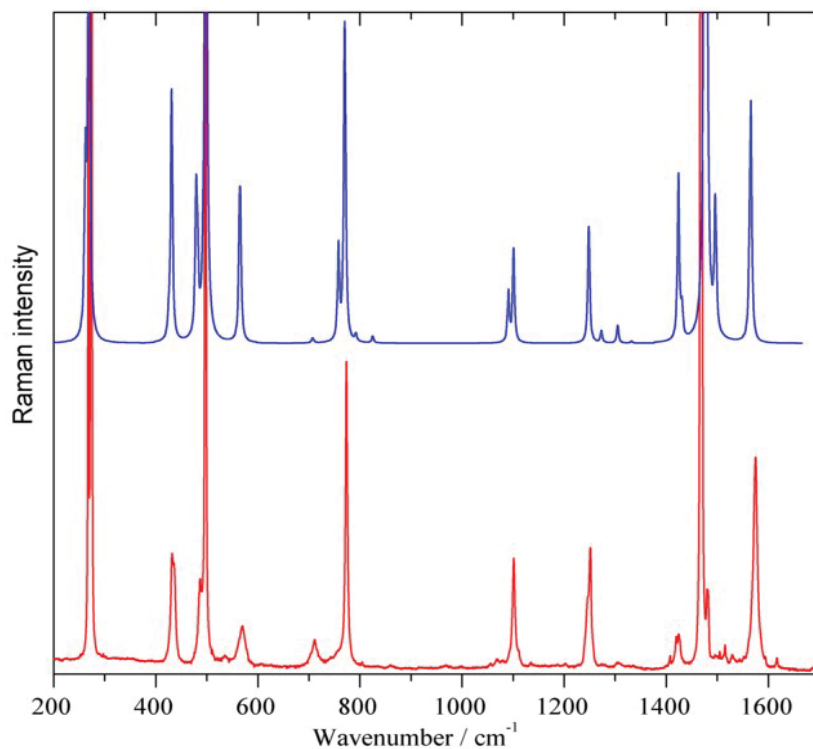


- Above 260K takes Fm3m structure with dynamical orientational disorder
- m3m point group lower than I_h molecular symmetry
- Selection rules very different from gas-phase.
- Intramolecular modes and factor group splitting seen.
- Try ordered Fm3 model for crystal spectral calculation.

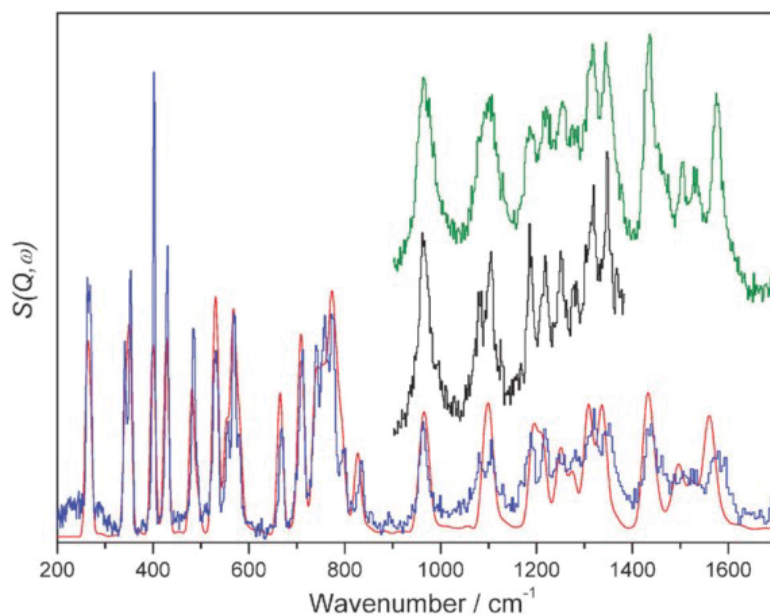
Parker et al, PCCP **13**, 7780 (2011)



GGA Raman spectrum of C_{60}

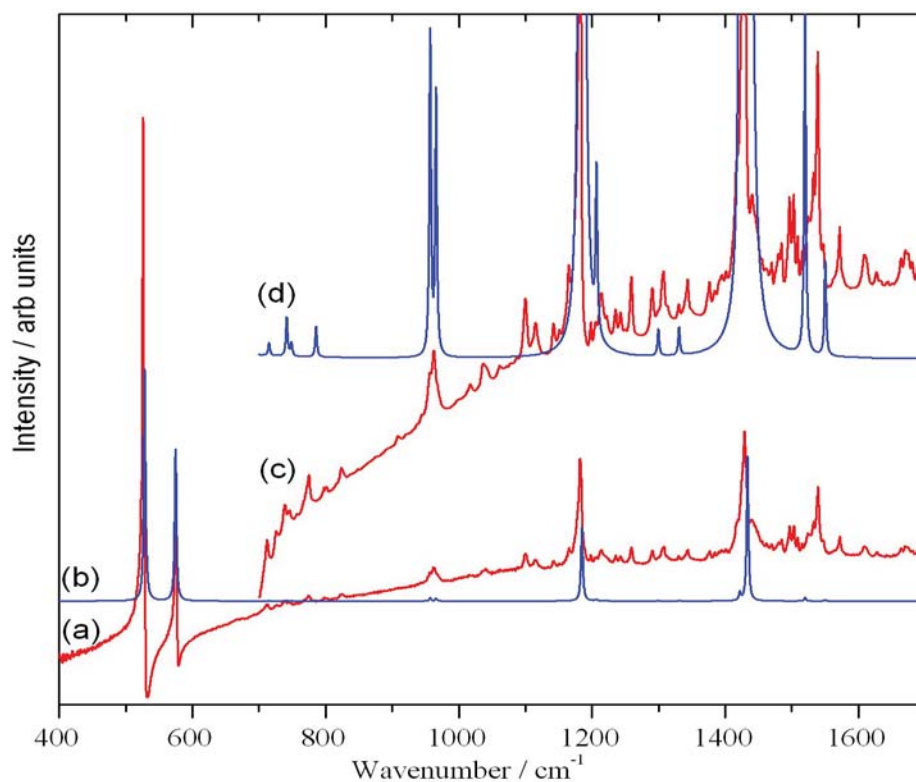


C_{60} INS -Tosca



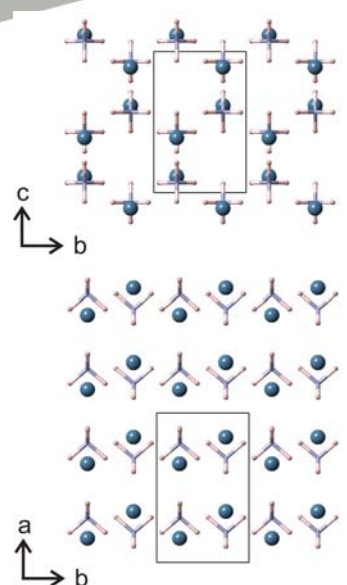


GGA infrared spectrum of C_{60}

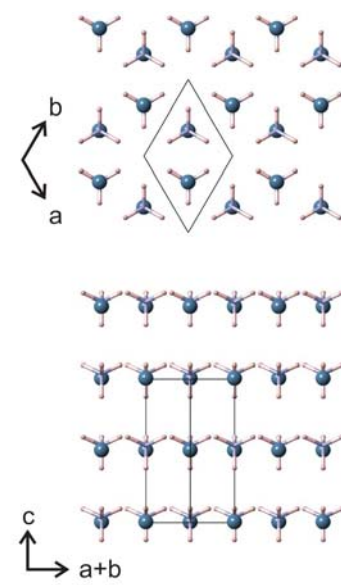


Structure and Transport in LiBH_4

Fast-ion conduction in LiBH_4



< 390 K
Orthorhombic (Pnma)



> 390 K
Hexagonal (P63/mmc)
Disordered
Superionic conductivity

> 560 K: liquid
> 650 K: decomposition

The Nature of BH_4^- Reorientations in Hexagonal LiBH_4

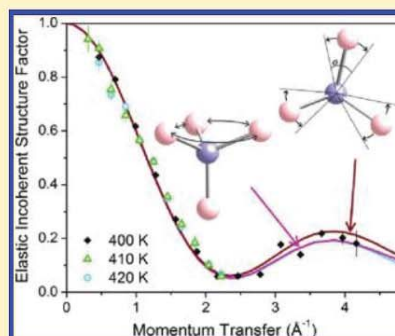
Nina Verdal,^{*,†} Terrence J. Udovic,[†] and John J. Rush^{†,‡}

[†]NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Dr., MS 6102, Gaithersburg, Maryland 20899-6102, United States

[‡]Department of Materials Science and Engineering, University of Maryland, 2135 Chemical & Nuclear Engineering Bldg., College Park, Maryland 20742-2115, United States

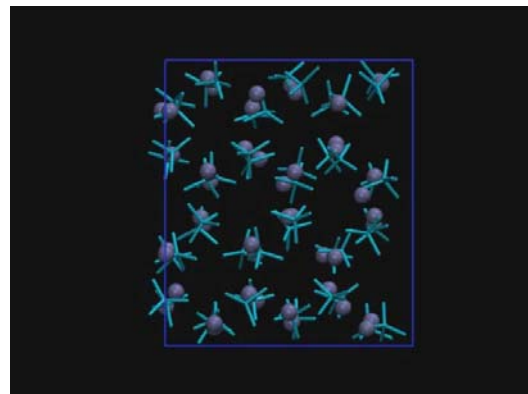
S Supporting Information

ABSTRACT: Lithium borohydride (LiBH_4) has lately been the subject of intense inquiry within the hydrogen storage community. Quasi-elastic neutron scattering spectra were measured for LiBH_4 in the high-temperature hexagonal crystal phase. The elastic incoherent structure factor associated with the rapid BH_4^- anion reorientations was determined at 400, 410, and 420 K for momentum transfers as high as 4.2 \AA^{-1} . The results strongly suggest a BH_4^- reorientational mechanism approaching quasi-free, trigonal-axis rotation of three borohydride H atoms, combined with reorientational jump exchanges between these delocalized “orbiting” H atoms and the remaining axial borohydride H atom. This mechanism is consistent with previously reported diffraction and spectroscopy studies.



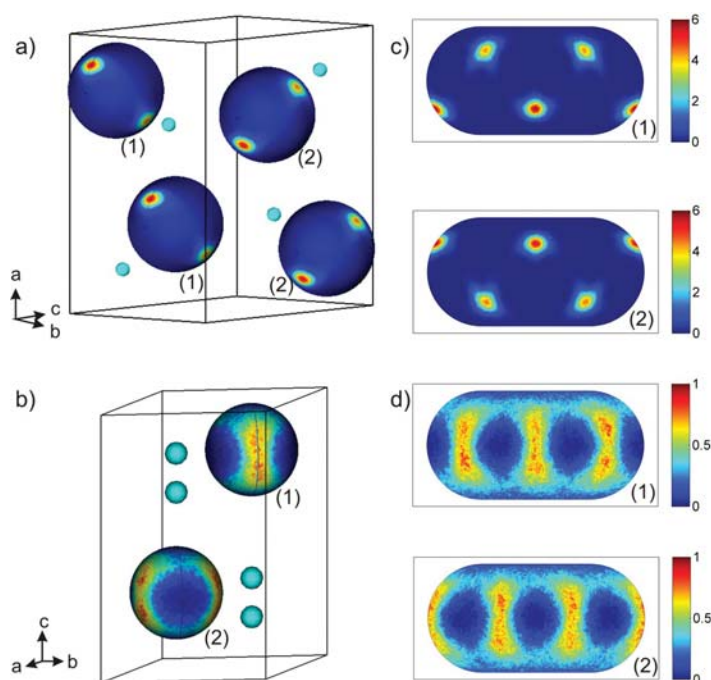
AIMD – computational details

- Code: CP2K
- Born-Oppenheimer molecular dynamics in isokinetic ensemble (Gaussian thermostat)
- Forces evaluated by DFT using the QUICKSTEP method
- Supercell: 288 atoms (48 formula units)
- Time step: 0.5 fs
- Run lengths 20-30 ps after equilibration
- PBE exchange-correlation functional
- Dual basis set (Gaussian DZ orbitals & plane waves up to 280 Ry) and Goedecker pseudopotentials are used



Equilibrium AIMD

BH4 rotational disorder:



298K

473K

Calculating diffusion by AIMD

Diffusion coefficient calculated by...

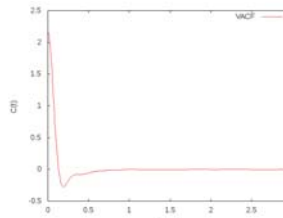
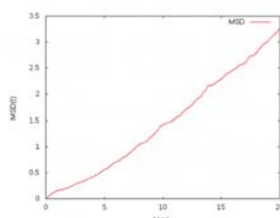
Einstein-Sutherland equation

$$D = \frac{1}{n} \frac{d\langle r^2(t) \rangle}{dt}$$

Green-Kubo formula

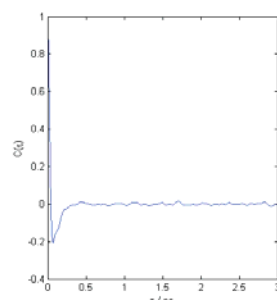
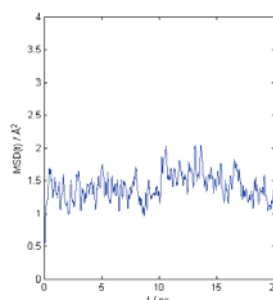
$$D = \frac{2}{n} \int_0^\infty dt \langle v(0) \cdot v(t) \rangle$$

Lennard-Jonesium
(mimicking liquid Argon)



Fast diffusion

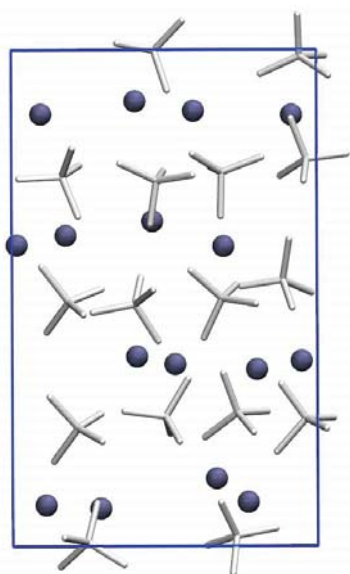
LiBH4 at 535 K



Diffusion by ion jumps
(rare events)
which are often
followed by a jump back
to the original position

Limits of AIMD: diffusion in fluids with $D > 10^{-5} \text{ cm}^2/\text{s}$

Nonequilibrium Molecular Dynamics



- An external field \mathbf{F}_e is applied that couples to a fictitious atomic property ("colour", c_i):

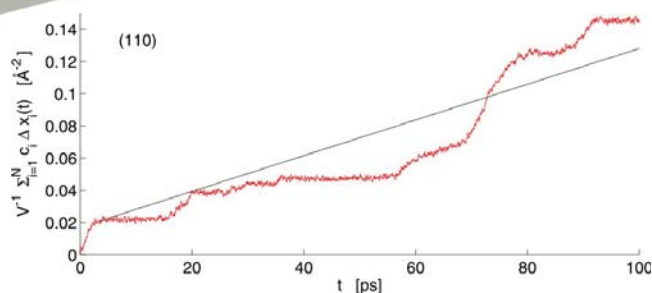
$$\dot{\mathbf{p}}_i = \mathbf{F}_i + c_i \mathbf{F}_e$$

- The (fictitious) field and its induced response are related by (real) transport coefficients:

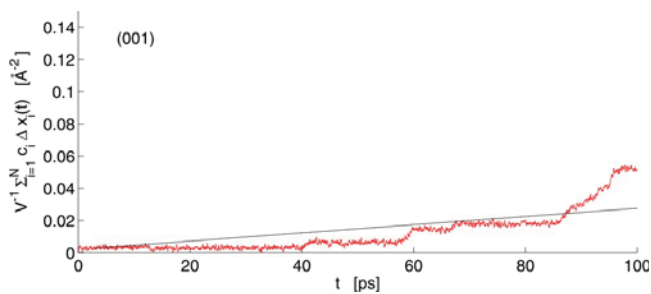
$$D = \frac{k_B T}{\rho_c} \lim_{t \rightarrow \infty} \lim_{F_e \rightarrow 0} \frac{\langle J_c(t) \rangle}{F_e}$$

- NEMD functionality implemented in CASTEP and CP2K
- ab initio* nature of the method allows mechanism discovery

Results – $F_e = 0.05 \text{ eV/\AA}$

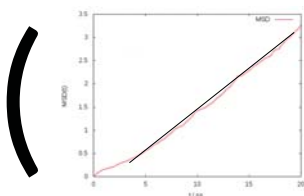


$$D_{\text{Li}} = 5.82 \cdot 10^{-6} \text{ cm}^2/\text{s}$$



$$D_{\text{Li}} = 1.34 \cdot 10^{-6} \text{ cm}^2/\text{s}$$

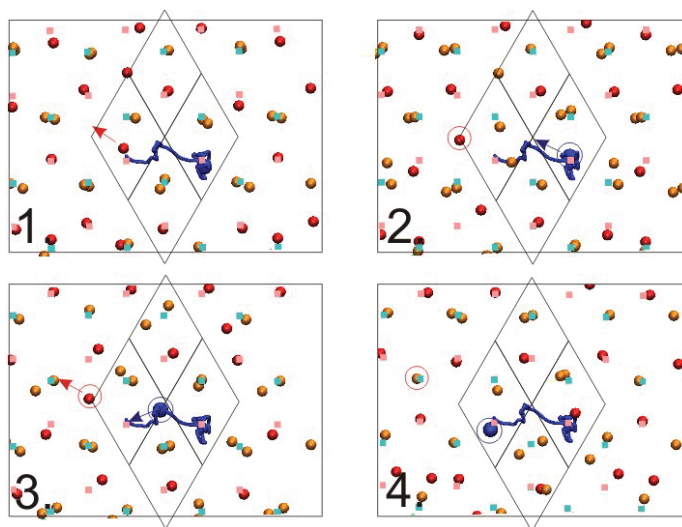
(Measured: $D_{\text{Li}} = 2.28 \cdot 10^{-6} \text{ cm}^2/\text{s}$)



Compare: $D = \frac{1}{n} \frac{d\langle r^2(t) \rangle}{dt}$ vs $D = \frac{k_B T}{\rho_c} \lim_{t \rightarrow \infty} \lim_{F_e \rightarrow 0} \frac{\langle J_c(t) \rangle}{F_e}$

Diffusion Pathway

Inspection of the NEMD trajectory:



hopping is via jumps from a lattice site into an empty interstitial site (2 & 3),
and from there on to another lattice site (4).

