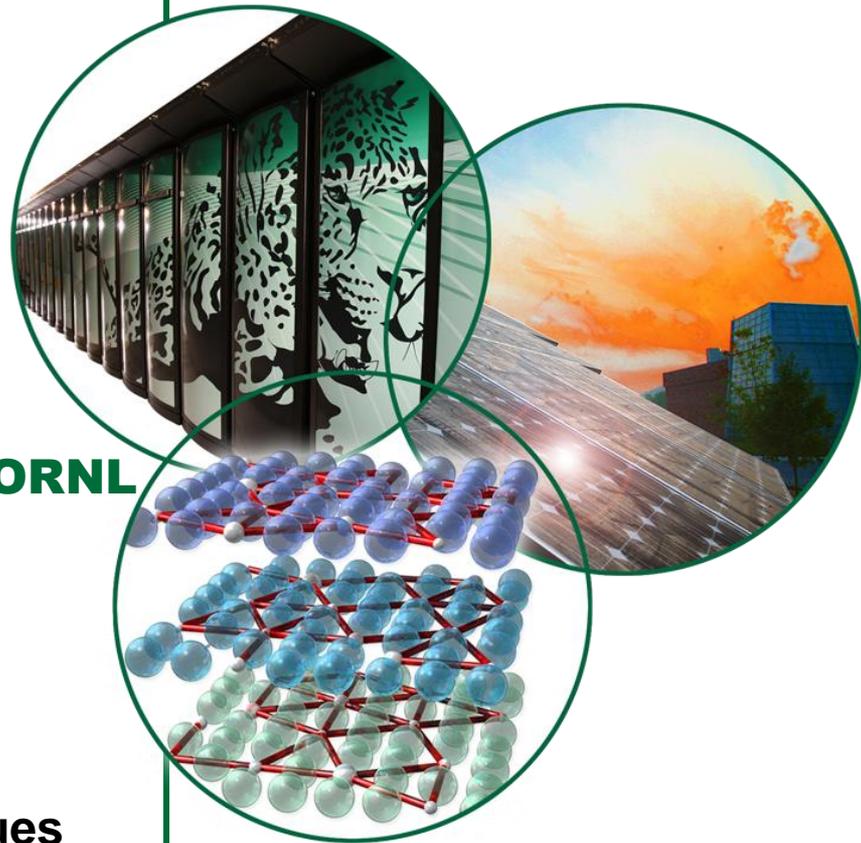


# What can we learn about the mobility of species in catalytic systems using quasielastic neutron scattering?

Eugene Mamontov

Neutron Scattering Science Division, ORNL

Workshop on Neutron Scattering Techniques for Studies in Catalysis, ORNL, Oak Ridge, TN, September 2010



# QENS-capable spectrometers in the US

**Backscattering** spectrometers – specifically designed for QENS, **disk chopper** spectrometers – often can be used too

Disk Chopper Spectrometer (DCS), NIST Center for Neutron Research

High Flux Backscattering Spectrometer (HFBS), NIST Center for Neutron Research

Cold Neutron Chopper Spectrometer (CNCS), SNS, ORNL

Backscattering Spectrometer (BASIS), SNS, ORNL

## Acknowledgement

Collaborators (ORNL): L. M. Anovitz, D. R. Cole, P. T. Cummings, L. Vlcek, W. Wang, D. J. Wesolowski

Scientific User Facilities Division, Office of Basic Energy Sciences (Spallation Neutron Source, ORNL)



SNS backscattering spectrometer, BASIS



# Elastic experiments probe structure, inelastic experiments probe dynamics

1 meV ~ 8 cm<sup>-1</sup> ~ 1 ps

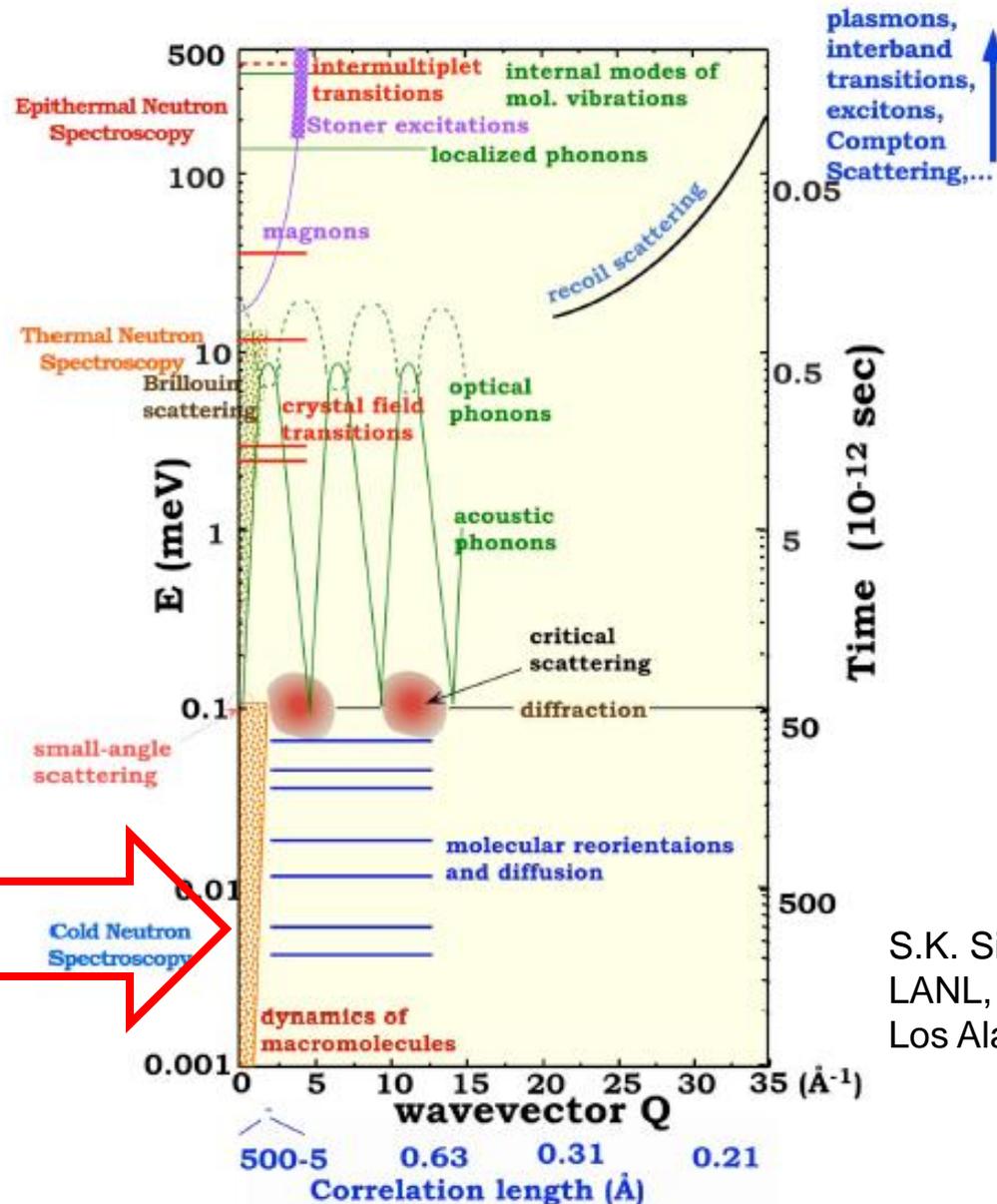
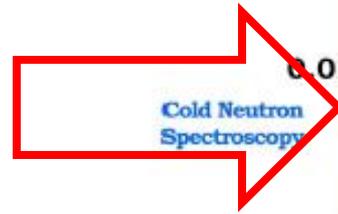
1 μeV ~ 0.008 cm<sup>-1</sup> ~ 1 ns

sub-ps (vibrations)

$$\tau = \tau_0 \exp(E_a/T)$$

ns (diffusion jumps)

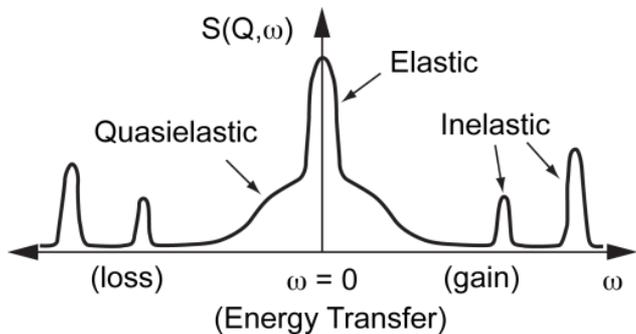
**YOU ARE HERE**



S.K. Sinha, 1985,  
LANL, LA-10227-C,  
Los Alamos, p.346

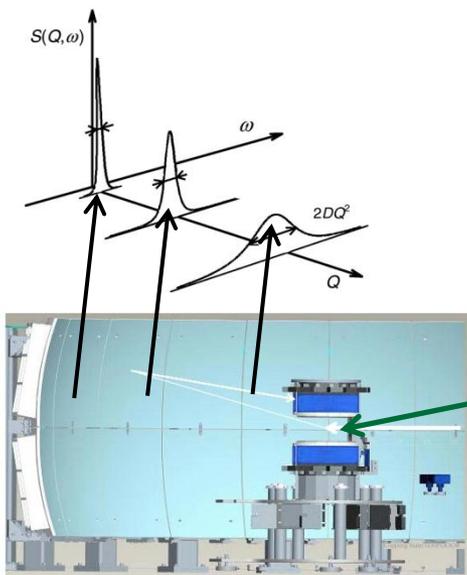


# How does a QENS experiment work?



- Unlike X-rays, neutrons have not only the “right” wavelength, but also the “right” energy to probe pico- to nano-second dynamics
- X-rays (keV): state of the art  $\Delta E/E$  yields  $\Delta E \sim 1 \text{ meV}$  – acoustic phonons
- Neutrons (meV): state of the art  $\Delta E/E$  yields  $\Delta E \sim 1 \text{ } \mu\text{eV}$  – diffusion jumps

Dynamic structure factor (x-rays or neutrons)

