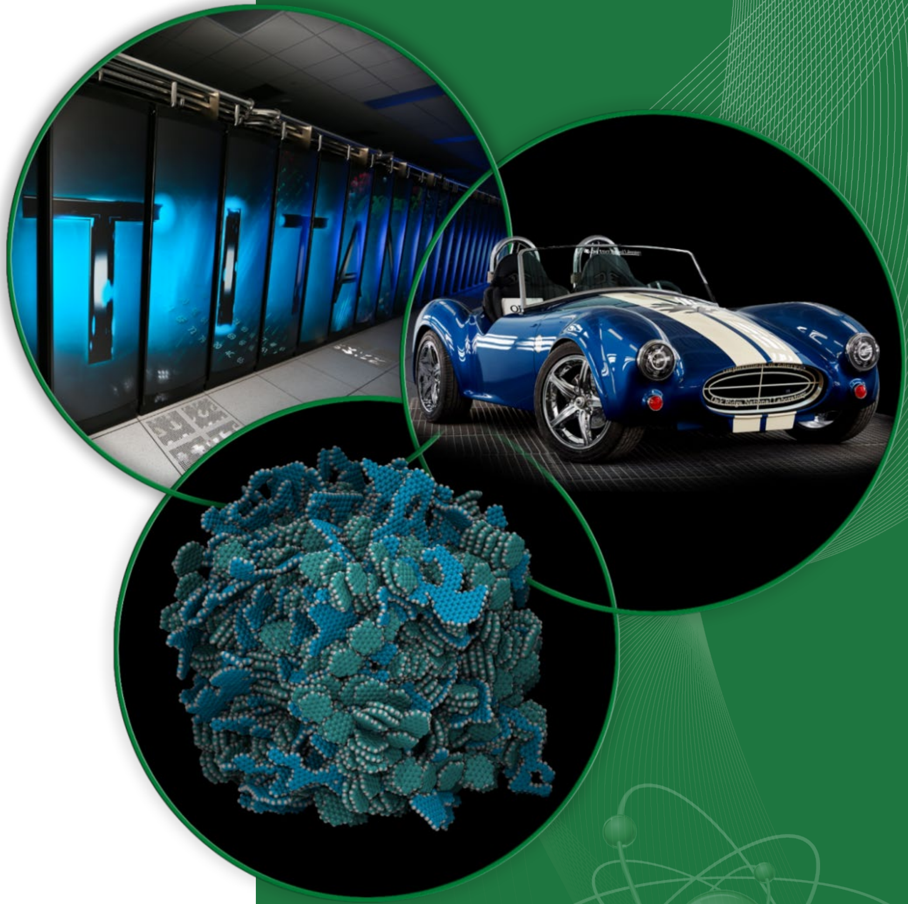
Quasi-Elastic Neutron Scattering



Niina Jalarvo

ORNL is managed by UT-Battelle
for the US Department of Energy

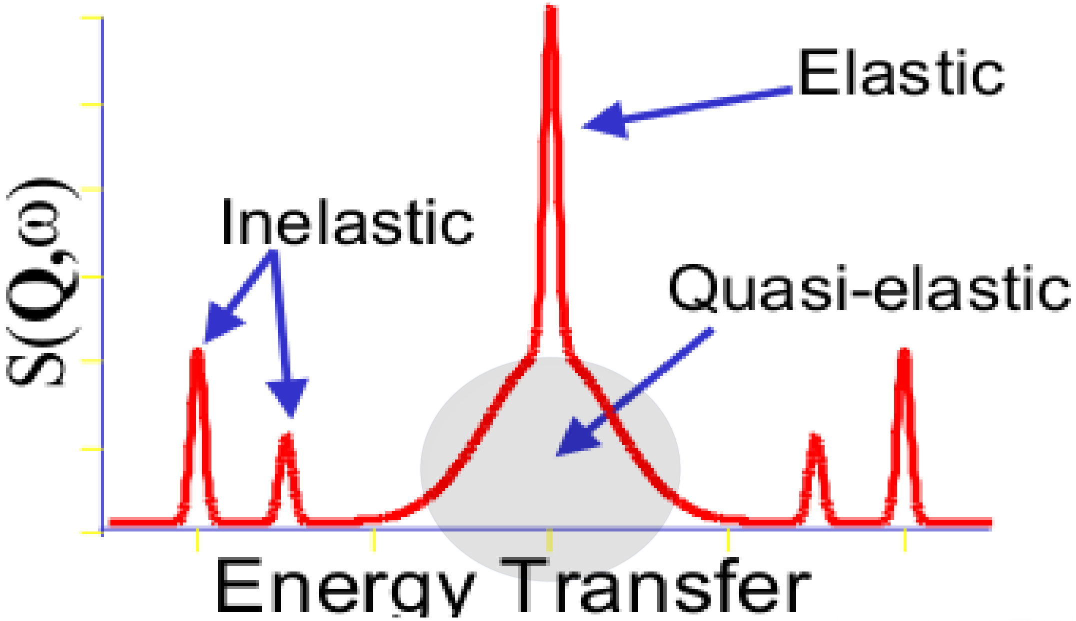
Oak Ridge National Laboratory

Overview

- INTRO to QENS
- QENS Instruments
- QENS Theory
- Science Examples

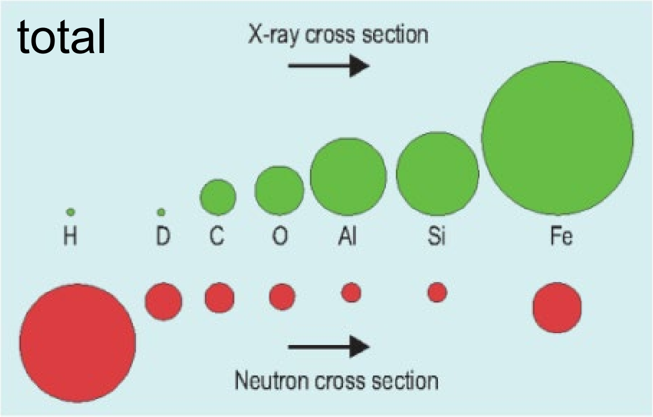
What is QENS

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 (σ)** – 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

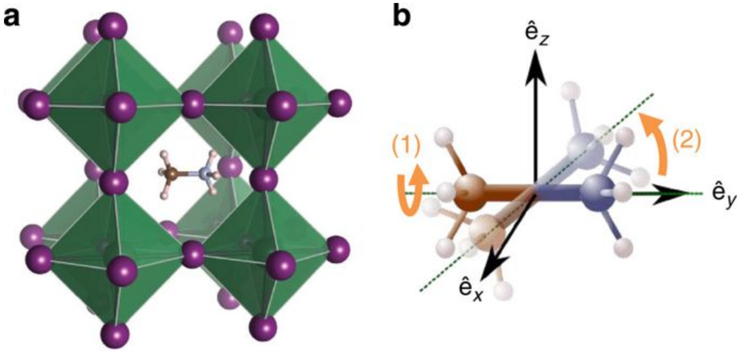
Probes slow dynamics

- Translational diffusion
- Molecular reorientations
- Relaxation processes

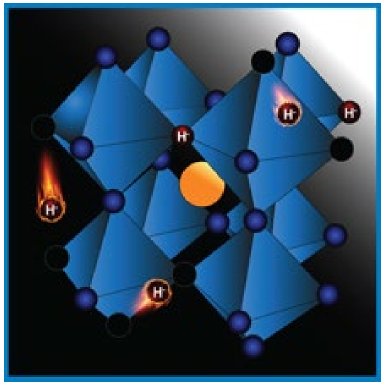
Applicable to wide range of scientific topics

- ***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

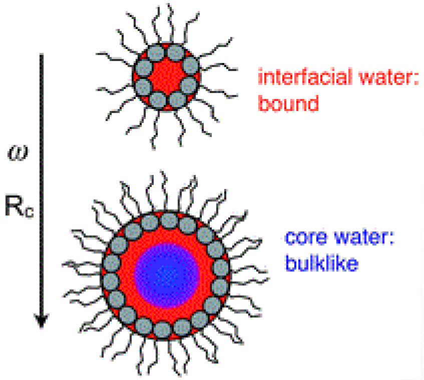
Results are comparable to Molecular Dynamics simulations



Nature Communications 6, 7124 (2015)

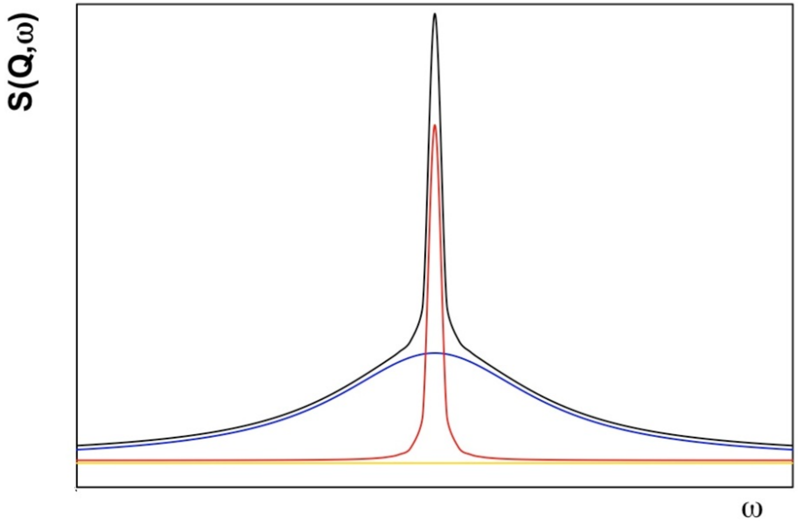


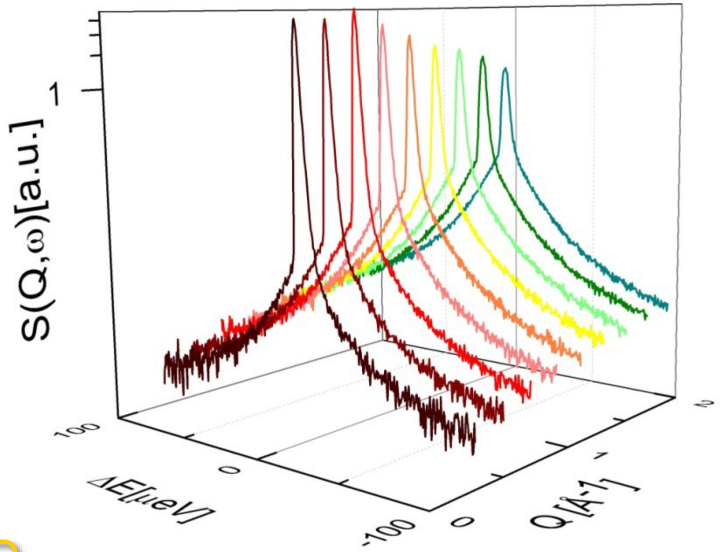
Journal of Physical Chemistry C, 123, 2019 (2019).



