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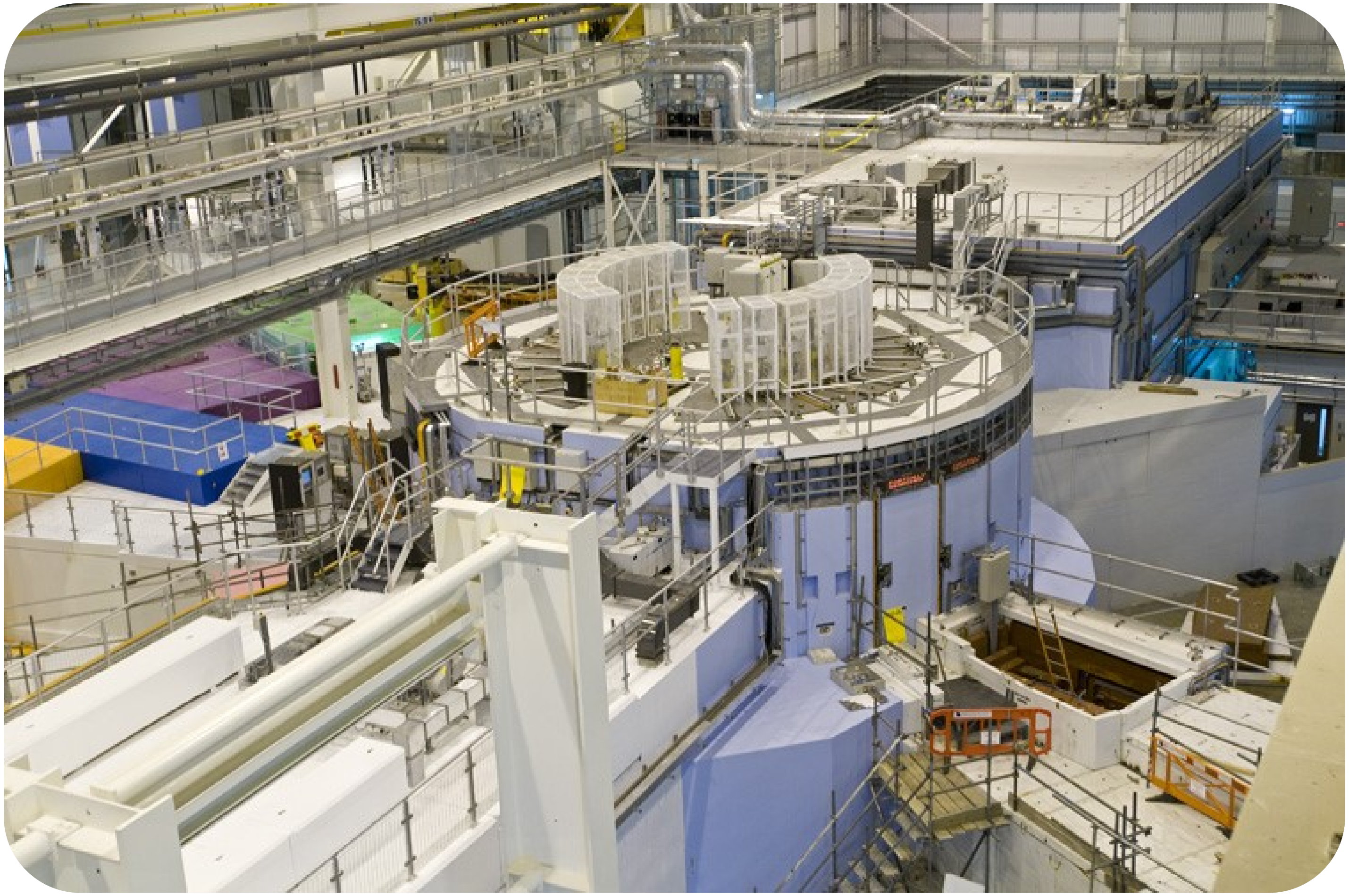
Spectroscopy at ISIS



Jeff Armstrong

Talk Layout

- What is neutron spectroscopy?
- Vibrational spectroscopy (TOSCA example)
- Quasi-elastic spectroscopy (OSIRIS example)
- Neutron Spectroscopy in Catalysis

(Example: Methanol production)

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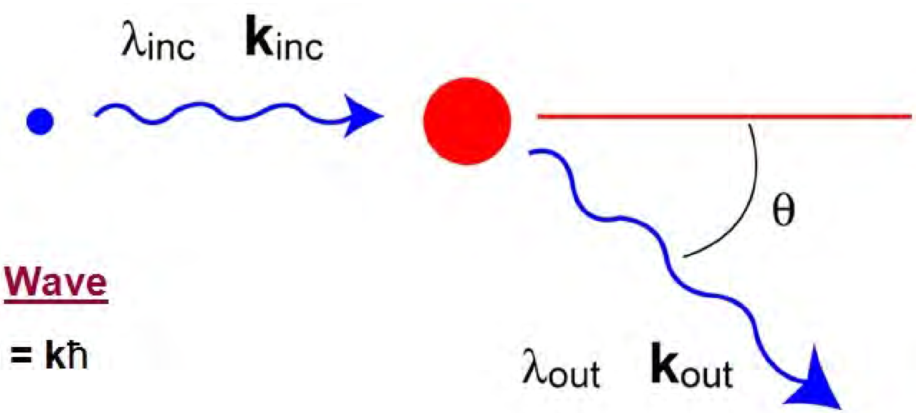
Basic principle of neutron spectroscopy



Particle

$E_{kin} = \frac{mV^2}{2}$

Wave

$\mathbf{p} = \mathbf{k}\hbar$

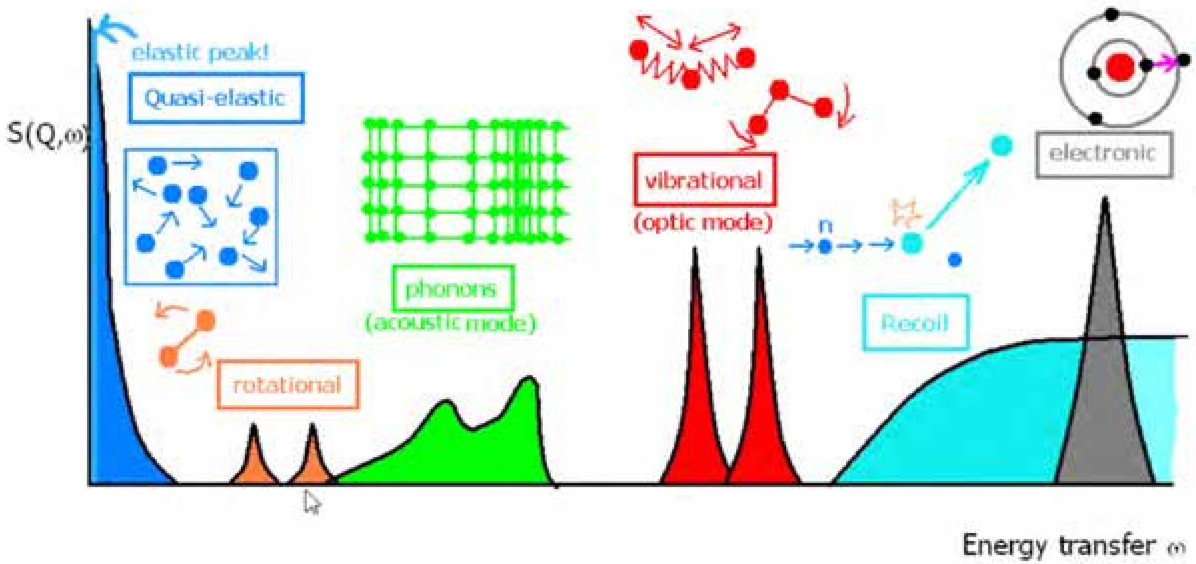
Scattering proces

$\hbar\omega = E_{out} - E_{inc} = \frac{m}{2}(V_{out}^2 - V_{inc}^2)$ information about microscopic motion

$\mathbf{Q} = \mathbf{k}_{out} - \mathbf{k}_{inc}$ information about microscopic structure

What motions can we study with Neutron Spectroscopy?