P.C. Aeberhard, S. Williams, D. Evans, K. Refson, and W.I.F. David, Physical Review Letters 108, 095901 (2012).



Integration of Simulation with experiment

Simulations used throughout whole experimental cycle –

- proposal – proof of interpretability
- experiment planning
- experiment steering
- data analysis and interpretation
- validated model used for deeper scientific insight.



Conclusions

Robust DFT electronic structure can serve as the engine for powerful new methods of structure search, materials design and spectroscopy

As in LiBH_4 even some crystal structures require a dynamic model to describe them properly.

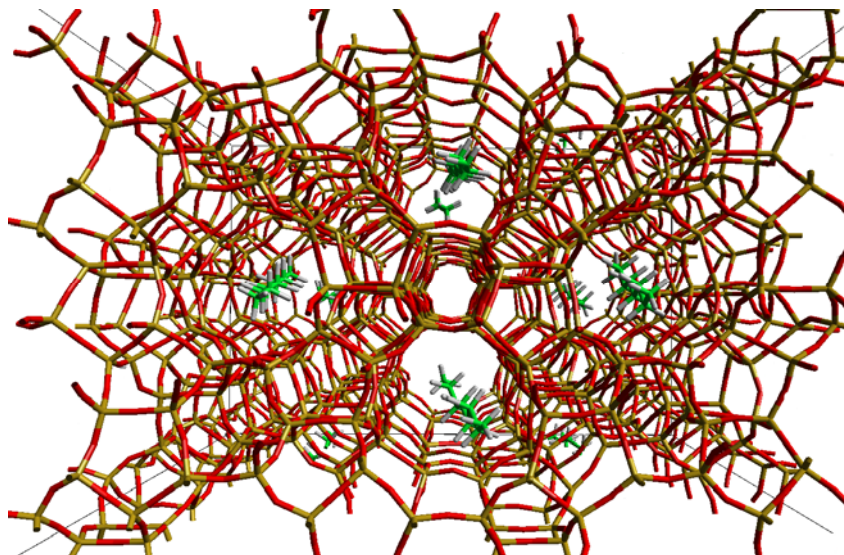
Inelastic peaks yield much more comprehensive scientific insight when interpreted with aid of a first principles lattice dynamics model.

Ab-initio lattice dynamics almost compulsory to Interpret and publish TOSCA experiments. >50%.



Acknowledgements

- Dr Matt Probert (York), Prof Chris Pickard (UCL), Prof Stewart Clark (Durham)
- Collaborators – LiBH_4
Bill David, Philippe Aeberhard, Oxford,
Stephen Williams, Denis Evans, ANU
- FUNDING – EPSRC, STFC
- Computer time EPSRC, NERSC, STFC, ANU, Oxford

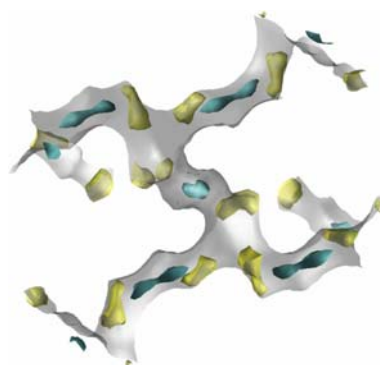


Diffusion of Hydrocarbons in Zeolites

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

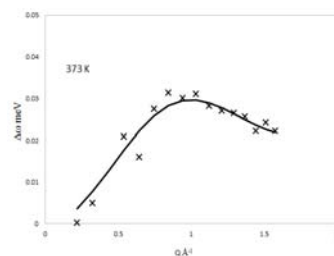
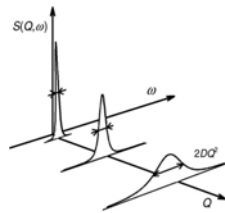
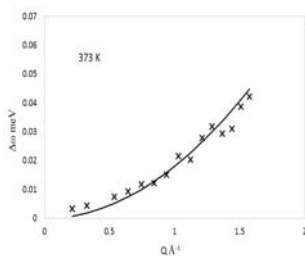


- The change of the spectral profile wrt neutron momentum transfer (Q) is related to the diffusion coefficient. (usually tracked from incoherent scattering of hydrogen atoms).
- Can probe the same length and time-scales similar to MD simulations.

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

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

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

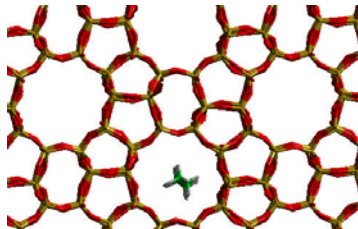
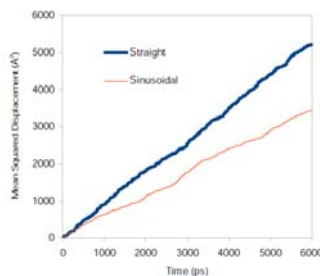


MD simulations for obtaining the diffusion coefficient



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

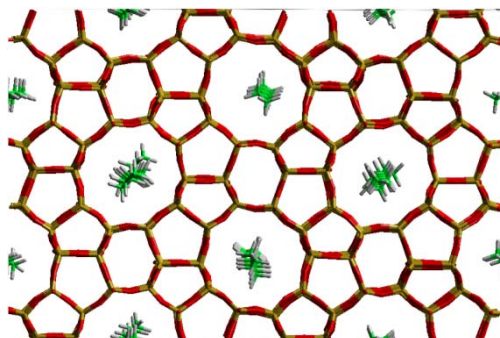


$$D_s = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle$$

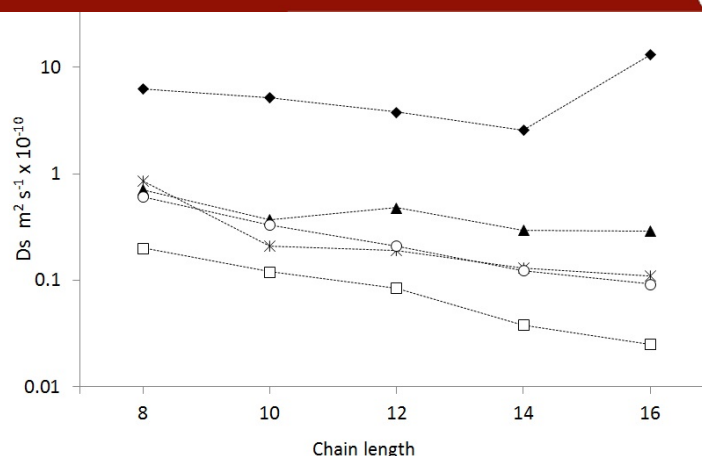
Longer *n*-alkanes in silicalite: Up-to-date models giving close agreement with QENS



- C₈ – C₂₀ 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.



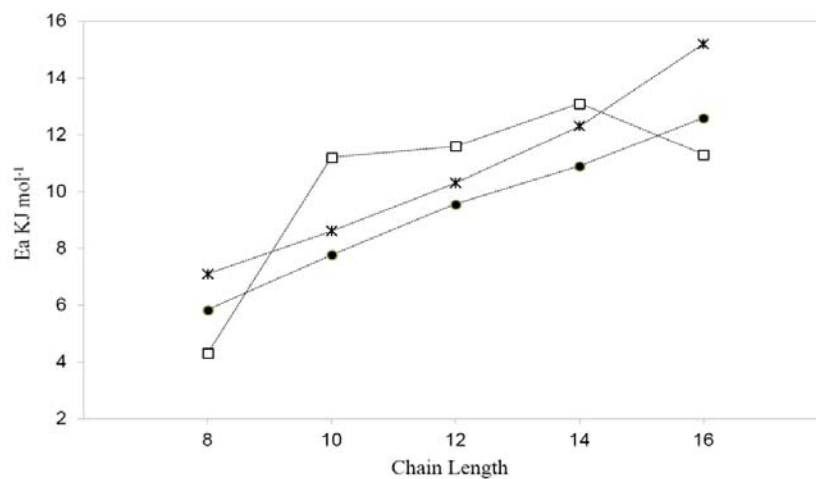
Diffusion coefficients: Compare simple MD models, hierarchical simulations, current study



A plot of the calculated diffusion coefficients from the current MD simulations (○), MD simulations at infinite dilution¹ (▲), 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.

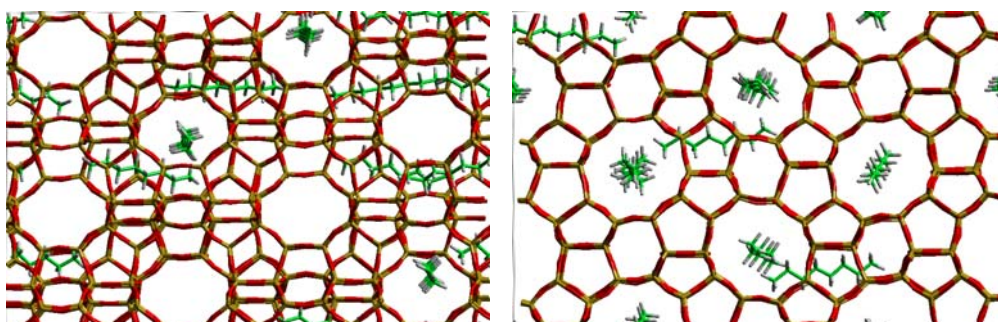
Activation energies: QENS, Hierarchical simulations, current MD simulations



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

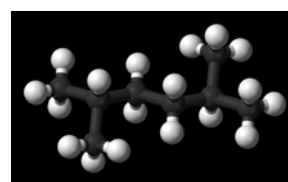
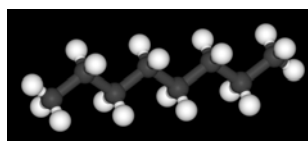
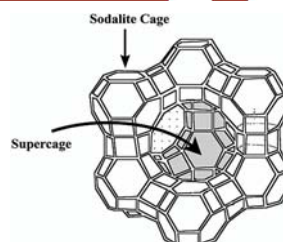


- Channel switching from straight to sinusoidal channel system for octane only
- Seen only at 350 and 400 K, and only in channels containing multiple molecules
- Static energy calculations to understand energetics of switching

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



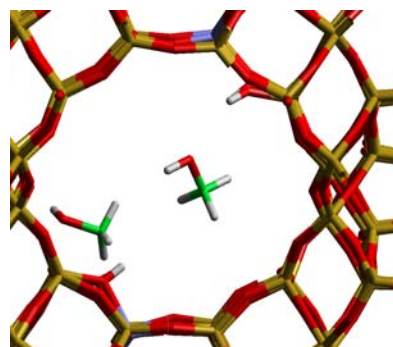
- Octane and dimethylhexane studied by QENS and MD in zeolite Y (Si/Al = 30) on OSIRIS
- Understand the difference in diffusion behaviour between the straight chain and branched isomer
- Still processing data from both methods to calculate diffusion coefficient...
- But some interesting parallels found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



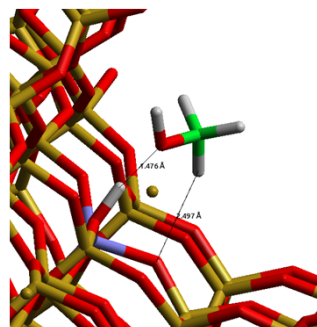
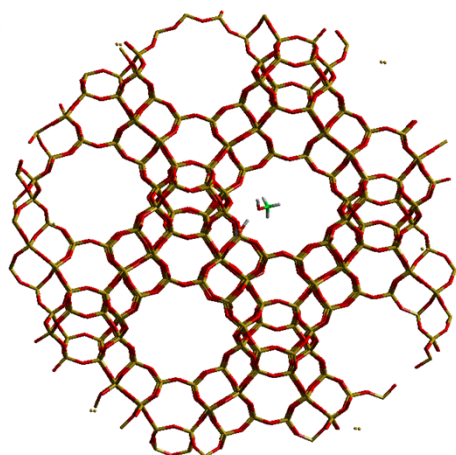
Methanol and dimethylether in zeolite Y



- 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

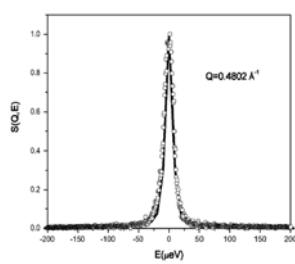


Future work – binding of methanol to zeolite frameworks to form methoxy species
INS + embedded cluster simulations

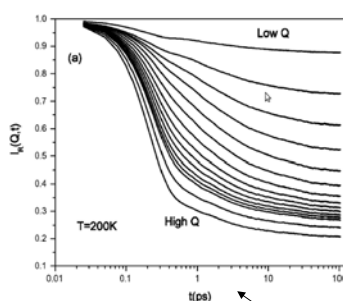


- INS observations show binding of methanol to the framework to form methoxy species in ZSM-5, not zeolite Y.
- Embedded cluster simulations an improvement on DFT studies to calculate the barriers to this process between the 2 frameworks

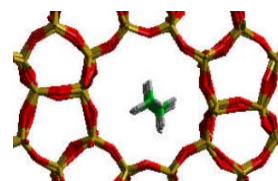
Future work – Rotational motions of octane isomers in ZSM-5



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



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



- 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

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

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



Science & Technology
Facilities Council



Crystalline Diffraction

An Introduction to Neutron Techniques in Catalysis

November 4th 2014



Martin Owen Jones

ISIS Facility, Rutherford Appleton Laboratory

- Neutron wavelength and energy 'just right' for condensed matter
structure and dynamics

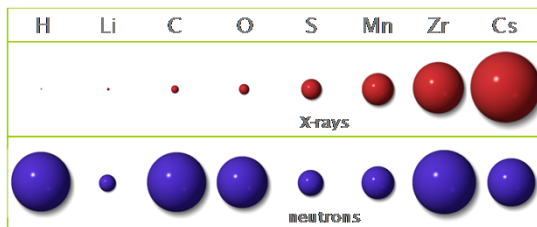
- Neutron cross-section
isotopic dependence

- H / D contrast
nuclear form factor

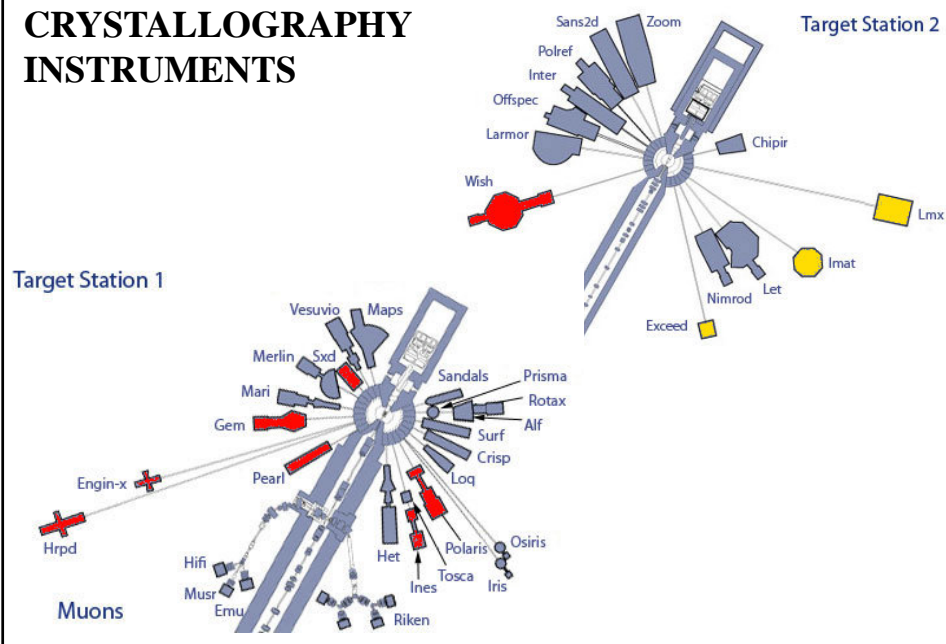
- Magnetic Moment
magnetic order & excitations

- Weak probe
theoretical interpretation

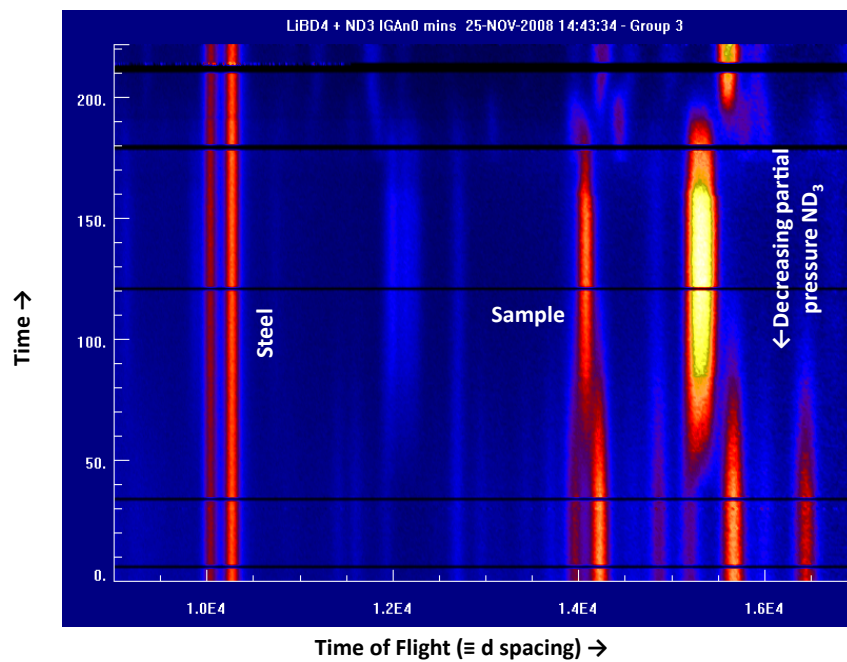
- Highly penetrating
bulk probe
complex SE



ISIS CRYSTALLOGRAPHY INSTRUMENTS

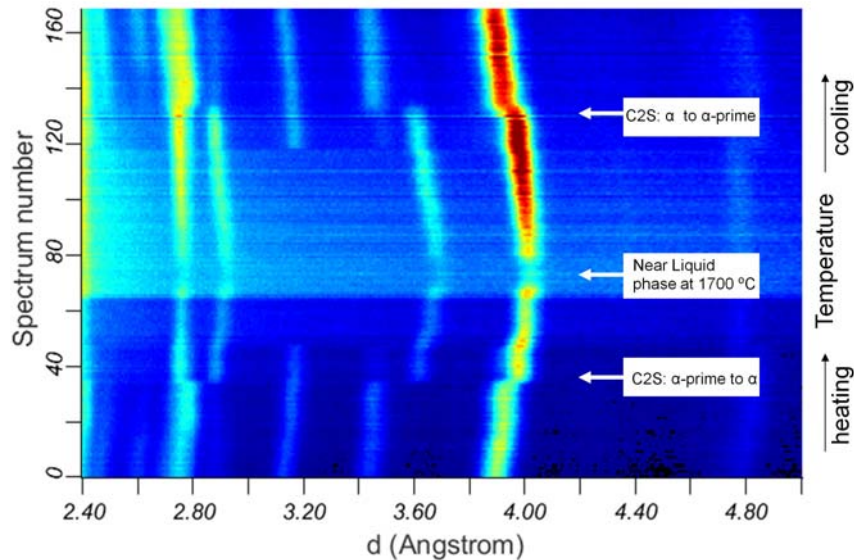


Determination of structure



Phase Transformations in steel

Phase formation at temperatures up to 1700°C (Tata steel).

