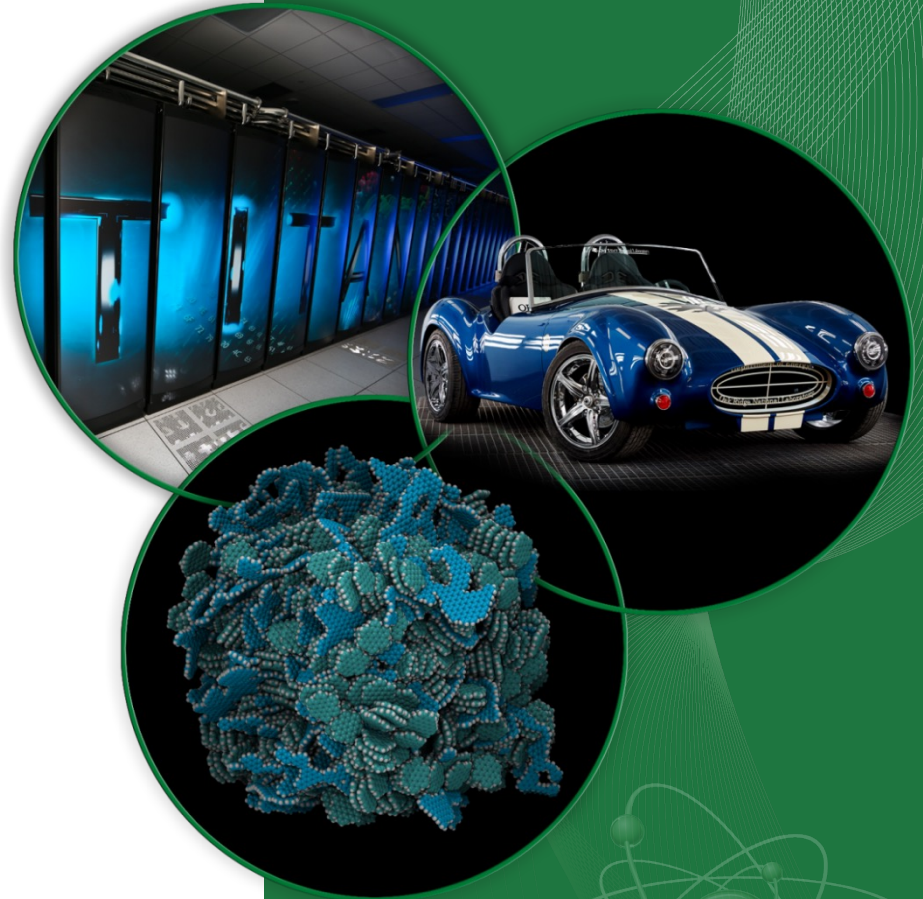


# Quasi-Elastic Neutron Scattering

Niina Jalarvo



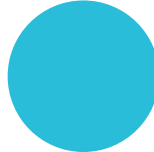
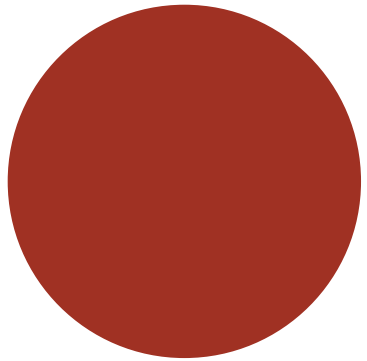
# Overview

INTRO to QENS

QENS Instruments

QENS Theory

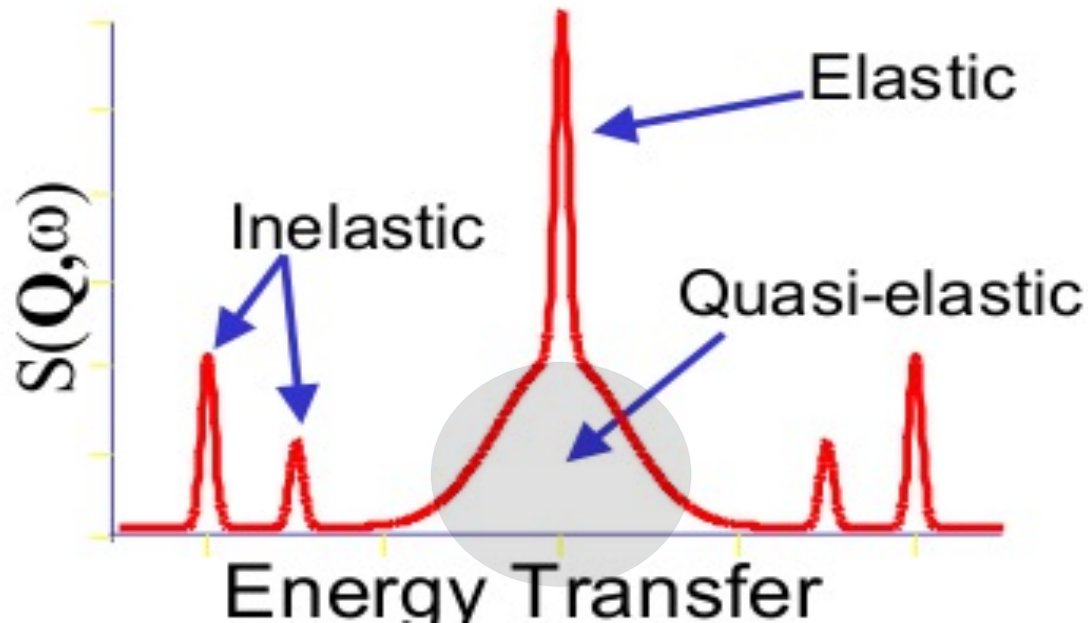
Science Examples



# What is QENS



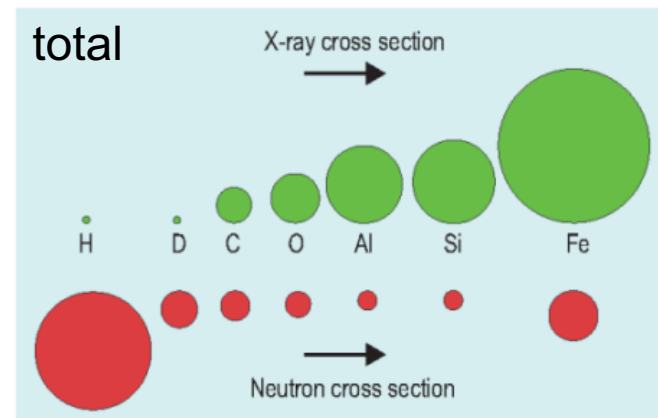
# Quasi Elastic Neutron Scattering QENS



- Quasi elastic neutron scattering is a limiting case of inelastic neutron scattering
- Doppler type of broadening of the elastic line due to a small energy transfer between the neutrons and the atoms in the sample

# Neutron-Material Interaction

- **Cross section ( $\sigma$ )** – Area related to the probability that a neutron will interact with a nucleus in a particular way (e.g. scattering or absorption)
- Light element sensitivity in presence of heavy elements
- Systems containing a reasonable proportion of H atoms, scattering from H tends to dominate
- Isotopic sensitivity
  - H-D contrast, H large incoherent cross-section
    - Use of deuteration/selective deuteration to suppress incoherent scattering
- Thermal neutron wavelengths (few Å's) are comparable to interatomic and intermolecular distances
- Thermal neutron energies (few meV's) comparable to energies of excitation in materials
  - => vibrations, librations, reorientations, diffusion, and relaxational processes can be observed



# What is QENS used for

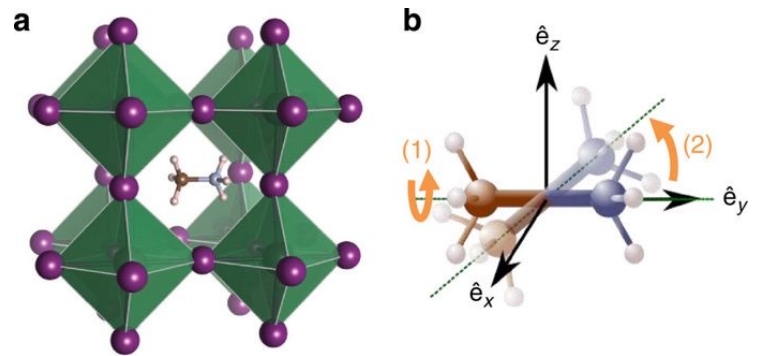
Probes slow dynamics

- Translational diffusion
- Molecular reorientations
- Relaxation processes

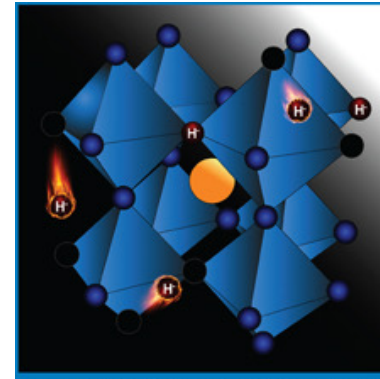
Applicable to wide range of scientific topics

- **Materials science:** fuel cells, batteries, hydrogen storage,
- **Soft Matter:** polymer nanocomposites and blends, organic photovoltaics, polymer electrolytes
- **Biology:** hydration water, dynamics of proteins
- **Chemistry:** water interfaces, ionic liquids, clays, porous media, complex fluids, surface interactions

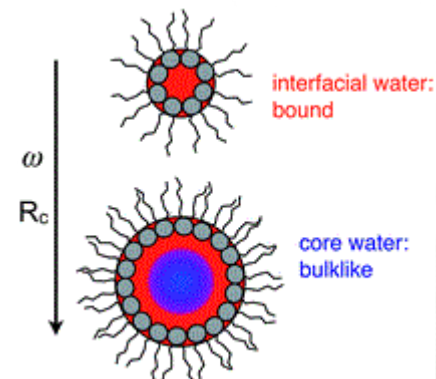
Results are comparable to Molecular Dynamics simulations



Nature Communications 6, 7124 (2015)