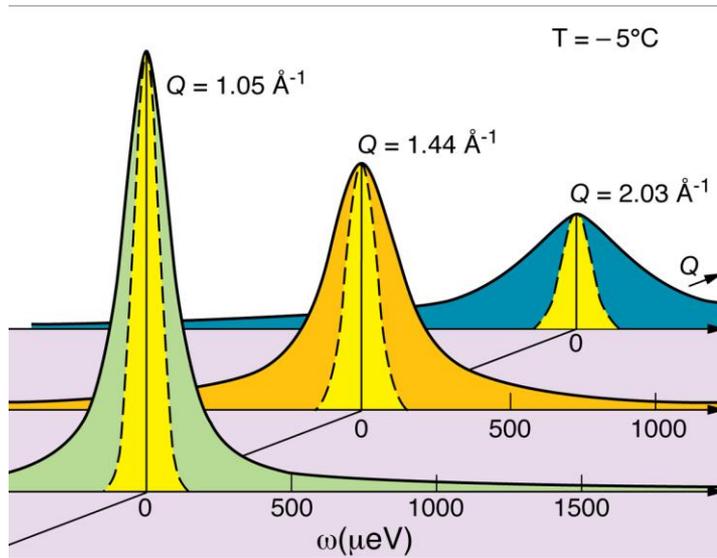


- BASIS/HFBS beam cross-section: 3 cm by 3 cm
- BASIS/HFBS sample holders ID: 29.0 mm; cylindrical inserts can provide a gap as narrow as 0.05 mm
- Samples are powders or liquids

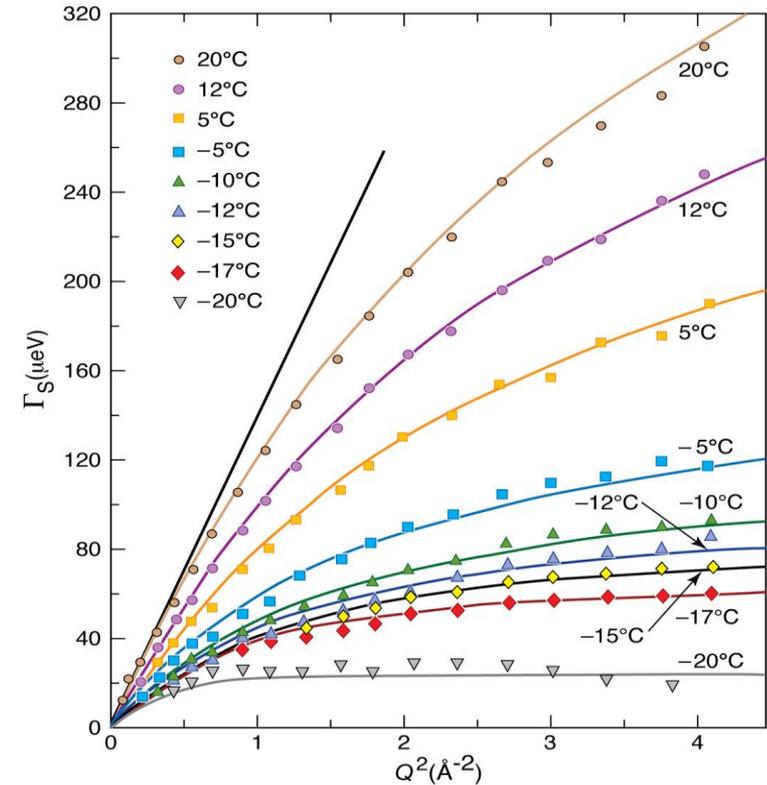
Both the relaxation times and diffusion process geometry are determined through the Q-dependence of the QENS broadening

$$Q_{\text{QENS}} = (4\pi/\lambda)\sin(\theta/2)$$

# Various types of dynamics probed by QENS: translational diffusion in bulk liquids



Supercooled water: data from Teixeira et al. (1985)