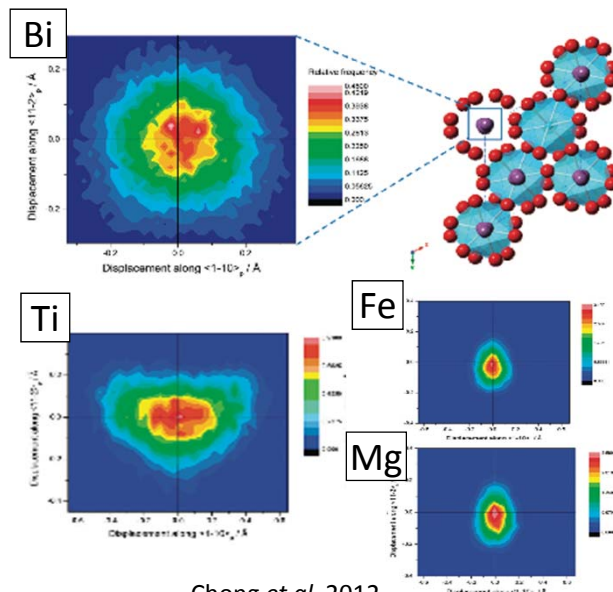


LOCAL STRUCTURES IN PEROVSKITES

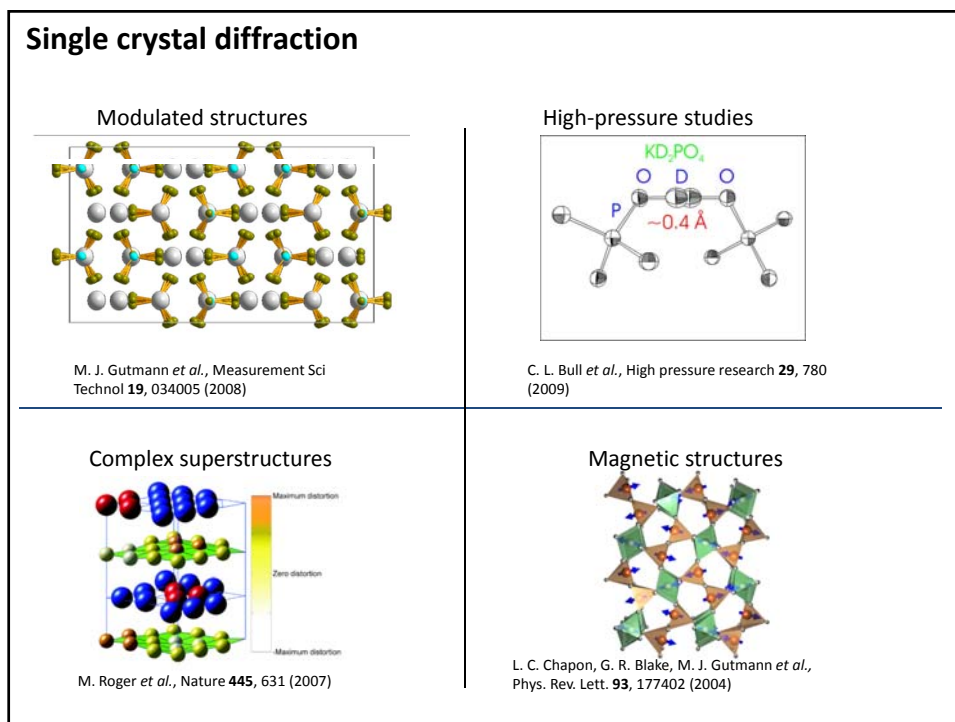
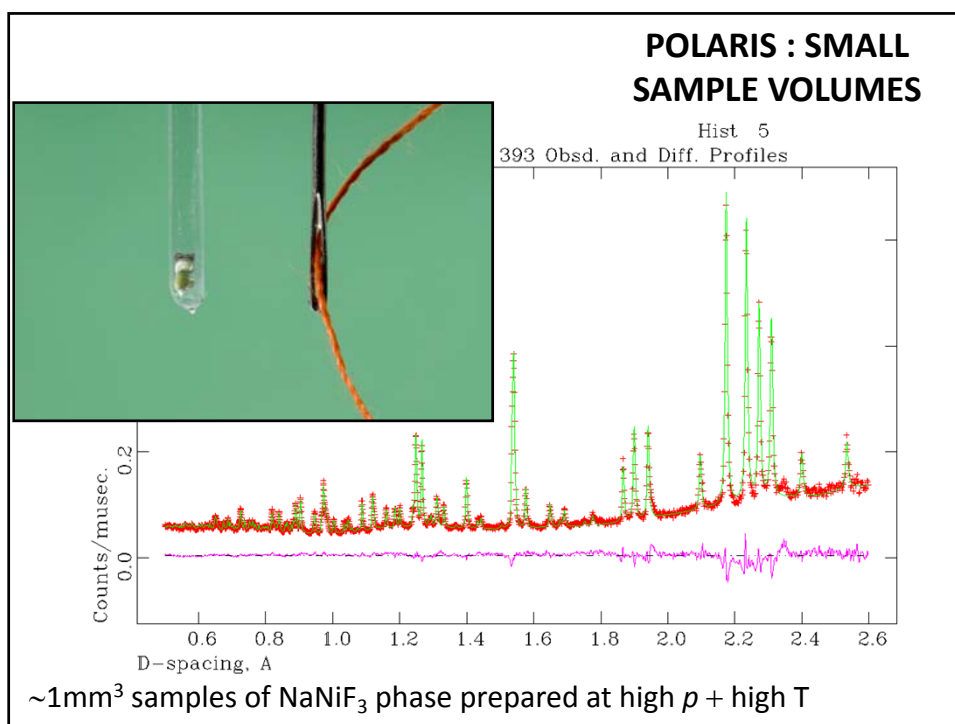
$\text{Bi}(\text{Ti}_{3/8}\text{Fe}_{2/8}\text{Mg}_{3/8})\text{O}_3$
possible lead-free
replacement for PZT
piezoelectric material.

RMC modelling of
provide insights
into several unexplained
aspects of earlier
crystallographic studies.

Locally monoclinic
clusters accounts for
micro-strain broadening
required for Rietveld
refinement using the
rhombohedral structural model.

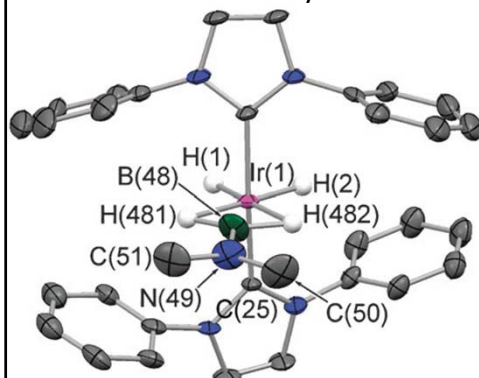


Chong *et al*, 2012

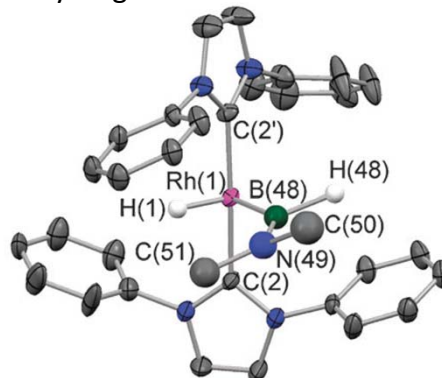


SXD : LOCATING HYDROGEN

Dimethylamine borane dehydrogenation.



18-electron aminoborane adduct



14-electron aminoboryl complex

SXD used to determine positions of H-atoms in metal complexes formed under catalytic conditions.

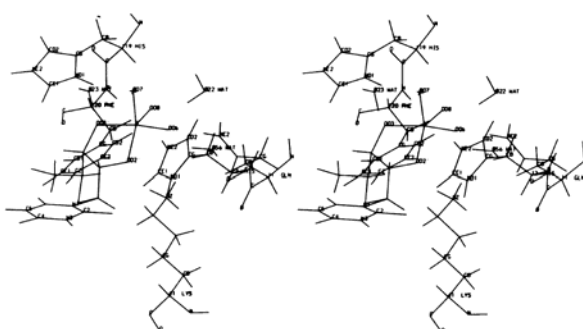
Tang *et al.* (2012)

Proc. Natl. Acad. Sci. USA
Vol. 80, pp. 3628–3631, June 1983
Biochemistry

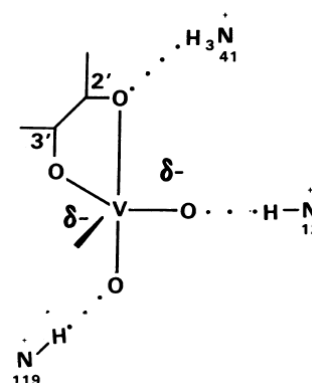
Active site of RNase: Neutron diffraction study of a complex with uridine vanadate, a transition-state analog

(catalysis/enzyme structure/refinement/hydrogen bonds)

ALEXANDER WLODAWER^{*†}, MARIA MILLER^{*†‡}, AND LENNART SJÖLIN[§]



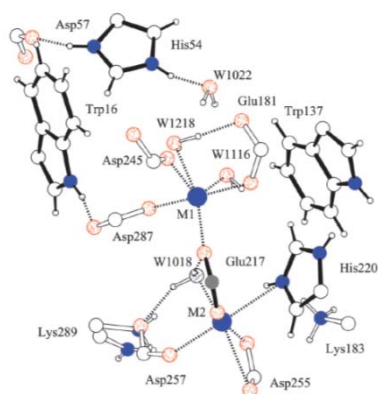
Determination of structure



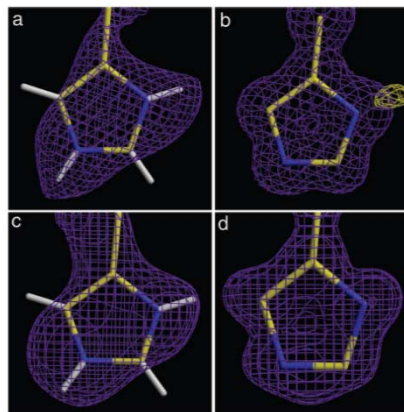
Observation and understanding of active-site

Locating active-site hydrogen atoms in D-xylose isomerase: Time-of-flight neutron diffraction

Amy K. Katz^{1,†}, Xinmin Li², H. L. Carrell³, B. Leif Hanson⁵, Paul Langan¹, Leighton Coates¹, Benno P. Schoenborn¹, Jenny P. Glusker¹, and Gerard J. Bunick^{1,††}



Crystal structure, active-site and hydrogen position determination

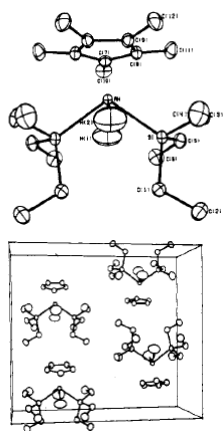


Nuclear density maps (a,c) and electron density maps (b, d) unambiguously identify deuterium atoms (white)

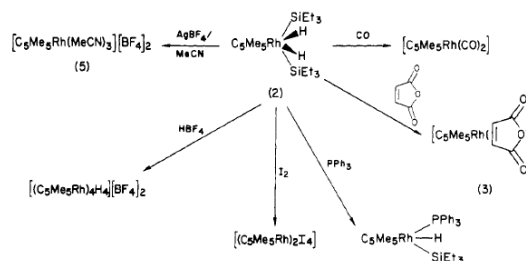
J. Am. Chem. Soc. **1984**, *106*, 5458–5463

Synthesis, X-ray, and Low-Temperature Neutron Diffraction Study of a Rhodium(V) Complex: Dihydridobis(triethylsilyl)-pentamethylcyclopentadienylrhodium

Maria-Jesus Fernandez,^{1a} Pamela M. Bailey,^{1a} Peter O. Bentz,^{1a} John S. Ricci,^{1b,c} Thomas F. Koetzle,^{*1b} and Peter M. Maitlis^{*1a}



Determination of structure



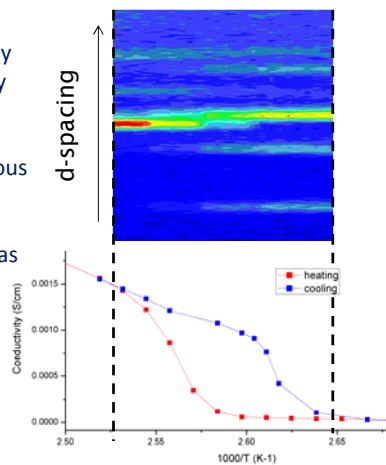
Elucidation of oxidation state (here Rh(V)) and information on mechanism

In-situ ionic conductivity analysis

- Simultaneous neutron diffraction and ionic conductivity measurements have been carried out at the ISIS facility
- Researchers from ISIS and Heriot Watt University have developed sample environment that allows simultaneous measurements of ionic mobility and structure
- Using the POLARIS neutron diffractometer, the team has been able to study lithium and proton conductivity in potential battery and proton conductor materials

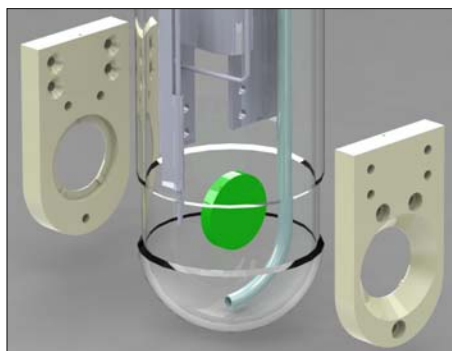


Ionic mobility and structure sample environment apparatus

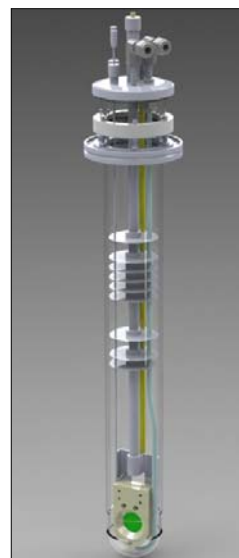


Typical ionic conductivity (lower) and neutron diffraction data collected simultaneously on the POLARIS diffractometer

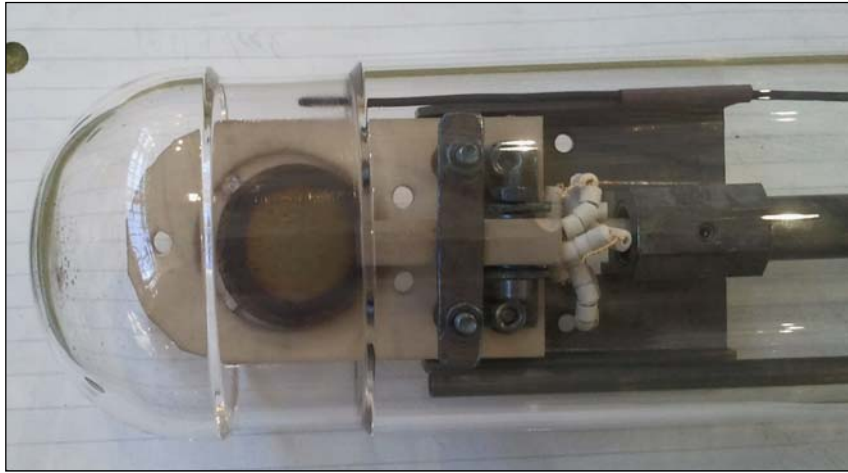
Hydrogen-ion conductivity



- Dense pellets painted with Pd electrodes
- Pellets held in closed end quartz tube
- Au contacts clamped to pellets
- Vials suspended in vacuum furnace
- Furnace mounted in POLARIS diffractometer