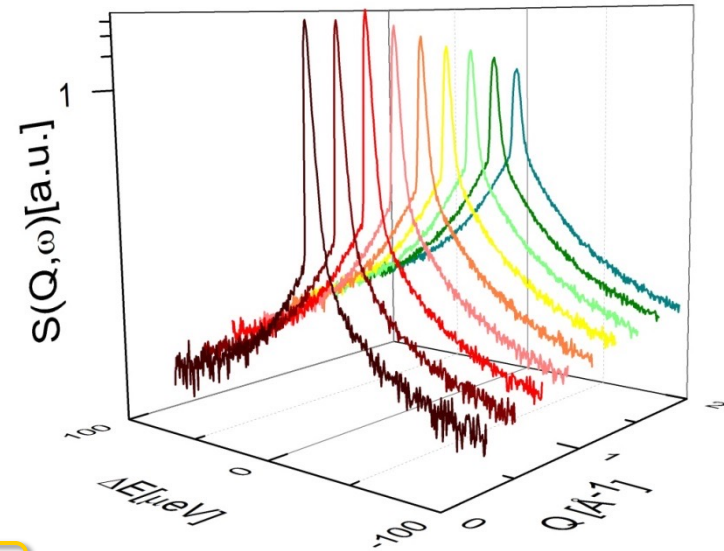
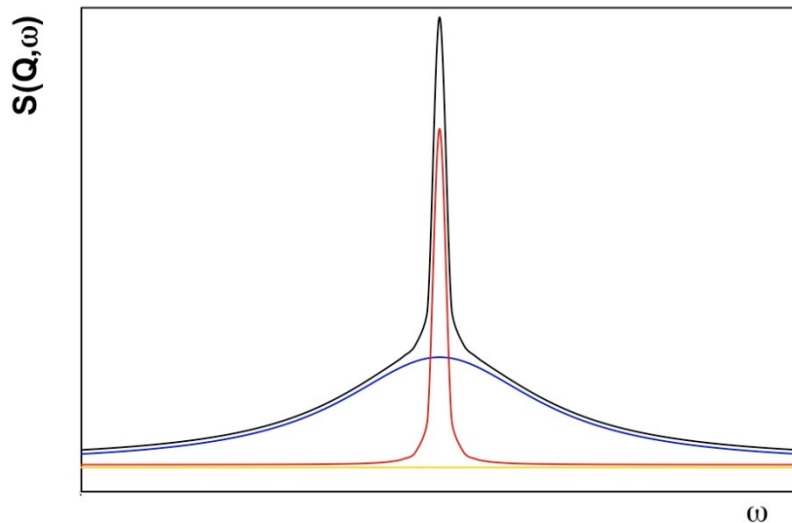


Journal of Physical Chemistry C, 123, 2019 (2019).



Soft Matter, 7, 12, 5745-5755 (2011)

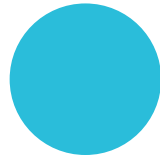
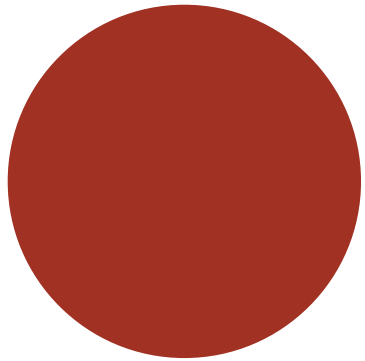
# QENS spectra



$$S(Q, \omega) = p_0 \delta(\omega) + \sum_{i=1}^n p_i \frac{1}{\pi} \frac{\Delta_i(Q)}{\omega^2 + \Delta_i^2} + B$$

Dynamic scattering function provides information on the sample states

- Elastic intensity** → Debye-Waller factor: Vibrational amplitudes
- Quasielastic intensity** →  $A_0 = \text{EISF}$  (ratio elastic/total): Geometry of motion
- Quasielastic broadening** → Width: Characteristic time scale / diffusion



# **QENS Instruments**





# QENS Instruments

Currently about 20 QENS spectrometers in the world (approximately 4 in the U. S., other locations include Germany, France, Switzerland, Japan and Australia)

## Backscattering Spectrometers

- High energy resolution
  - Resolution determined by the instrument (final energy of neutrons fixed)
  - Access to slower dynamics on nanosecond to picosecond time scale
  - Dynamic range limited

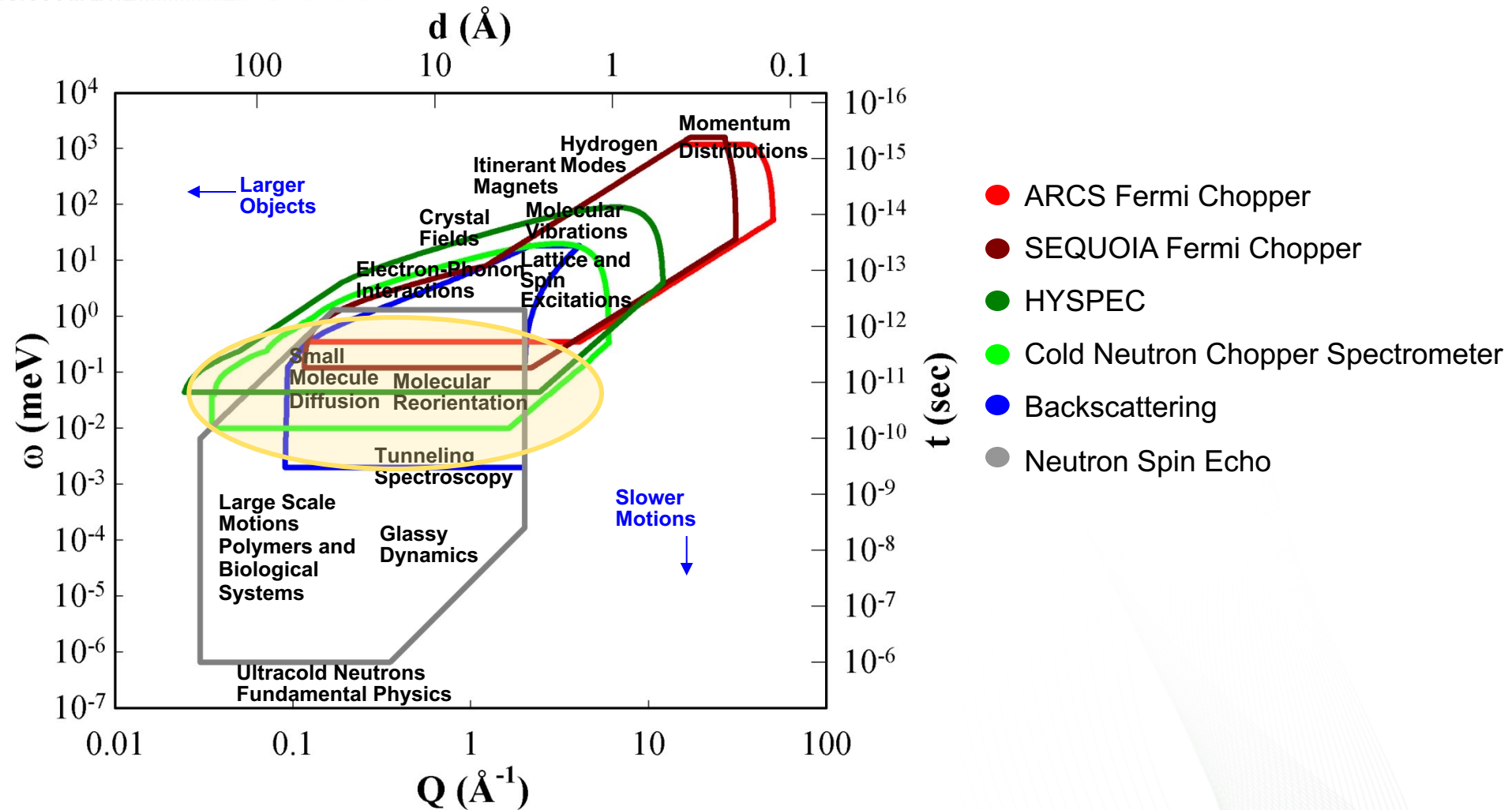
## Time-of-Flight Spectrometers


- Lower energy resolution
  - Resolution can be varied by changing the energy of incoming neutrons
  - Access to dynamics on picosecond time scale
  - Larger dynamic range accessible

# QENS and Neutron Scattering Instruments

- Dynamics in sample measurable
  - Length scales set by Q range (depends on neutron  $\lambda$ )
    - $Q = 2\pi/d$
    - $0.1 \text{ \AA}^{-1} < Q < 4 \text{ \AA}^{-1} \rightarrow 60 \text{ \AA} > d > 1.6 \text{ \AA}$
  - Time scales set by the elastic energy resolution
    - higher resolution  $\rightarrow$  longer times/slower motion (ns time scales accessible)
    - lower resolution  $\rightarrow$  shorter times/faster motion (ps time scales accessible)
- interchange
  - dynamic range / resolution / count rate
  - Neutron  $\lambda$  vs Q
    - large  $\lambda \rightarrow$  high resolution  $\rightarrow$  long times/slow motions
    - large  $\lambda \rightarrow$  limited Q-range, limited length scales

# The SNS Inelastic Instrument Suite



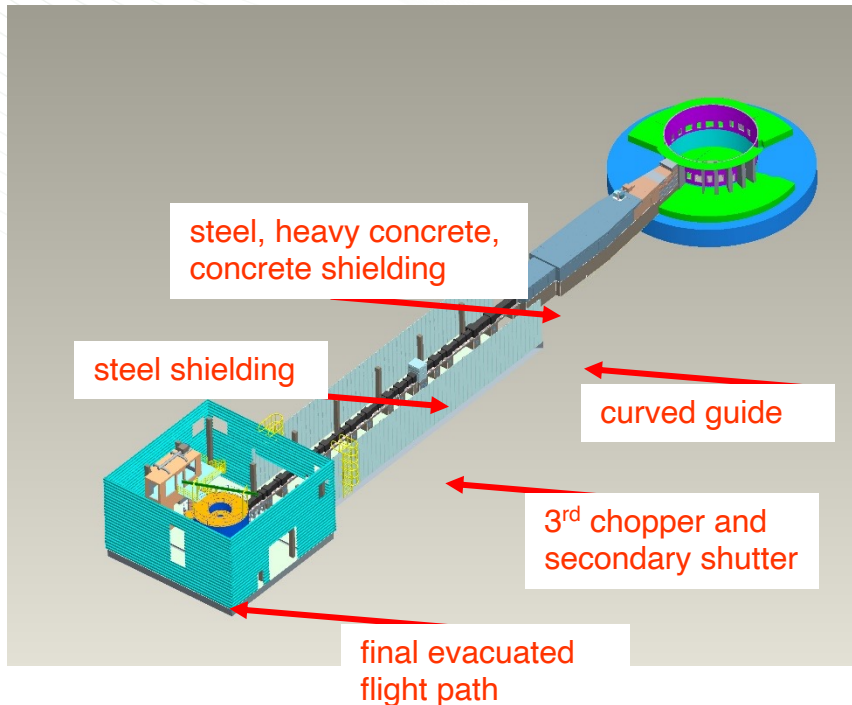
A large, blue, cylindrical structure with a spiral staircase, likely a backscattering spectrometer, is shown in a laboratory setting. The structure is mounted on a platform and has a metal railing around the top. The background shows a large industrial or laboratory space with various equipment and structural elements.