- Neutron spectroscopy can access the full range of structural and dynamic regimes
- Typically neutron spectrometers are designed to obtain E or Q resolution within a specific region



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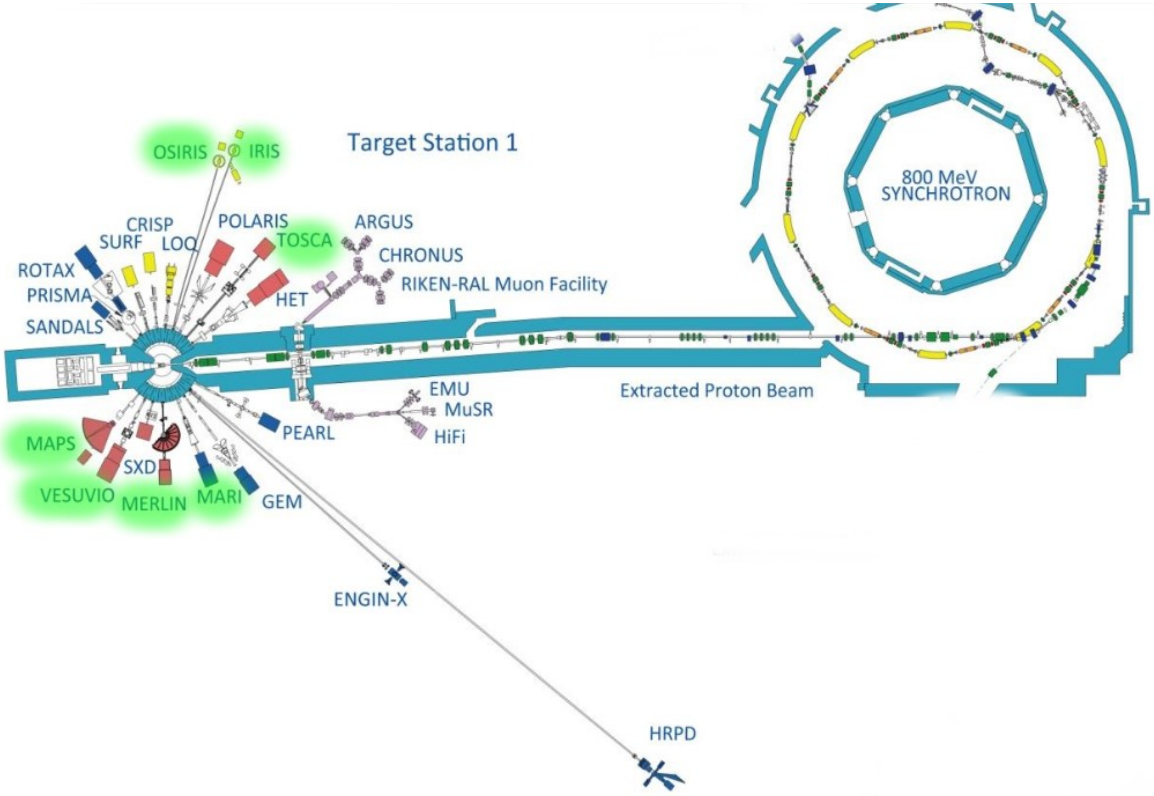
Inelastic and Quasi-elastic (QENS) spectrometers at ISIS (shown in green)



- OSIRIS
- IRIS
- TOSCA
- MAPS
- VESUVIO
- MERLIN
- MARI

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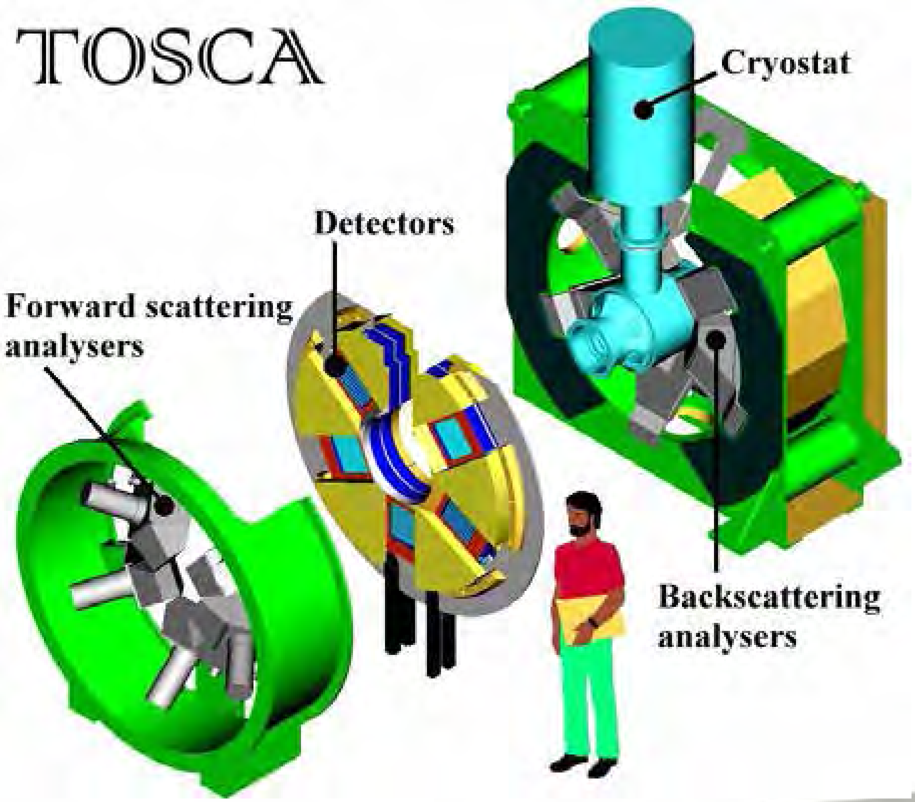
TOSCA(vibrational spectroscopy with neutrons)

Advantages of neutrons:

- High sensitivity to hydrogen
- No selection/transition rules
- Penetrate into the bulk
- Possibility of using deuteration to distinguish peaks
- Broad band (0-4000cm^{-1})



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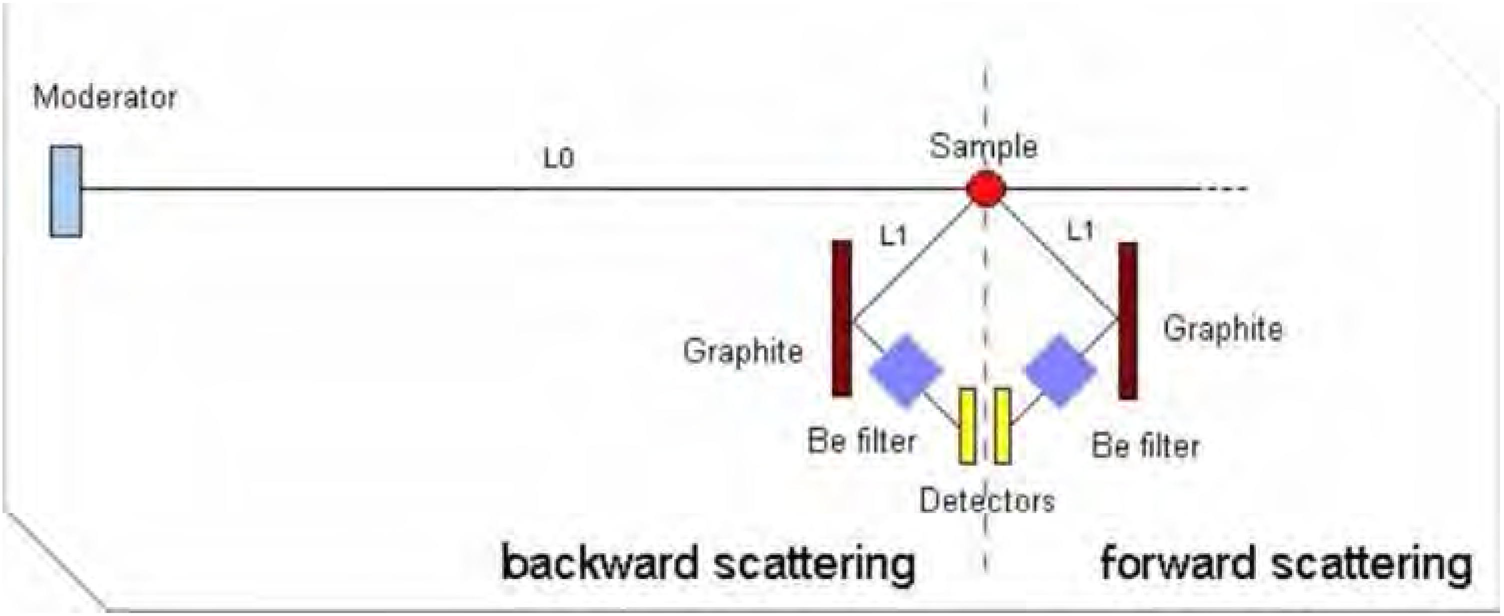
TOSCA(Principle of operation)