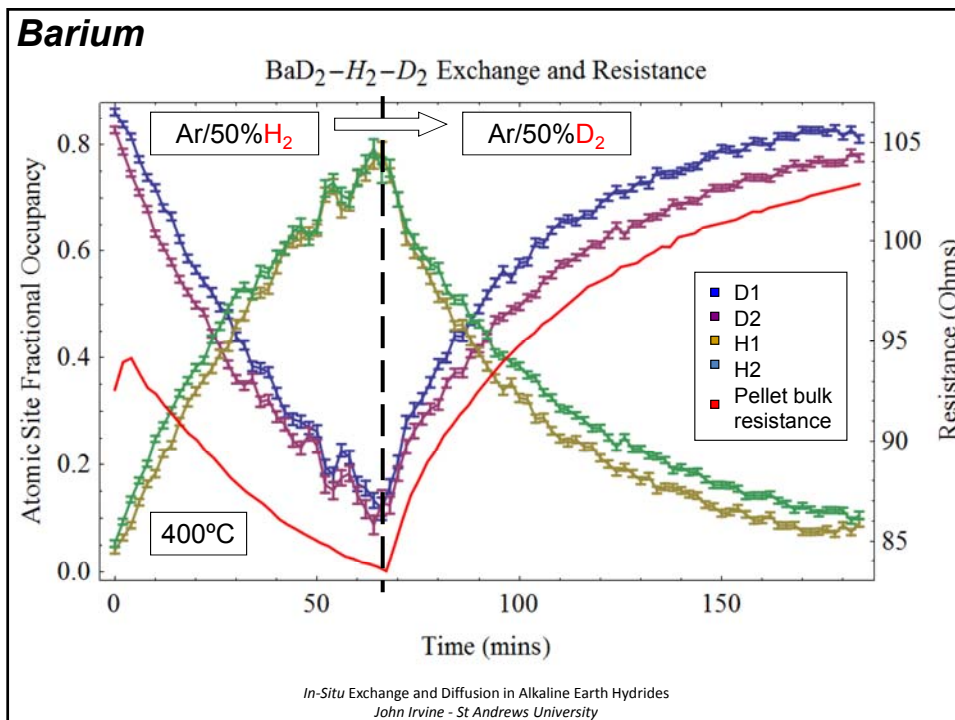


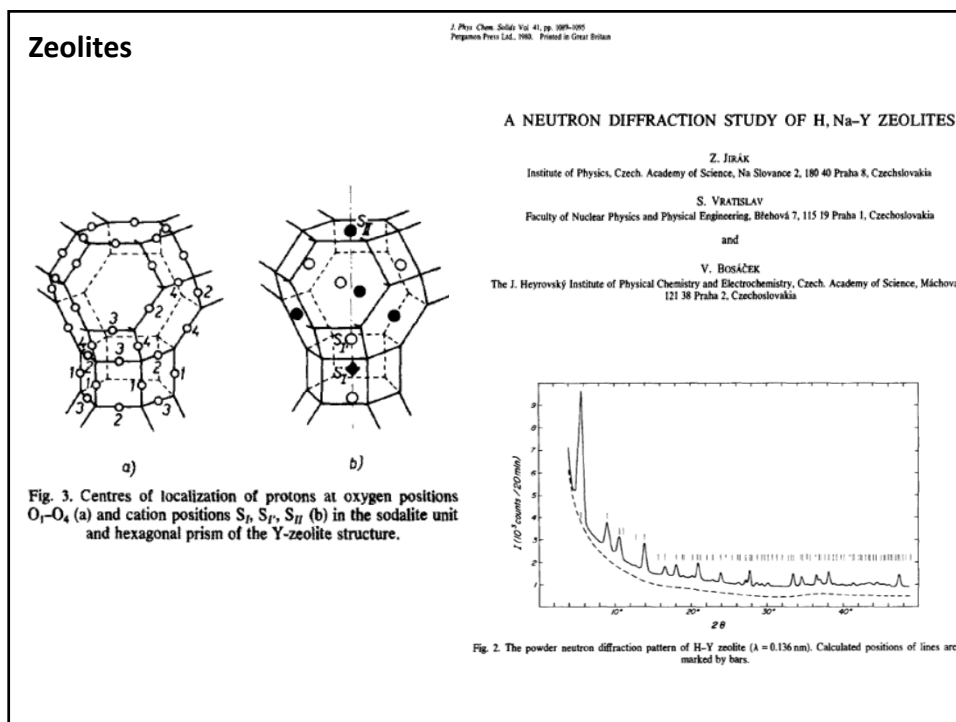
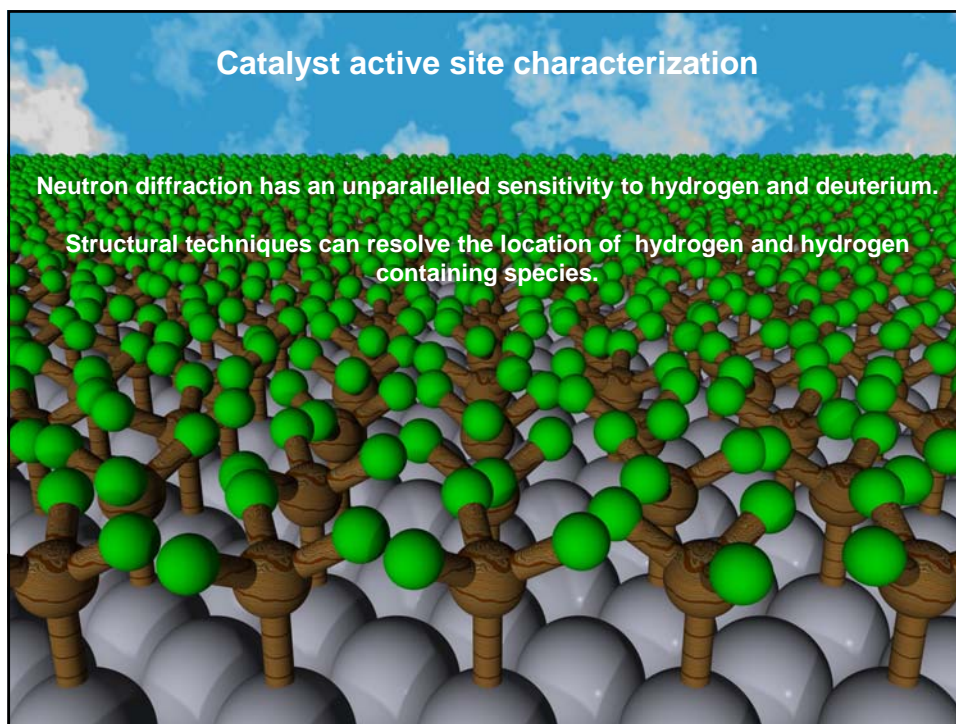
*In-Situ Exchange and Diffusion in Alkaline Earth Hydrides
John Irvine - St Andrews University*



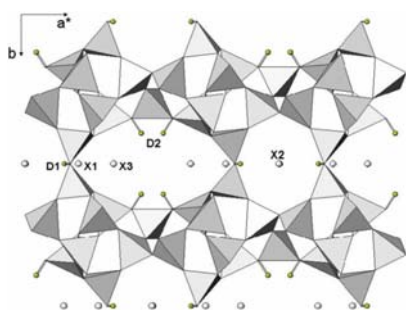
Sample set up – Barium pellet (post tests)

In-Situ Exchange and Diffusion in Alkaline Earth Hydrides
John Irvine - St Andrews University





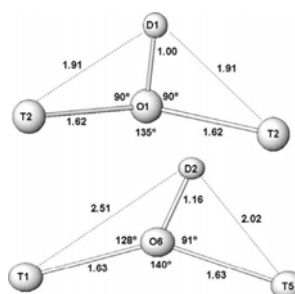
Active site position, geometry and proton mobility in acidic zeolites



Brønsted acid (D) and water molecule (X) sites.

Permitting the proton mobility and the activity of the catalyst to be tracked.

Neutron diffraction can identify the Brønsted acid (D) and water molecule (X) sites and the geometry of the active sites



Geometry of the active sites

Cheetham et al, *Microporous and Mesoporous Materials* **123** (2009) 15–20

J. CHEM. SOC., CHEM. COMMUN., 1984

1337

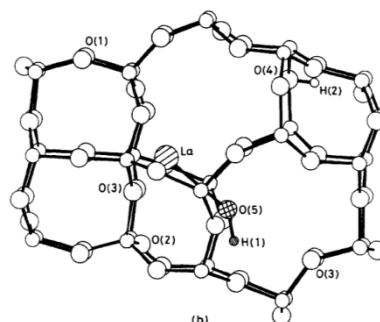
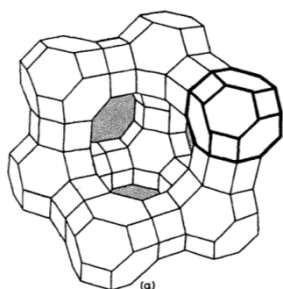
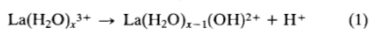
The Direct Observation of Cation Hydrolysis in Lanthanum Zeolite-Y by Neutron Diffraction

A. K. Cheetham,^a M. M. Eddy,^a and J. M. Thomas^b

^a University of Oxford, Chemical Crystallography Laboratory, 9, Parks Road, Oxford, OX1 3PD, U.K.

^b University of Cambridge, Department of Physical Chemistry, Lensfield Road, Cambridge, CB2 1EP, U.K.

Neutron diffraction studies on a partially dehydrated sample of lanthanum zeolite-reveal the locations of the hydrogen atoms, thus providing direct evidence for the cation hydrolysis and Brønsted acidity that account for the catalytic activity of this faujasite zeolite.



ILL

The Interaction of Sorbates with Acid Sites in Zeolite Catalysts: A Powder Neutron Diffraction and ^2H NMR Study of Benzene in H-SAPO-37

J. Am. Chem. Soc. **1995**, *117*, 4328–4332

L. M. Bull,[†] A. K. Cheetham,^{*,‡} B. M. Powell,[‡] J. A. Ripmeester,[‡] and C. I. Ratcliff[‡]

[†]Contribution from the Materials Department, University of California, Santa Barbara, California 93106, [‡]AECL Research, Chalk River Laboratories, Chalk River, Ontario, Canada, and [‡]Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, Canada

Received October 28, 1994[¶]

Neutron diffraction reveals that benzene is only located above the six-ring and in the plane of the 12-ring, and that protons are only found at the O(2) site

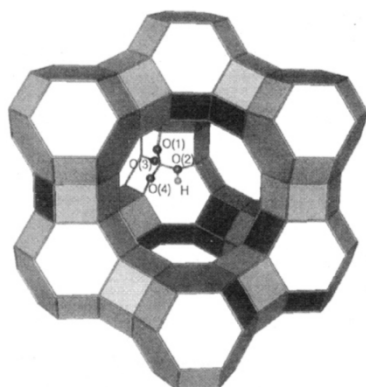


Figure 2. The faujasite structure showing the positions of the four oxygens sites that may be protonated and the observed location of the proton at O(2).

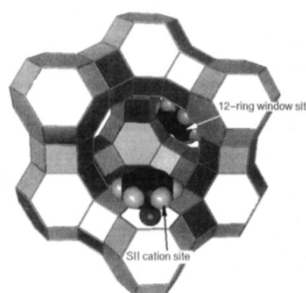
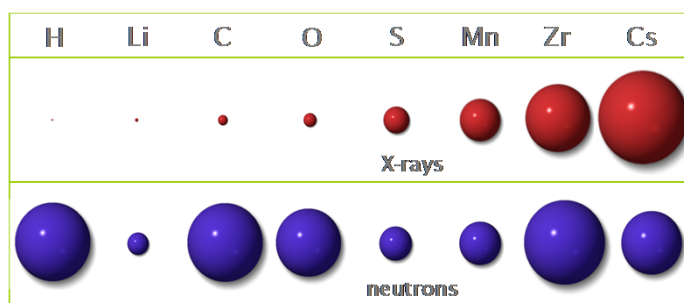


Figure 1. The adsorption sites for benzene in Na-Y as observed from neutron diffraction¹ above the Si cation and in the plane of the 12-ring window.

Neutron cross-section - isotopic dependence



Locate a very small amount of Ti or Fe in ZSM-5

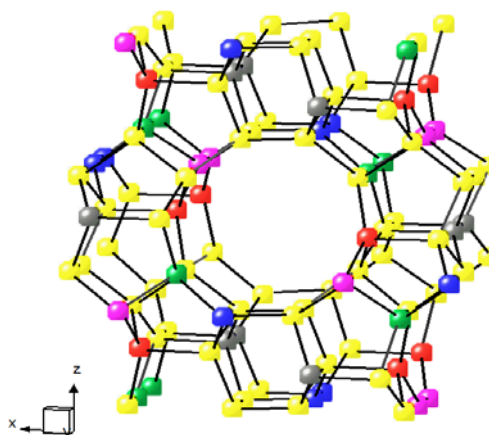
X-rays

Atomic scattering lengths based on atomic number - Ti is fairly similar to Si

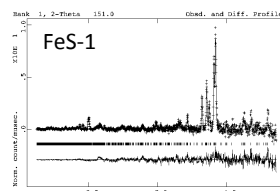
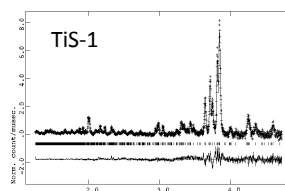
Neutrons

scattering cross-section is a complex function of nuclear properties

Ti: -3.4 fm Si: +4.1 fm

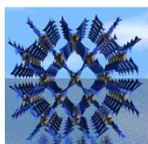


T3-red(4% Ti)
T7-blue (4% Ti)
T8-green (12% Ti)
T10-gray (5% Ti)
T12-magenta (6% Ti)



Collective neutron (and X-ray) processes

- UK researchers have created a low cost, new material that can capture harmful gases
- The porous material, NOTT-300, has the potential to reduce fossil fuel emissions through cheaper and more efficient capture of polluting gases such as carbon dioxide (CO₂) and sulfur dioxide (SO₂)
- TOSCA and WISH at ISIS used to determine crystal structure and locate CO₂ and SO₂ within the pores

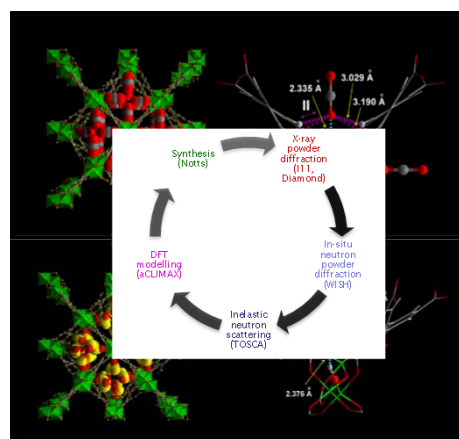


The crystal structure of NOTT-300



Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host

Sihai Yang, Bill David, Timmy Ramirez-Cuesta *et al* 4 887-894 (2012)



View of CO₂ (top) and SO₂ (bottom) sited in the pore of NOTT-300(Al) as determined by PXRD (I11 Diamond), inelastic neutron scattering (TOSCA, ISIS) and DFT analysis (aClimax, ISIS).

Hydrogen Adsorption in a Highly Stable Porous Rare-Earth Metal-Organic Framework: Sorption Properties and Neutron Diffraction Studies

Junhua Luo,^{*,†} Hongwu Xu,^{†,‡} Yun Liu,^{§,¶} Yusheng Zhao,^{*,†} Luke L. Daemen,[†] Craig Brown,[§] Tatiana V. Timofeeva,[#] Shengqian Ma,[‡] and Hong-Cai Zhou[‡]

LANSCE-12 and EES-6, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, NIST Center for Neutron Research, Gaithersburg, Maryland 20899, Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, Department of Natural Sciences, New Mexico Highlands University, Las Vegas, New Mexico 87701, and Department of Chemistry & Biochemistry, Miami University, Oxford, Ohio 45056

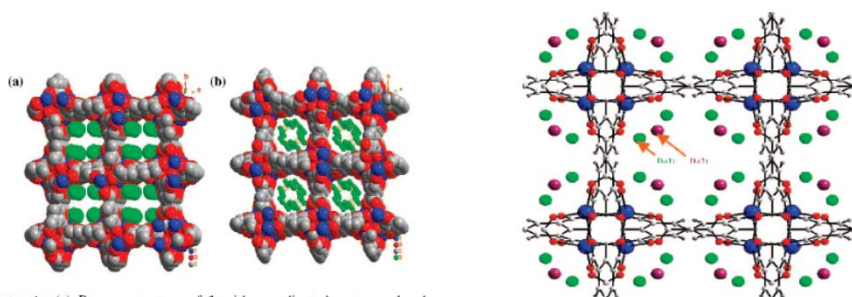


Figure 1. (a) Porous structure of **1** with coordinated water molecules (green) inside, and (b) hydrogen clusters formed inside **1a**.

Figure 3. First and second H₂ adsorption sites in **1a**.

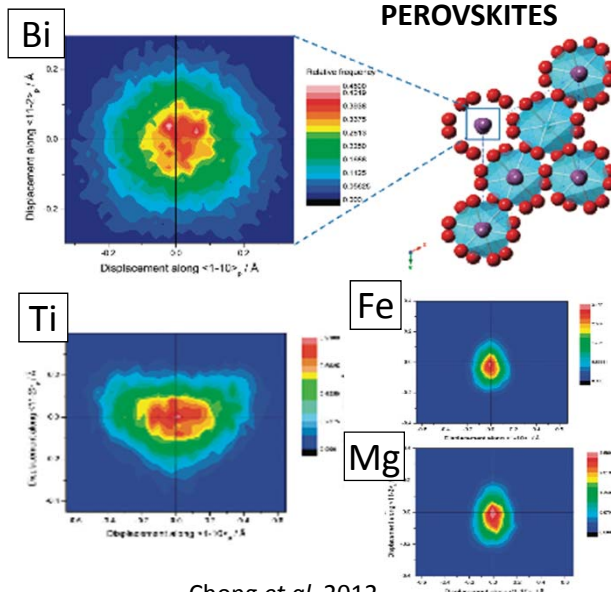
Local Structure

Bi(Ti_{3/8}Fe_{2/8}Mg_{3/8})O₃
possible lead-free
replacement for PZT
piezoelectric material.