**BASIS**  
**backscattering**  
**spectrometer at SNS**

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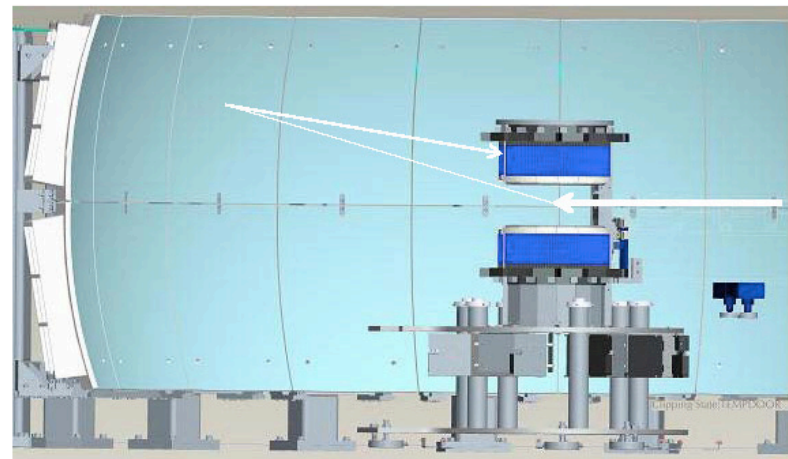
# BASIS overview

**B**Ackscattering **S**ilicon **S**pectrometer is a high-energy resolution, wide-dynamic range inverted geometry neutron spectrometer built on BL2 and facing a decoupled supercritical hydrogen, centerline-poisoned moderator



- Incident Flight Path - 84 m moderator-sample position
  - Curved Guide: 10 cm wide x 12 cm tall, 1000 m radius of curvature, line-of-sight at 31 m
  - Straight Guide: 10 cm wide x 12 cm tall
  - Converging Funnel: last 7.7 m; exit 3.25 cm x 3.25 cm, stops 27.5 cm from sample
- Chopper System
  - 3 bandwidth/frame overlap choppers at 7, 9.25 and 50 m
  - Operation at 60 (standard), 30, 20, 15, 12, or 10 Hz
  - Bandwidth (full choppers transmission) of about 0.5 Å at 60 Hz

# Instrument Specifications



|                           | Si111   | Si311   |
|---------------------------|---|---|
| Elastic energy            | 2.08 meV  | 7.63 meV  |
| Bandwidth                 |   |   |
| 60 Hz                     | $\pm 100 \mu\text{eV}$                            | $\pm 660 \mu\text{eV}$                            |
| 30 Hz                     | $\pm 200 \mu\text{eV}$                            | $\pm 1700 \mu\text{eV}$                           |
| Elastic resolution (HWHM) | $3.6 \mu\text{eV}$                                | $15 \mu\text{eV}$                                 |
| Q range (elastic)         | $0.2 \text{ \AA}^{-1} < Q < 2.0 \text{ \AA}^{-1}$ | $0.4 \text{ \AA}^{-1} < Q < 3.8 \text{ \AA}^{-1}$ |

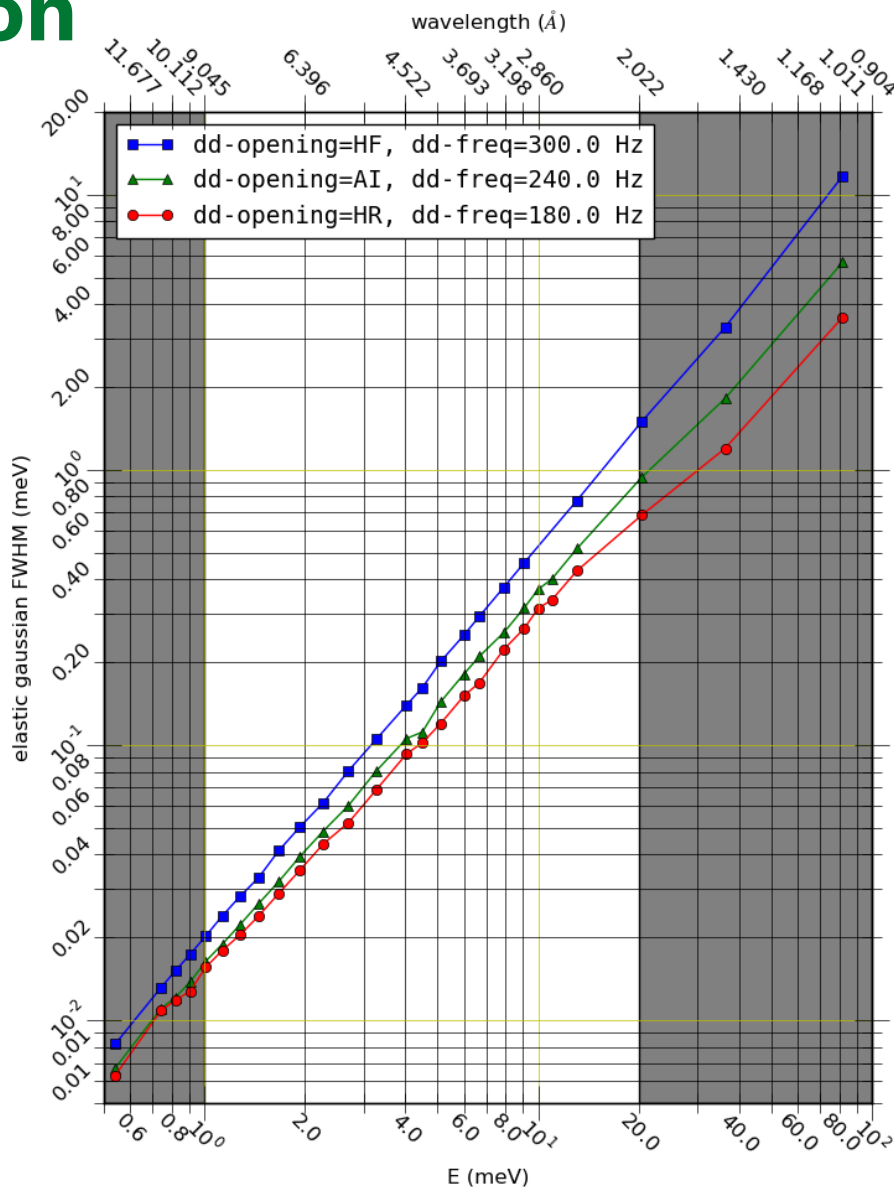
- Radial Collimator – restricts analyzer view of the sample
- Final Evacuated Flight Path - 2.5 m sample - analyzer,  $\sim 2.23$  m analyzer – detector
- Detector Choice – LPSD  $^3\text{He}$  tubes

A woman with short blonde hair, wearing a white long-sleeved shirt and blue jeans, stands on the left side of the frame, smiling. She is positioned next to a large, complex metal structure made of dark grey beams and lighter grey vertical supports. The structure appears to be part of a large scientific instrument. The background is a dimly lit industrial or laboratory setting with a concrete floor and various cables and pipes. The overall lighting is low, with some highlights on the metal surfaces.

# CNCS Cold Neutron Chopper Spectrometer

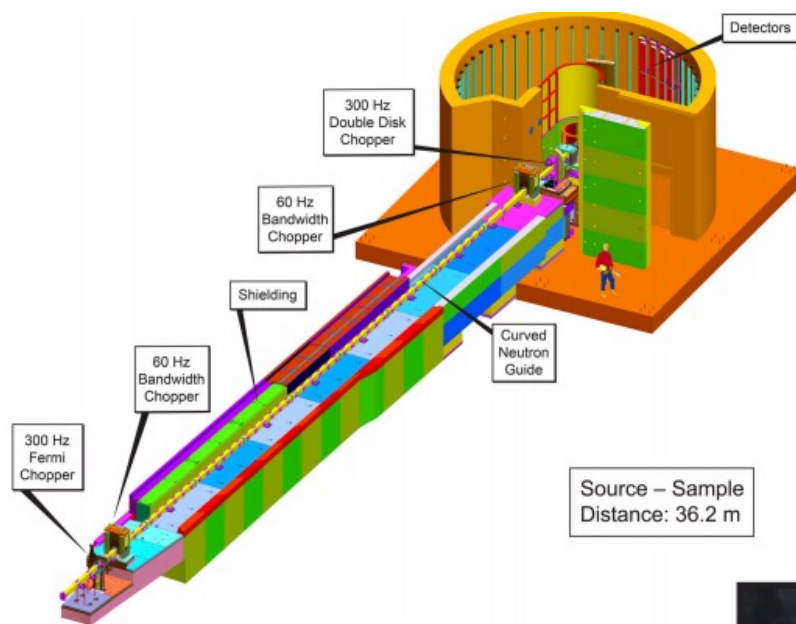
# Instrument Description

- direct-geometry, multi-chopper inelastic / QENS spectrometer designed to provide flexibility in the choice of energy resolution
  - best at low incident energies (2 to 50 meV).
  - typical experiments use energy resolutions between 10 and 500  $\mu\text{eV}$ .