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

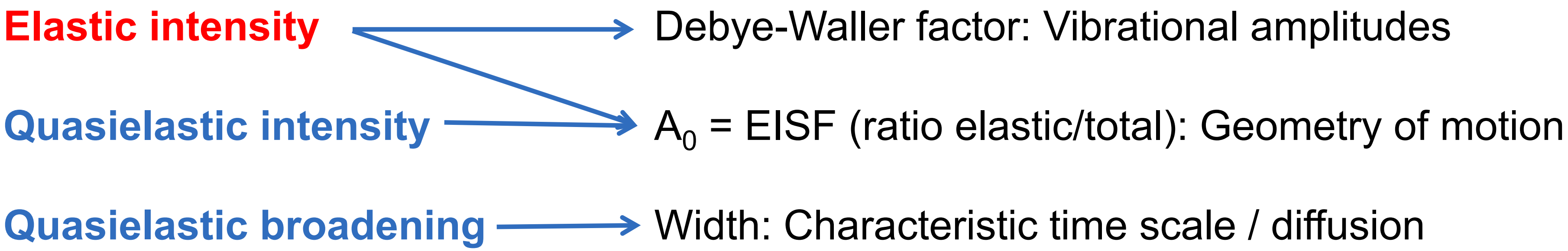
QENS spectra





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

Dynamic scattering function provides information on the sample states



Elastic intensity → Debye-Waller factor: Vibrational amplitudes

Quasielastic intensity → A_0 = 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

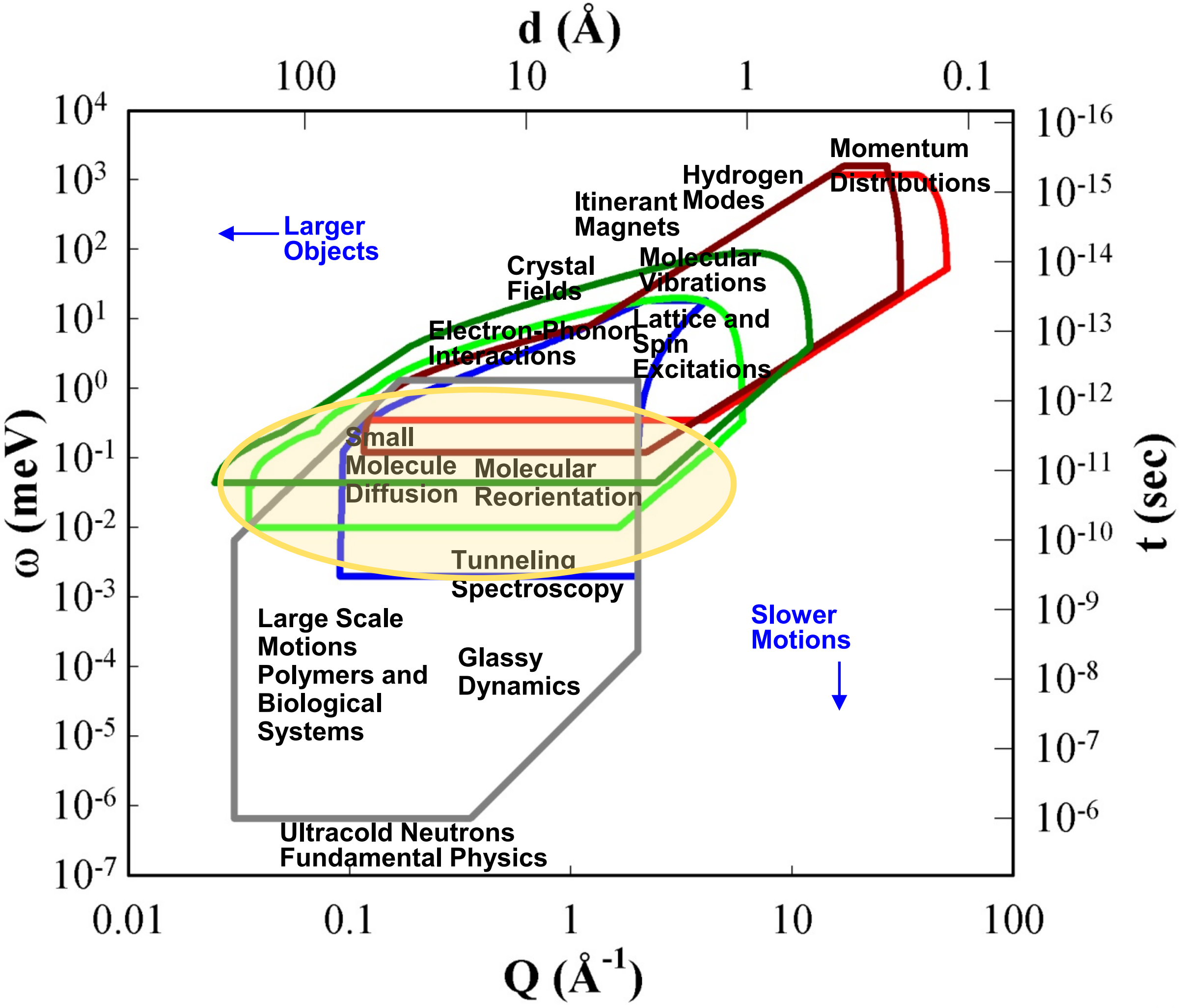
Time-of-Fligth Spectrometers

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

The SNS Inelastic Instrument Suite



- 🟥 ARCS Fermi Chopper
- 🟥 SEQUOIA Fermi Chopper
- 🟩 HYSPEC
- 🟩 Cold Neutron Chopper Spectrometer
- 🟦 Backscattering
- ● Neutron Spin Echo

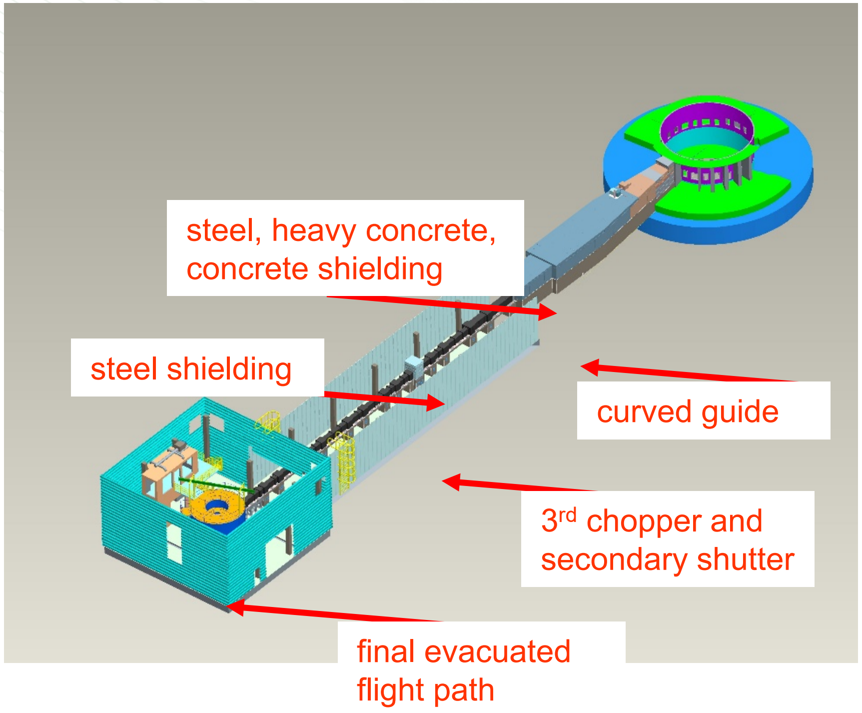
BASIS backscattering spectrometer at SNS

SNS


Front-End Building
BASIS
Klystron Building
Central Helium Liquefaction Building
Linac Tunnel
Ring
Radio-Frequency Facility
Target
Future Target Building
Support Buildings
Central Laboratory and Office Complex
Center for Nanophase Materials Sciences
Joint Institute for Neutron Sciences
01-04517/arb

BASIS overview

BAckscattering SIlicon Spectrometer 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

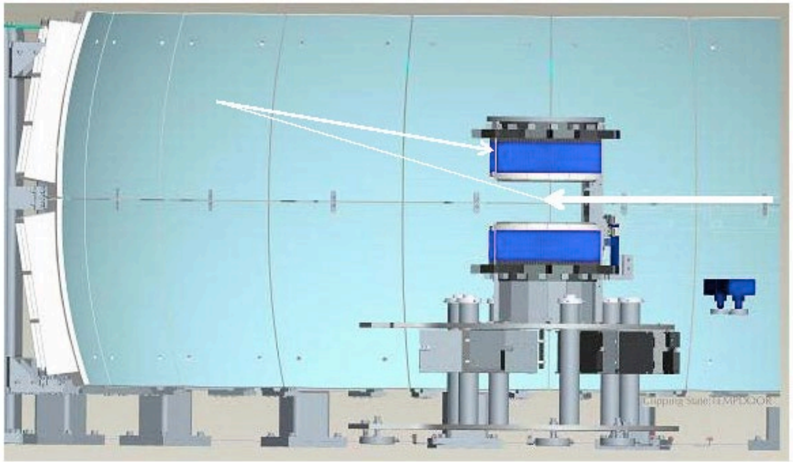
- Bandwidth (full choppers transmission) of about 0.5 Å at 60 Hz

Instrument Specifications

LABORATORY MANAGEMENT

SNS: No. 1 in Neutron Science

Completed on time, on budget, and on scope, the $1.4 billion Spallation Neutron Source will make Oak Ridge National Laboratory (ORNL) the world's foremost center for the study of neutron sciences. With 24 instruments and 2,000 scientists visiting each year, SNS will provide technological advances of lasting benefit to America's scientific, business, and industrial sectors. Among these anticipated discoveries will be lightweight plastics for more energy-efficient aircraft, superconducting wires that carry more power at less cost, fuel cells that power emission-free vehicles, and drug delivery systems that release medicines precisely when the body needs them. As a group of European scientists concurred during their visit to ORNL, "America now has the greatest facility in the world for the study of materials." UT-Battelle, LLC, manages ORNL for the U.S. Department of Energy. UT-Battelle, LLC, is composed of the University of Tennessee and Battelle.