- Systems are measured at low T (typically ~10K)
- Spectra obtained on the order of ~1 hour

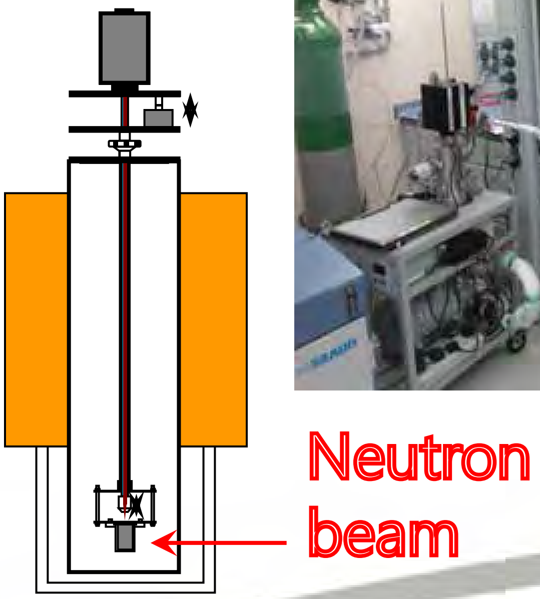
What can we tell from vibrational spectroscopy?

- Biology (e.g. polypeptides, nicotinic acid)
- Chemistry (e.g. Catalysis, fuel cell catalysts, understanding hydrogen bonds)
- Energy (e.g. binding of H2 in zeolites)
- Physics (Ferroelectrics)

"In-situ" studies at ISIS

- A mobile catalysis rig is available at ISIS
- Many of our neutron experiments can be performed with "in-situ" gas handling (e.g. absorption studies)
- We also have the capability to measure neutron/Raman spectra simultaneously

Specialised sample sticks



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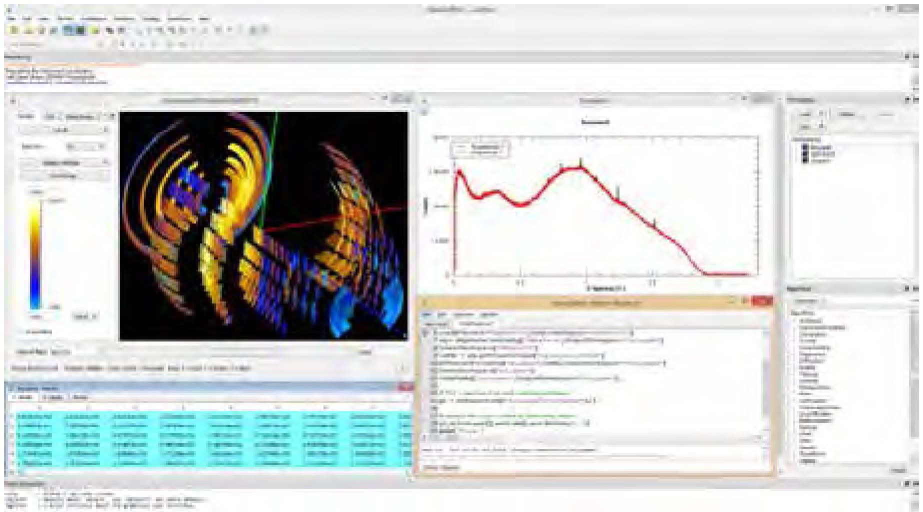
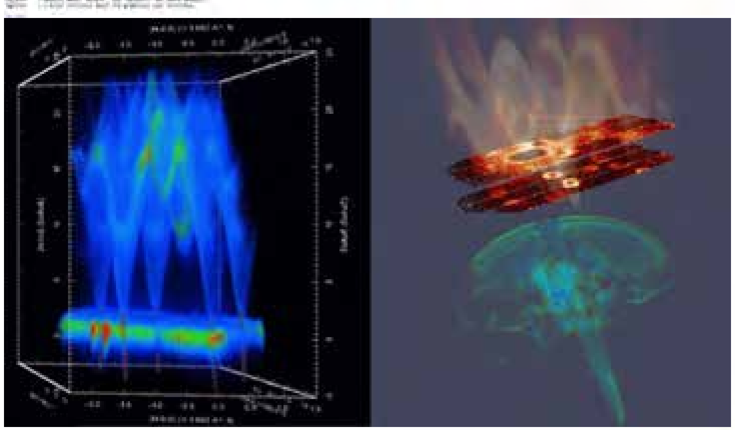
MANTiD (Data analysis made easy)





- ISIS provides its own professional data analysis software suite
- Raw data reduction is performed at the click of a button
- Fitting of data to models is provided through easy to use GUIs

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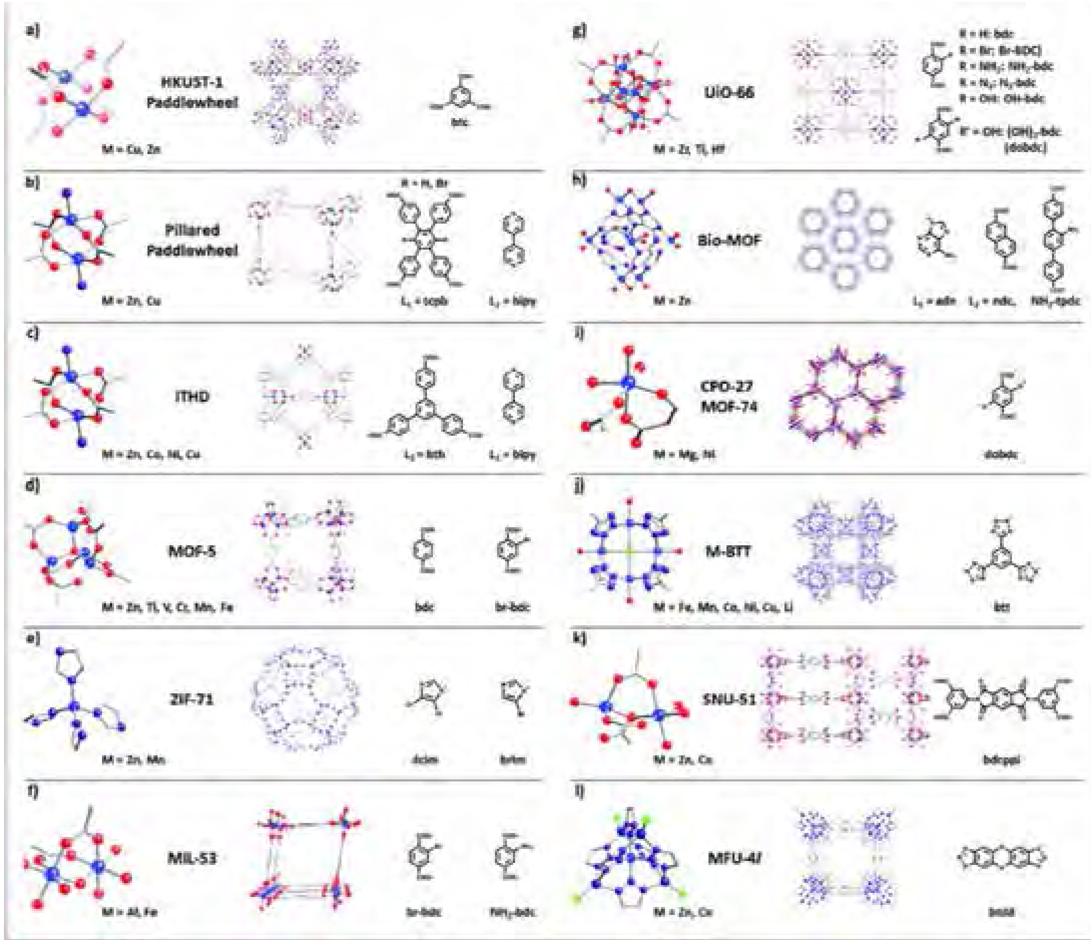
Metal Organic Frameworks

Metal ion clusters coordinated to organic ligands



Tuneable properties via linker/metal selection

- Gas storage
- CO_2 capture
- Microelectronics/dielectrics
- Photocatalysis
- Drug encapsulation

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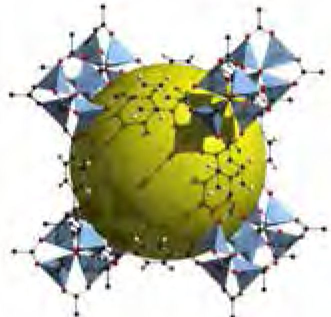
Intelligent design of MOFs

How can neutrons help?