# Specifications



Source-sample distance

36.2 m

Sample-detector distance

3.5 m

Angular coverage

Horizontally:  $-50^\circ - +140^\circ$

Vertically:  $\pm 16^\circ$

Energy resolution

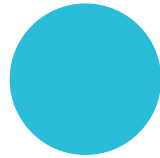
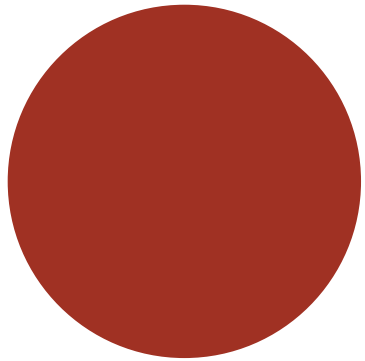
10 – 500  $\mu\text{eV}$

Incident energy range

0.5 – 80 meV

Momentum transfer range

0.05 – 10  $\text{\AA}^{-1}$



# **QENS theory**



# Incoherent vs Coherent Neutron Scattering

Different atoms and isotopes have different coherent and incoherent scattering cross sections

| Element       | $\sigma_{\text{coh}}$ (barns) | $\sigma_{\text{inc}}$ (barns) |
|---------------|-------------------------------|-------------------------------|
| Hydrogen (H)  | 1.8                           | 79.9                          |
| Deuterium (D) | 5.6                           | 2.0                           |
| Carbon (C)    | 5.6                           | 0.001                         |
| Oxygen (O)    | 4.232                         | 0                             |

If the scattered neutron waves from the different nuclei have RANDOM relative phases (no interference)  
=> **INCOHERENT SCATTERING**

If the scattered neutron waves from the different nuclei have definite relative phases, they can interfere  
=> **COHERENT SCATTERING**

**DYNAMICS**

**Protonated** sample to observe single particle dynamics (quasielastic) and for the inelastic spectrum to weight hydrogen vibrations.

**STRUCTURE**

**Deuterated** sample to obtain structure and collective excitations.

**Deuteration** can help to **suppress** dynamics of particular groups

# QENS - Incoherent and Coherent Scattering

- Large proportion of QENS experiments focus on dynamics of hydrogenous samples

$$S(Q, \omega) = S_{inc}(Q, \omega) + S_{coh}(Q, \omega)$$

No information about structure  
Dominated by H dynamics

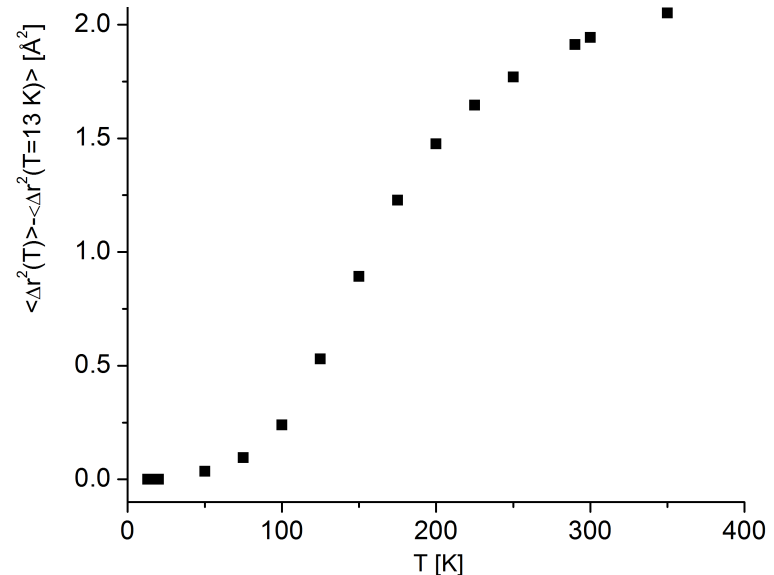
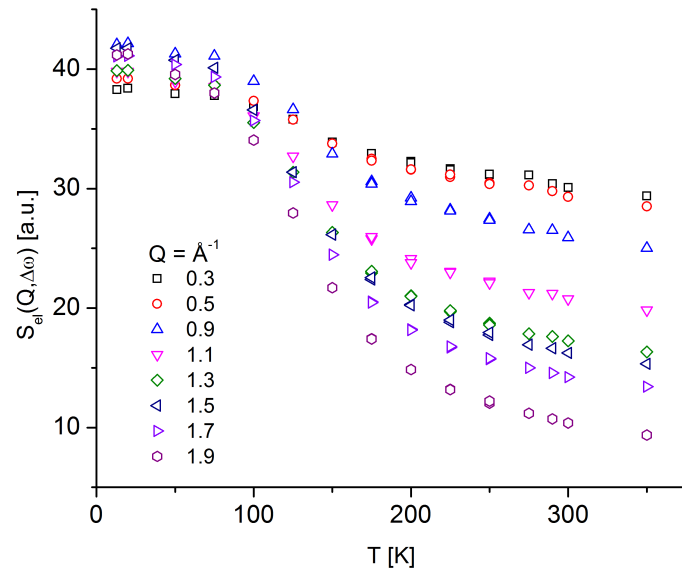
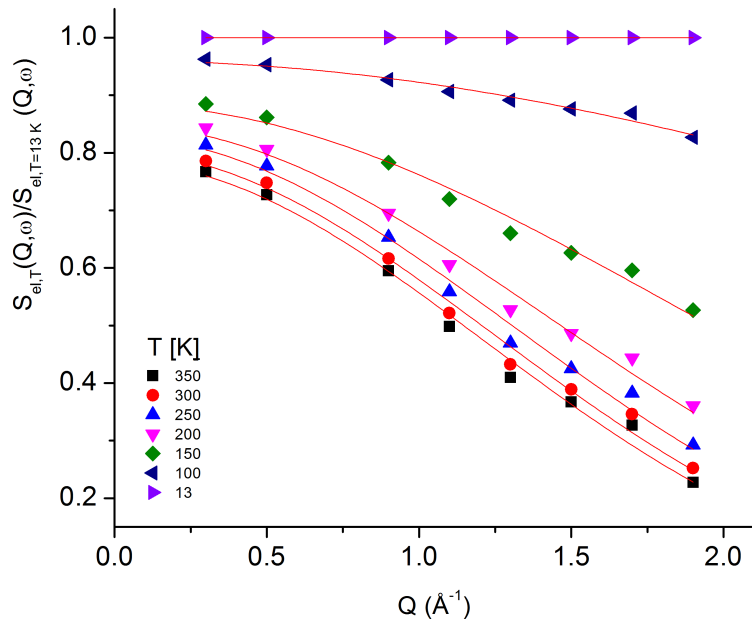
Contaminates QENS signal (Bragg peaks)

- Coherent QENS signal observable e.g. oxide ion diffusion
- Mixed coherent and incoherent QENS signal e.g. lithium or sodium diffusion

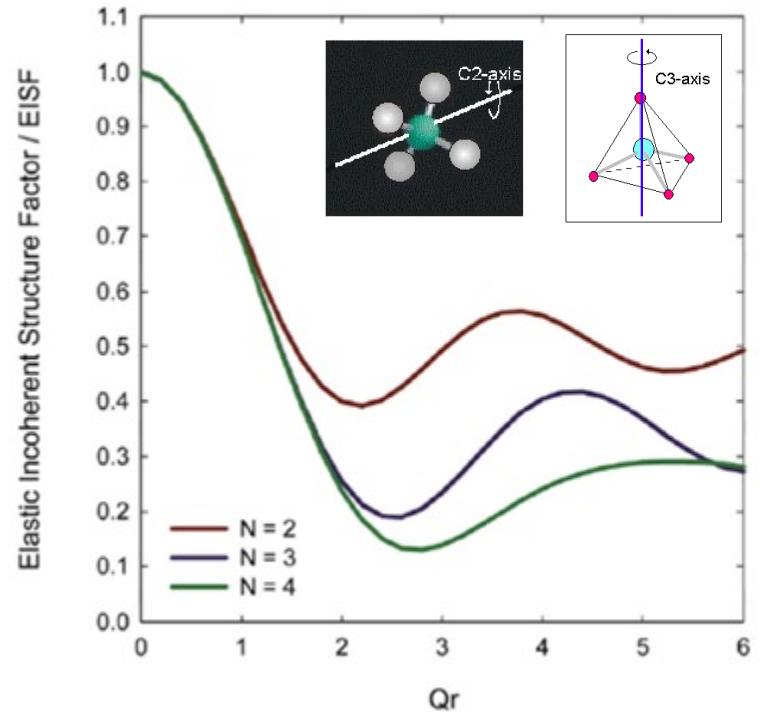
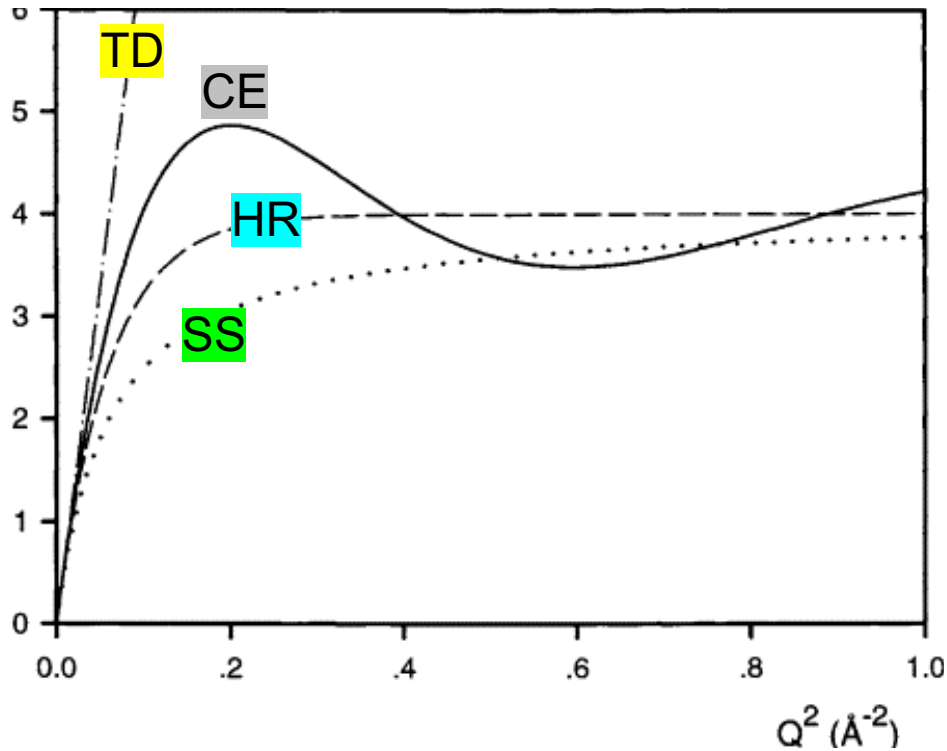
# Elastic Window Scan