RMC modelling of
provide insights
into several unexplained
aspects of earlier
crystallographic studies.

Locally monoclinic
clusters accounts for
micro-strain broadening
required for Rietveld
refinement using the
rhombohedral structural model.

GEM : LOCAL STRUCTURES IN PEROVSKITES



Chong *et al*, 2012

Neutron Diffraction Investigation of Ordered Oxygen Vacancies in the Defect Pyrochlores, $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ and $\text{PbTiNb}_2\text{O}_{6.5}$

Electrocatalysts for O_2 reduction and evolution

R. A. BEYERLEIN,¹ H. S. HOROWITZ, J. M. LONGO,
AND M. E. LEONOWICZ

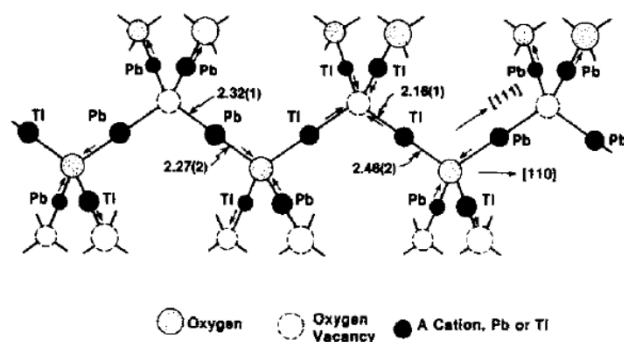
*Exxon Research and Engineering Co., Corporate Research Labs,
Annandale, New Jersey 08801*

AND J. D. JORGENSEN² AND F. J. ROTELLA²

Argonne National Laboratory, Argonne, Illinois 60439

Determine
oxygen vacancy
ordering

Origin of catalytic
behaviour



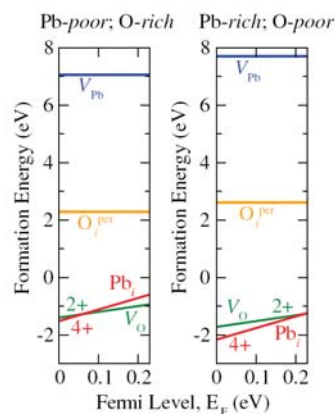
JOURNAL OF SOLID STATE CHEMISTRY 51, 253-265 (1984)

Mystery of car battery material solved

- researchers from Oxford University, the University of Bath, Trinity College Dublin and ISIS have helped to reveal what makes lead oxide such a powerful electrical conductor
- Using theoretical calculations, the group were able to show that oxygen vacancies can form very easily in lead oxide and that oxygen vacancies give metallic behaviour by freeing up electrons to carry electrical current
- Neutron diffraction experiments on Polaris confirmed that commercial lead oxide powder is oxygen-deficient by showing that oxygen sites were 1.6% vacant



A lead-acid battery



Formation energies for intrinsic defects under O-rich (left) and O-poor (right) conditions



Nature of the Band Gap and Origin of the Conductivity of PbO_2 Revealed by Theory and Experiment

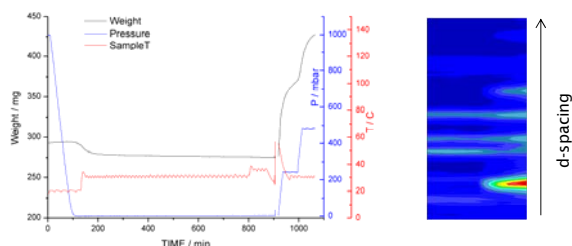
David O. Scanlon, Bill David, Martin Owen Jones *et al.* 107 246402 (2011)

In-situ gravimetric and structural characterisation

- Scientists from the University of Oxford and ISIS have developed sample environment to simultaneously study the structure and thermogravimetric properties of hydrogen storage materials – the intelligent gravimetric analysis apparatus for neutrons, IGAⁿ
- The apparatus allows controlled gas, temperature (to 500°C) and pressure (20bar) environments to be used to investigate gas uptake, desorption and cycling in hydrogen storage materials on the HRPD, WISH and GEM neutron diffractometers at ISIS

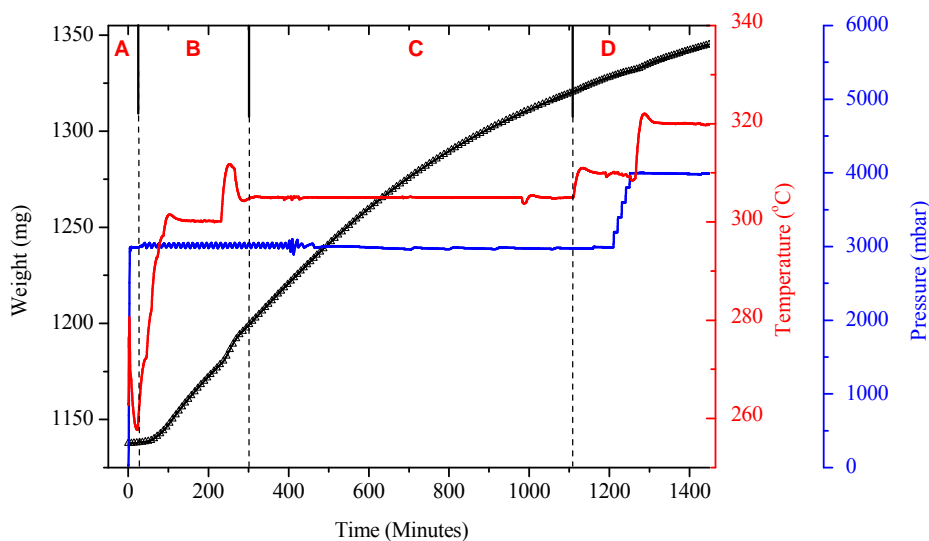


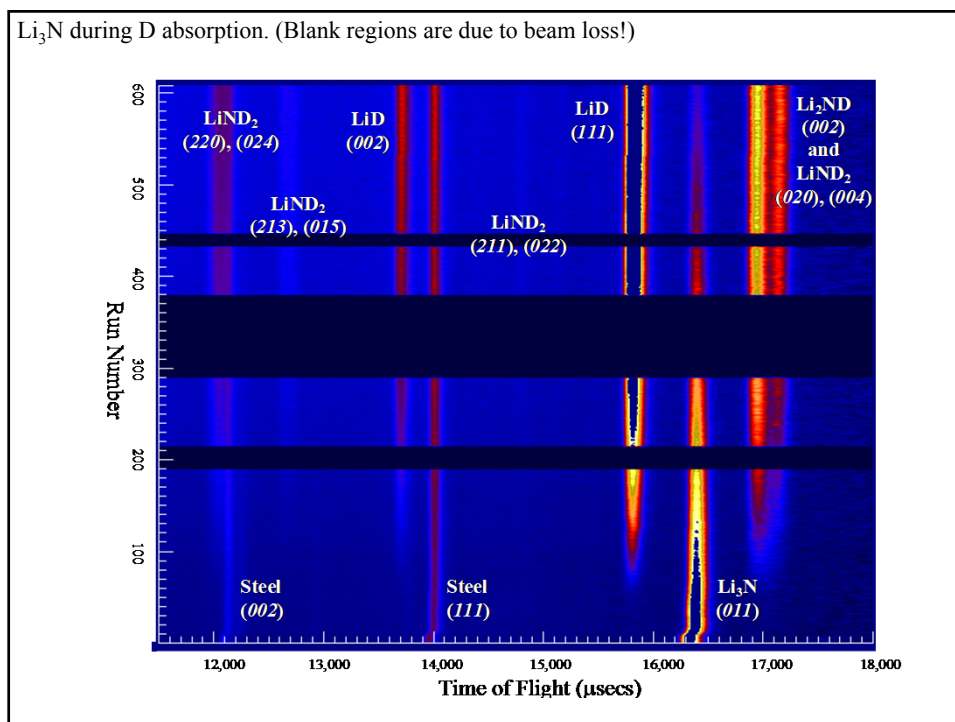
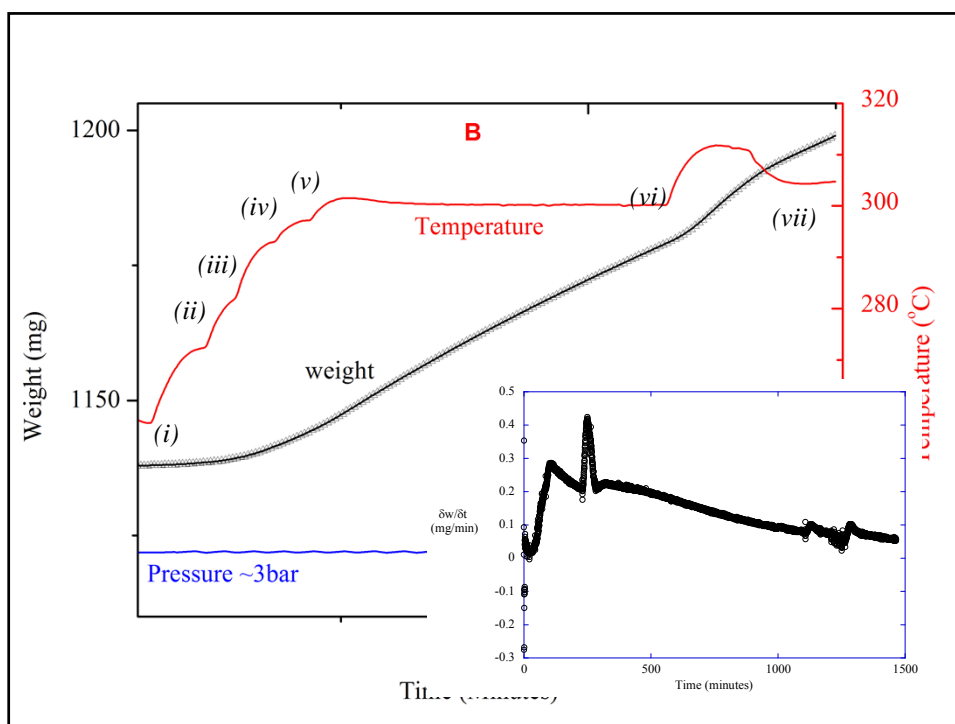
The IGAⁿ apparatus

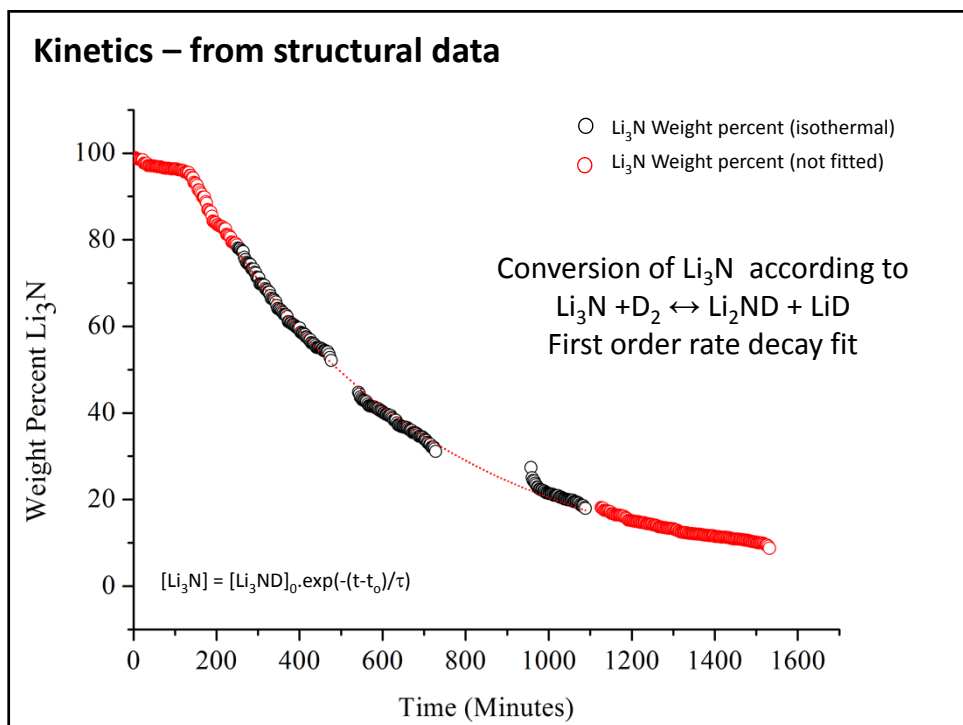
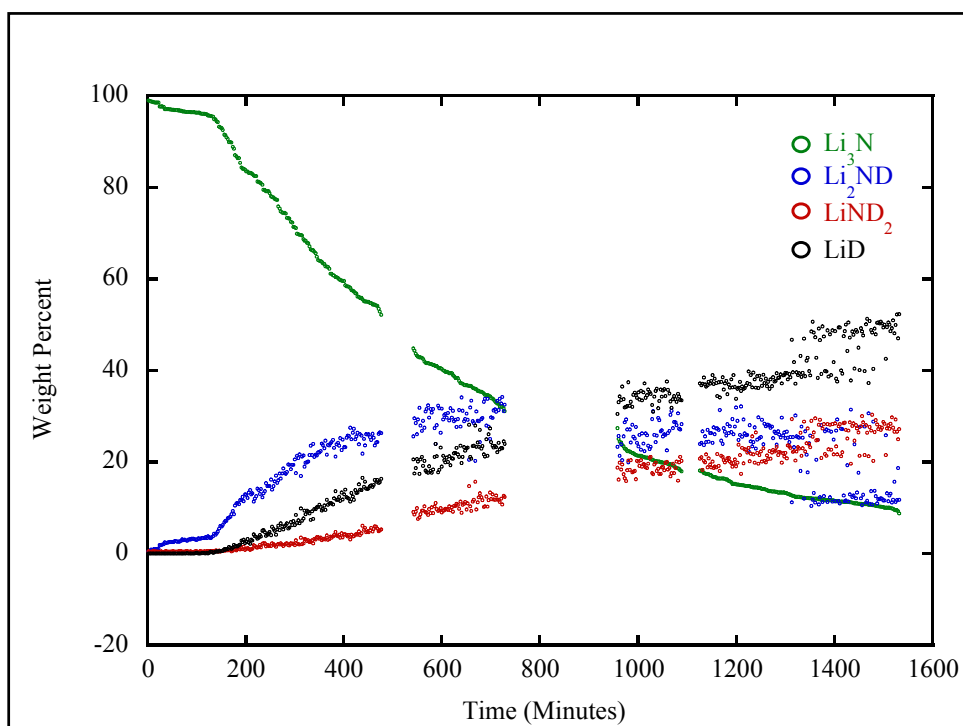


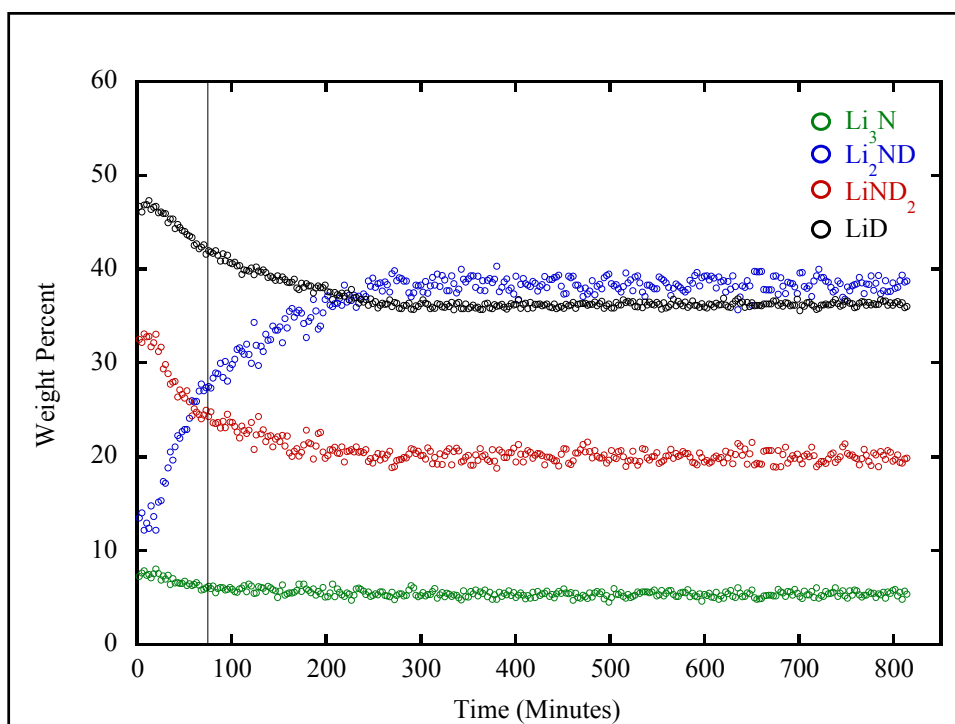
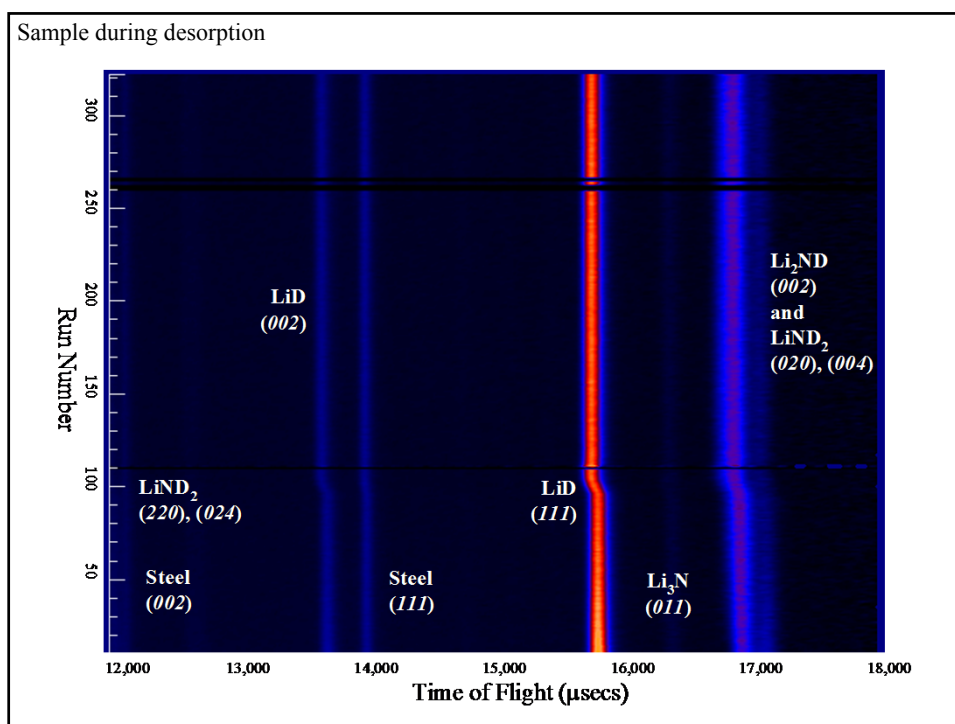
Sample thermogravimetric (left) and diffraction (right) data collected on the GEM neutron diffractometer using the IGAⁿ