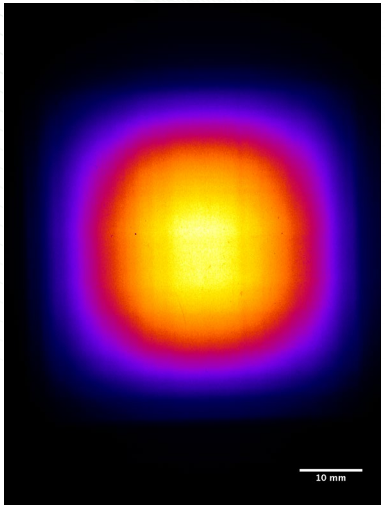


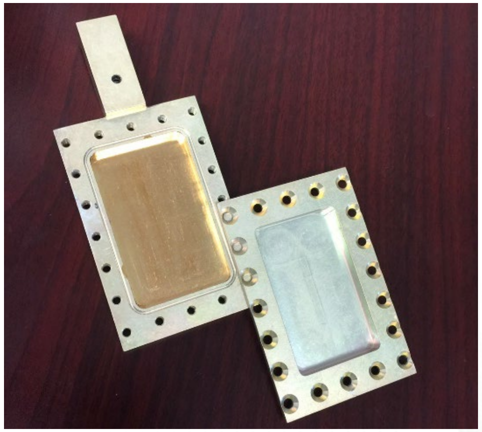
	Si111	Si311
Elastic energy	2.08 meV	7.63 meV
Bandwidth 60 Hz 30 Hz	±100 µeV ±200 µeV	±660 µeV ±1700 µeV
Elastic resolution (HWHM)	3.6 µeV	15 µeV
Q range (elastic)	0.2 Å^{-1} < Q < 2.0 Å^{-1}	0.4 Å^{-1} < Q < 3.8 Å^{-1}

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

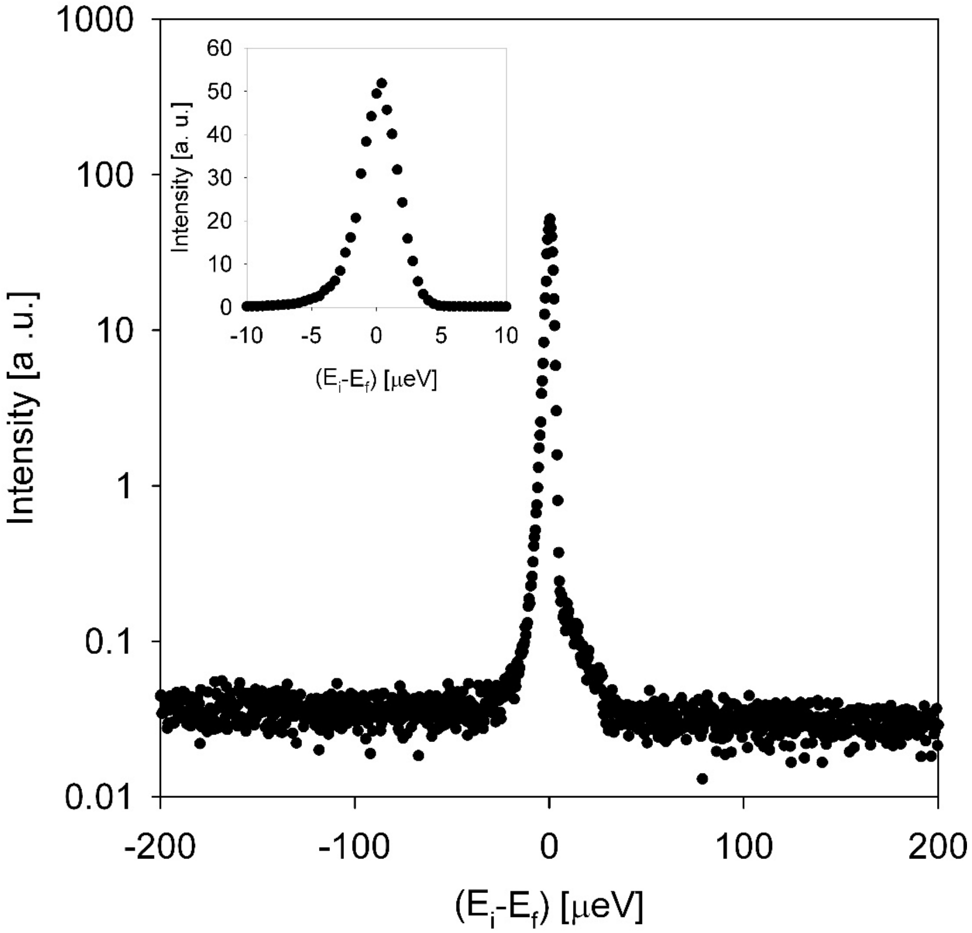
Sample

- Typical sample holders: annular cylindrical or flat plate
  - Keep sample thin to avoid multiple scattering effects
  - Transmission probability ~ 95 %



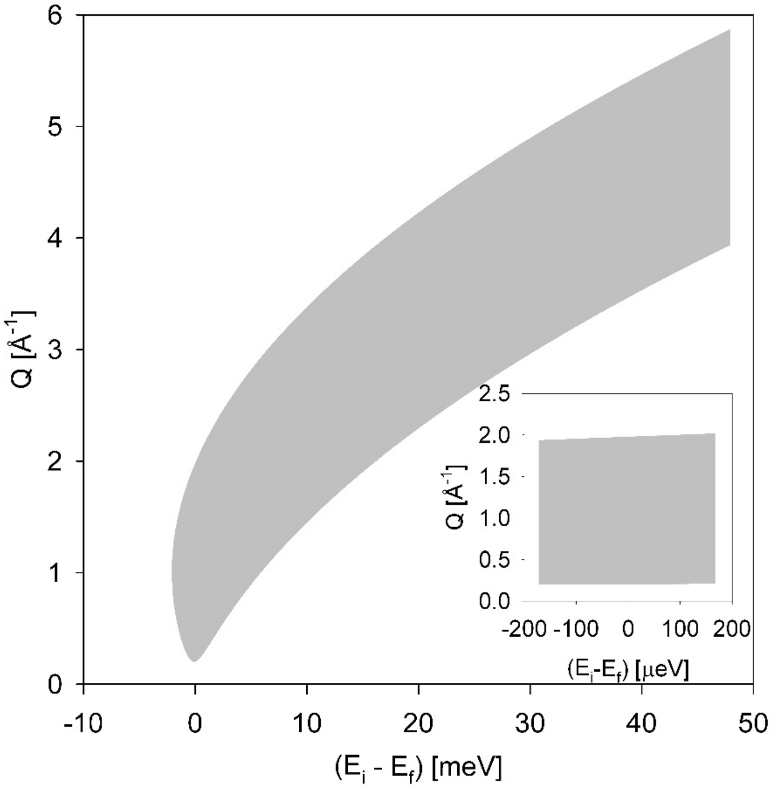


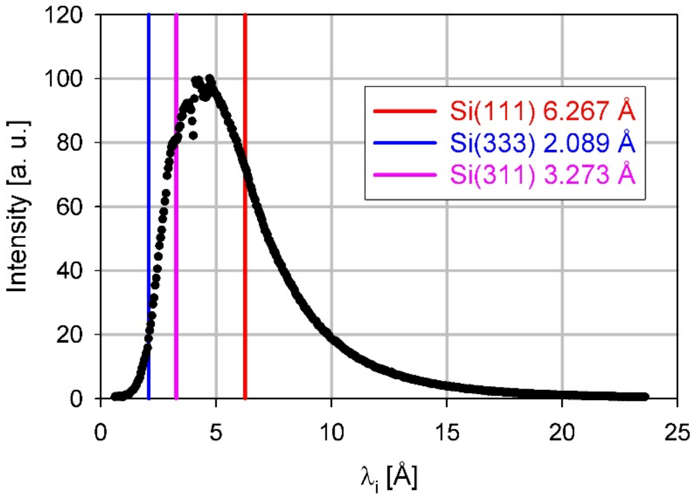
Vanadium Standard

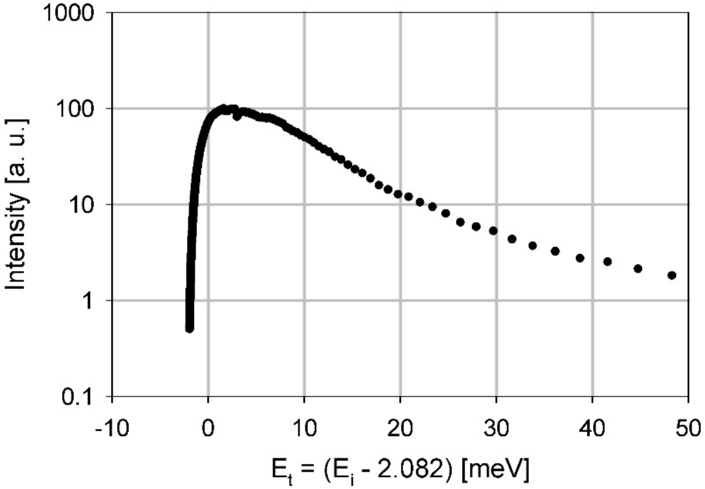


- Energy resolution (Q-averaged): 3.6 μeV (FWHM)
- Signal-to-background ratio (at the elastic line): better than 1000:1
- Dynamic range: variable (affects counting statistics, but not the energy resolution)

Incident spectrum and (Q,ω) coverage







- Incident band (full chopper opening): (60/ν)*[0.5 Å], where ν = 60, 30, 20, 15, 12, 10 Hz