- Elastic intensity scan as a function of temperature is a typical approach to estimate dynamic transitions.
- Resembles a DSC scan, i.e. locate transition temperature at which the dynamics enter the time window of the neutron spectrometer.
- Derive MSD using Gaussian approximation

$$S_{el}(Q, \omega) = A * e^{-Q^2 \langle r^2 \rangle / 3}$$



# QENS diffusion models

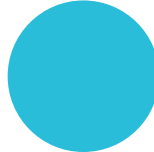
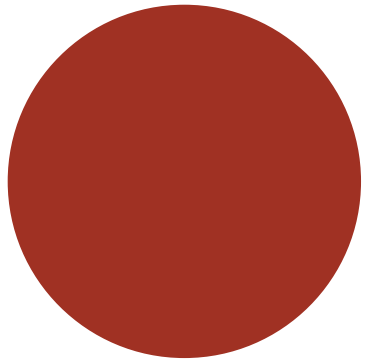


- **(TD)** Translational Diffusion following Fick's law
- **(CE)** Chudley-Elliott -model, jump diffusion on a lattice
- **(SS)** Singwi-Sjölander -model, alternation between oscillatory motion and directed motion
- **(HR)** Hall-Ross –model, jump diffusion within a restricted volume

## Spatially restricted diffusion

- Jumps between 2, 3, ... n sites
- Rotational diffusion on a circle
- Diffusion on a sphere
- Diffusion inside a sphere, cylinder

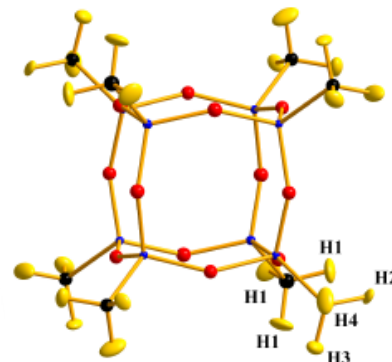
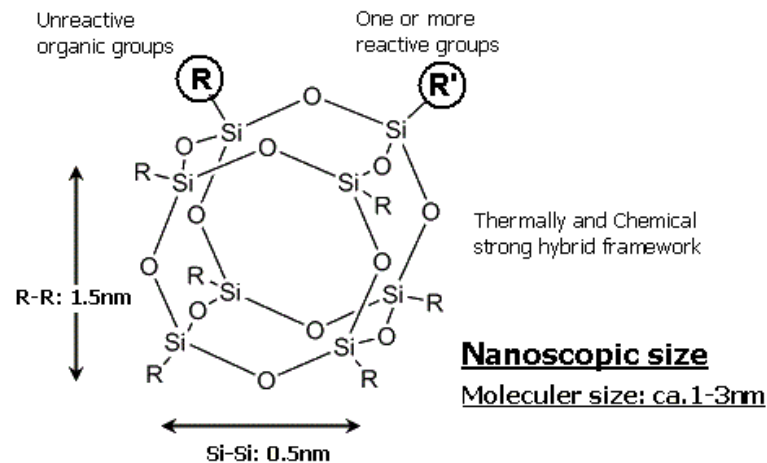
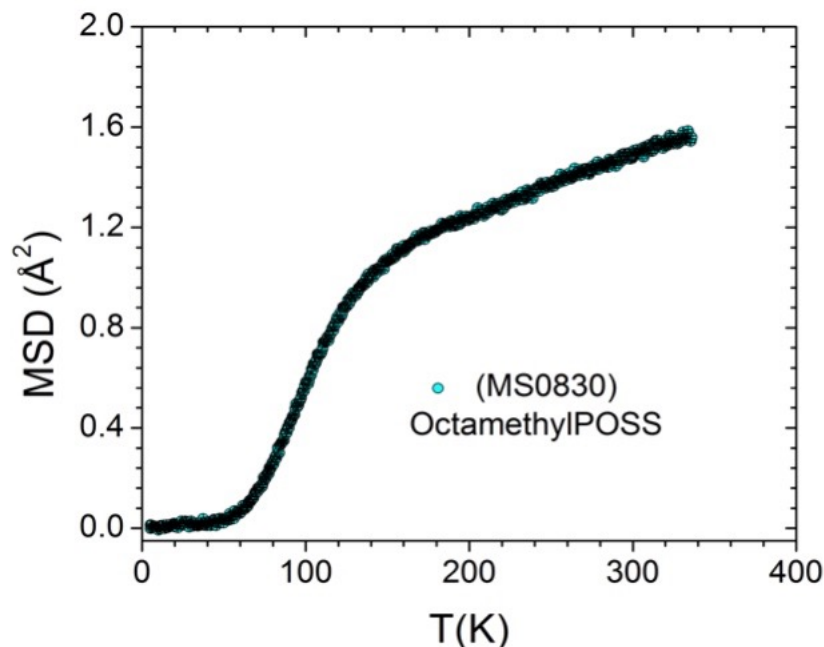
**Angular dependency gives access to fundamental processes**



**QENS - Science  
examples** |

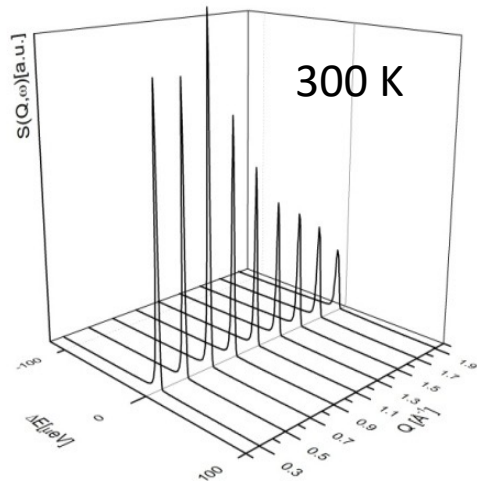
# Science Example 1: Molecular Reorientation

- Polyoligosilsesquioxane Ligand Dynamics
- How do ligand dynamics contribute to the functionalities of POSS?



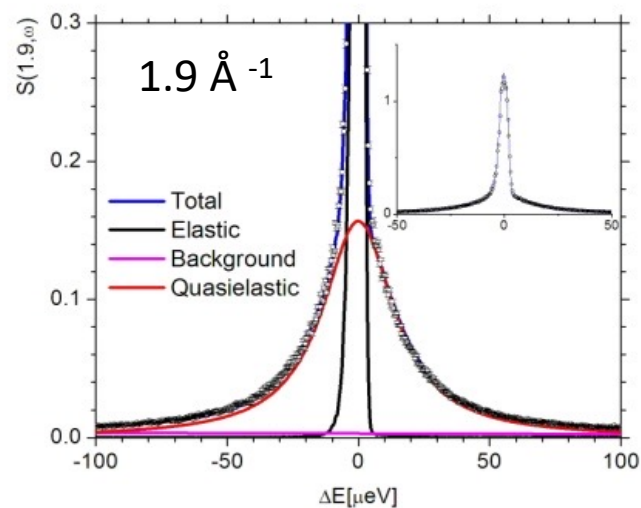
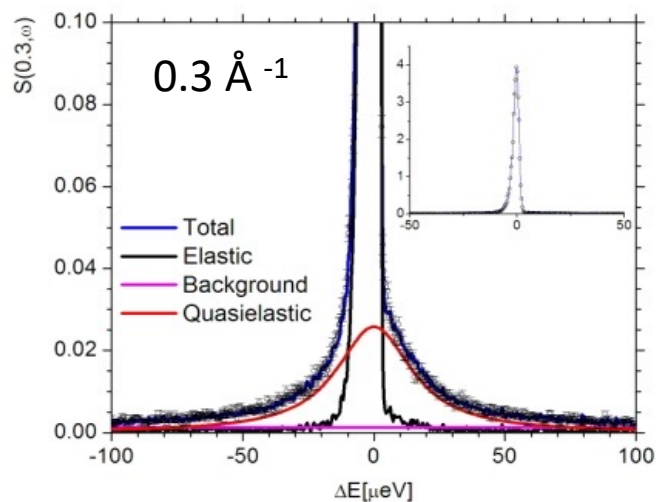