$\Gamma$  (HWHM) is Q-dependent

Low Q:  $\Gamma = \hbar D Q^2$ ; obtain D

High Q,  $\Gamma = \hbar / \tau_0$ ; obtain residence time and jump length

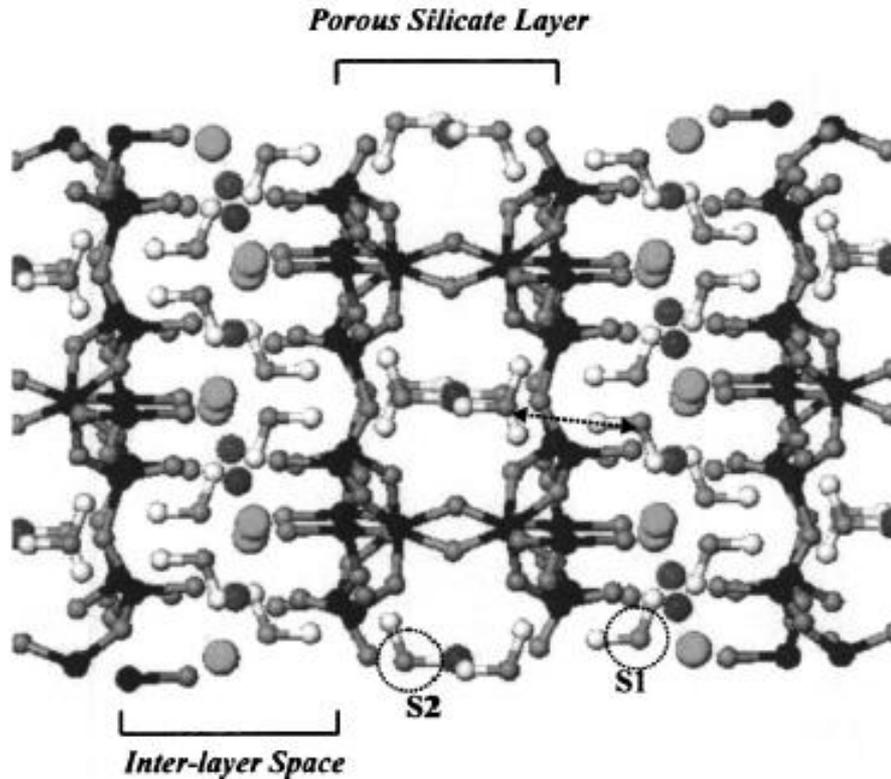
- Translational Motion

$$T(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma^2(Q) + \omega^2}$$

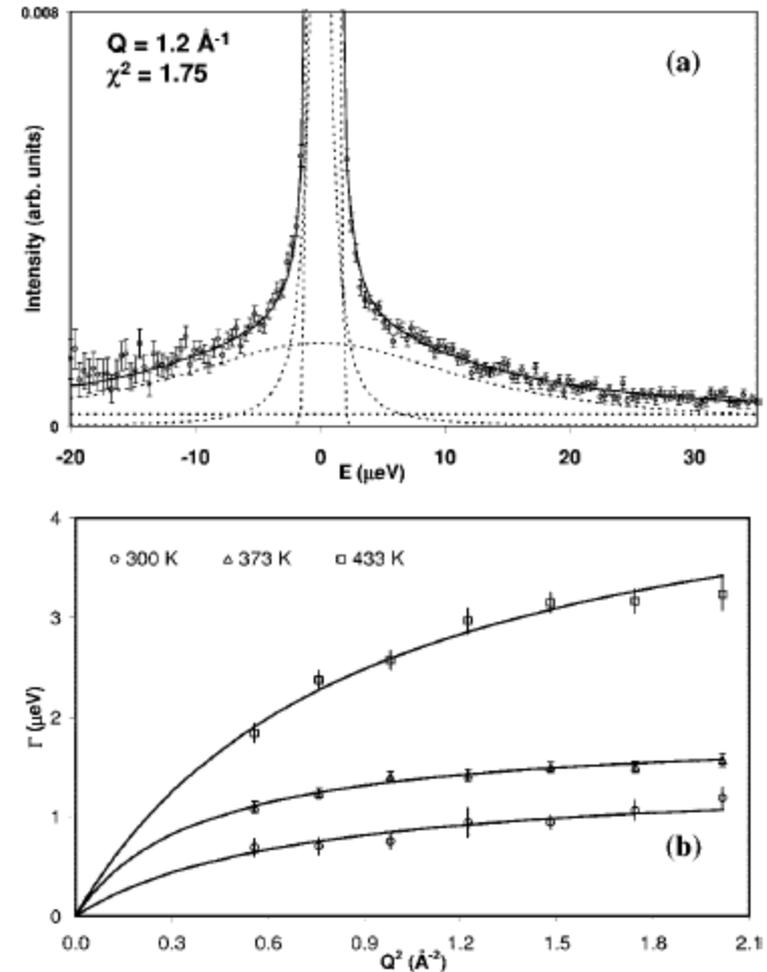
- Jump Diffusion

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

# Various types of dynamics probed by QENS: translational diffusion in confined liquids

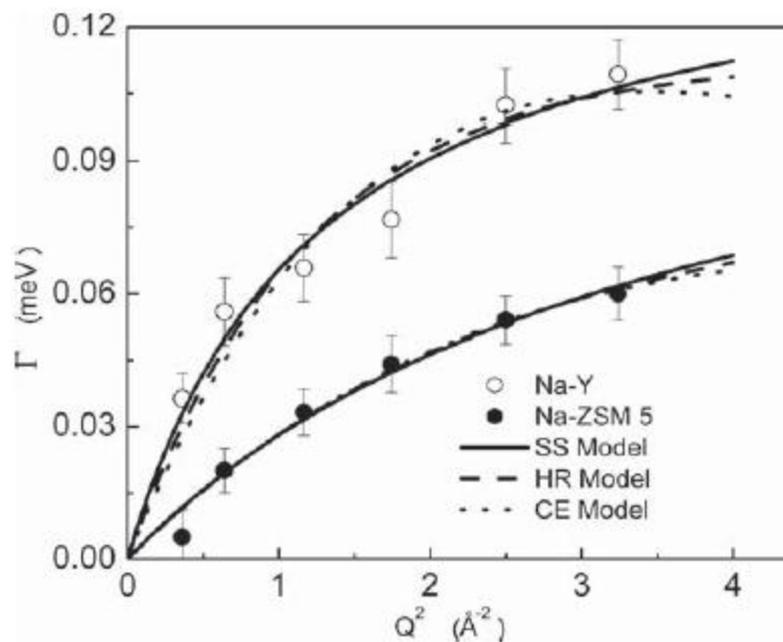
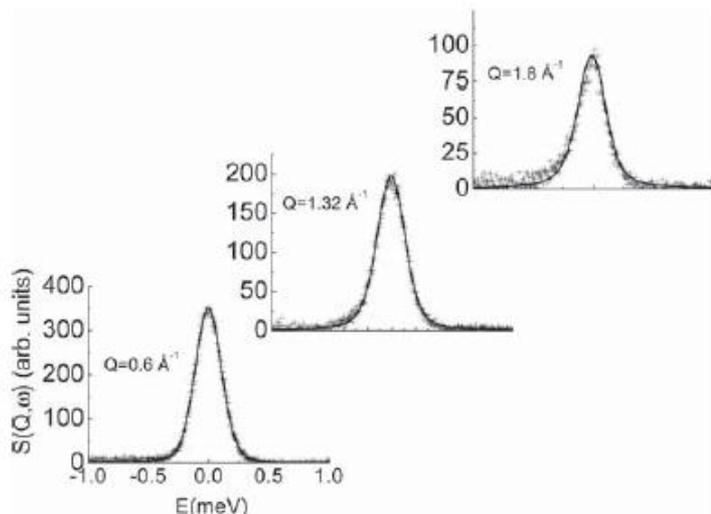
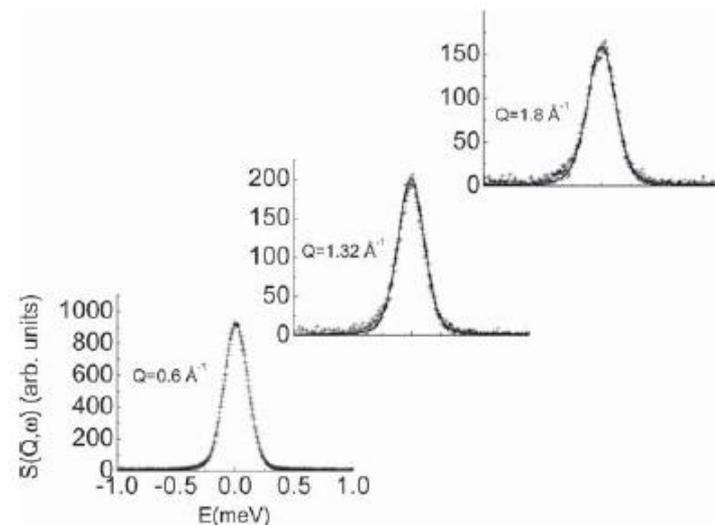
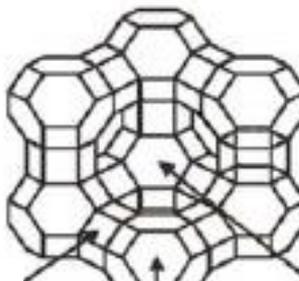
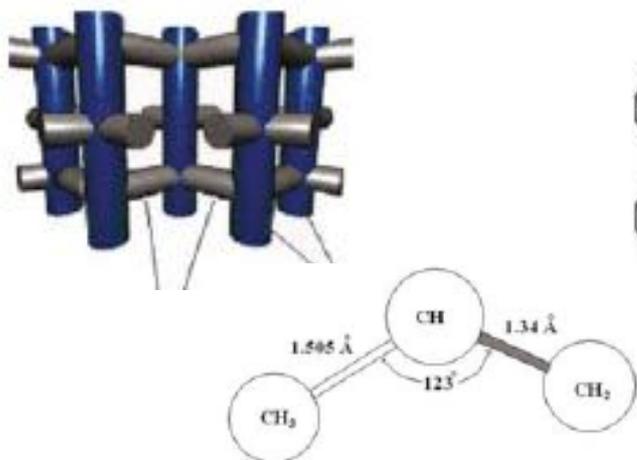


Water in a nanoporous layered silicate AMH-3, an interesting zeolite-clay-like hybrid material: data from Nair et al. (2005)

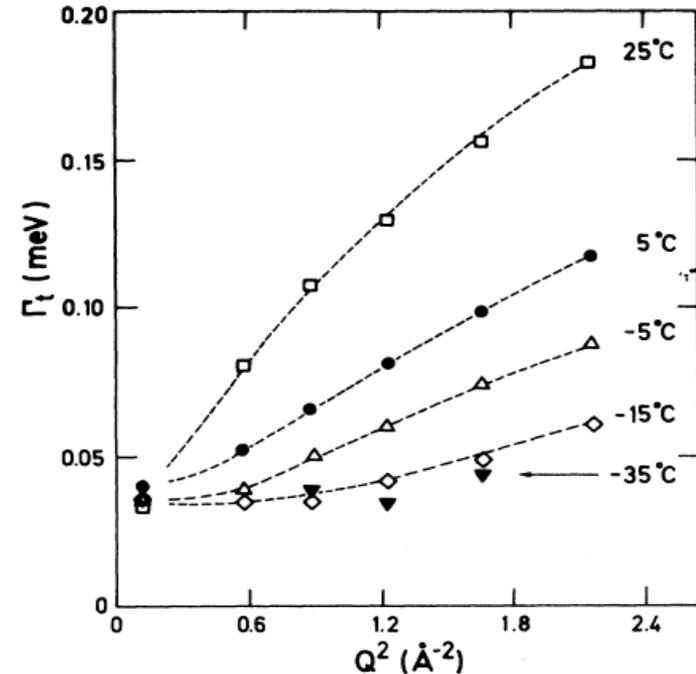
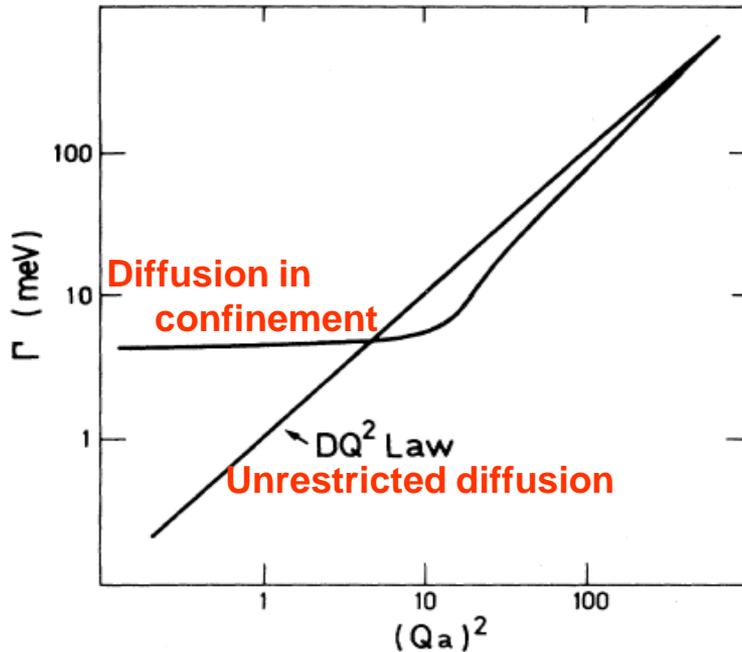


# Various types of dynamics probed by QENS: translational diffusion in confined liquids

Propylene in Na-Y and Na-ZSM5 zeolites:  
data from Sharma et al. (2009, 2010)



# Various types of dynamics probed by QENS: deducing nano-confinement size



When diffusing molecules cannot penetrate the borders of the pores, the QENS broadening at low  $Q$  no longer follows  $\Gamma = \hbar D Q^2$  law

For example, for diffusion in a spherical pore of radius  $a$ ,  $\Gamma = 4.33\hbar D/a^2$  for  $0 < Qa < 3.3$ ; the confinement radius  $a$  can be obtained

Water in Vycor pores: data from Bellissent-Funel et al. (1995)

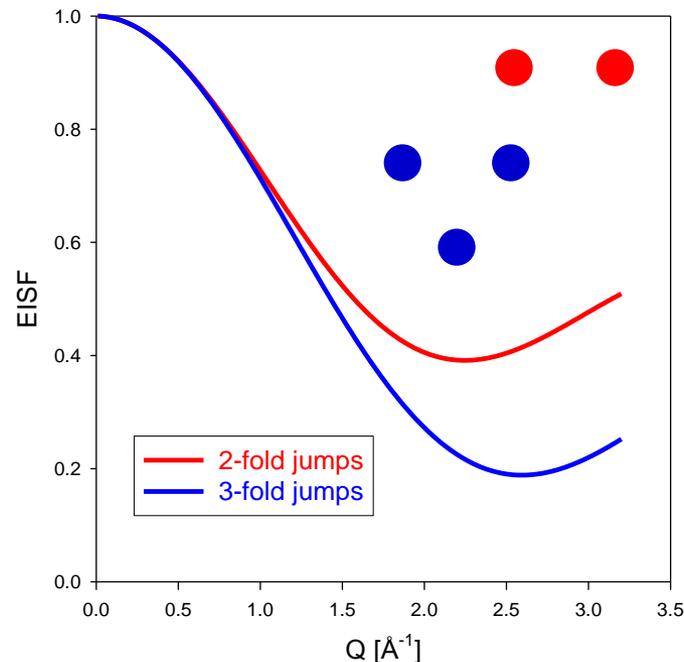
# Various types of dynamics probed by QENS: localized (non-translational) diffusion jumps

For localized diffusion, there is an elastic scattering due to “spatial restriction”

Elastic Incoherent Structure Factor = Elastic/(Elastic+Quasielastic)

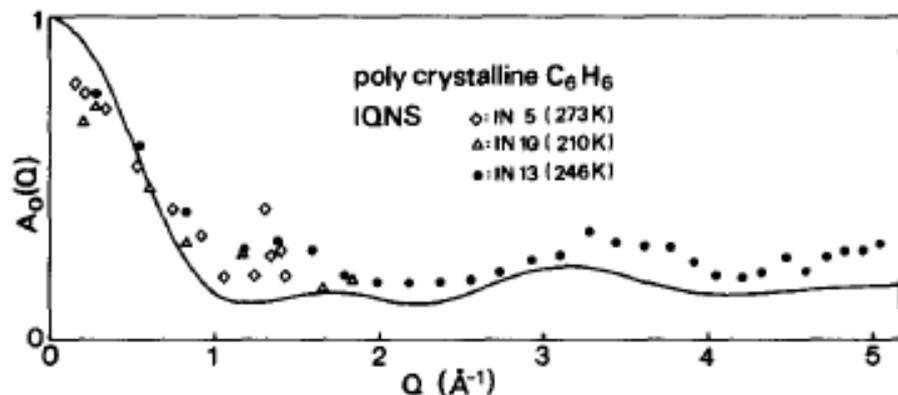
Physical meaning of EISF(Q): the probability that, within the resolution time of the QENS measurement, the particle does not leave the volume  $\sim 2\pi/Q$

Measuring EISF(Q) is an excellent way to deduce the geometry of the corresponding restricted motion



From the data fits, we get the characteristic size and (sometimes) geometry of the confinement