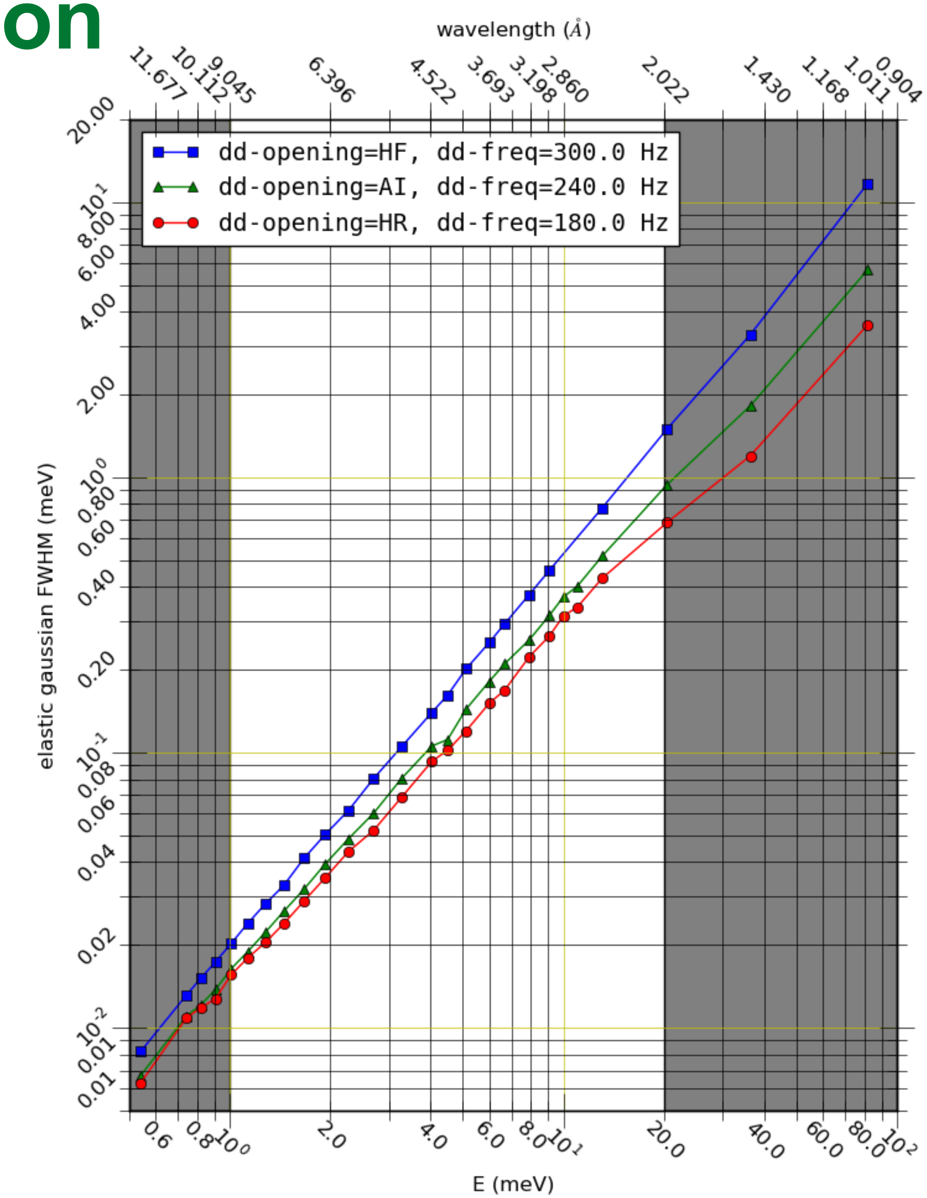
- Inelastic resolution: $\delta E \approx 0.001 * E_i$ at high energy transfers

1 Hz signal (no frame overlap), 1/v efficiency corrections applied

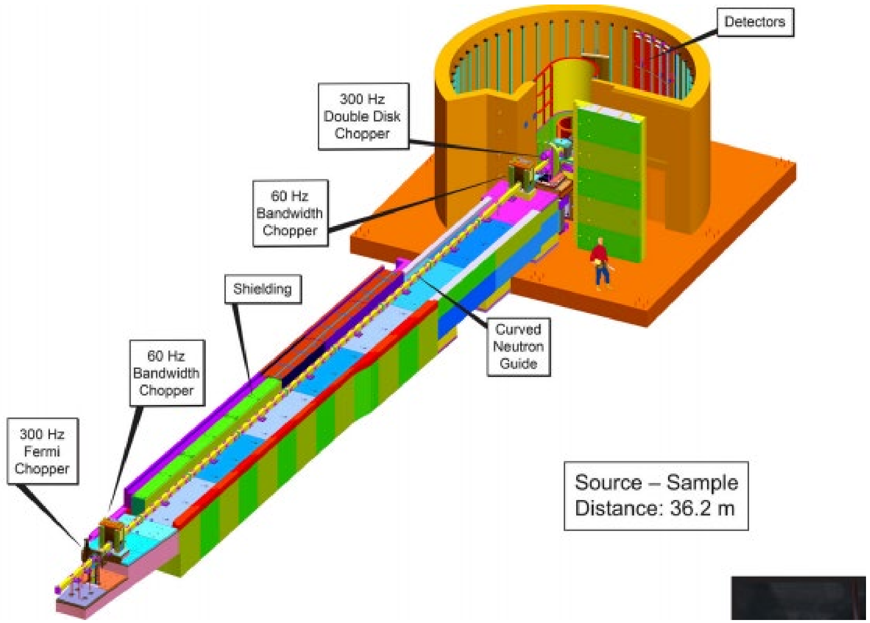
CNCS Cold Neutron Chopper Spectrometer

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 μeV.



Specifications



Source-sample distance	36.2 m
Sample-detector distance	3.5 m
Angular coverage	Horizontally:−50° – +140° Vertically:±16°
Energy resolution	10 – 500 μeV
Incident energy range	0.5 – 80 meV
Momentum transfer range	0.05 – 10 Â−1

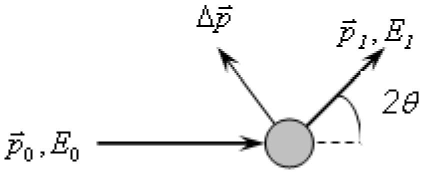
QENS theory

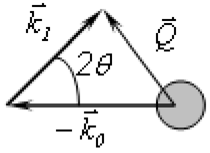
Scattering Kinematics

The collision of two objects (e.g. neutron and sample atom) can be described in terms of momentum and energy conservation.

Neutron scattering events are described by means of energy and momentum transfer.

$$\boxed{\begin{aligned}\hbar\vec{Q} &= \hbar\vec{k}_1 - \hbar\vec{k}_0\\ \hbar\omega &= E_1 - E_0\end{aligned}}$$

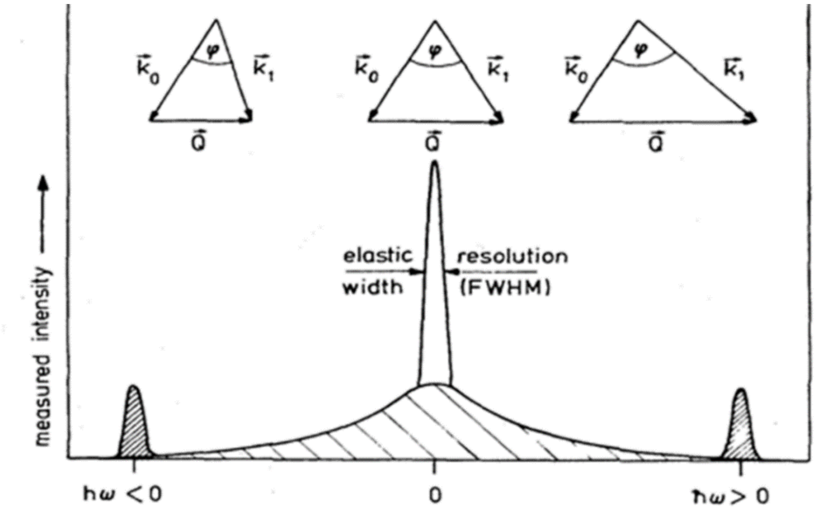




$\hbar\omega = 0 \longrightarrow$ **ELASTIC** scattering

$\hbar\omega \neq 0 \longrightarrow$ **INELASTIC** scattering

$\hbar\omega \approx 0 \longrightarrow$ **QUASIELASTIC** scattering



Incoherent vs Coherent Neutron Scattering

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

Element	σ_{coh} (barns)	σ_{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)
=> *IN*COHERENT 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

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

No information about structure
Dominated by H dynamics

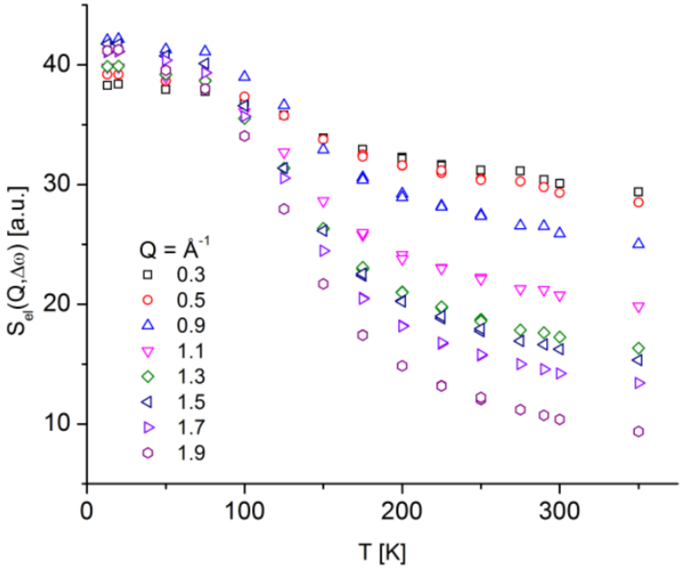
Contaminates QENS signal (Bragg peaks)

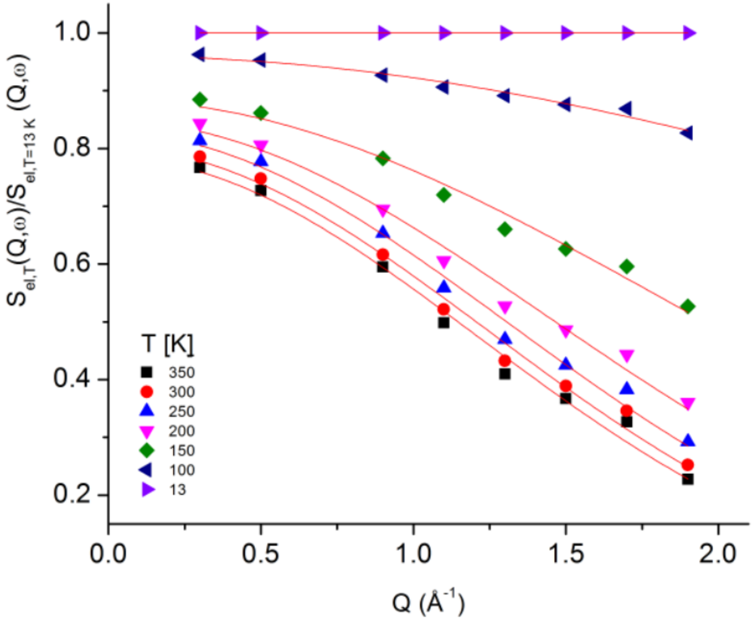
- Coherent QENS signal observable e.g. oxide ion diffusion
- Mixed coherent and incoherent QENS signal e.g. lithium or sodium diffusion