# Science Example 1: Molecular Reorientation

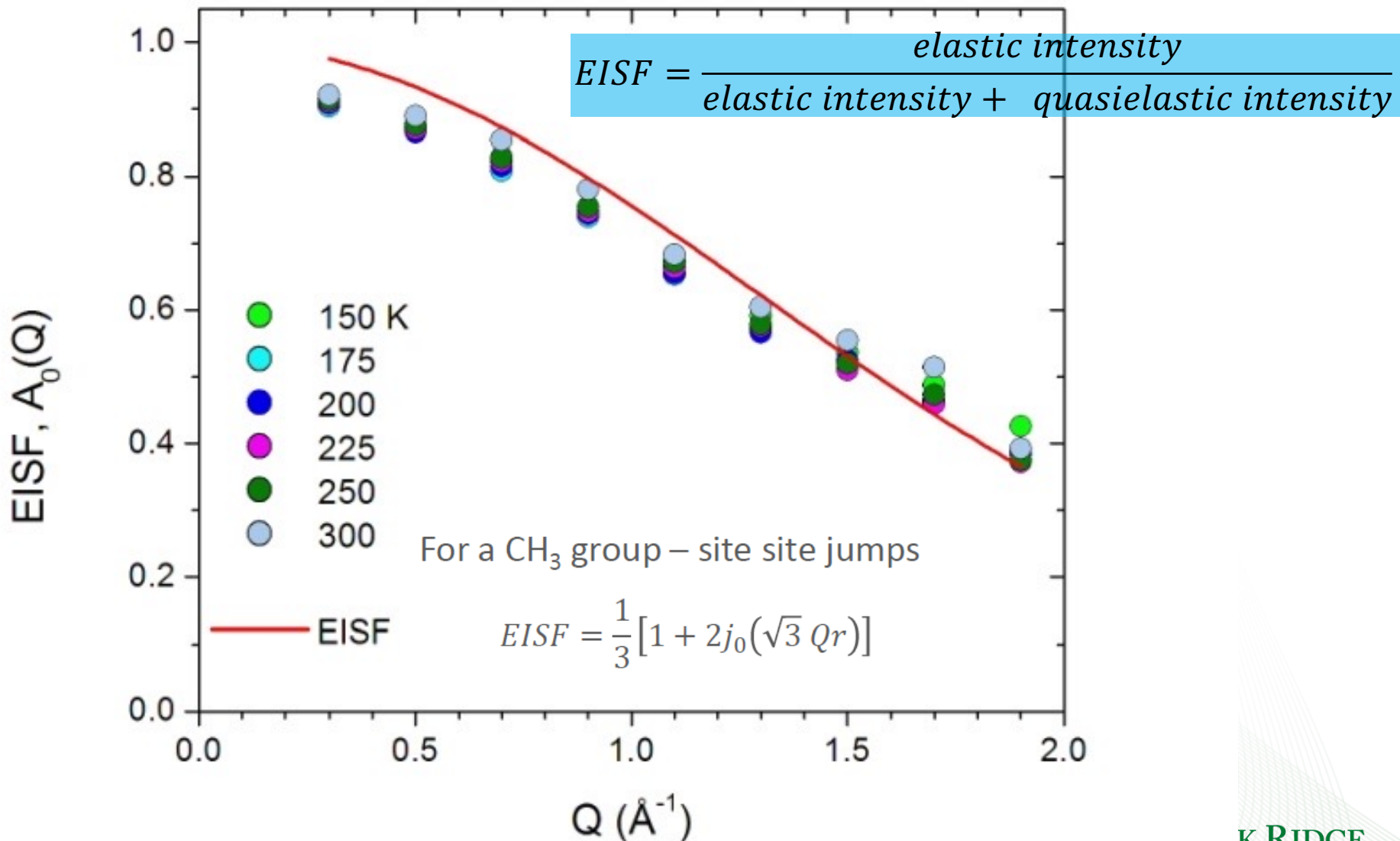


Octamethyl POSS @ BASIS

$$S(Q, \omega) = f \left[ p_0 \delta(\omega) + \sum_{i=1}^n p_i \frac{1}{\pi} \frac{\Delta_i(Q)}{\omega^2 + \Delta_i^2} \right] \otimes R(Q, \omega) + B$$



# Science Example 1: Molecular Reorientation

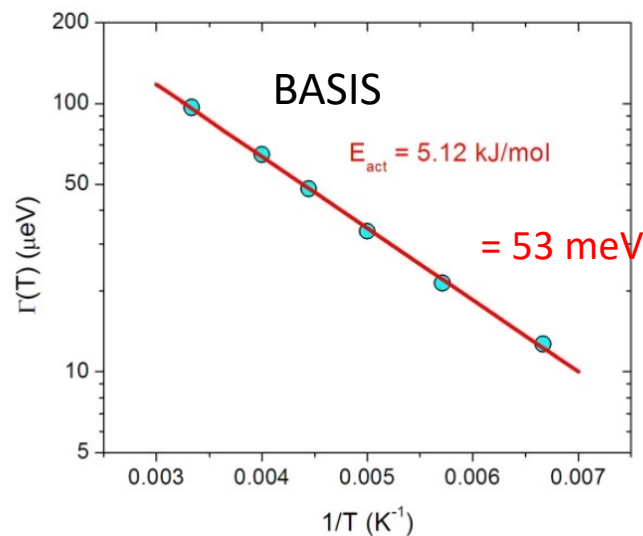


# Science Example 1: Molecular Reorientation

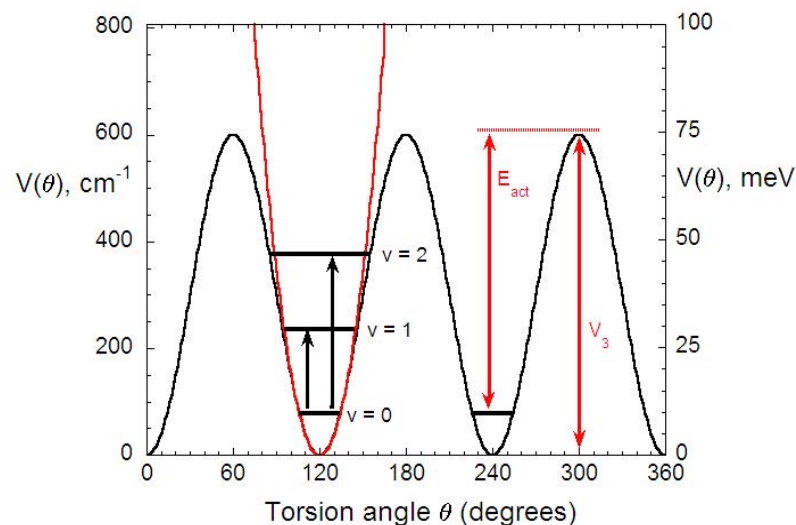
$$V(\theta) = \frac{V_3}{2} (1 - \cos 3\theta)$$

$$H\psi_n(\theta) = E_n\psi_n(\theta)$$

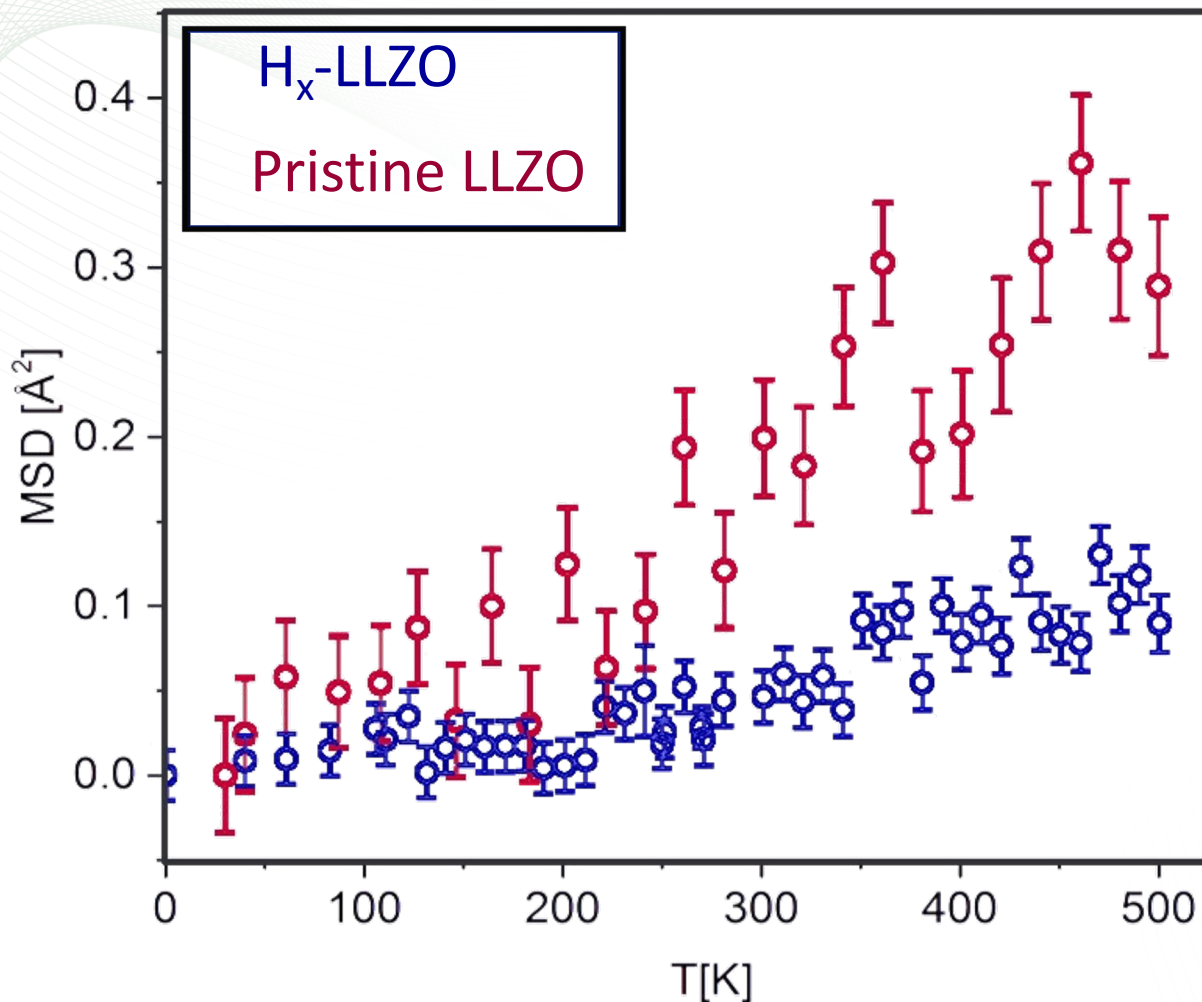
$$\rightarrow V_3 = 74.4 \text{ meV (7.18 kJ/mol)}$$