# Various types of dynamics probed by QENS: deducing geometry of localized diffusion jumps



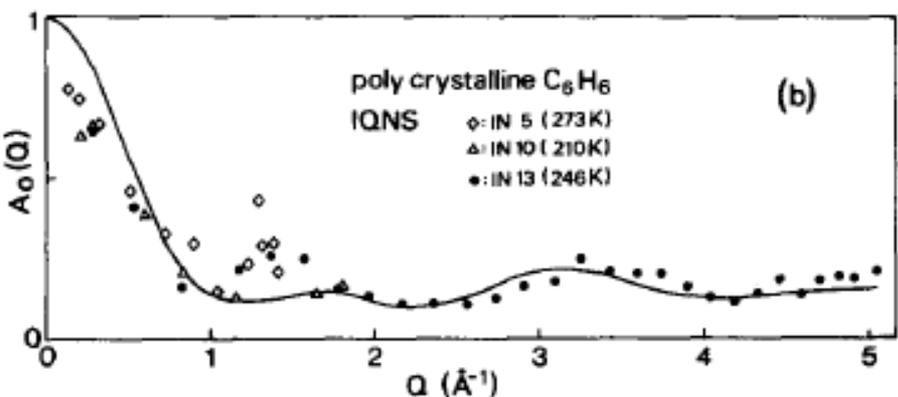
Random 6-fold jump model

$$S_{\text{inc}}(Q, \omega) = A_0(Q)\delta(\omega) + [1 - A_0(Q)]L\left(\frac{1}{\tau_c}\right)$$

$$A_0(Q) = \frac{1}{6} \sum_{j=1}^6 \frac{\sin(2Qa \sin \pi j/6)}{2Qa \sin \pi j/6}$$

$$L\left(\frac{1}{\tau_c}\right) = \frac{1}{\pi} \frac{1/\tau_c}{\omega^2 + (1/\tau_c)^2}$$

one Lorentzian term



Single step jump model (only  $\pm 60^\circ$  jumps) – better describes the data

$$S_{\text{inc}}(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^5 A_l(Q)L\left(\frac{1}{\tau_l}\right)$$

$$A_l(Q) = \frac{1}{6} \sum_{j=1}^6 \frac{\sin(2Qa \sin \pi j/6)}{2Qa \sin \pi j/6} \cos \frac{\pi lj}{3}$$

$(l = 0, \dots, 5)$

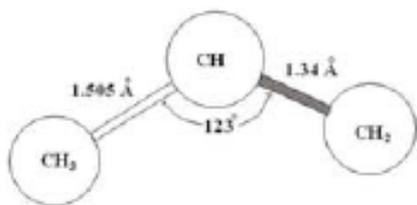
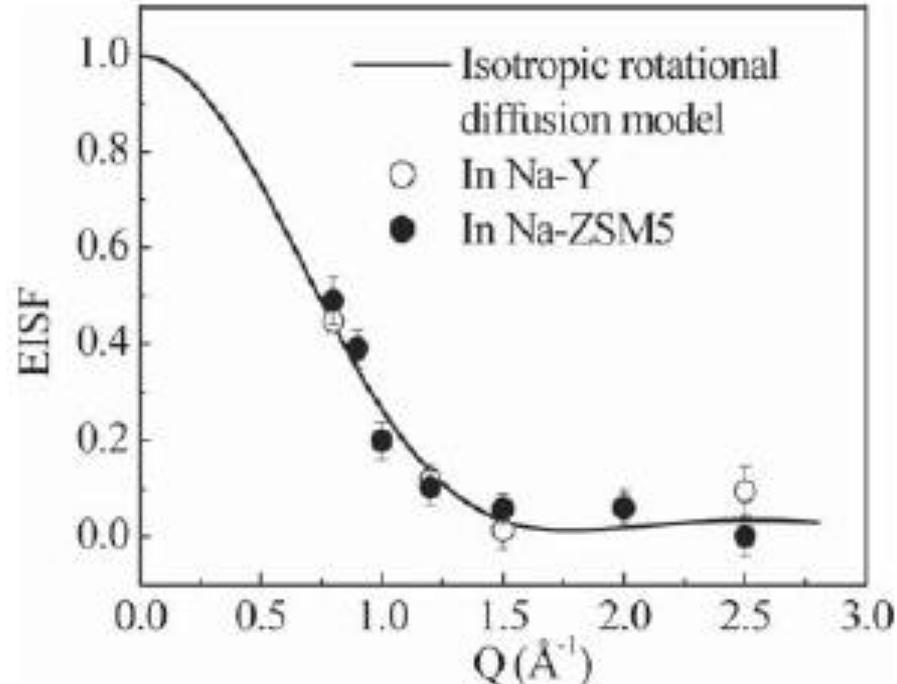
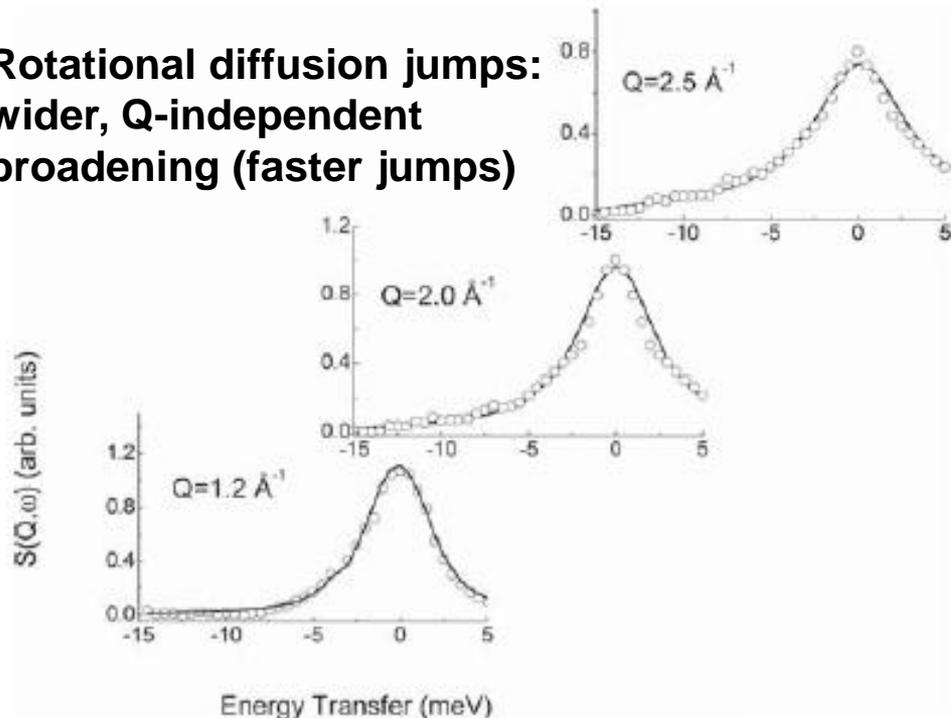
$$\tau_l = \frac{\tau_c}{2 \sin^2(\pi l/6)}$$

three Lorentzian terms

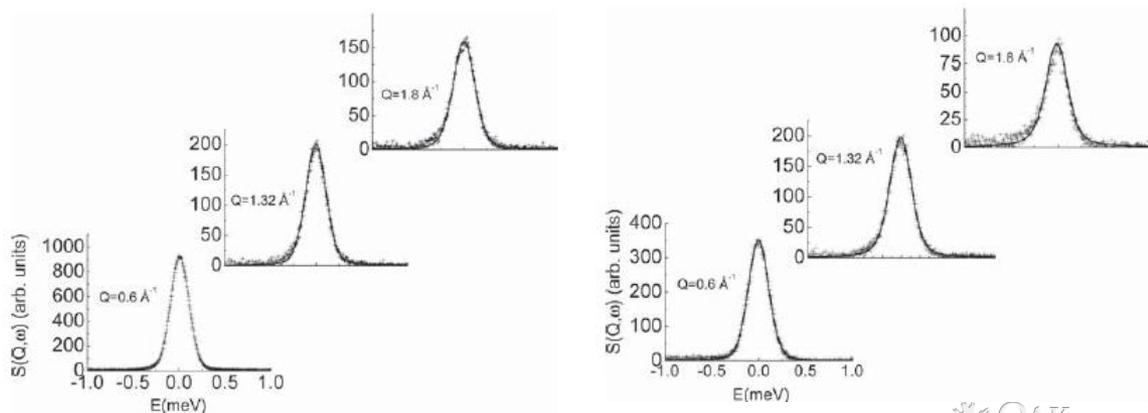
Reorientation of benzene molecules in the crystalline state: data from Fujara et al. (1988)

# Various types of dynamics probed by QENS: deducing geometry of localized diffusion jumps

Rotational diffusion jumps:  
wider, Q-independent  
broadening (faster jumps)



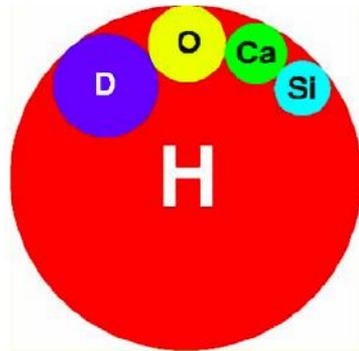
Propylene in Na-Y and Na-ZSM5 zeolites:  
data from Sharma et al. (2009, 2010)



Translational diffusion jumps: narrower,  
Q-dependent broadening (slower jumps)