- Lattice dynamics underpins the elasticity and the structural stability
- Also their thermomechanical behaviour
- Understanding the origin of low frequency modes is more challenging as there are no stereotypical vibrations for standard chemical groups
- We therefore need to use density functional theory to understand the microscopic origin of each vibration



Current challenges for MOFS:

- Structural stability over a wide range of conditions
- How does one optimise gas storage through topology?
- Manufacture on commercially relevant scale

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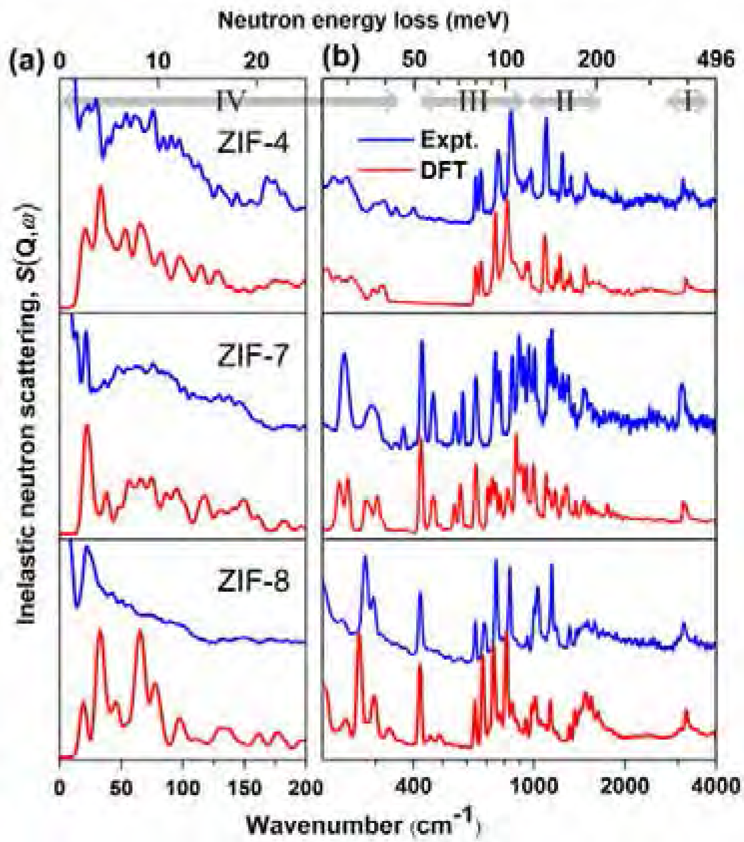
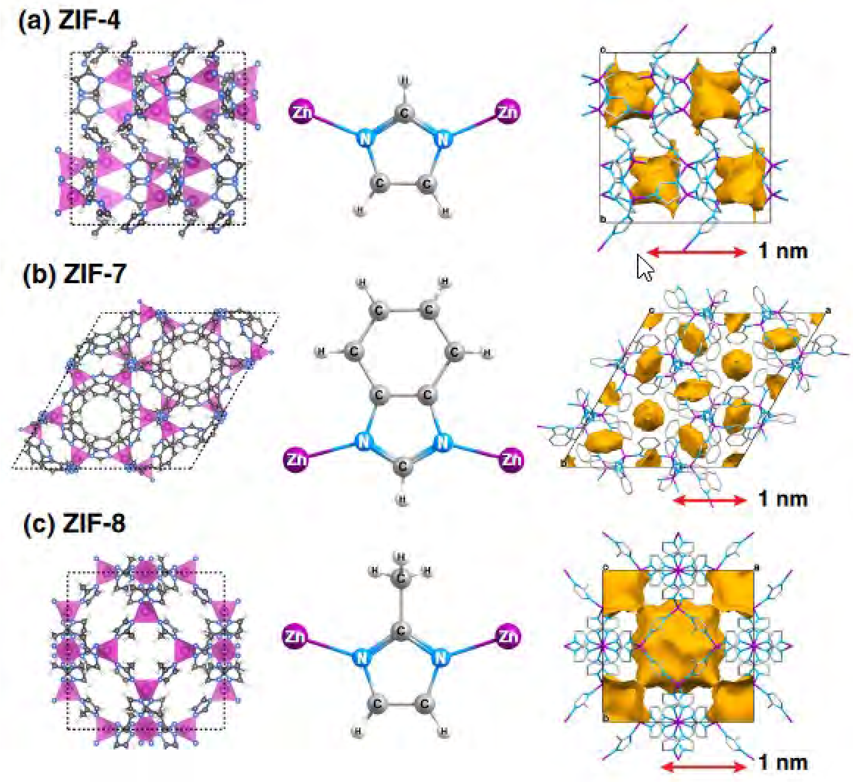
Zeolitic Imidazolate frameworks (neutrons & theory)





Tetrahedrally coordinated transition metal ions, connected by imidazolate linkers

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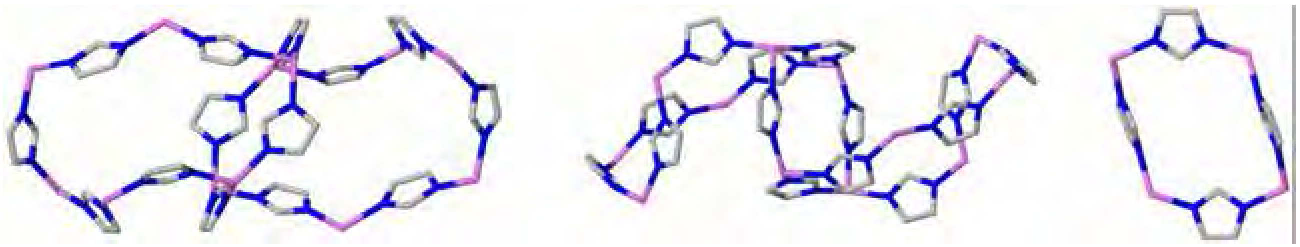
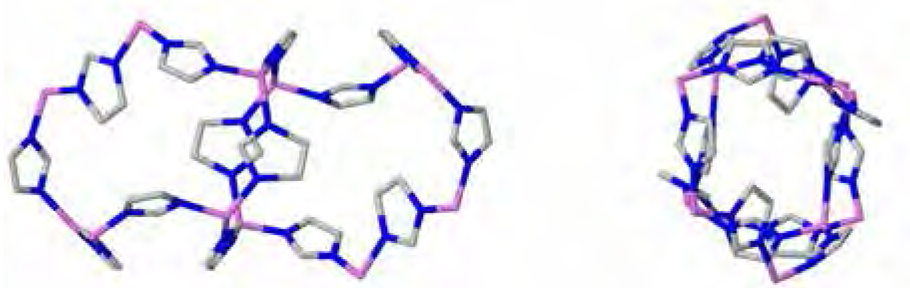
Identification of specific modes
ZIF-4 (low frequency modes)

Soft mode
0.2 THz



- Soft mode suggests the possibility of phase transition through shearing

Gate-opening
1 THz



- This soft stretching combined with the gate-opening is probably responsible for the anomalous gas absorption isotherms which are reported

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How to apply for time at ISIS

- Two standard proposal rounds (October & April)
- Rapid access
- Xpress (short immediate access)