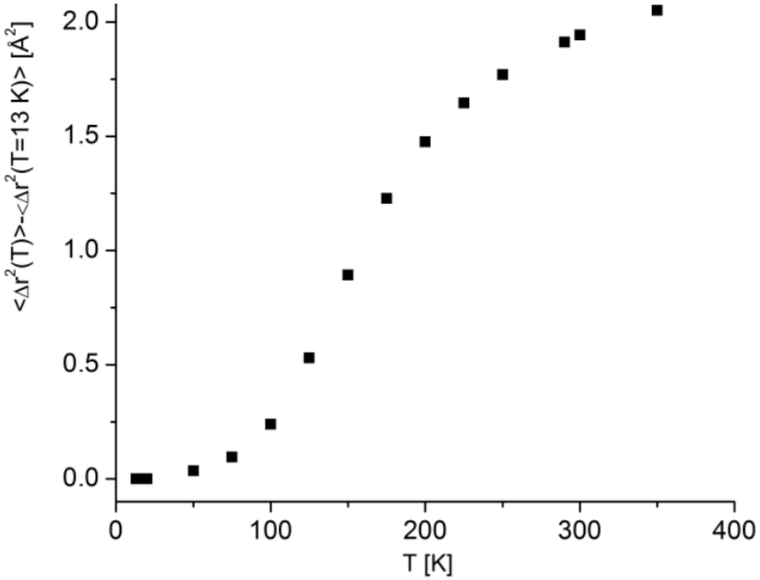
Elastic Window Scan

- 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

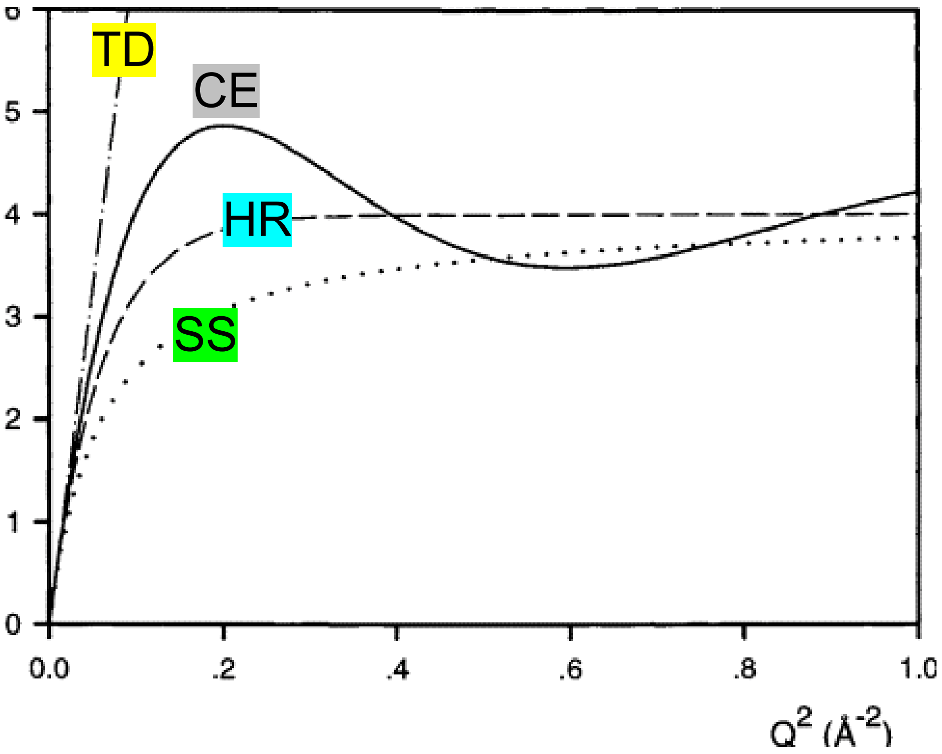
$$S_{el}(Q,\omega) = A * e^{-Q^2\left\langle r^2\right\rangle/3}$$

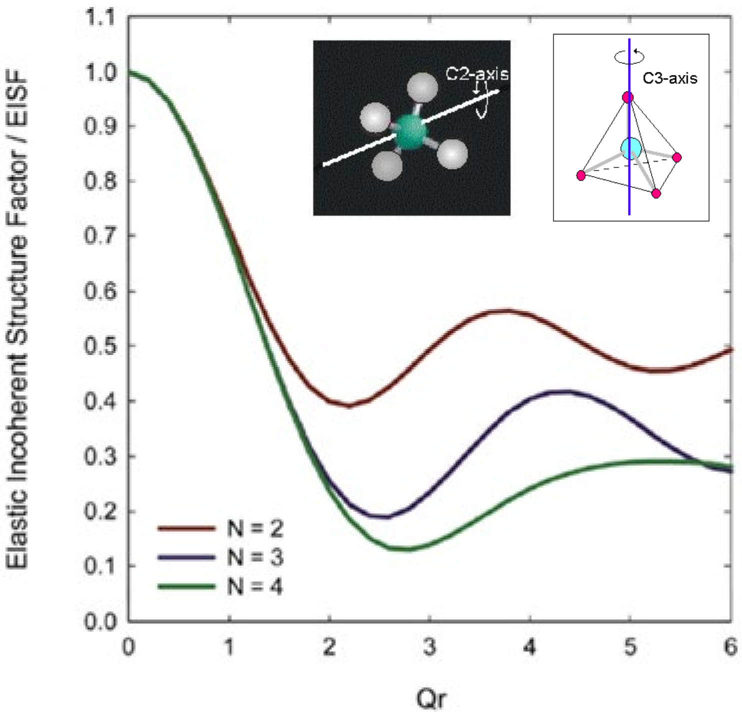






QENS diffusion models





- (TD) Translational Diffusion following Fick’s law
- (CE) Chudley-Elliot -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

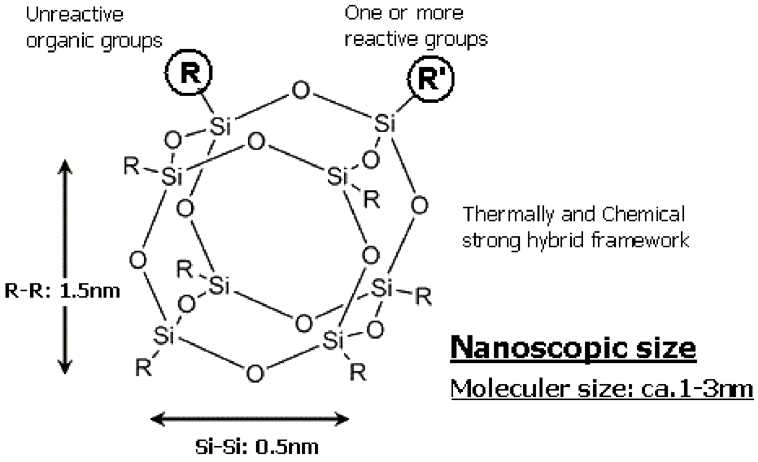
- Jumps between 2, 3, … n sites
- Rotational diffusion on a circle
- Diffusion on a sphere
- Diffusion inside a sphere, cylinder

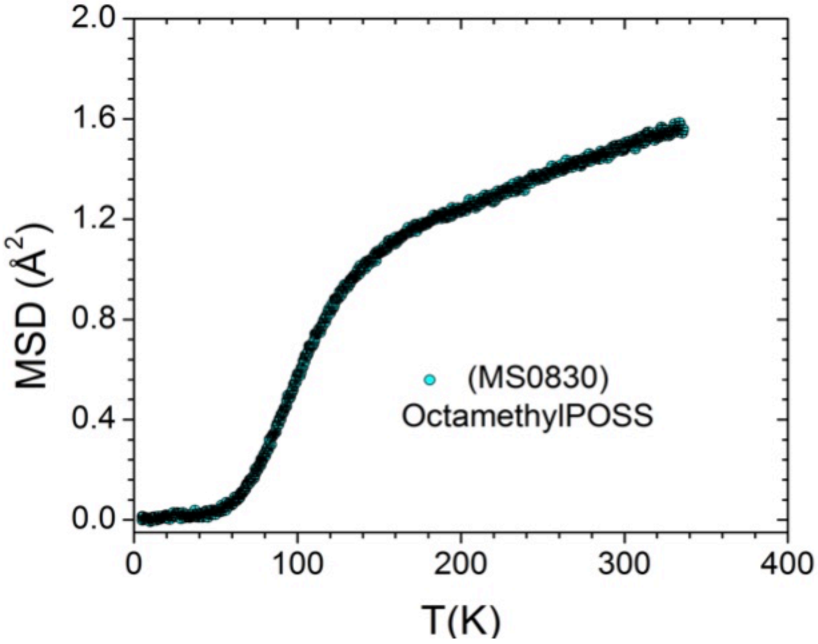
Angular dependency gives access to fundamental processes

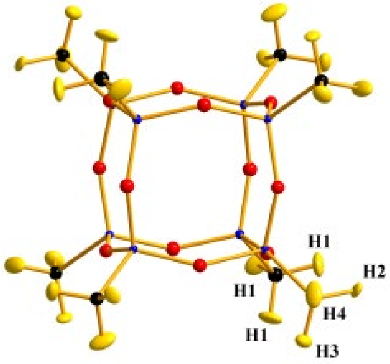
QENS - Science examples

Science Example 1: Molecular Reorientation

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

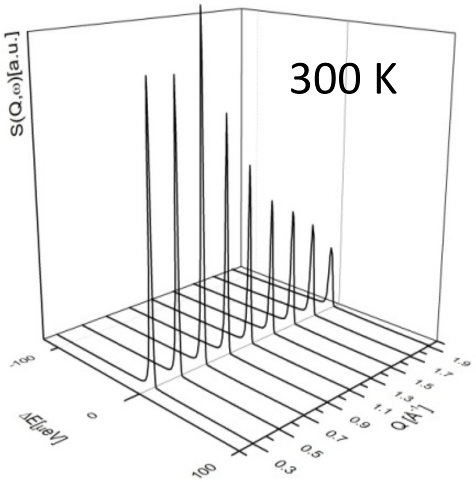






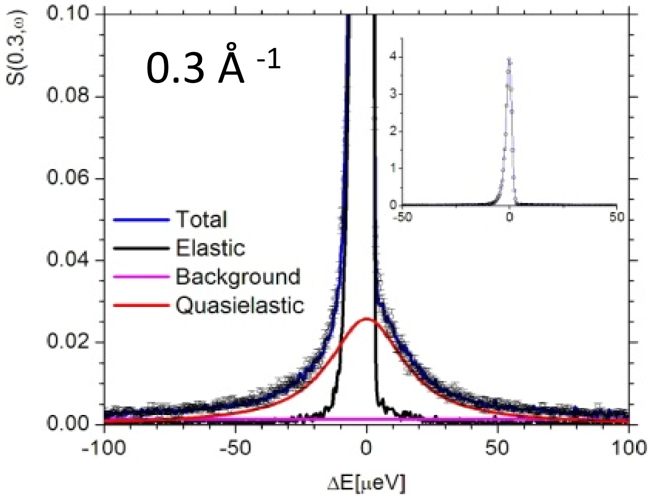
Jalarvo N., *et al, Journal of Physical Chemistry C,* **118,** 10, 5579-5592 (2014)