Barrier for methyl rotation

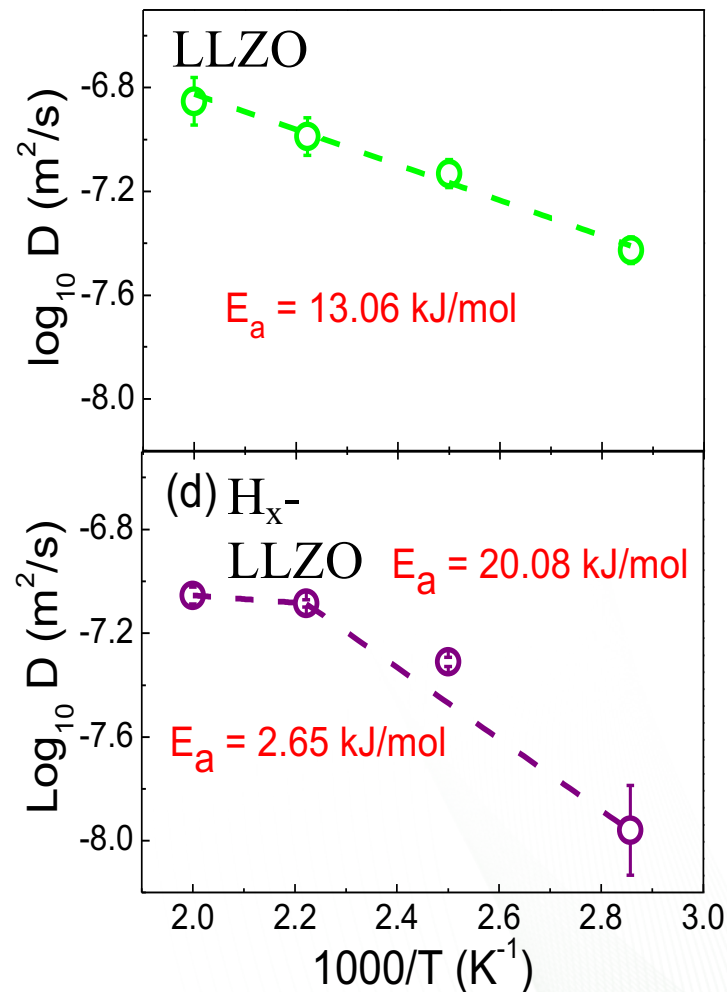
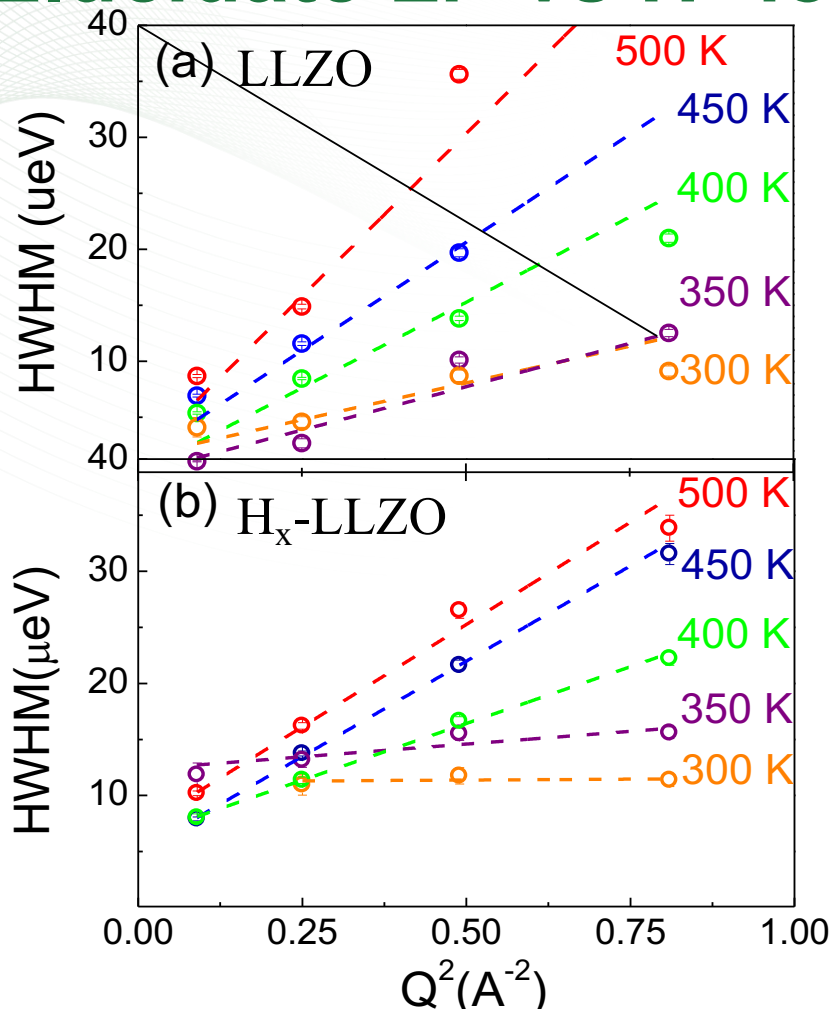


# Science example 2: Elucidate $\text{Li}^+$ vs $\text{H}^+$ ion diffusion



$\text{H}^+$  ions were found to be immobile while  $\text{Li}^+$  ion maintained a desired mobility in the solid electrolyte  $(\text{Li}_{6.25-x}\text{H}_x\text{Al}_{0.25})\text{La}_3\text{Zr}_2\text{O}_{12}$

# Science example 2: Elucidate Li<sup>+</sup> vs H<sup>+</sup> ion diffusion



H<sup>+</sup> ions are found to be immobile while Li<sup>+</sup> ions maintain mobility in H-LLZO at the operating temperature range of ALBs.

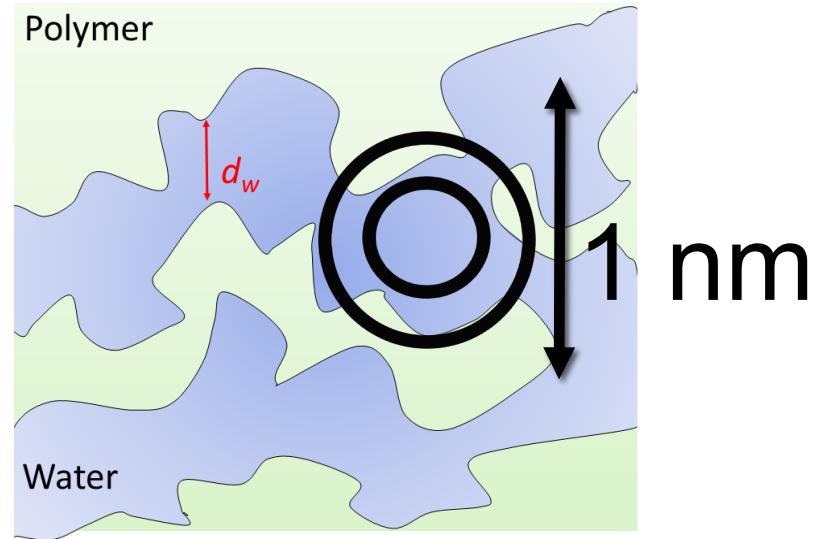
# Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

Ionic conductivity and water transport are key properties for applications

Depends on water content

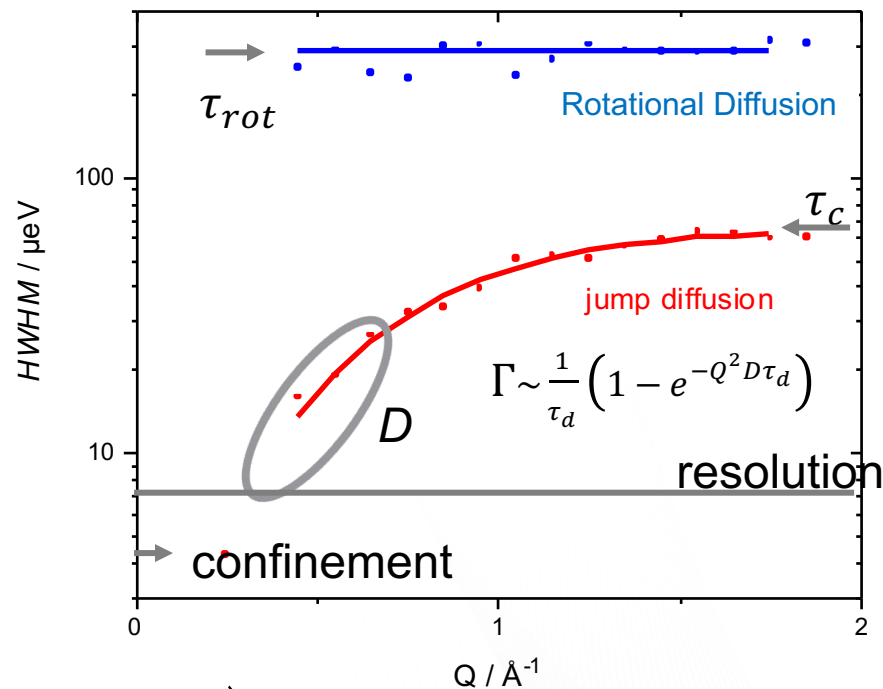
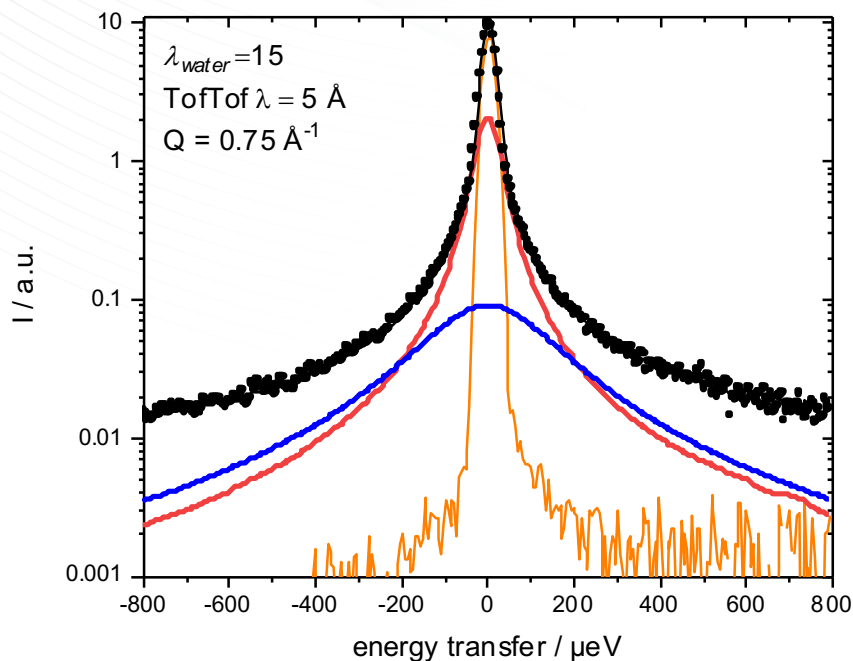
Water transport in AEM  
multiscale problem