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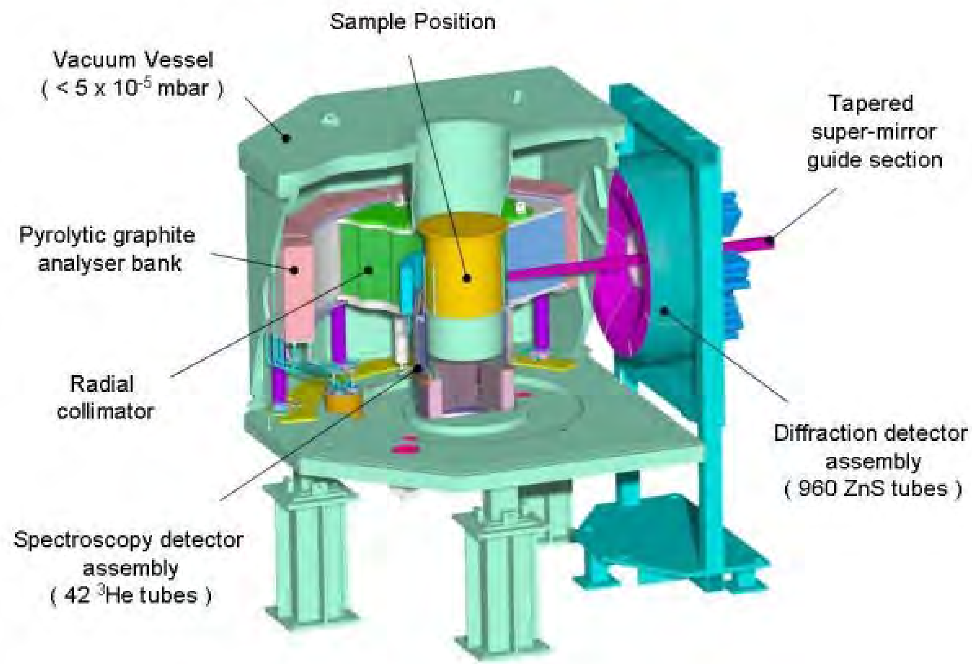
OSIRIS (Quasi-elastic neutron spectrometry)



- Spectroscopy & diffraction capabilities
- High temperature studies (~1200K)

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What can we tell from Quasi-elastic spectroscopy?

- Time-scales (pico-seconds/nano-seconds)
- Chain dynamics/rotations (e.g. rotational freq)
- Diffusion (single particle dynamics especially hydrogen)
- Analytical models can be invoked to get diffusion coefficients
- For more complex systems the use of simulation is often required
- Especially when coherent and incoherent signals are mixed, or we simply have a weak signal (i.e. hard to fit analytic functions)

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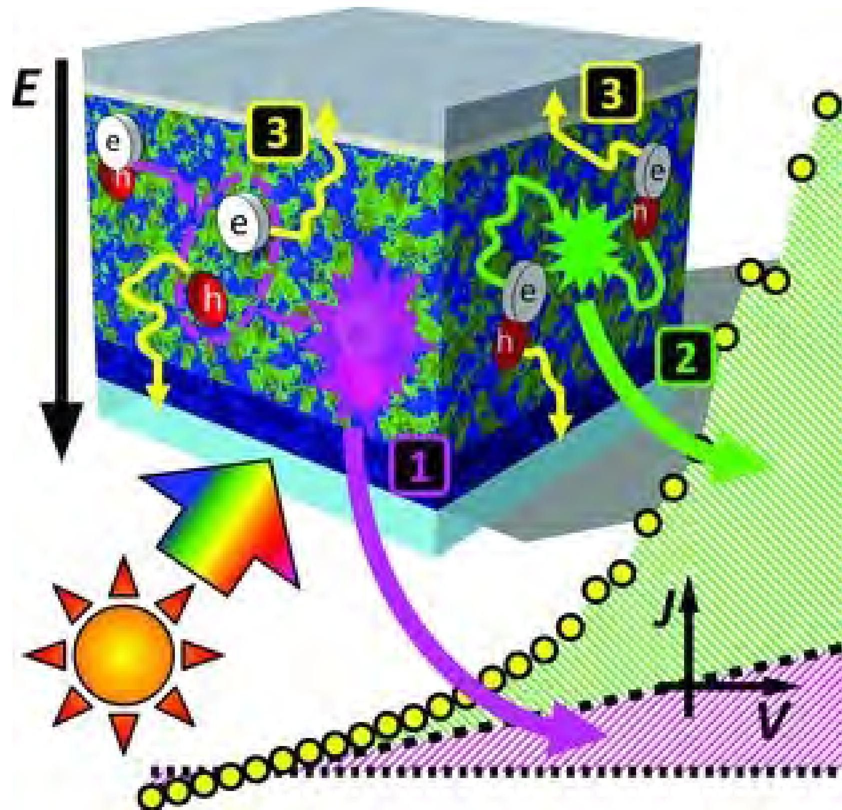
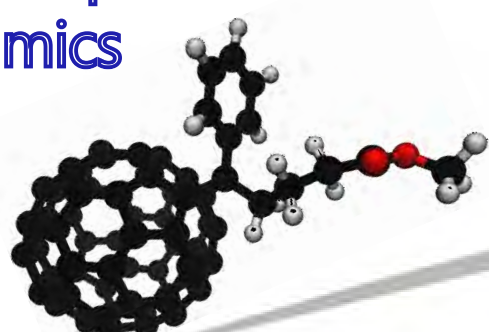
Organic photovoltaics (PCBM)

- PCBM is the most promising electron acceptor candidate
- We lack understanding of how morphology is effected by temperature and solvent preparation method
- In fact little is known about PCBM's phase behaviour and dynamics





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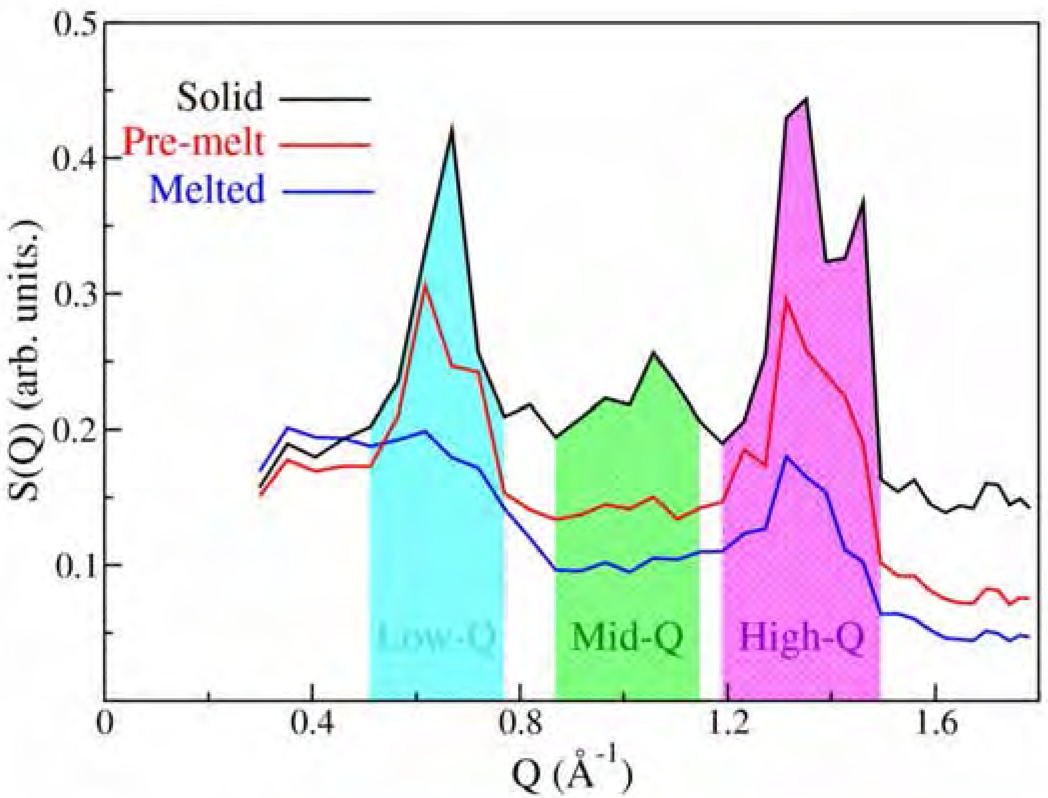
Step 1, understand the structure