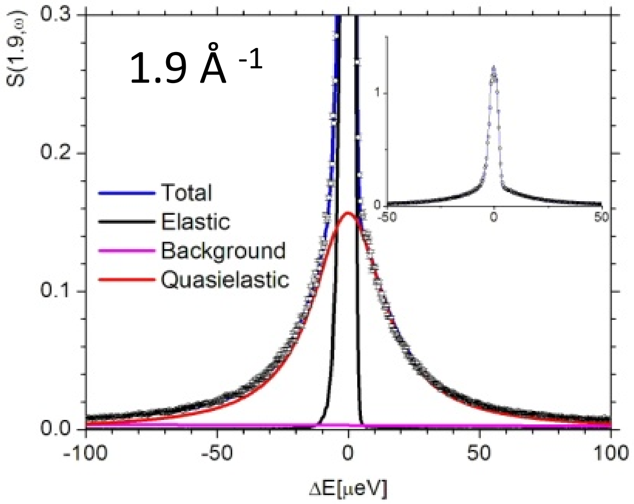
Science Example 1: Molecular Reorientation



Octamethyl POSS @ BASIS

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

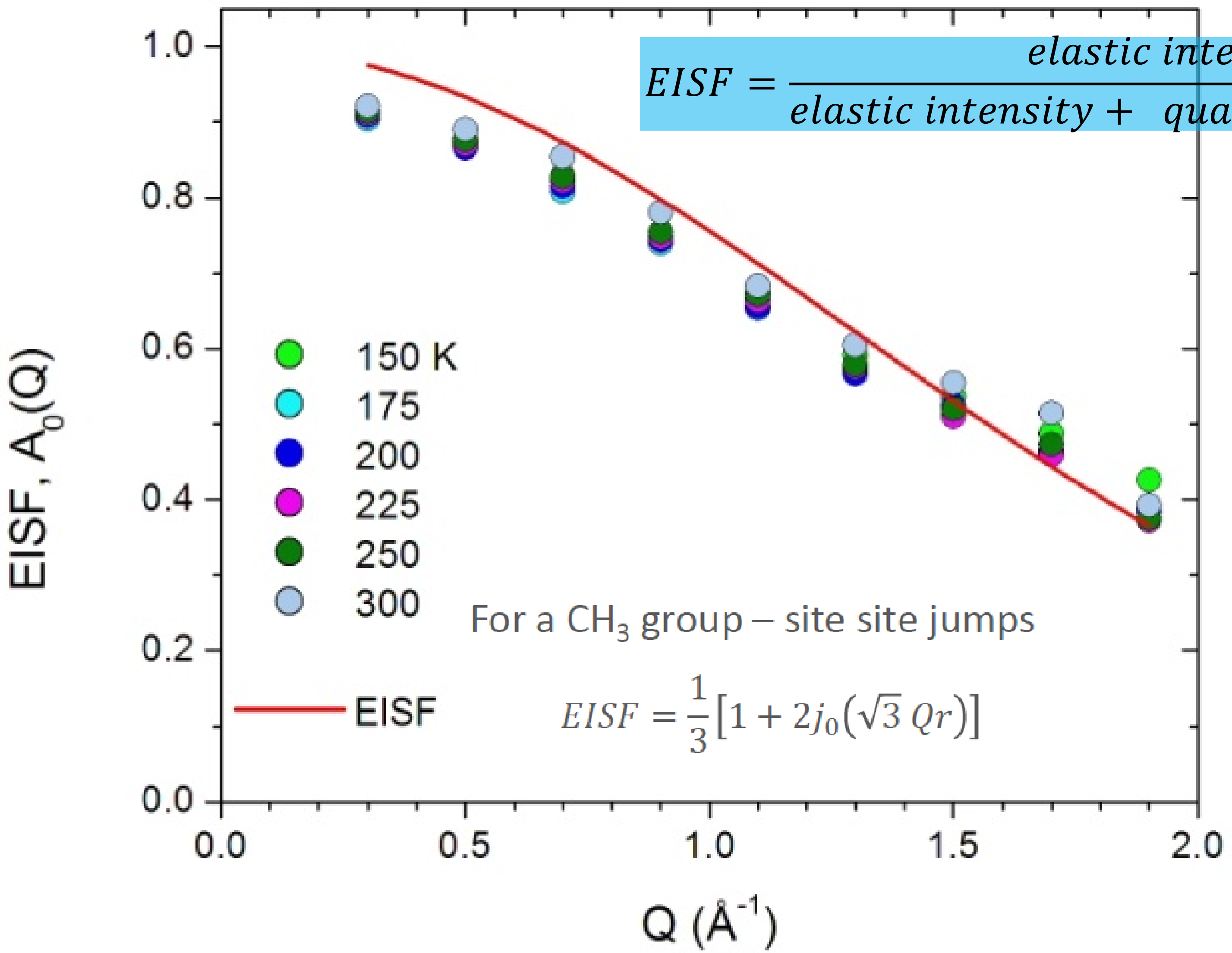




Jalarvo N., *et al, Journal of Physical Chemistry C,* **118,** 10, 5579-5592 (2014)

Science Example 1: Molecular Reorientation

$$EISF = \frac{elastic\ intensity}{elastic\ intensity + \ quasielastic\ intensity}$$

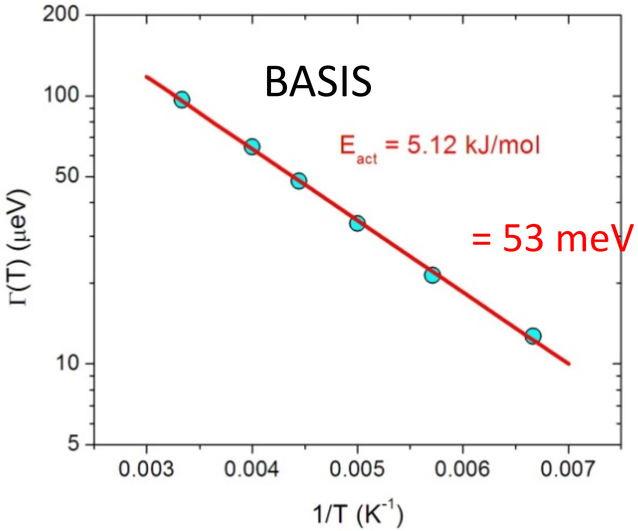


For a CH_3 group – site site jumps

$$EISF = \frac{1}{3}\left[1 + 2j_0\left(\sqrt{3}\,Qr\right)\right]$$

Jalarvo N., *et al, Journal of Physical Chemistry C,* **118,** 10, 5579-5592 (2014)