# Various types of dynamics probed by QENS: beyond hydrogen-bearing molecules

Total neutron scattering cross-section



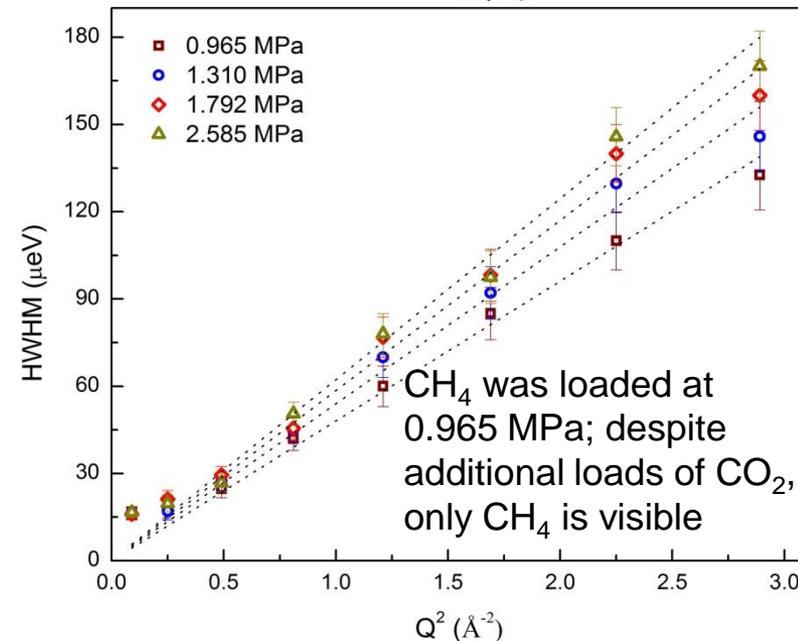
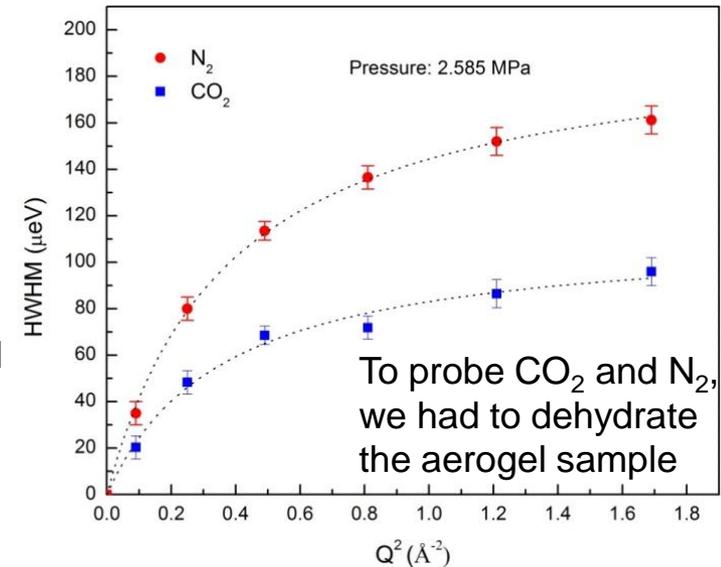
Hydrogen dwarfs all the other elements due to its huge **incoherent** scattering cross-section:

$$\sigma_{\text{coh}} = 1.76 \text{ barn}, \sigma_{\text{inc}} = 80.26 \text{ barn}$$

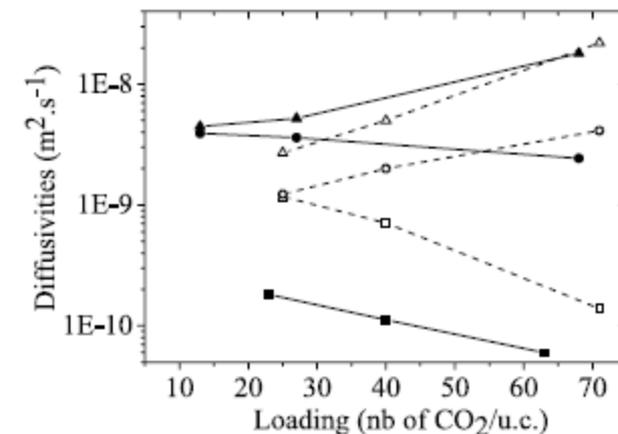
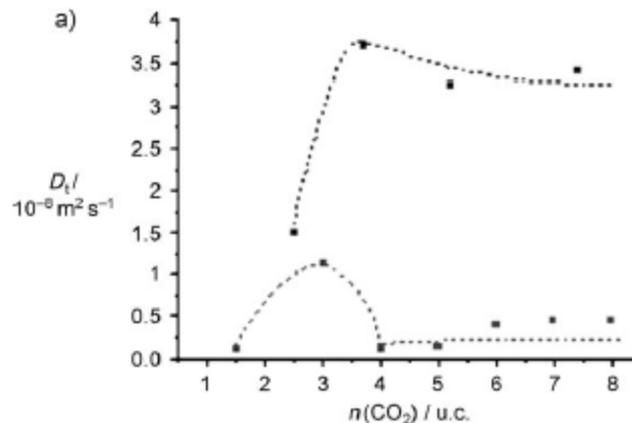
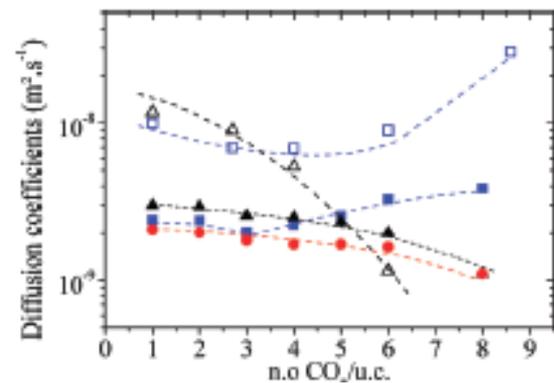
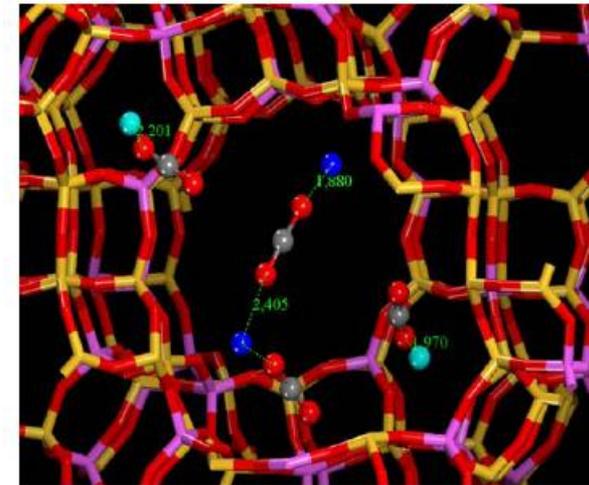
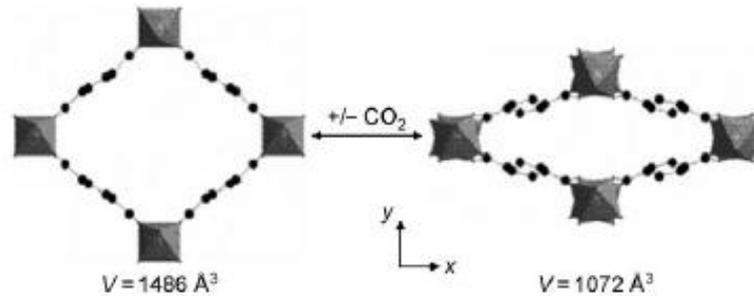
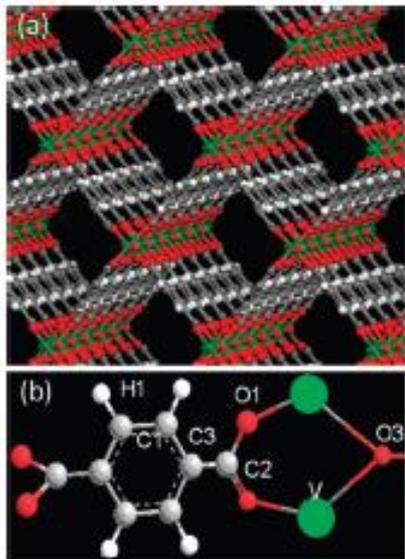
In presence of hydrogenated species, other molecules are almost invisible to QENS

Either probe non-hydrogenous species alone (e.g., make sure there is no adsorbed water!), or use deuterated components to study mixtures

CH<sub>4</sub>/CO<sub>2</sub> in carbon aerogel at ambient temperature: data from Chathoth et al. (BASIS experiment, manuscript in preparation)



# Various types of dynamics probed by QENS: CO<sub>2</sub> diffusion in various matrices (MOFs, zeolites, etc)



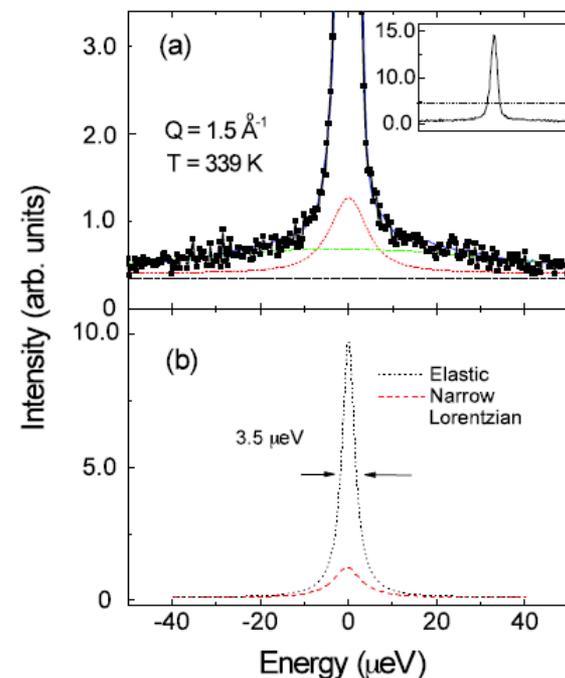
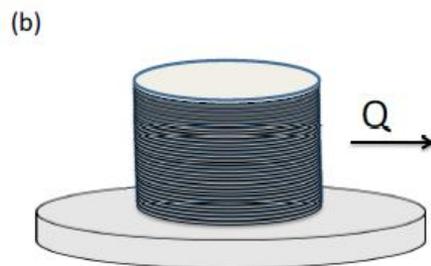
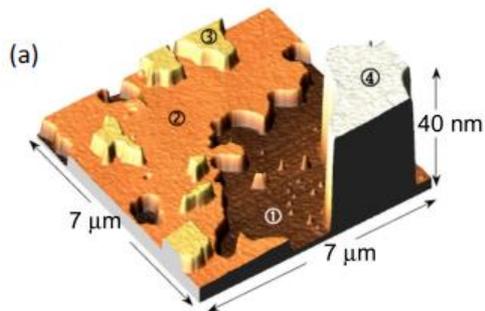
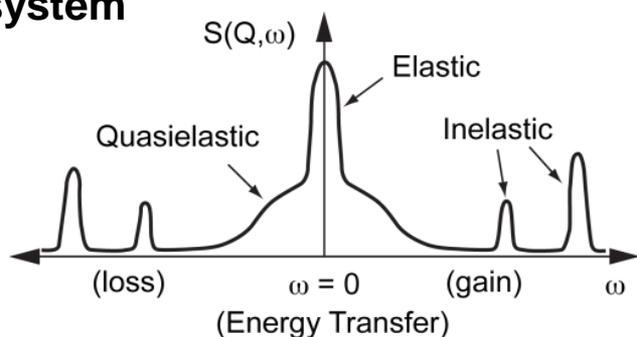
Diffusivity of CO<sub>2</sub> in various matrices as a function of load: data from Jobic et al. (2007, 2008, 2009)

# Diffusion on oriented wafers: next frontier?

Beyond powder averaging: QENS from oriented samples is sensitive to in- and out-of-plane motions

But the optimal amount of hydrogen in 3 cm by 3 cm neutron beam is a few millimole

Difficult to run a QENS experiment with much less than a millimole of H in the system



Solid alkane  $\text{C}_{32}\text{H}_{66}$  nanoparticles on Si(100) wafers: data from Taub et al. (BASIS experiment, EPL, in press)

100 double-side polished Si(100) wafers, 0.3 mm thick, very good quality QENS data obtained from 10 monolayer system in several hours per temperature point

What does it take to get a good quality data from 1 monolayer system?