OSIRIS provides both structural and dynamic information



- We are able to see structural changes on the length scales of nanoscopic molecules/structures
- For PCBM we see three distinct structural regions (Low, Mid and High-Q)

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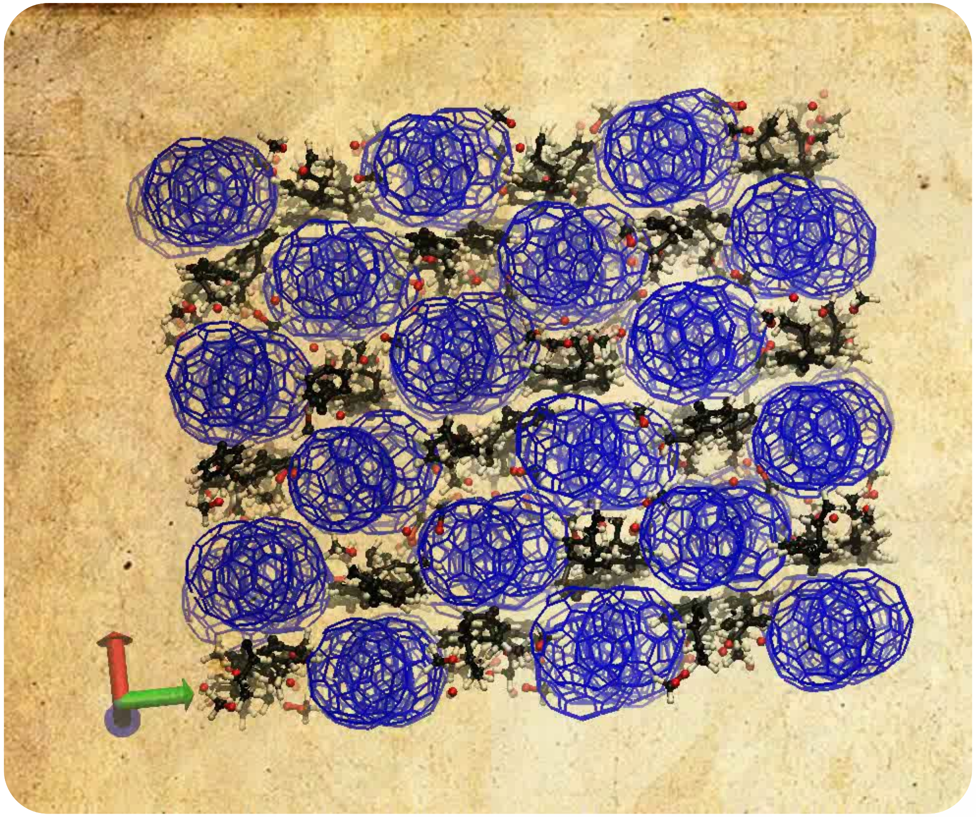
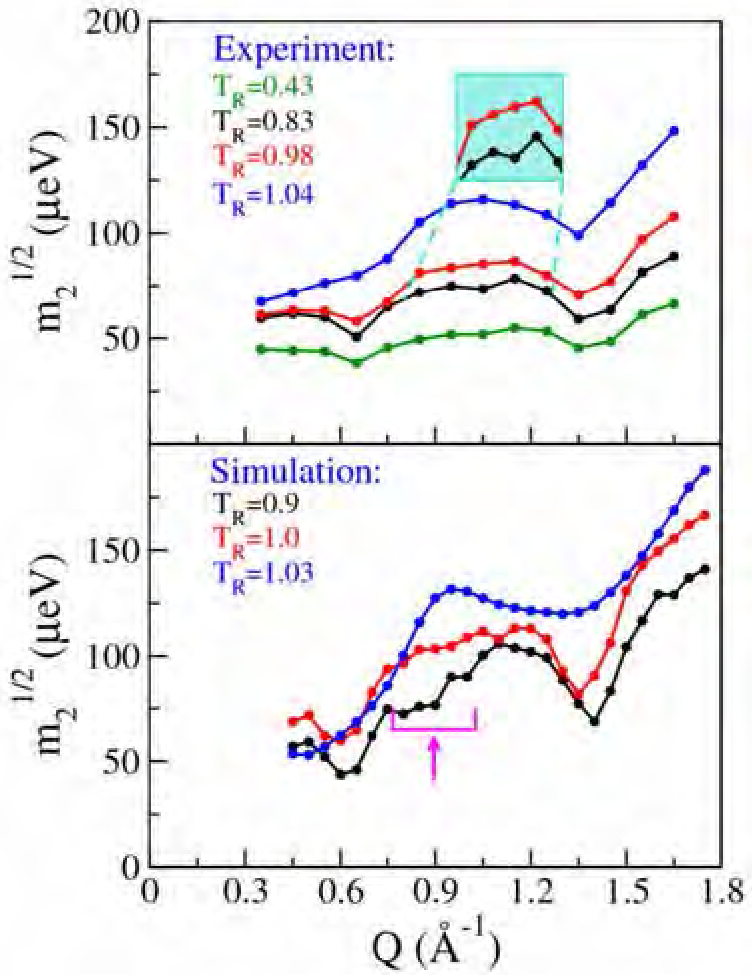
Classical Molecular Dynamics



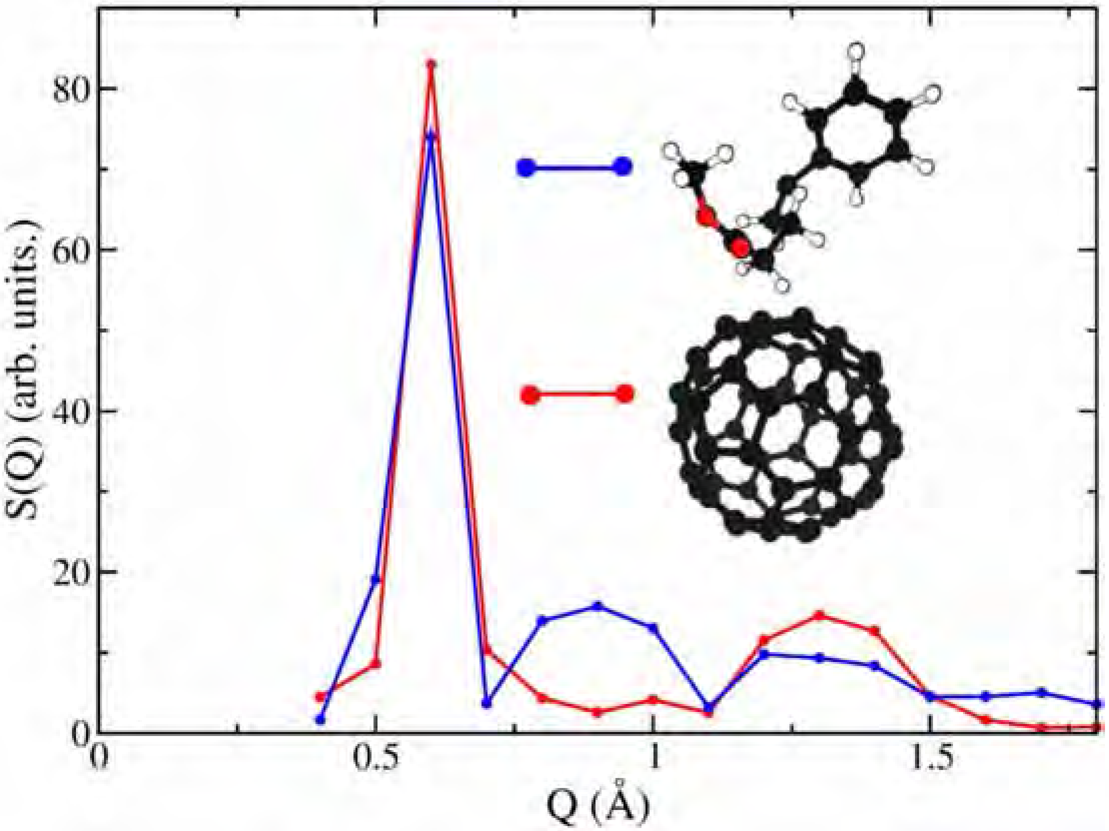
- Ideal models may be used to understand the dynamic structure factor of simple systems
- For more complex system however we should use simulation to understand the microscopic origin of a given signal