Absorption



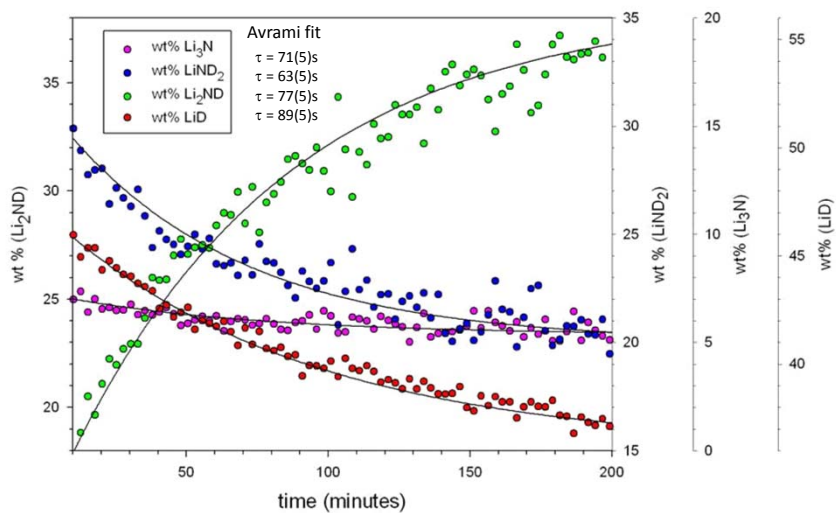




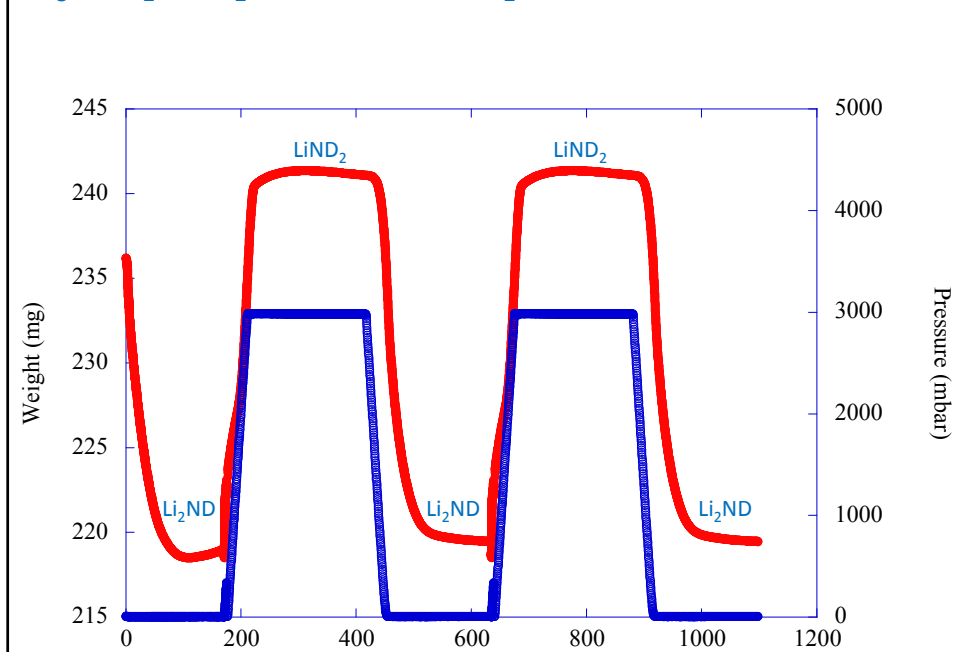


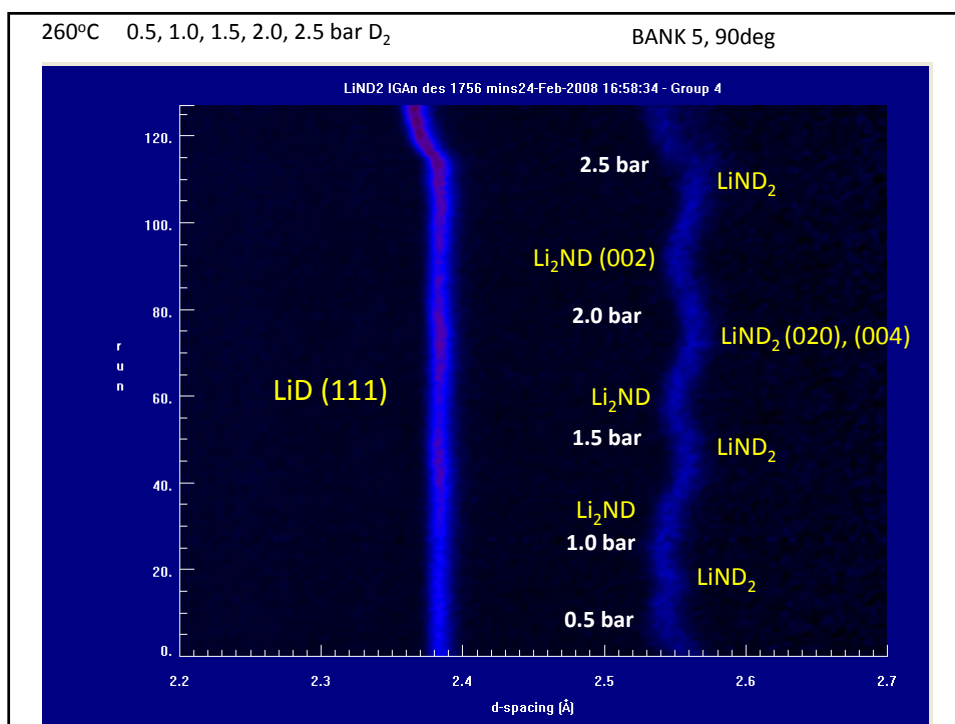
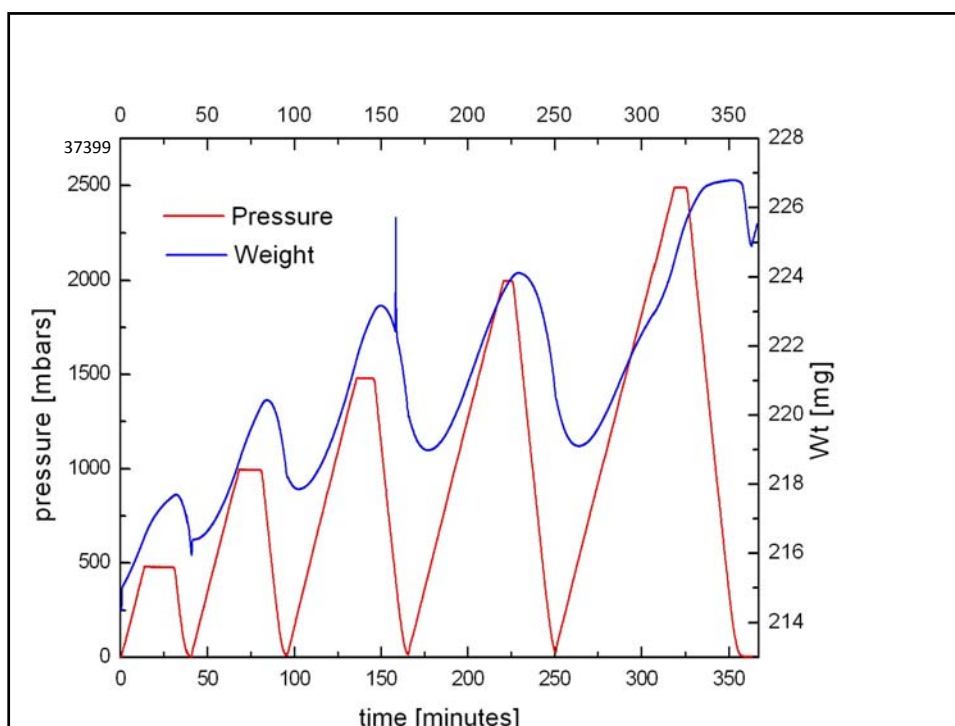
Kinetics – from structural data

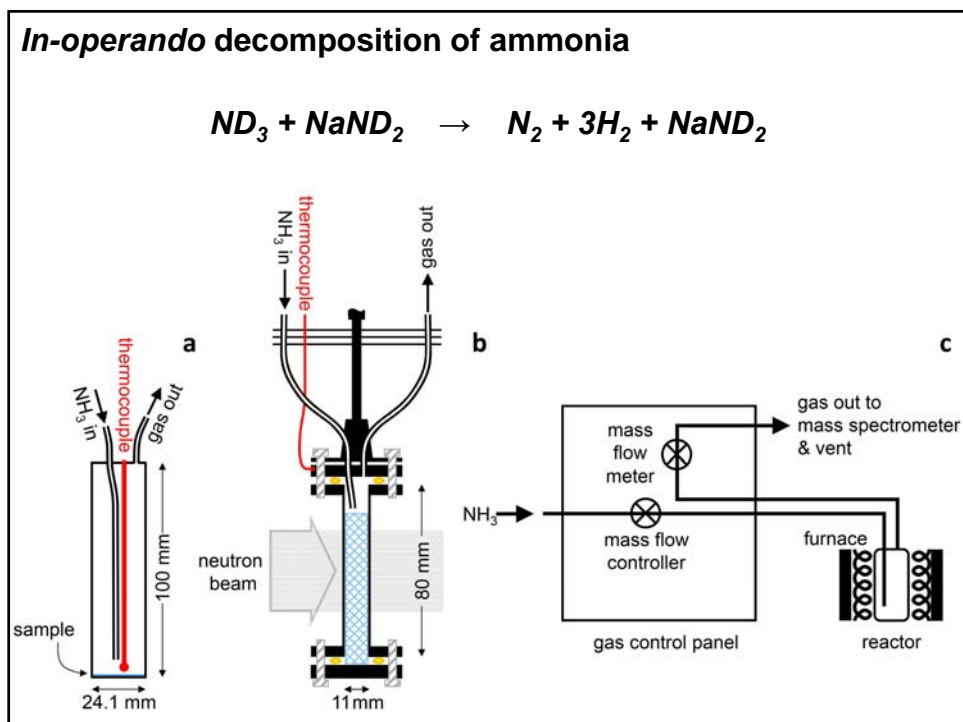
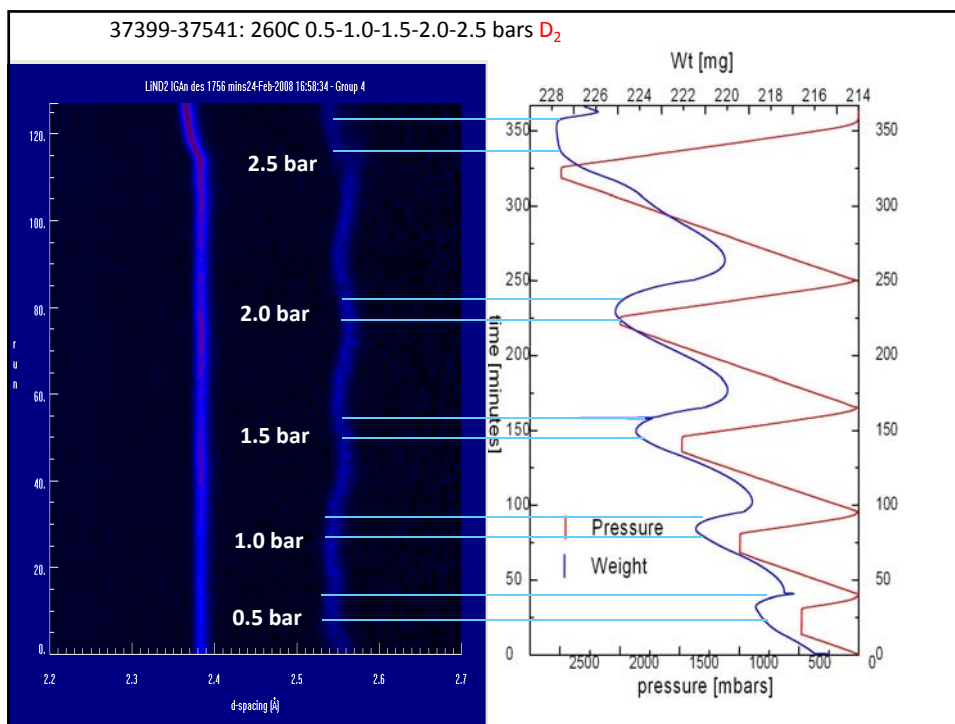
Conversion of Li_3N according to
 $\text{Li}_3\text{N} + \text{D}_2 \leftrightarrow \text{Li}_2\text{ND} + \text{LiD} \leftrightarrow \text{LiND}_2 + 2\text{LiD}$



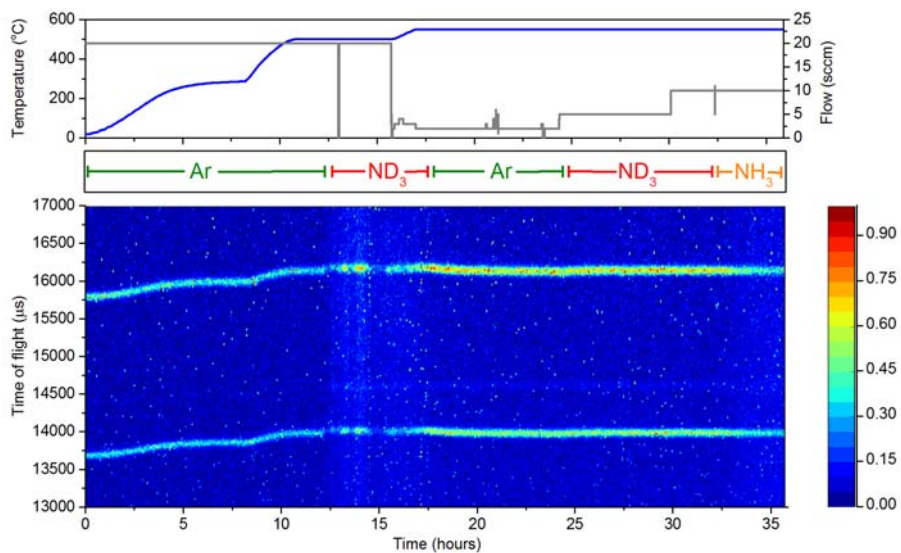
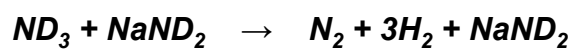
$\text{Li}_3\text{N} + \text{D}_2 \leftrightarrow \text{Li}_2\text{ND} + \text{LiD} \leftrightarrow \text{LiND}_2 + 2\text{LiD}$



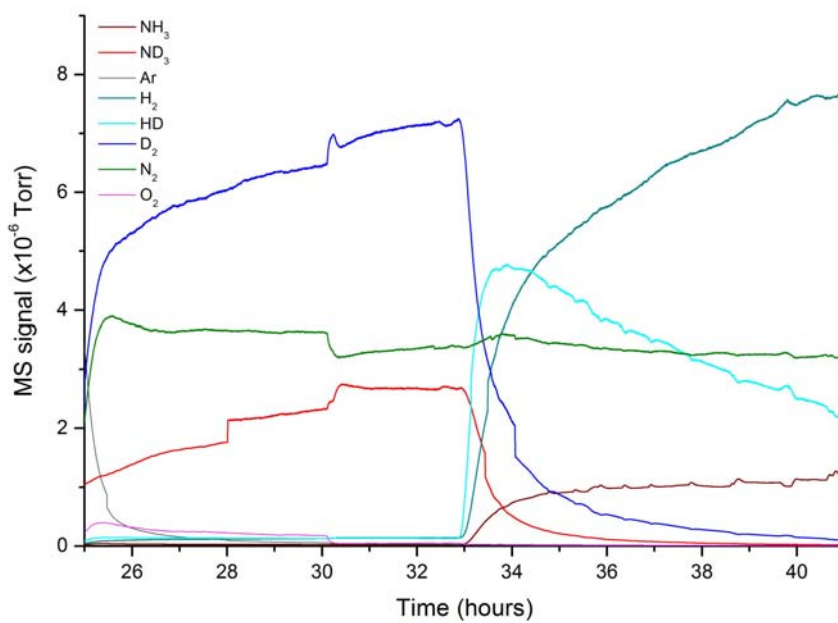




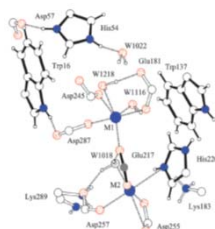
In-operando decomposition of ammonia



In-operando - kinetics and mechanism



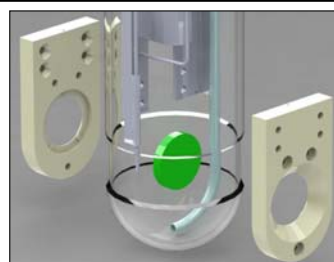
Summary



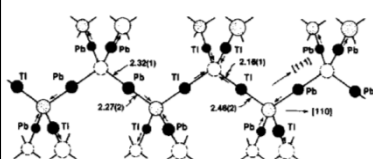
Crystal structure,
active-site, mechanism,
activity and more



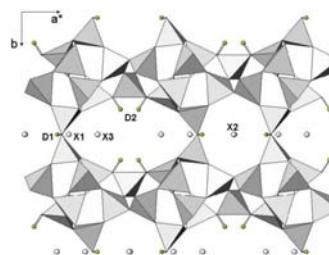
Structure, kinetics and
thermodynamics of
processes.