Science Example 1: Molecular Reorientation



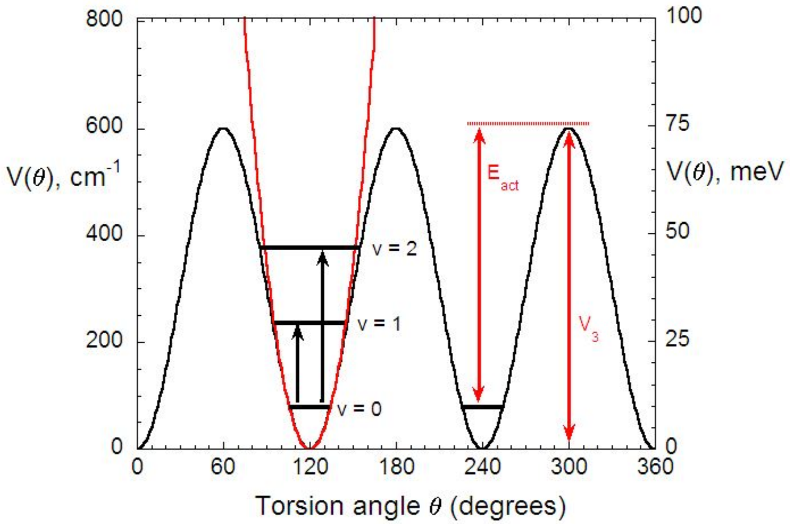
= 53 meV

$$V(\theta) = \frac{V_3}{2}(1 - cos3\theta)$$

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

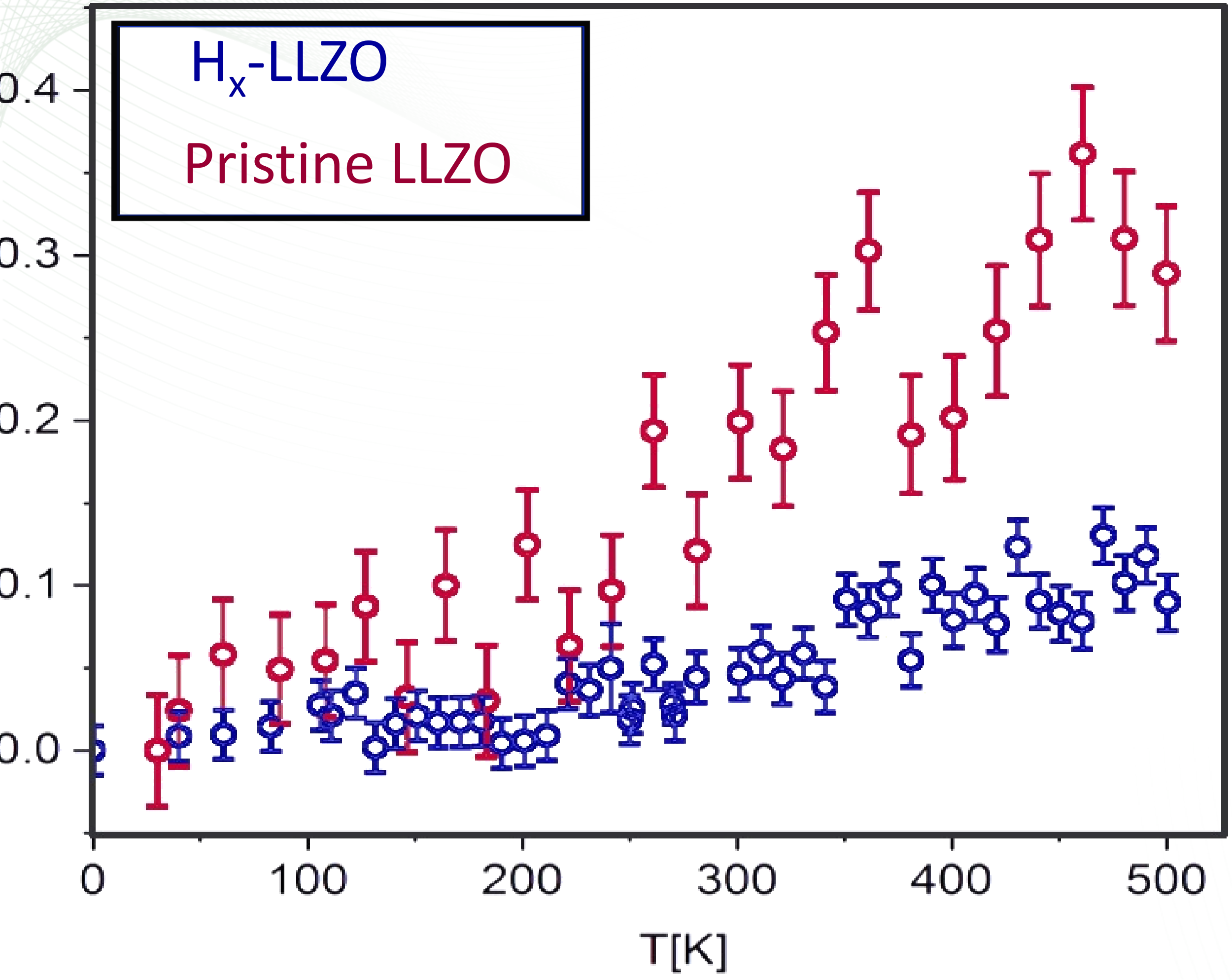
-> V_3 = 74.4 meV (7.18 kJ/mol)

Barrier for methyl rotation



Jalarvo N., *et al, Journal of Physical Chemistry C,* **118,** 10, 5579-5592 (2014)

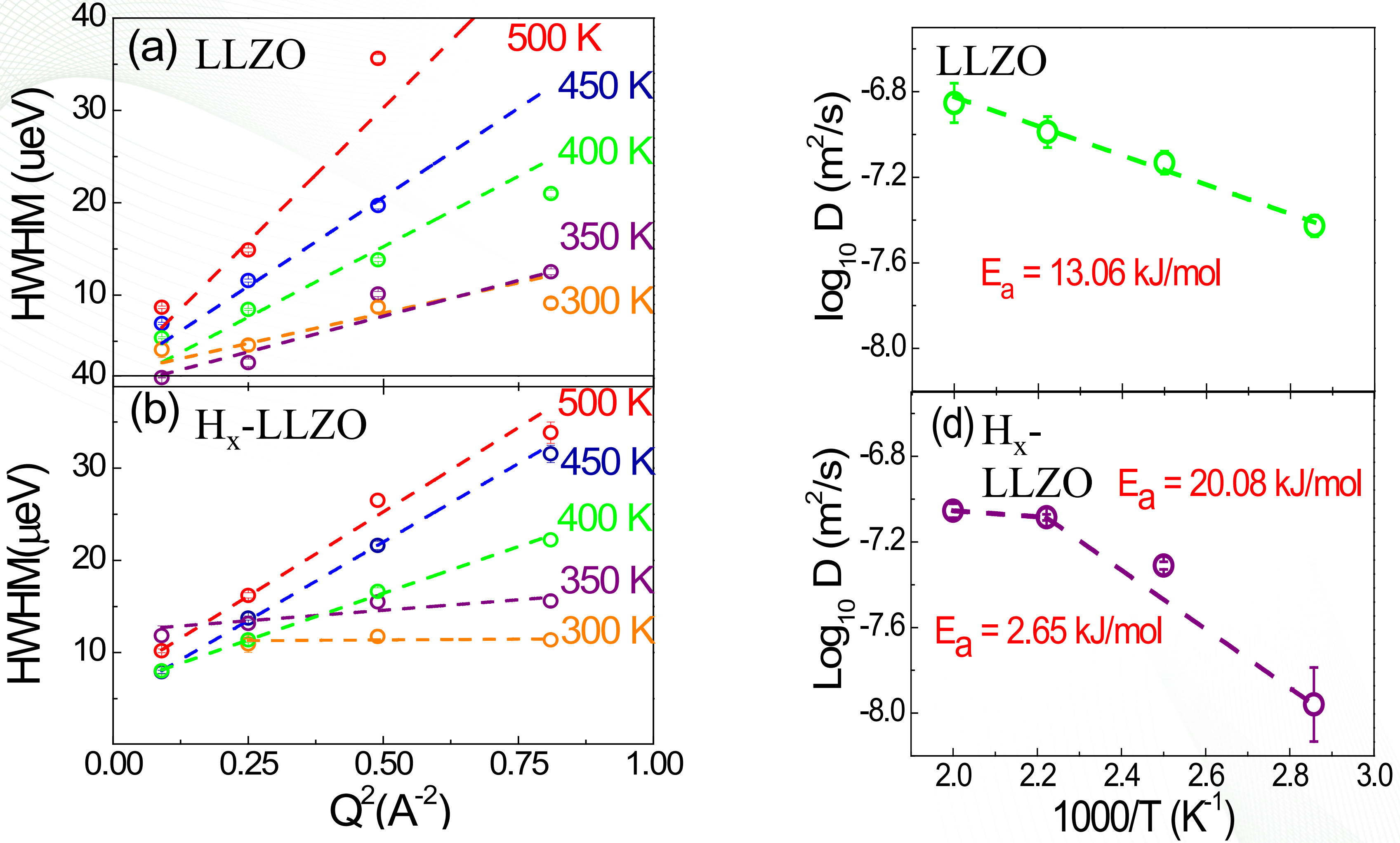
Science example 2: Elucidate Li^+ vs H^+ ion diffusion



H^+ ions were found to be immobile while Li^+ ion maintained a desired mobility in the solid electrolyte $(Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}$

Xiaoming Liu, *et al, Energy & Environmental Science,* **12,** 3, 945-951 (2019).

Science example 2: Elucidate Li^+ vs H^+ ion diffusion

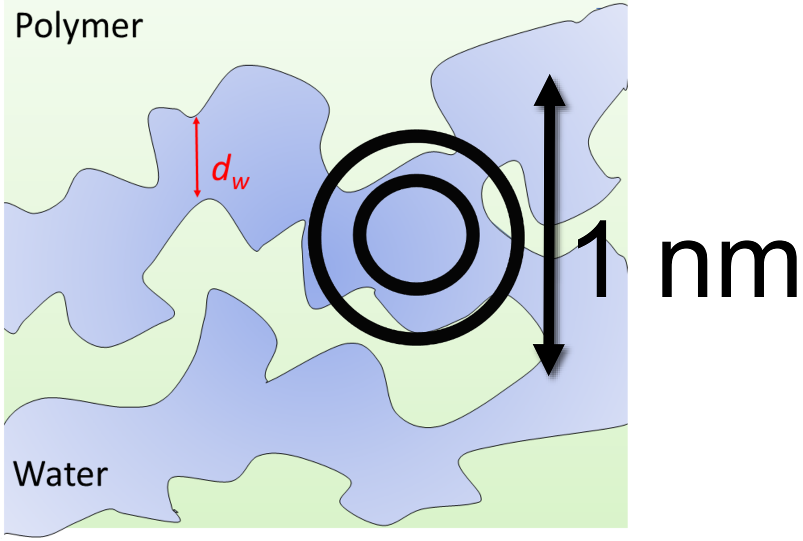


H^+ ions are found to be immobile while Li^+ ions maintain mobility in H-LLZO at the operating temperature range of ALBs.

Xiaoming Liu, *et al, Energy & Environmental Science,* **12,** 3, 945-951 (2019).

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

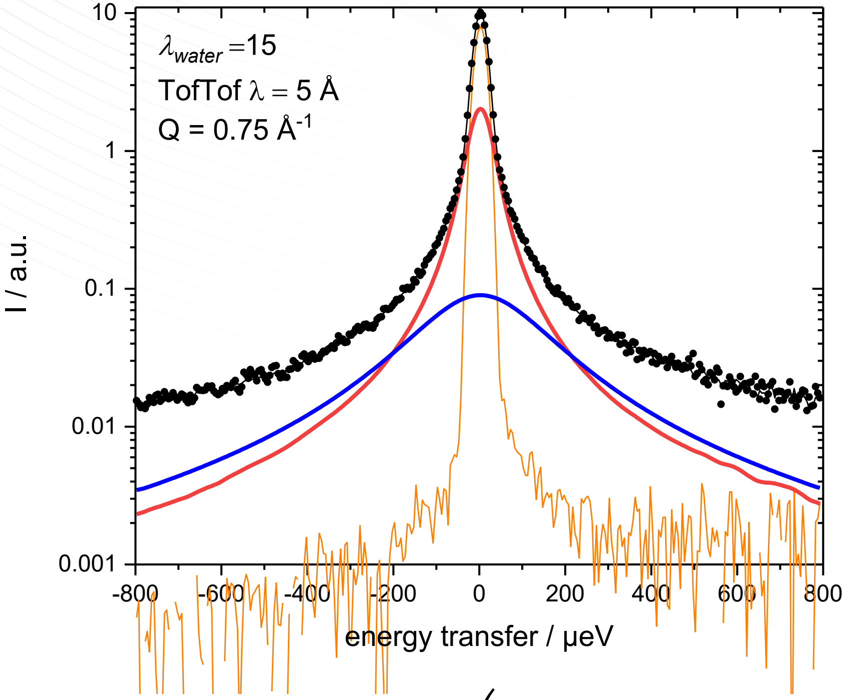
- Ionic conductivity and water transport are key properties for applications
  - Depends on water content
- Water transport in AEM multiscale problem
  - Investigation of transport in multiple time- and length scales for structure – function insight