Comparing experiment and simulation (dynamics)



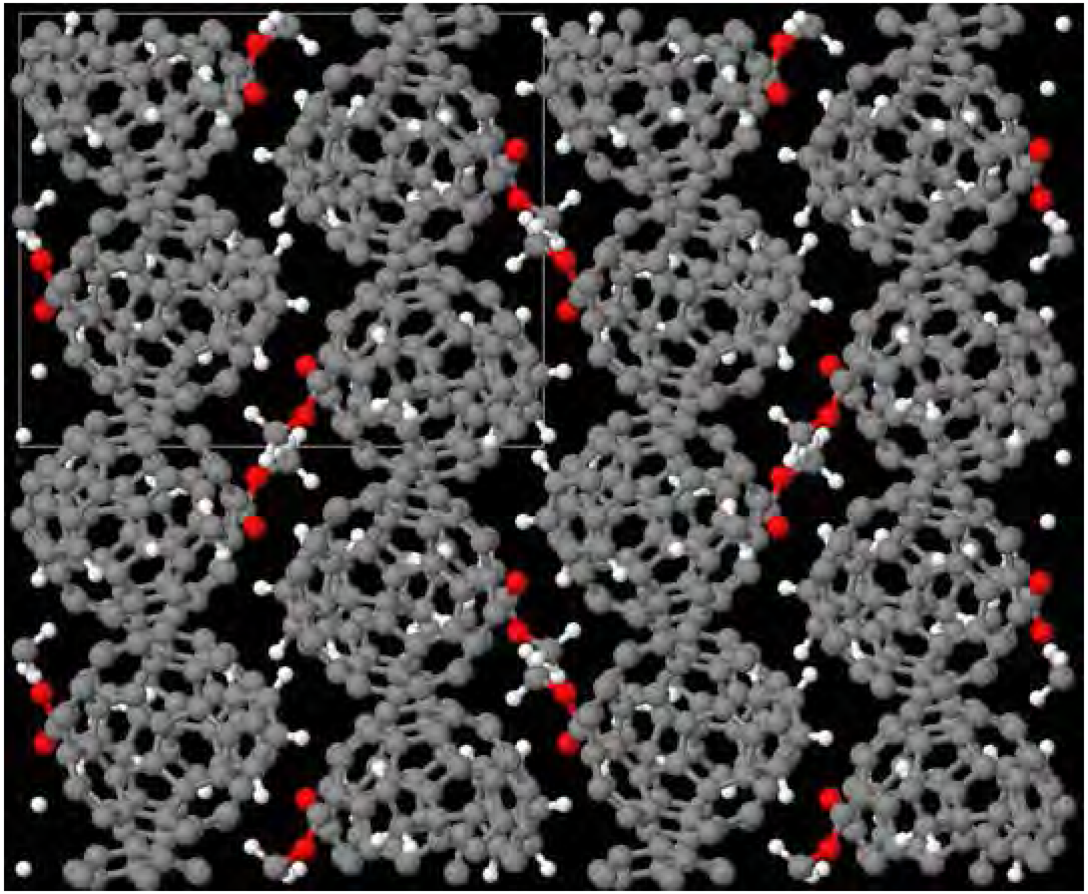
- We provide a direct comparison with classical simulation is through convolution with the instrument resolution
- Comparison is semi-quantitative
- Each loss of structure is accompanied by an increase in dynamics

Microscopic origin explained



- Simulation also has the benefit that we can decompose the signal's origin into structural units
- Here we see that the chain is responsible for the Mid-Q structural correlations

Precise modes which cause melting of the chains (through density functional theory)



- Precise insight into the soft modes which may stimulate the melting mechanism through DFT
- This may be compared directly with TOSCA spectra

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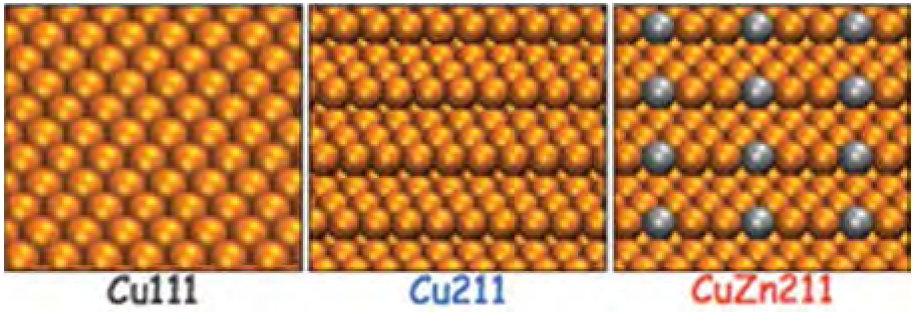
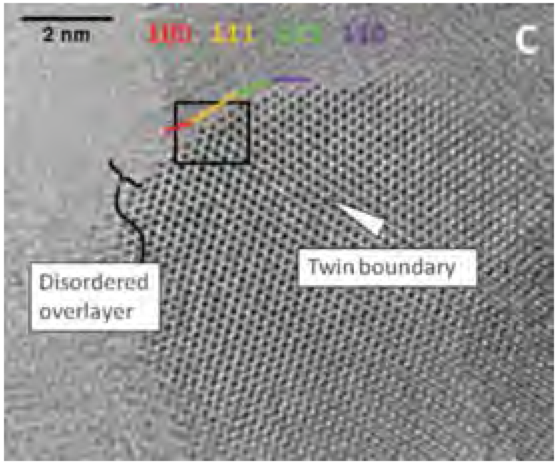
Catalysis (Methanol production)

- For 50 years Cu catalysts on Oxide supports have been very successful in the synthesis of methanol



- The exact reaction mechanism is surprisingly poorly understood



- Recent studies have suggested models for CO_2-coverting sites as CuZn(211) bi-metallic stepped facets

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Catalysis (Methanol production)

Reaction scheme involves many intermediates

$$H_2(g) + 2^* \leftrightarrow 2H^*$$

$$CO_2(g) + H^* \leftrightarrow HCOO^*$$

$$HCOO^* + H^* \leftrightarrow HCOOH^* + {}^*$$

$$HCOOH^* + H^* \leftrightarrow H_2COOH^* + {}^*$$

$$H_2COOH^* + {}^* \leftrightarrow H_2CO^* + OH^*$$

$$H_2CO^* + H^* \leftrightarrow H_3CO^* + {}^*$$

$$H_3CO^* + H^* \leftrightarrow CH_3OH(g) + 2^*$$

$$OH^* + H^* \leftrightarrow H_2O(g) + 2^*$$

$$CO(g) + {}^* \leftrightarrow CO^*$$

$$CO^* + H^* \leftrightarrow HCO^* + {}^*$$

$$HCO^* + H^* \leftrightarrow H_2CO^* + {}^*$$

- It is hypothesised that methanol formation occurs through different mechanisms and intermediates depending on whether Zn is present or absent
- Studied Cu/ZnO & Cu/MgO catalysts
- Two different syngas feeds (CO/H_2 & CO_2/H_2)