Conductivity and structure of
materials, in harsh
environments

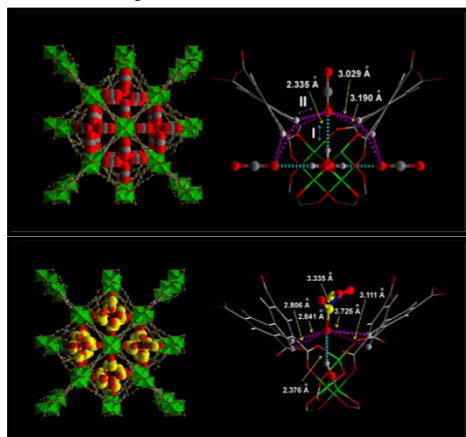


Defect structure and origin of
catalytic activity



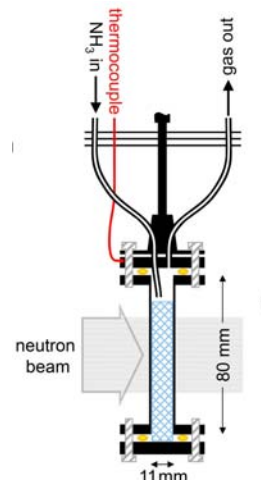
Zeolite crystal structure,
active-site of powders

Summary



Technique combination

Provides fundamental understanding
of how and why catalysts work



Highly penetrating neutron allows In-situ and in-operando
studies at technologically significant temperatures, pressures and
environments

Acknowledgements

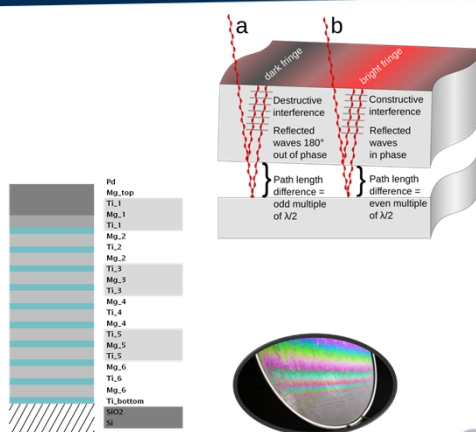
Bill David	(STFC / ISIS / Oxford)
Josh Makepeace, Hazel Hunter, Thomas Wood	(STFC)
Sam Callear	(STFC / ISIS)
Timmy Ramirez Cuesta	(STFC / ISIS)
Marco Sommariva	(STFC / ISIS)
Keith Refson	(STFC / ISIS)
Matthias Gutmann	(STFC / ISIS)
Steve Hull	(STFC / ISIS)
Felix Fernandez-Alonso	(STFC / ISIS)
John Irvine, George Carins	(St Andrews)



Neutron Reflectivity for Catalysis

Maximilian Skoda

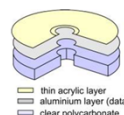
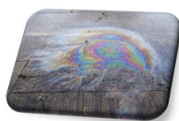
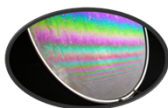
What is reflectometry?



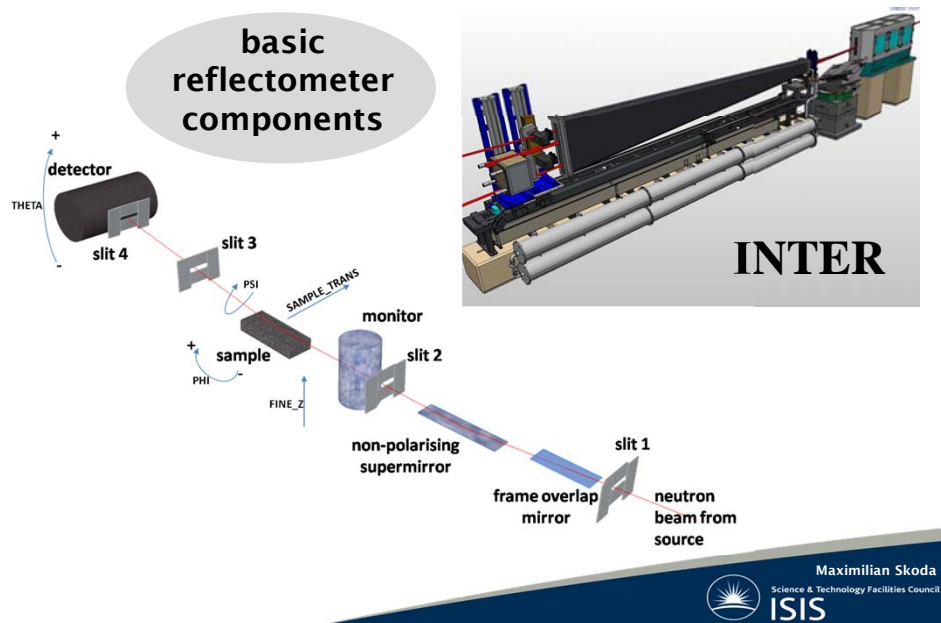
In a nutshell...

- (light) waves traverse a layered structure containing layers of a certain thickness
- for one given wavelength (of radiation), there are bright regions arising from constructive interference and dark regions, where waves cancel each other out
- angular distribution and spacing between dark and bright regions allows the calculation of the layer thickness

measure
layered
structures



What is a Reflectometer?



Reflectometers



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- SURF
- CRISP
- INTER
- OffSpec
- PolRef

- D17
- FIGARO
- SuperADAM



HIGH FLUX ISOTOPE REACTOR
SPALLATION NEUTRON SOURCE

- Liquids
- MR



- Platypus

NIST, HZB, FRM2, ...

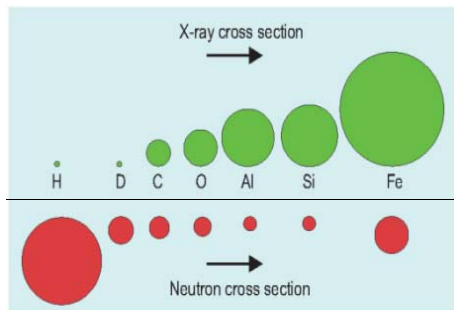
Lots more...

http://material.fysik.uu.se/Group_members/adrian/reflect.htm



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Neutron Scattering Lengths



This property can be expressed as 'refractive index':

$$n = \frac{k_1}{k_0} = 1 - \alpha - i\beta, \quad \alpha = \frac{N\lambda^2 Z_{re}}{2\pi}, \quad \beta = \frac{\lambda\mu}{4\pi}$$

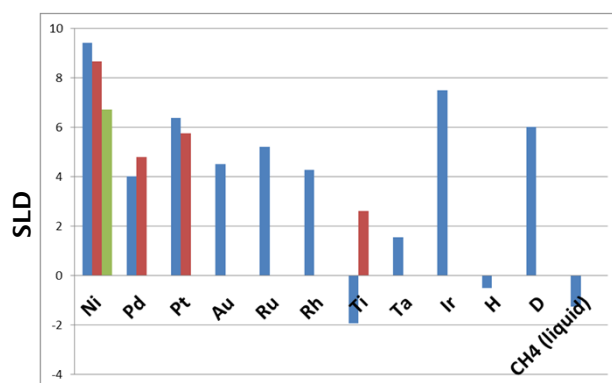
} **X-rays**

$$n = \frac{k_1}{k_0} = 1 - \lambda^2 A - i\lambda B, \quad A = \frac{Nb}{2\pi}, \quad B = \frac{N(\sigma_a + \sigma_i)}{4\pi}$$

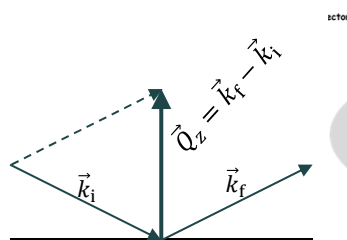
} **neutrons**

Fig. 2. Neutron and x-ray scattering cross-sections compared. Note that neutrons penetrate through Al much better than x rays do, yet are strongly scattered by hydrogen.

Relevant Materials

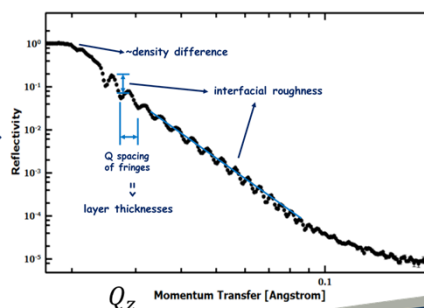


How do we measure?



a 'typical' measurement

$$Q_z = \frac{4\pi}{\lambda} \sin \theta$$



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http://www.ncnr.nist.gov/instruments/magik/calculators/calcR_wf.html

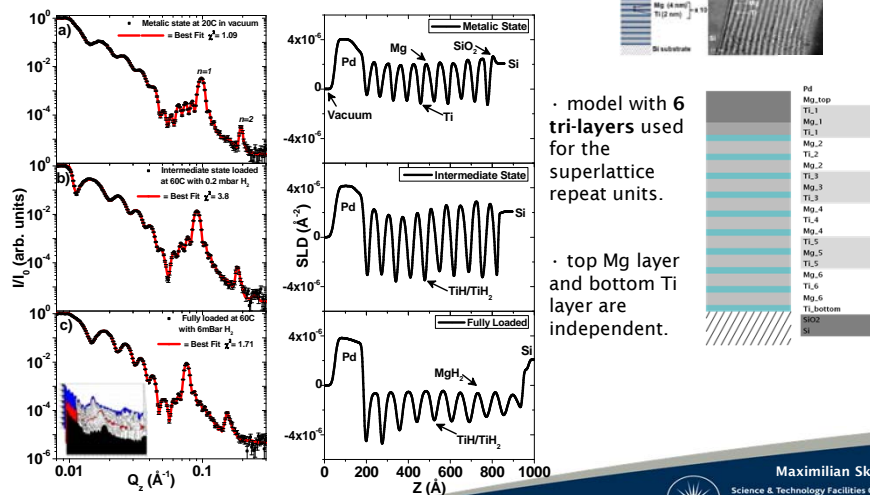


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Example 1

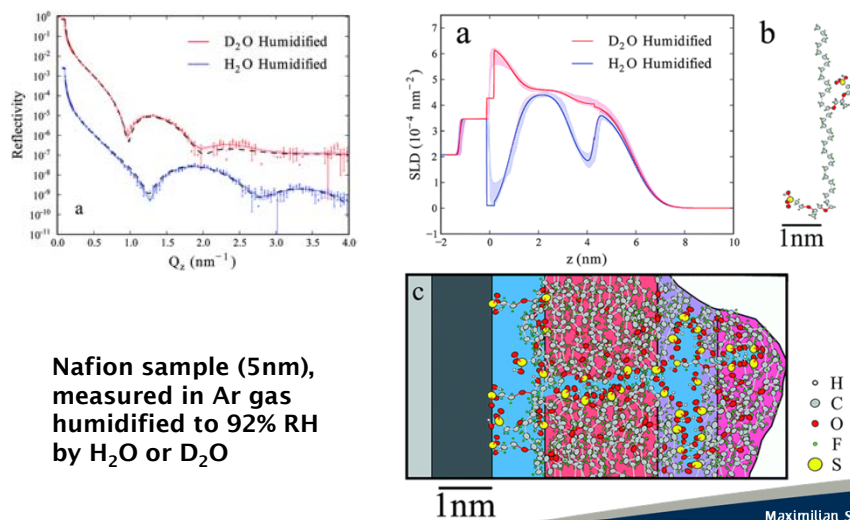
Hydrogen loading in Mg/Ti 10 bilayer sample



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Example 2

Nafion® hydration and lamellar phase segregation



DeCaluwe et al. - DOI: 10.1039/C4SM00850B (Paper) Soft Matter, 2014, 10, 5763-5776



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Practicalities

- **Sample size**
 - the bigger the better (obviously)
 - $1 \times 1 \text{ cm}^2$ just feasible
- **Uniformity**
 - in thickness
 - in roughness
- **Film thickness**
 - 1 nm to 100s of nm
 - consider resolution
- **Sample environment**
 - common: ambient to 200°C OR cryogenic
 - solid-air (vacuum), solid-liquid, air-liquid, liquid-liquid (more tricky)
 - controlled gas, humidity etc
 - maximum pressure limited by entry windows
- **Assess feasibility by modelling prior to proposal and discuss with instrument scientist**



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Small-Angle Neutron Scattering at ISIS

Sarah Rogers

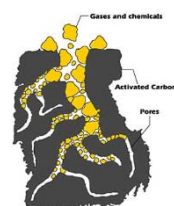
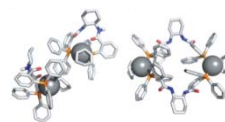
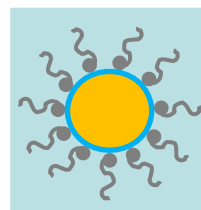
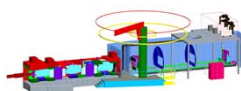


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Overview:

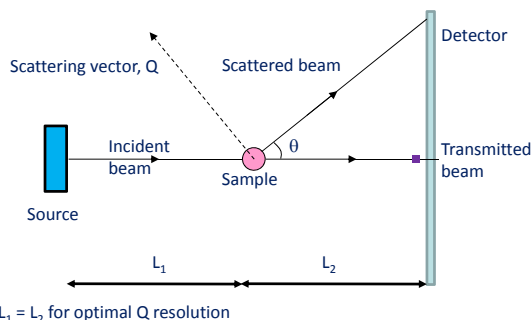
- What is SANS
- Why use neutrons and ISIS?
- Sample Environment
- Science examples:
 - Engineering – metal alloys at elevated temperatures
 - Chiral catalysts based on the Trost ligand
 - Nanoparticles – CaCO_3
 - Time-resolved measurements – polymer crystallization
 - Porosity in activated carbons
- Summary
- Acknowledgements





SANS Transmission Geometry

Materials studied include surfactants, polymers, liquid crystals, nanoparticles, porous materials, lipids and fibres



Lengthscales, 10s to 100s nm, are explored in reciprocal space by detecting the number of scattered neutrons as a function of Q . Q is inversely proportional to distance, D , by the approximation:

$$Q = \frac{2\pi}{D}$$

Units are either \AA^{-1} or nm^{-1} i.e. the smaller the value of Q the bigger the object

Q is also related to wavelength and the scattering angle by:

$$Q = \frac{4\pi \sin\left(\frac{\theta}{2}\right)}{\lambda}$$

Q (size) range is varied by altering θ or λ .

$L_1 = L_2$ for optimal Q resolution

Allows the bulk properties of a material:

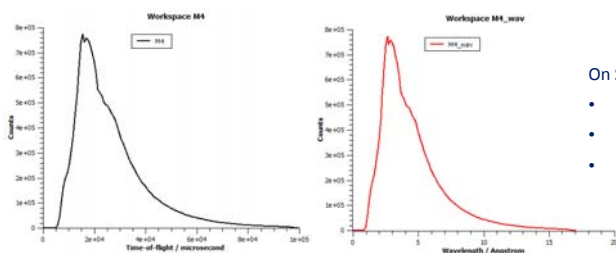
- Size
- Polydispersity
- Shape/Structure
- Particle Interaction

$$I(Q) = (\rho_p - \rho_m)^2 N_p V_p^2 P(Q) S(Q)$$



Why Use Neutrons and ISIS?