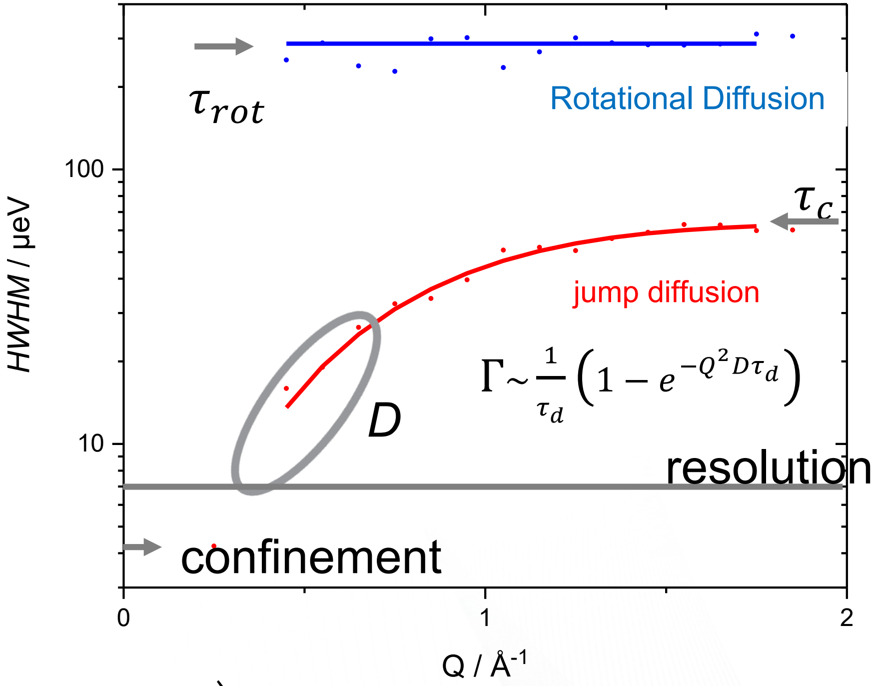


J. Melchior, *et al,* Journal of Membrane Science 586, Pages 240-247 (2019)

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

TOFTOF: time-of-flight spectrometer





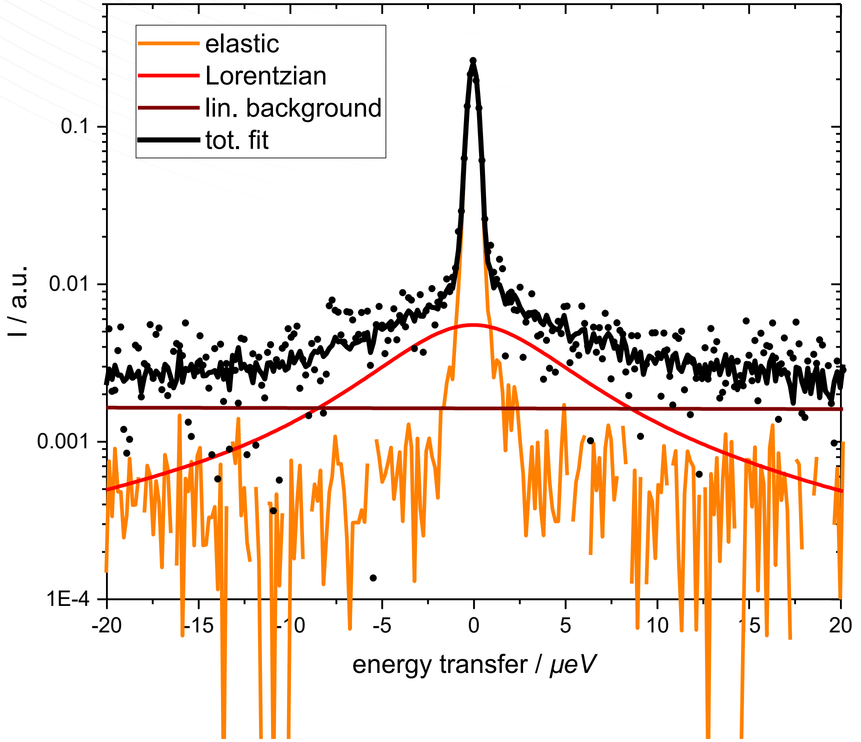
$$S(Q,\omega) = f\left(a_0(Q)\delta + \sum_n \frac{a_n(Q)}{\pi}\left(\frac{\Gamma}{\omega^2+\Gamma^2}\right)\right) \otimes Res + Backg$$

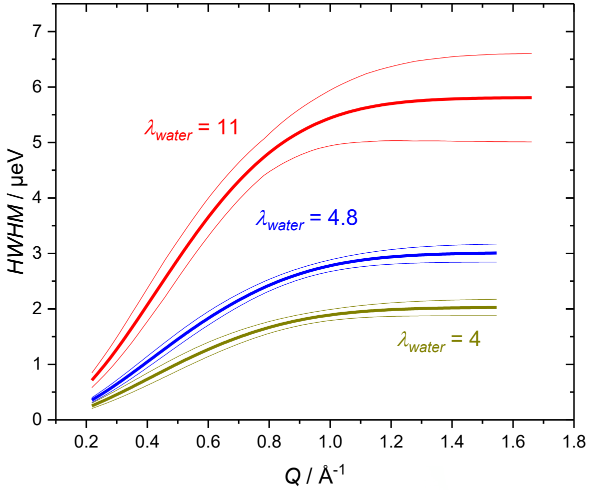
J. Melchior, *et al,* Journal of Membrane Science 586, Pages 240-247 (2019)

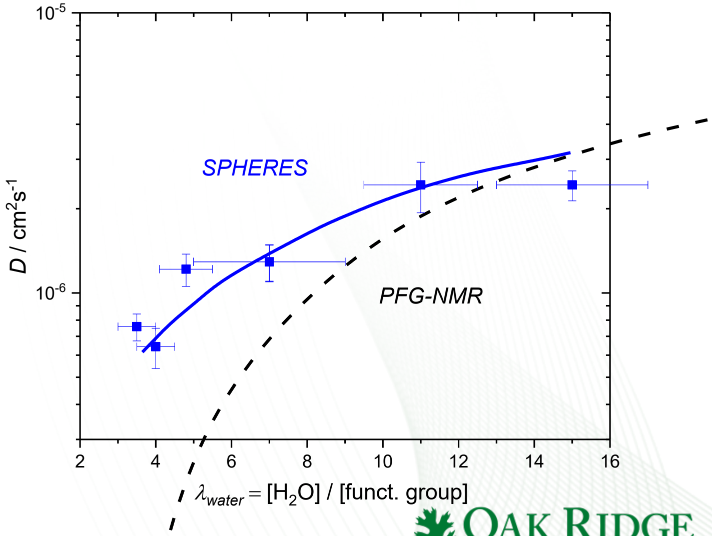
Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

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

SPHERES: high-resolution backscattering spectrometer

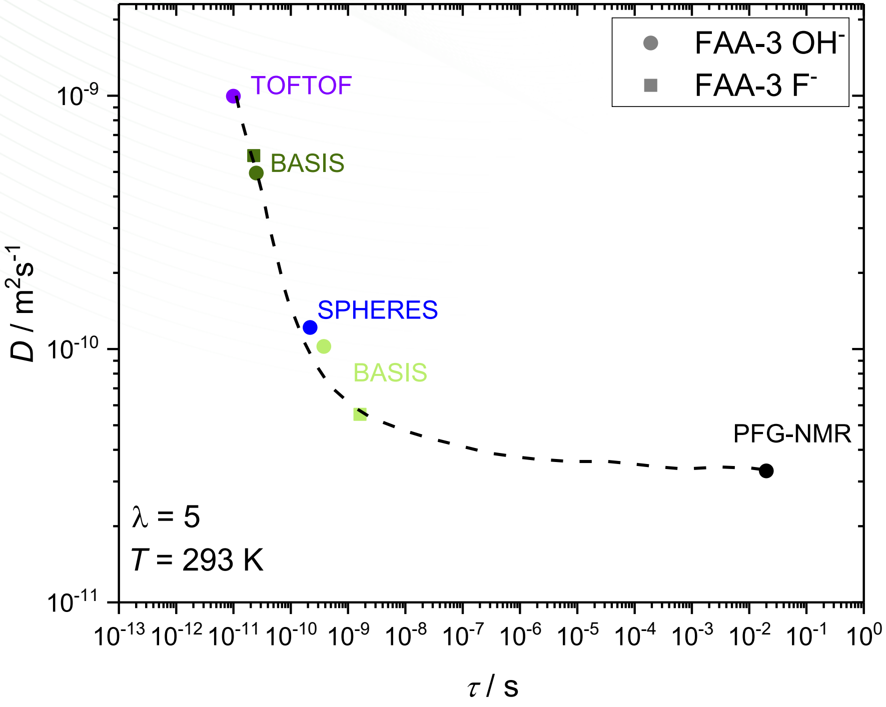


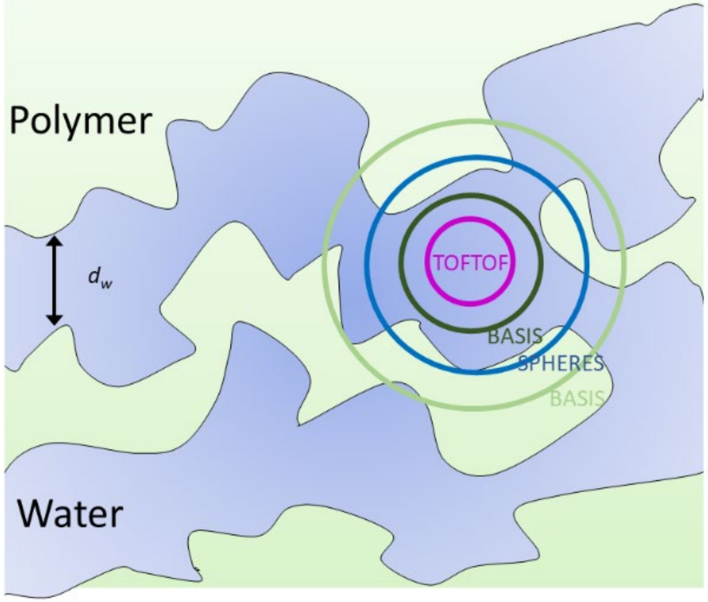




J. Melchior, *et al,* Journal of Membrane Science 586, Pages 240-247 (2019)

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





J. Melchior, *et al,* Journal of Membrane Science 586, Pages 240-247 (2019)

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 (μsec 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).