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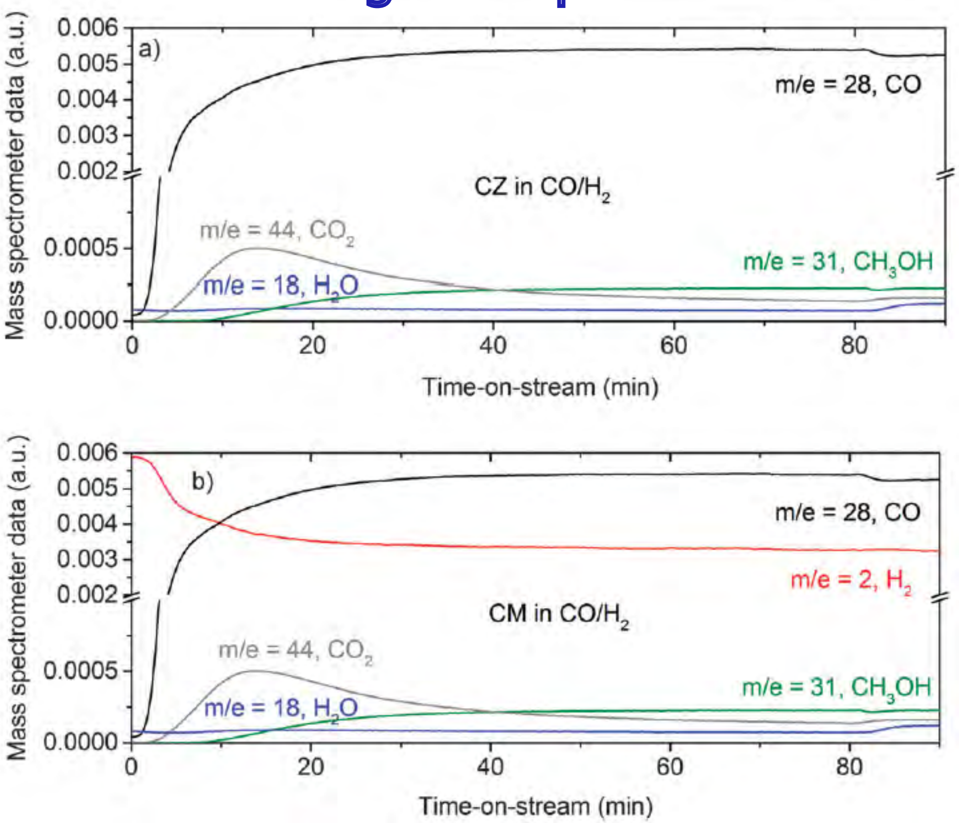
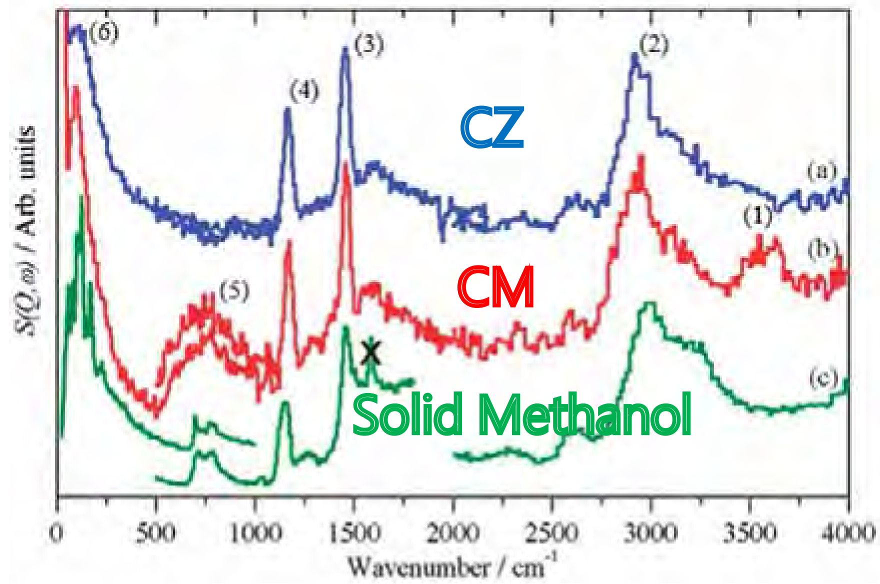
Methanol formation in CO/H_2

Exhaust gas composition





Chemisorbed methoxy is clearly identified from the spectra

We see the conversion of CO to CO_2 via reaction with hydroxys on the oxides (confirmed by neutron spectra)

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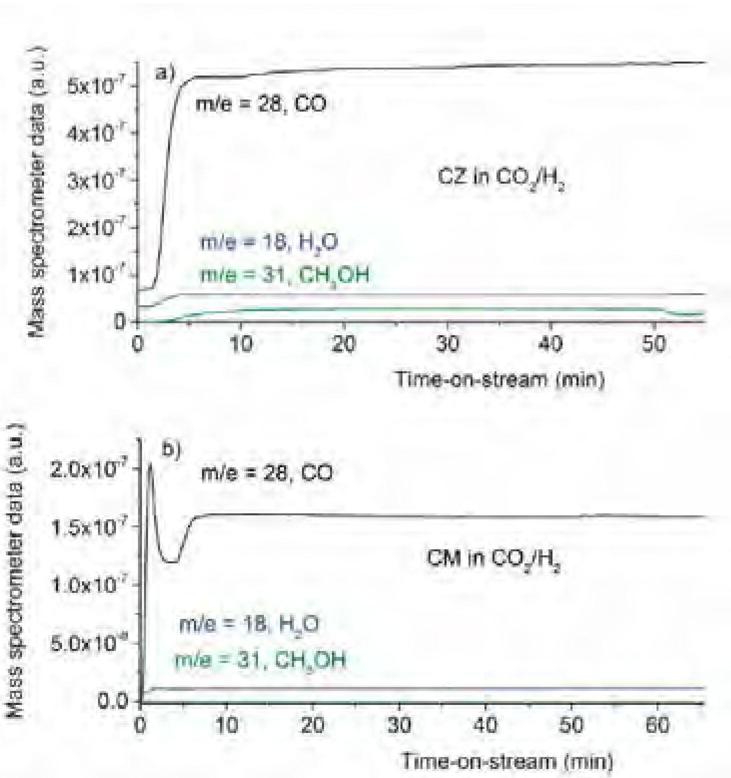
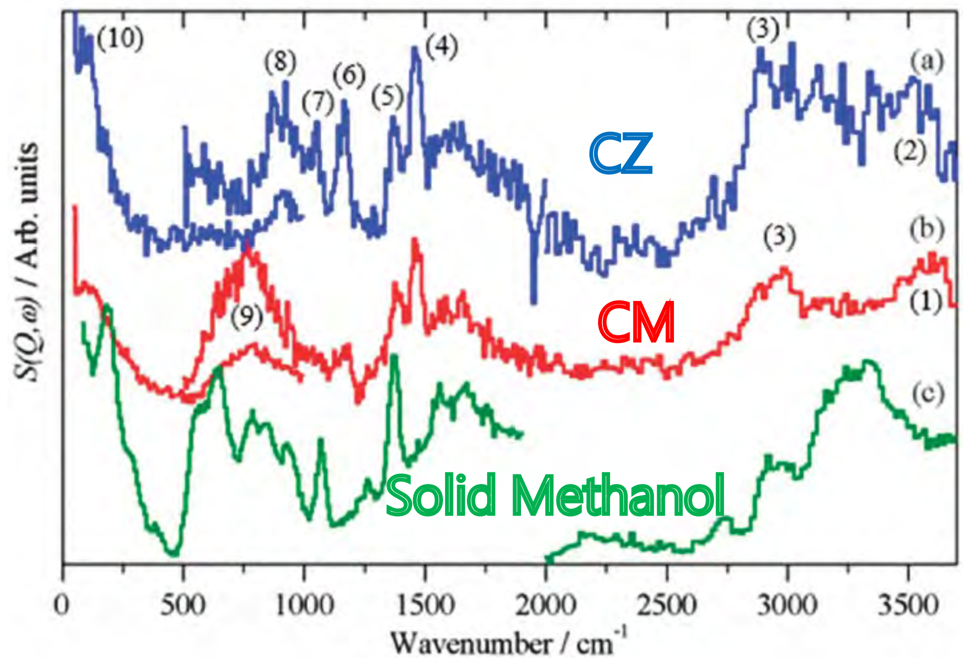
Methanol formation in CO_2/H_2

Exhaust gas composition



Creating of CO from reverse water shift reaction
CM favours this over methanol synthesis (hence smaller quantities)



- Again chemisorbed methoxy is seen
- This time however we also see formate
- Additionally CZ shows the presence of hydroxyls

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Findings

- Chemisorbed methoxy present in all cases
- CO_2/H_2 shows the production of formate
- In the case of CM, both methoxy and formate compete for space on the Cu, as the area under the curves is the same
- For CZ this is not the case and we also see hydroxyls, which show positions consistent with being on the Cu, thus also competing for space with formate

In Summary

- Neutron spectroscopy can be used to target a wide range of problems spanning many different scientific disciplines

- Neutrons are particularly sensitive to Hydrogen, which means they can tackle problems that other spectroscopies cannot

- ISIS provides the framework, both practical and software to allow non-specialists to easily use the facility