Investigation of transport in multiple time- and length scales for structure – function insight



# Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

TOFTOF: time-of-flight spectrometer

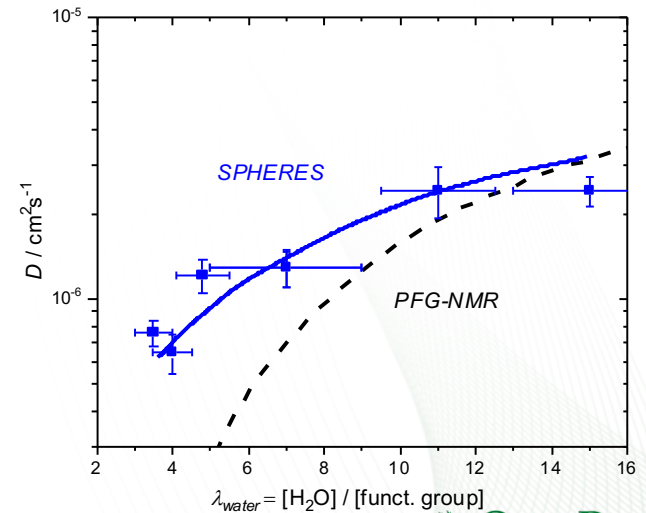
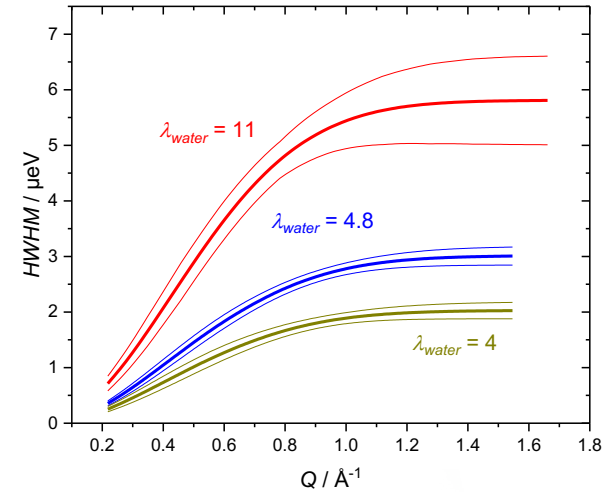
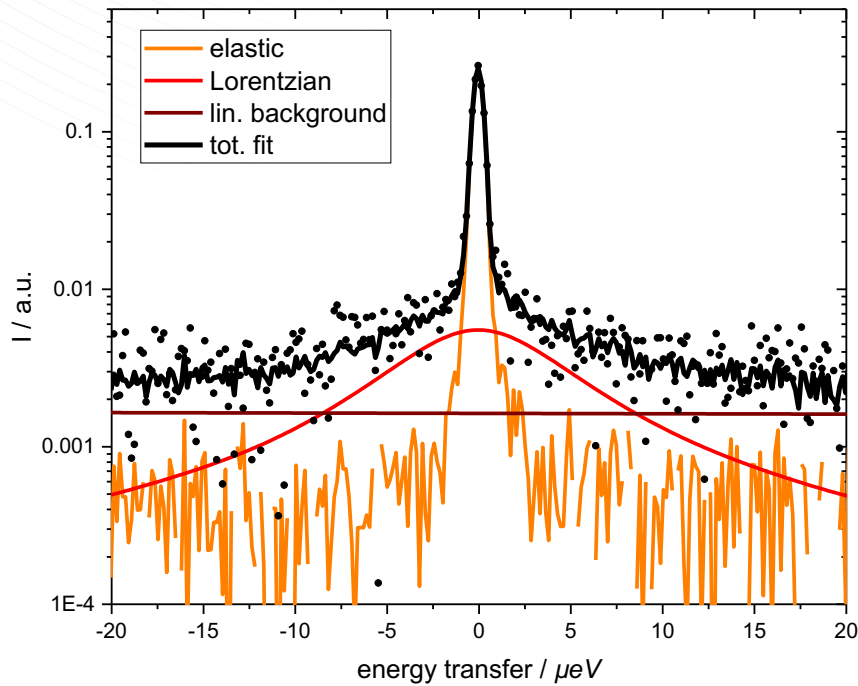


$$S(Q, \omega) = f \left( a_0(Q) \delta + \sum_n \frac{a_n(Q)}{\pi} \left( \frac{\Gamma}{\omega^2 + \Gamma^2} \right) \right) \otimes Res + Backg$$

# Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

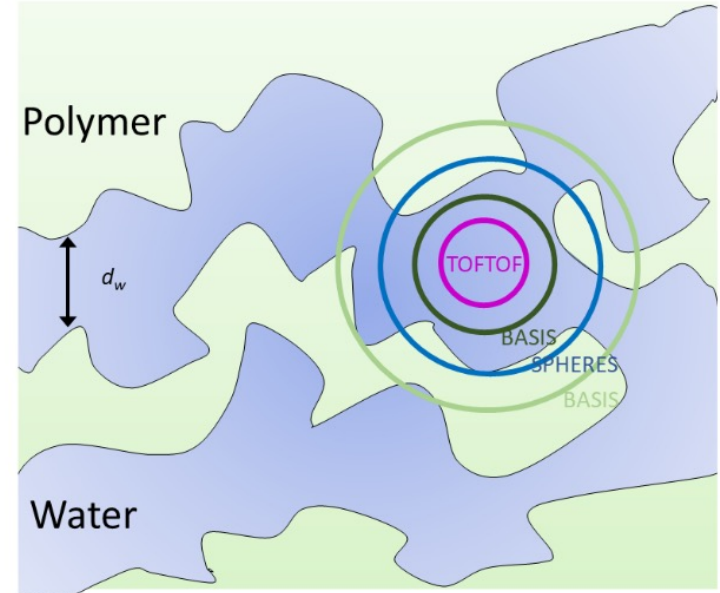
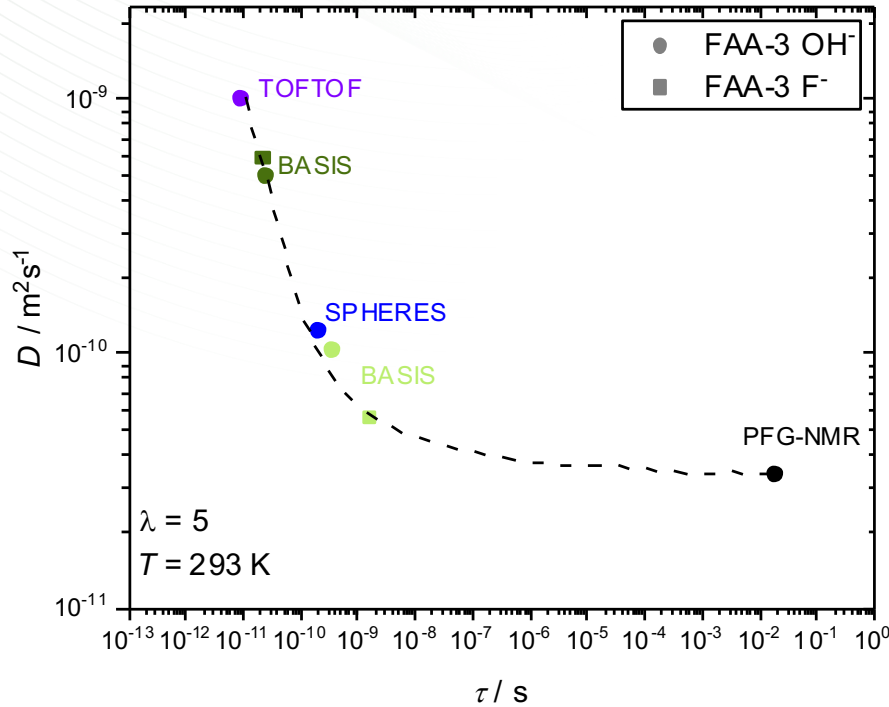
$$\Gamma \sim \frac{1}{\tau_d} \left(1 - e^{-Q^2 D \tau_d}\right)$$

**SPHERES: high-resolution  
backscattering spectrometer**





# Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS



# Summary:

- QENS is an unique technique to measure diffusive dynamics providing exclusive information about the geometry of the diffusion
  - accessible through Q-dependence
  - Large range of time scales available depending of the selected QENS instrument ( sub-picosecond  $< t <$  nanosecond ( $\mu\text{sec}$  for NSE)
  - Hydrogen sensitivity
- Instrument selection is a critical decision
  - resolution to match the time scale of the diffusion process
  - Q range to match the diffusion length scale
- Suitable technique to study dynamics in large variety of materials and science problems.

- Questions?

- Literature:

- Quasielastic Neutron Scattering, M. Bee (Bristol, Adam Hilger, 1988).
- Quasielastic Neutron Scattering and Solid State Diffusion, R. Hempelmann (2000).