- High penetrating power that allows the structure in the bulk of a material to be probed
- They are non-destructive and therefore delicate samples can be studied
- They do not significantly perturb the system under study and so the results from experiments can be clearly interpreted
- The neutron has a magnetic moment which allows the study of magnetic structures
- Neutrons scatter from materials by interacting with the nucleus of an atom (rather than the electron as with X-rays)...this is very useful!
- ISIS is a spallation source and operates in time-of-flight mode. This means that a large simultaneous Q -range is achievable (without moving detectors) as white beam of delivers a broad wavelength range of neutrons. This is very useful for time-resolved measurements



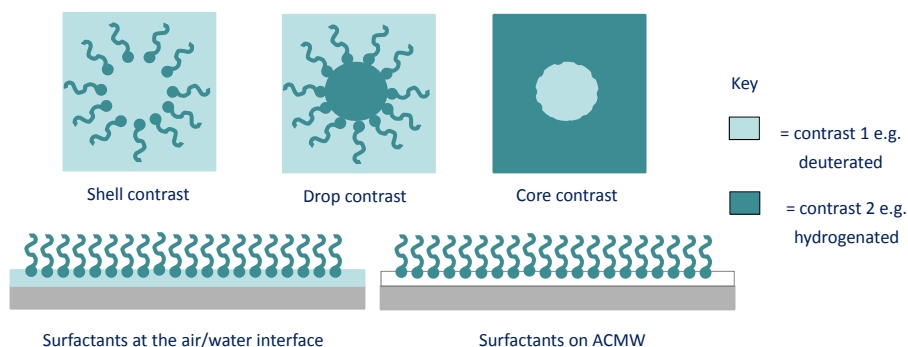
On Sans2d:

- Wavelength range = $1.75 - 17.5 \text{ \AA}$
- Q -range = $0.001 - 3 \text{ \AA}^{-1}$
- Size range $\approx 3 - 6000 \text{ \AA} = 0.3 - 600 \text{ nm}$



Unique insights from Contrast Variation

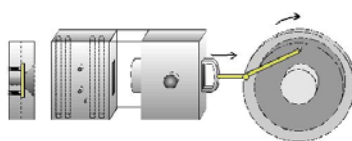
- The neutron scattering power of atoms varies, randomly, from element to element and isotope to isotope
- Light atoms e.g. hydrogen, can be distinguished from heavier atoms, such as metals
- Also isotopes of the same element can have substantially different scattering powers: by altering the isotopic content of a sample (switching the solvent H_2O to D_2O , for example) or by using isotopic substitution within a molecule specific area of interest within the system under investigation can have their scattering power enhanced without changing the chemical properties of the sample



The Sample Environment

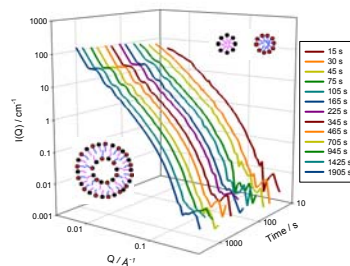
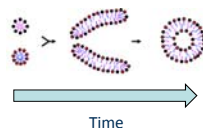
Extensive available sample environments allow a broad range of science to be studied via SANS at ISIS

- Sample changer
- Tumblers
- Rheometer
- Pressure cells
- T-jump cell
- Furnace
- Cryostat
- Magnets
- *In situ* DLS and UV-vis
- Stopped-flow (see figure)



- Synchronized data collection
- event mode allows data to be time sliced after the experiment

Micelles \rightarrow Bilayer disks \rightarrow Vesicle



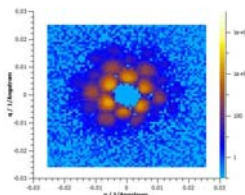
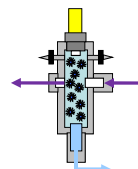
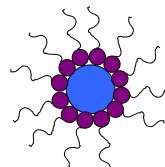


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The Science

- **Surfactant chemists**
 - Structure of particle stabilized foams
 - Micellization in $sc\text{-CO}_2$ using ISIS p-cell
 - Templating of nanoparticles with micelles and microemulsions using stopped-flow
- **Industry**
 - Fuel additives
 - *In-situ* rheology of industrially relevant polymer systems
- **Biologists**
 - Drug encapsulation and delivery systems
 - Interaction of nanoparticles with lung surfactant
- **Engineers**
 - Creep cavitation in stainless steel welds
- **Polymer scientists**
 - Interfacial structure of solar cell polymers at air-solid interfaced via GISANS
 - Polymer structure in solution for templating
- **Physicists**
 - Flux line lattice measurements in high T_c superconductors with 17T magnet

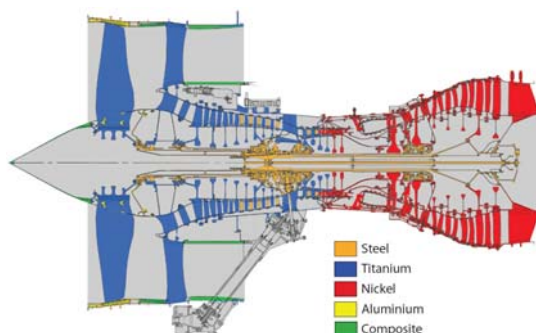


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Engineering

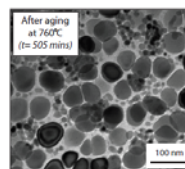
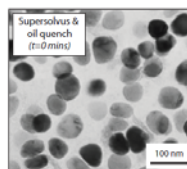
Collaboration between [Dr H. Stone \(University of Cambridge\)](#) and the [ISIS SANS team](#) characterizing nickel-base superalloys as used in aero-engine turbine discs. These materials exhibit both exceptional mechanical properties and superior corrosion resistance at high temperatures. The PhD student working on this study is sponsored by Rolls-Royce.





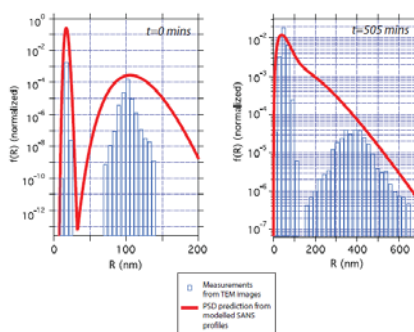
Why SANS?

- Processes must be studied *in-situ*
- Large penetrating power of neutron allows structures buried deep in materials to be studied
- Lengthscales being probed are ideal for SANS



The Experiment and Results

- Ni alloy composed of γ' $\text{Ni}_3(\text{Al, Ti, Ta})$ precipitates
- *In-situ* heating of sample using a furnace is used to mimic heat treatments during manufacturing process
- SANS results validate computer models of precipitates
- Understanding of these important alloys is improved

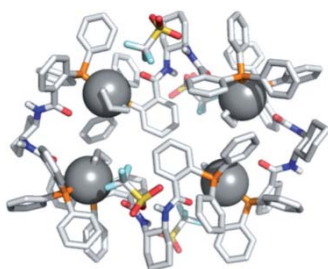


Ref: Collins, D.M. et al. *Met Trans A* 2011, 42A (1), 49-59



Chiral Catalysts Based on the Trost Ligand

Work carried out by Prof J. Eastoe (University of Bristol) and Prof G. Lloyd-Jones (University of Edinburgh) monitoring the changes in aggregation structure of the Trost ligand *in-situ* whilst it is participating in a catalytic cyclic reaction. This system is of interest as the catalyst has uniquely high selectivity and activity for chiral syntheses in organic media. The PhD student working on this study is sponsored by Merck.



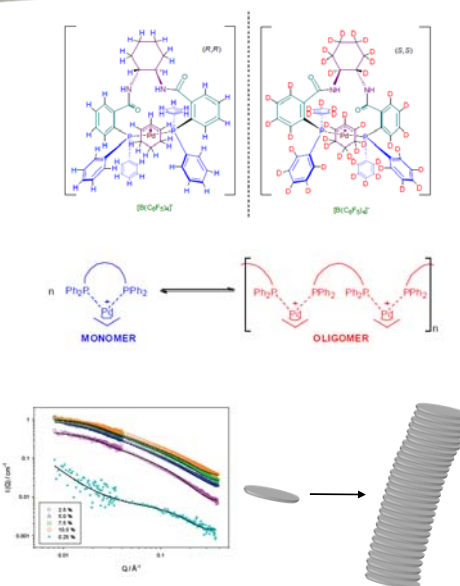


The System

- The chiral complex guides incoming nucleophile on one side of the bound substrate
- Slightly different conditions trigger remarkable shift in selectivity: loses the all-important chiral selectivity
- Root cause of this activity switch is thought to be oligomerisation

The Experiment and Results

- SANS used to study the aggregated structures
- Initial disc shape structures are $\sim 19 \text{ \AA}$
- Further aggregation takes place and rod like structures form which are $\sim 19 \text{ \AA}$ in radius and $\sim 200 \text{ \AA}$ long
- Both contrast steps were used to confirm these results
- Further measurements altering reaction conditions are planned

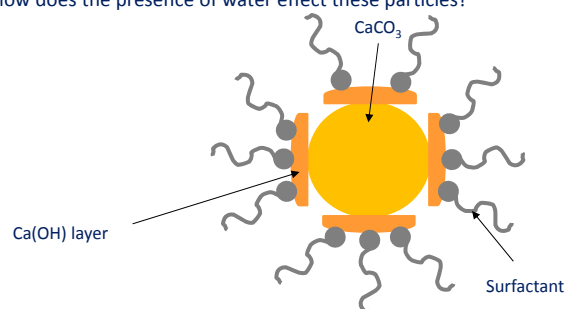


Ref: Faraday Discuss 2010, 145, 27 - 47



Nanoparticles

Work carried out by Dr P. Dowding (Infineum) and Dr A. Routh (University of Cambridge) studying overbased sulfonate engine oil additives (OBSAs). These OBSAs consist of calcium carbonate nanoparticles – CaCO_3 - stabilized by a sulfonate surfactant. The stability of these particles is crucial for their correct performance. The combustion process can produce a considerable amount of water: how does the presence of water effect these particles?





Proposed Structure

Amorphous CaCO_3 core (< 10 dia.nm) surrounded by a monolayer of alkyl aryl sulfonate surfactant

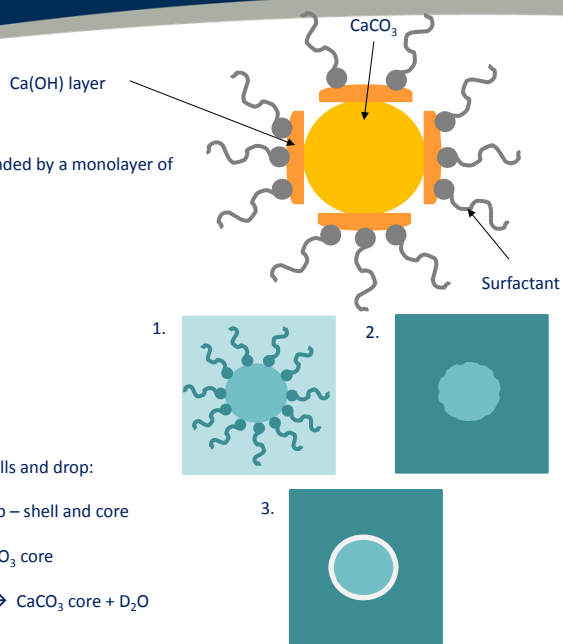
Three possible locations of water molecules:

- Water-in-oil microemulsions
- Throughout the CaCO_3 particles
- Surface of the particles

The Experiment

Used contrast variation SANS to see core, shells and drop:

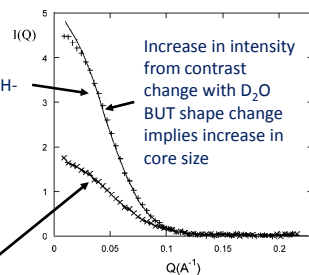
1. H-surf + CaCO_3 in D-cyclohexane \rightarrow Drop – shell and core
2. H-surf + CaCO_3 in H-cyclohexane \rightarrow CaCO_3 core
3. H-surf + D_2O + CaCO_3 in H-cyclohexane \rightarrow CaCO_3 core + D_2O 'shell'



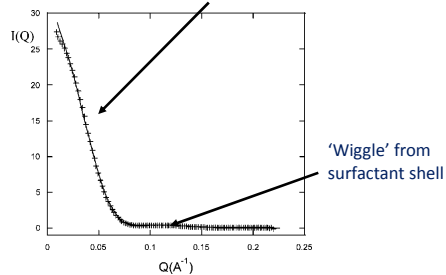
Results

CaCO_3 + surfactant doped with D_2O in H-cyclohexane

Undoped CaCO_3 + surfactant in H-cyclohexane

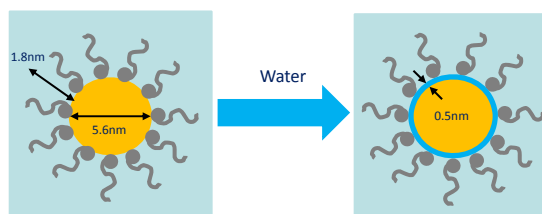


Undoped CaCO_3 + surfactant in D-cyclohexane



- CaCO_3 particles are spherical with dia. ~ 5.6 nm
- Surfactant monolayer is of thickness ~ 1.8 nm
- Water layer inserts between the calcium cation at the surface of the particle and the sulfonate anion

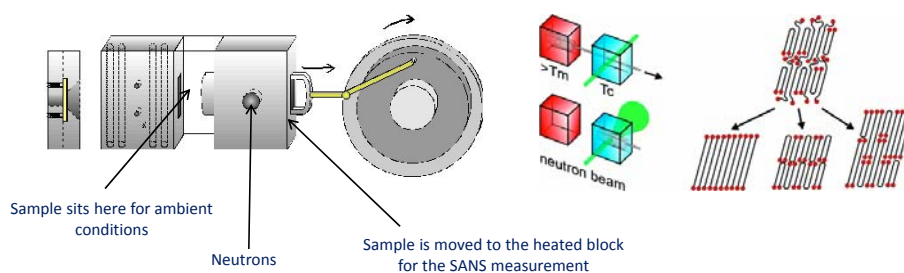
Ref: Langmuir 2008, 24, 3807 - 3813





Time-Resolved Measurements

Collaboration between Prof G. Ungar (University of Sheffield) and the ISIS SANS team studying transient phases in polymer crystallization using a temperature jump (T-jump) cell designed for SAS beamlines

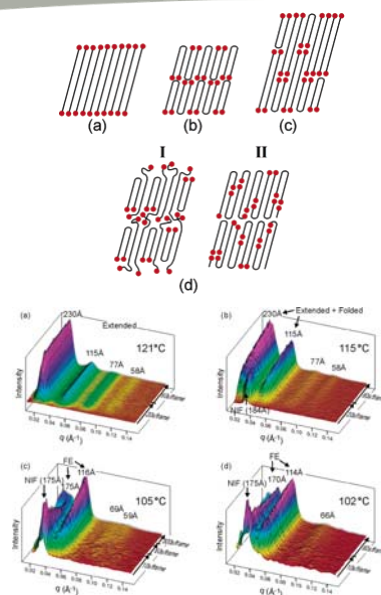


Why Real-Time SANS?

- Polymer crystallization is a highly non-equilibrium process
- SAS is a powerful technique for studying lamellar structures
- Using selectively deuterated segments, SANS can provide information of the location and state of order of such segments

The Experiment and Results

- Material C₁₂D₂₅C₁₉₂H₃₈₄CHDC₁₁D₂₃ used
- Lamellar structures possible are (a) extended chain form, (b) once-folder chain form, (c) triple-layer mixed folded-extended (FE) form and (d) alternative models for the noninteger folded (NIF) form (see Figure)
- NIF form has a lifetime of ~ 1minute – time resolution achievable via SANS
- Real-time SANS 'snap shots' reveal structural changes with time and temperature

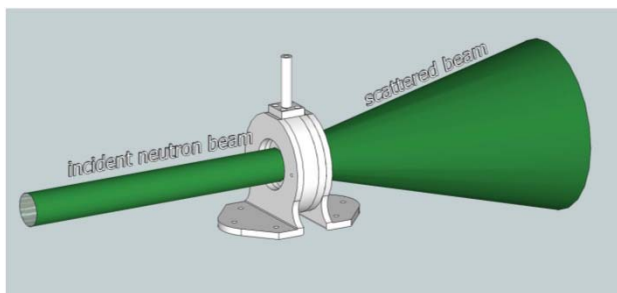
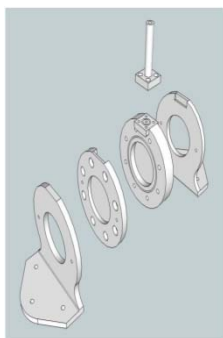


Ref: Zeng, X.B. et al. *Macromolecules* 2005, 38 (17), 7201-7204



Porosity in Activated Carbons

Collaboration between Prof K. Ross (University of Salford) and the ISIS SANS team studying the porosity of activated carbon using a gas handling rig designed for SANS beamlines. Contrast matching measurements were made using mixtures of H/D toluene which allowed the carbon density of different length scales to be obtained.



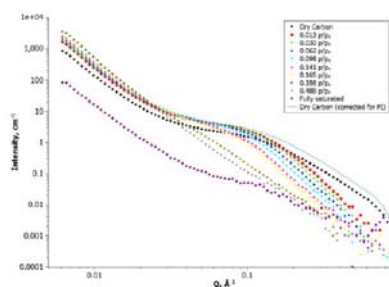
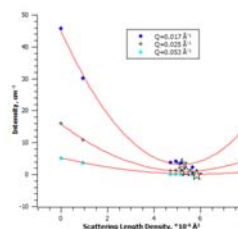
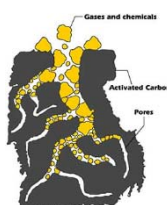
Why Use SANS?

- Nanoscale 'slit pores' where adsorbate molecules interact with both walls is best for H_2 storage
- Standard methods of measuring porosity overestimates pore volumes as condensation of the gas increases the apparent carbon density
- Using SANS and contrast matching liquids circumvents these difficulties

The Experiment and Results

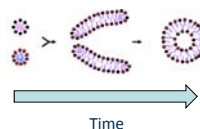
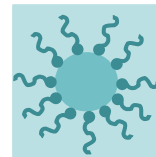
- Mixtures of H/D toluene were used to match the scattering from carbon at different densities
- Data shows fractal behaviour at the larger lengthscales and a well defined hump at atomic scales caused by the activation (oxidation) process
- Minimum pore radius and accessible pore volumes were found as a function of toluene partial pressure

Ref: Carbon 2012, 50 (14), 5062-5075

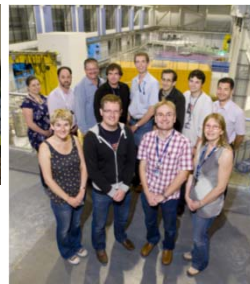


Summary:

- SANS is a very useful techniques for determining the size, polydispersity, orientation and structure of a wide range of disordered materials in the bulk
- When combined with the broad sample environment available the science and systems studied using SANS is incredibly varied
- *In-situ* and real time measurements possible
- Any questions?



THANKS to.....



The University
Of Sheffield.



For listening!