What does it take to get a good quality data from 1 monolayer system of **small hydrogen-bearing molecules**?

# Surface water on oxide nano-powders

- The samples for studying **dynamics** need to be **nano-powders** (to provide sufficient signal from the surface area of the sample); need to get at least a few  $\text{m}^2$  (better some tens of  $\text{m}^2$ ) of the hydrated surface in approximately  $10 \text{ cm}^2$  neutron beam
- Any hydrophilic surfaces exposed to atmosphere, including oxides, attract molecular water from the ambient environment
- Neutron scattering is sensitive to the dynamics of surface water, despite the presence of the hydrated matrix (because of the huge H incoherent scattering cross-section!)
- It helps if the powders exhibit a single dominant surface (e.g., nano-rutile –  $\text{TiO}_2$ , nano-cassiterite –  $\text{SnO}_2$ )

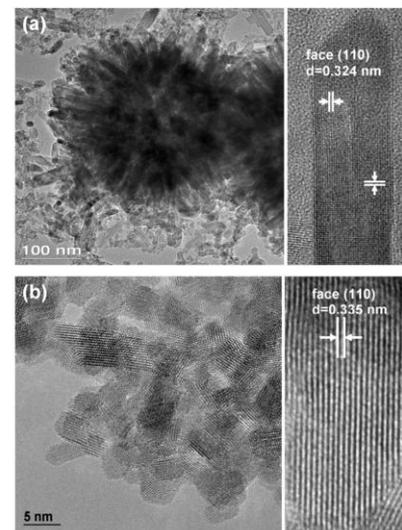


No sample, just the “substrate.”



In a few hours, the sample has formed.

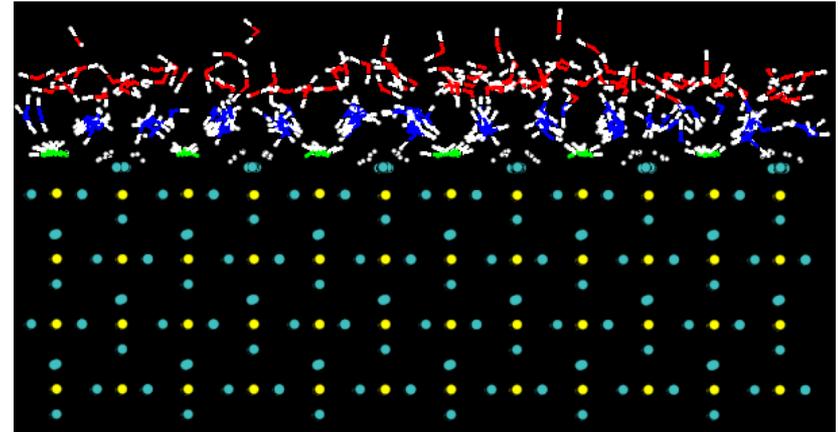
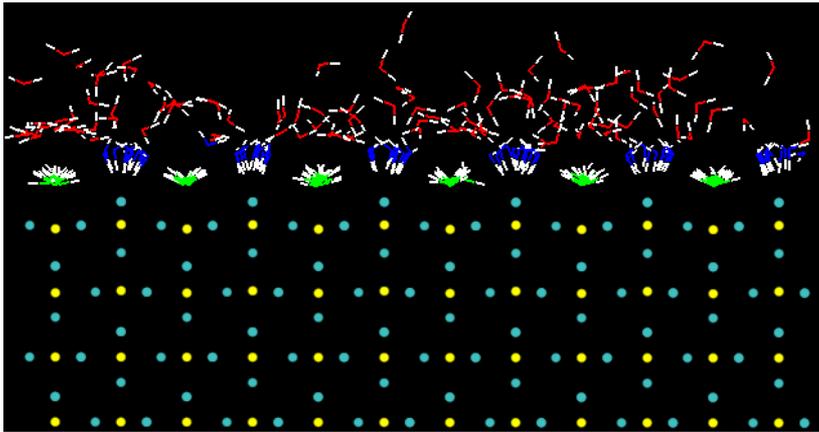
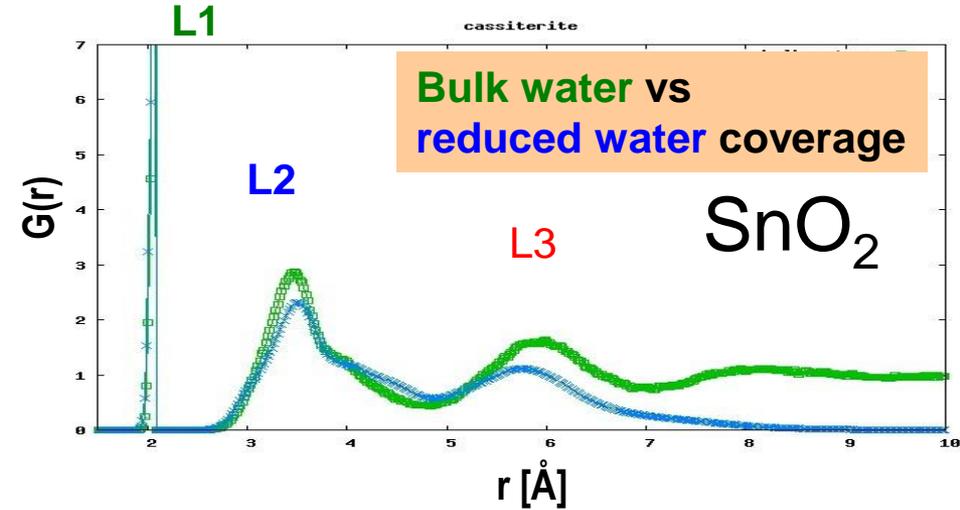
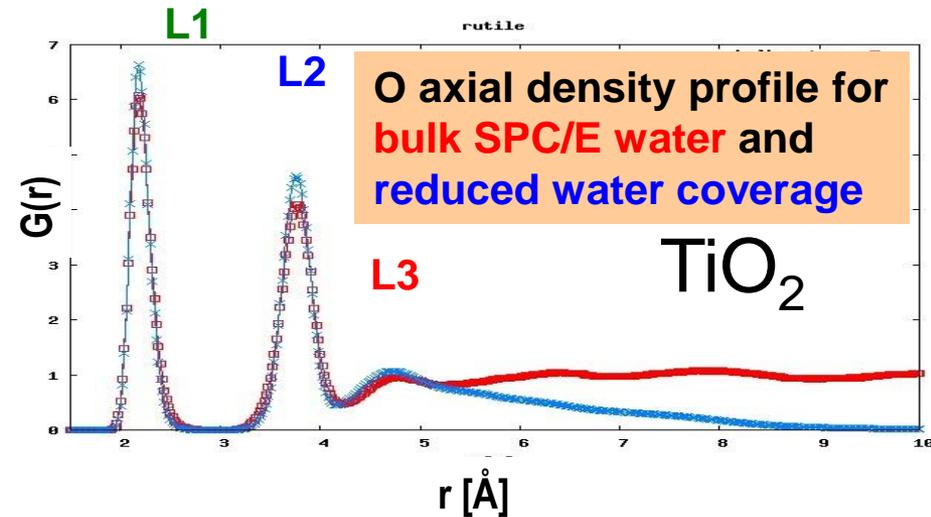
- How do we know if the hydration water is on the powder surface?
- Simple way: by weight uptake.
- Fancy way: spectroscopy (IR, Raman...)



Sample holders ID: 29.0 mm; cylindrical inserts are used to reduce the amount of hydrated powder in neutron beam

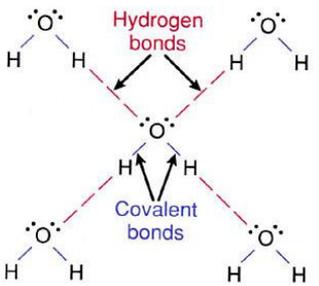


# What do we know about the STRUCTURE (MD)?



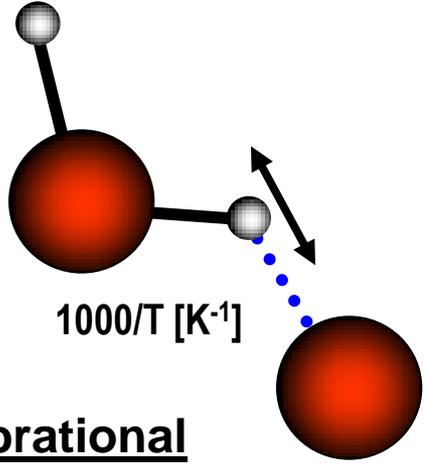
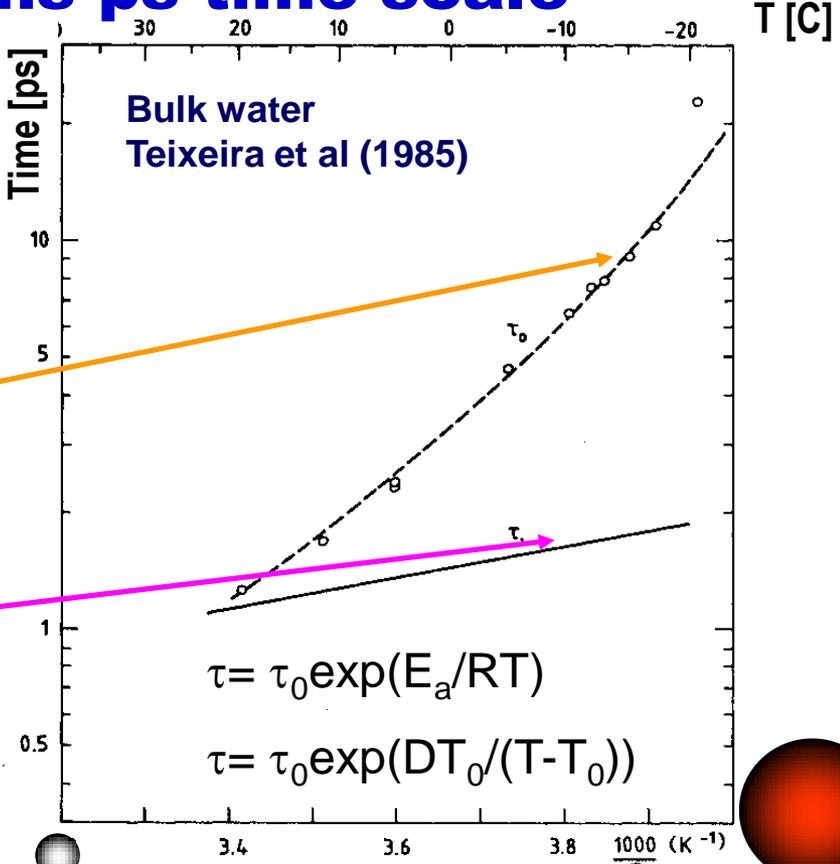
- Layered structure, very similar to the structure of bulk water in contact with the surface
- Under ambient conditions, about three layers are formed,  $L_1$ ,  $L_2$  and  $L_3$
- $L_1$  is the innermost, may consist of OH or  $\text{H}_2\text{O}$
- $L_2$  is still somewhat structured, consists of  $\text{H}_2\text{O}$
- $L_3$  is the outermost, liquid-like layer of  $\text{H}_2\text{O}$

# Reference point - established QENS results for bulk water: 2 mechanisms on ns-ps time scale

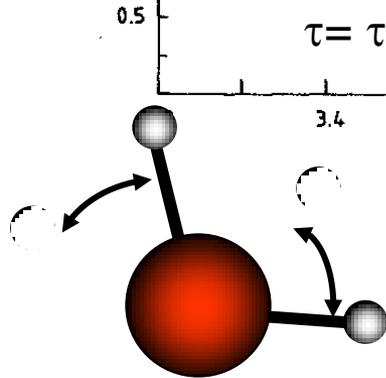


In bulk water, **translational** motions occur when at least three bonds are simultaneously broken and involve rearrangement of neighboring molecules. This is a complex, cooperative process, with non-Arrhenius temperature dependence.

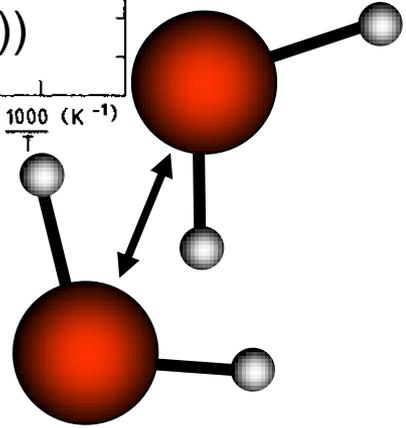
**Rotational** motions are localized (within the "cage"), simple, thermally activated, with Arrhenius temperature dependence.



**Vibrational**  
(harmonic oscillation)



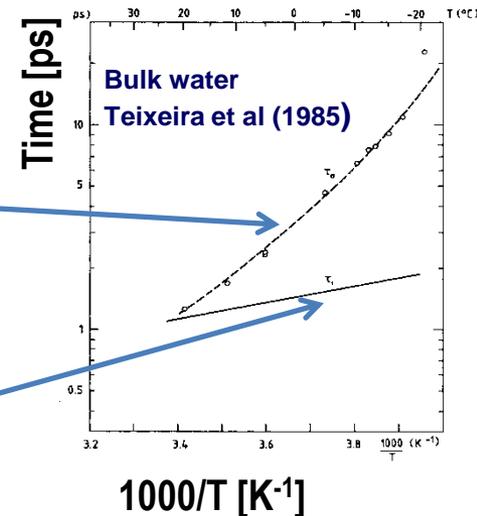
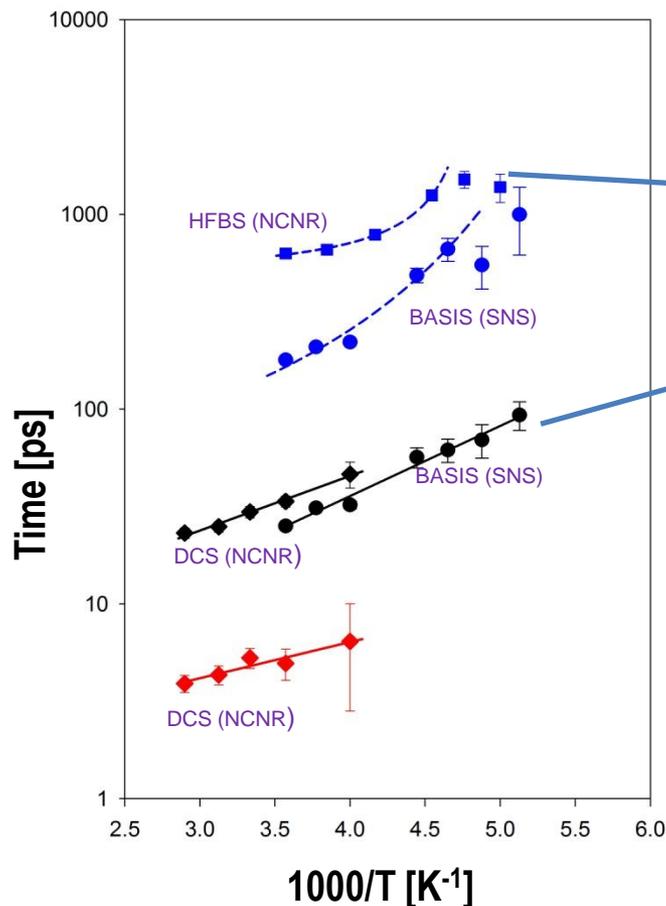
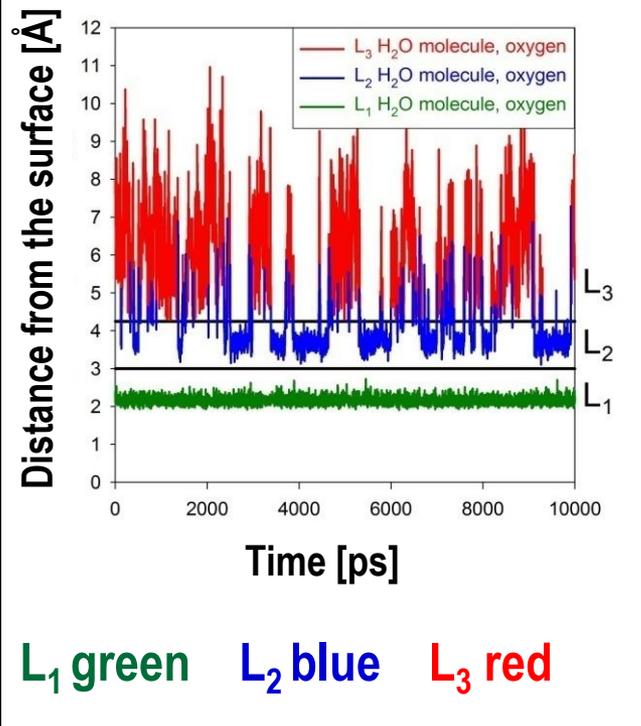
**Reorientational**  
(isotropic rotation)



**Jump Translational**

# Dynamics of surface water on rutile

MD trajectory of two molecules:  
At  $t=0$  one is in  $L_1$  and the other in  $L_3$

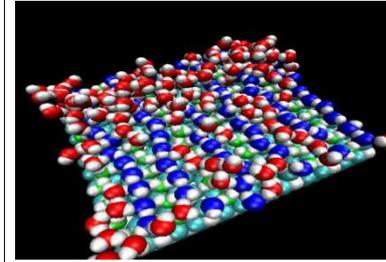
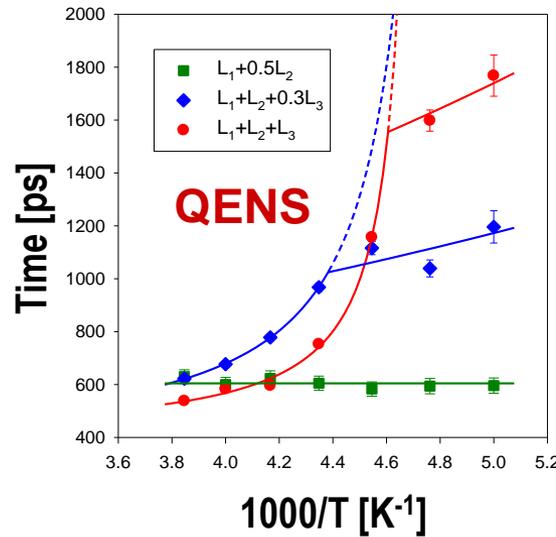
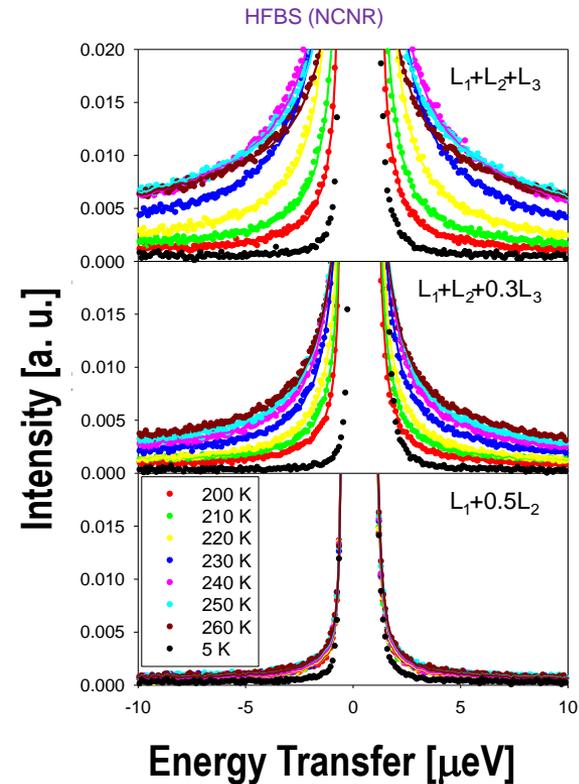


- Mamontov, Wesolowski, Vlcek, Cummings, Rosenqvist, Wang, Cole, *Journal of Physical Chemistry C* 112, 12334 (2008).

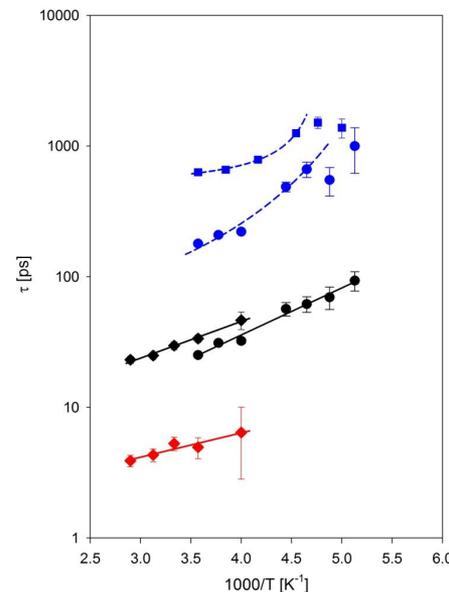
- Hundreds of ps ( $L_2$  -  $L_3$  exchange)—has an appearance of rotational component, but only because of the “confinement” effect; physically is more like translational component in bulk.
- Tens of ps (all layers)—very similar to the rotational component in bulk.
- ps ( $L_3$  only)—translational, under-bonded, fast - no analogy in bulk.

# Water on rutile, slowest component: super-Arrhenius behavior only for hydration level $> L_2$

- Mamontov, Vlcek, Wesolowski, Cummings, Rosenqvist, Wang, Cole, Anovitz, Gasparovic, *Physical Review E* 79, 051504 (2009)

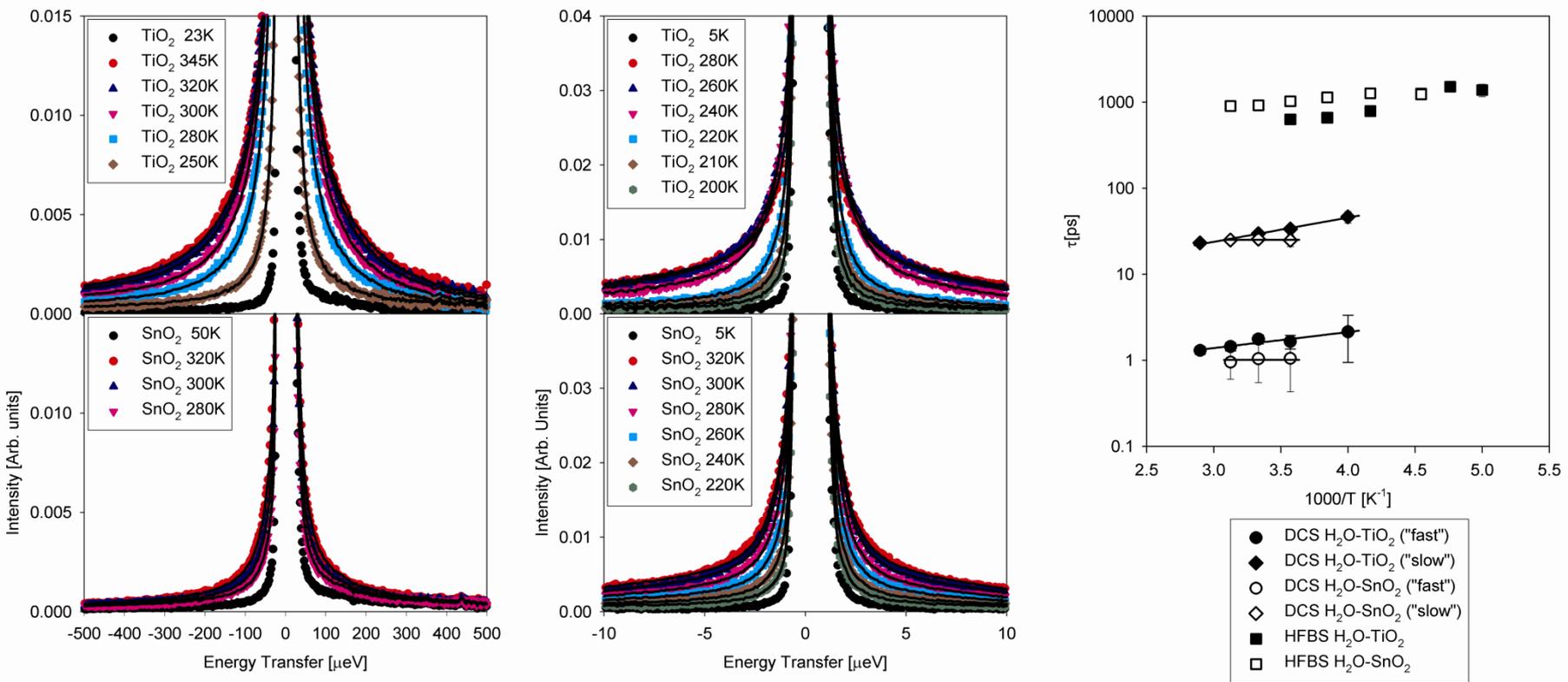


- Non-Arrhenius behavior (and the dynamic crossover) is suppressed at low hydration levels; needs to be more than a monolayer of **mobile** water (not counting  $L_1$ ).
- This is intuitive: needs to be more than one layer for layer-exchange dynamics.



- It takes just above 1 layer of **mobile** water for this mobile water to behave qualitatively bulk-like

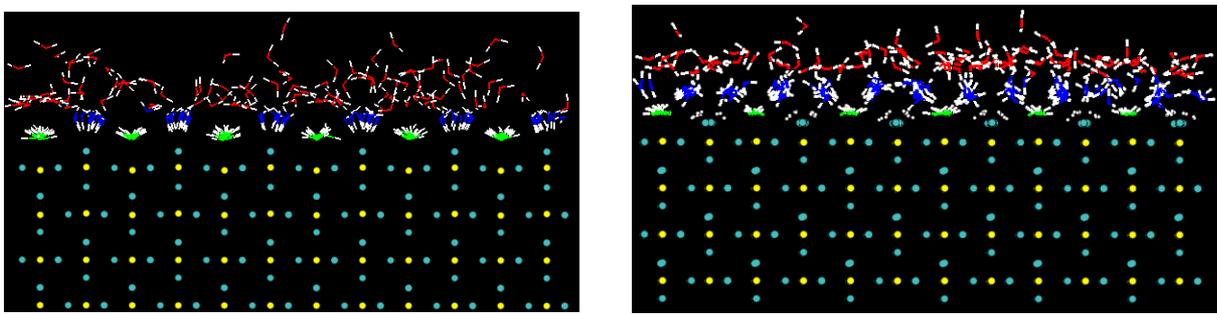
# Generic vs. surface-specific dynamics features



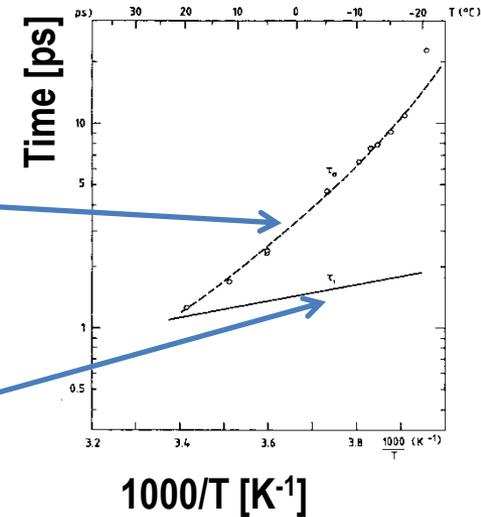
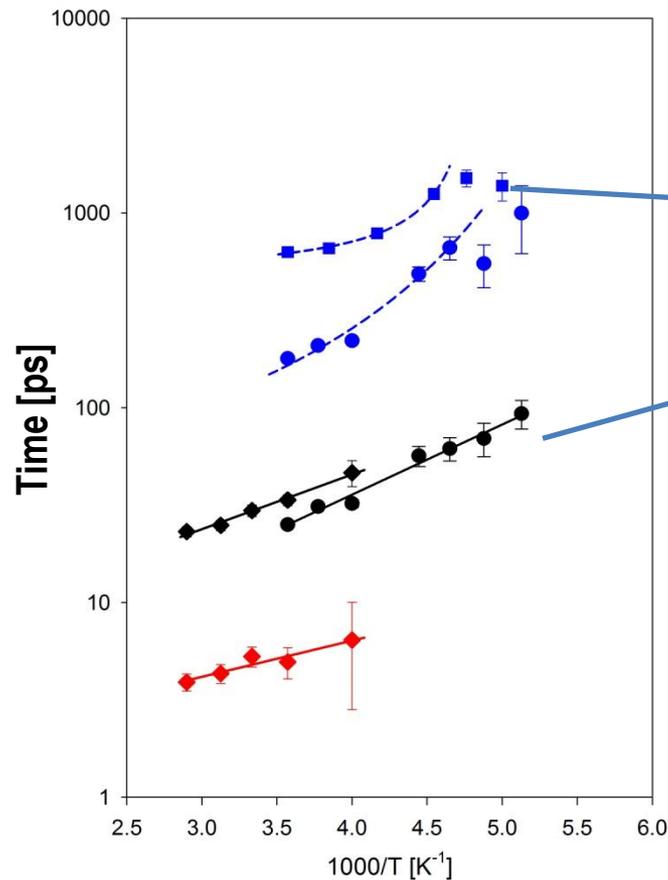
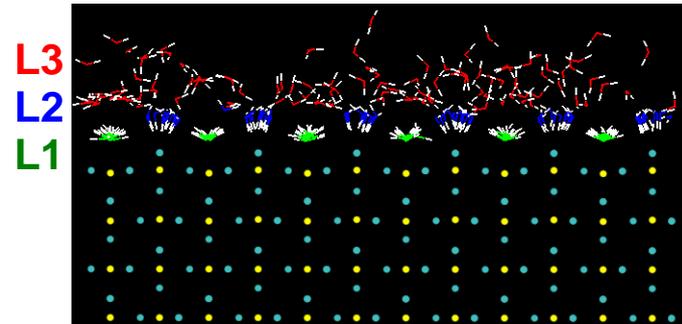
The influence of the surface may be through:

The surface-specific structure of (and interactions with) the  $L_1$  and  $L_2$  layers

The overall hydration level (how much of  $L_3$  is present) – dielectric constant of the matrix?



# Conclusion



- We learned some fine details about surface water behaviour (three dynamic components):**
- Slow dynamics (100s ps – 1 ns):** L2-L3 exchange jumps (analogous to translational jumps in bulk water); gets suppressed and eventually disappears at low hydration levels.
  - Intermediate dynamics (10s ps – 100s ps):** Localized (rotation-like) motion is all layers (but mostly L2 and L3) (analogous to rotational jumps in bulk water).
  - Fast dynamics (picoseconds):** Under-bonded L3 molecules **(no analogy in bulk water)**.