SPETTROSCOPIA DI NEUTRONI

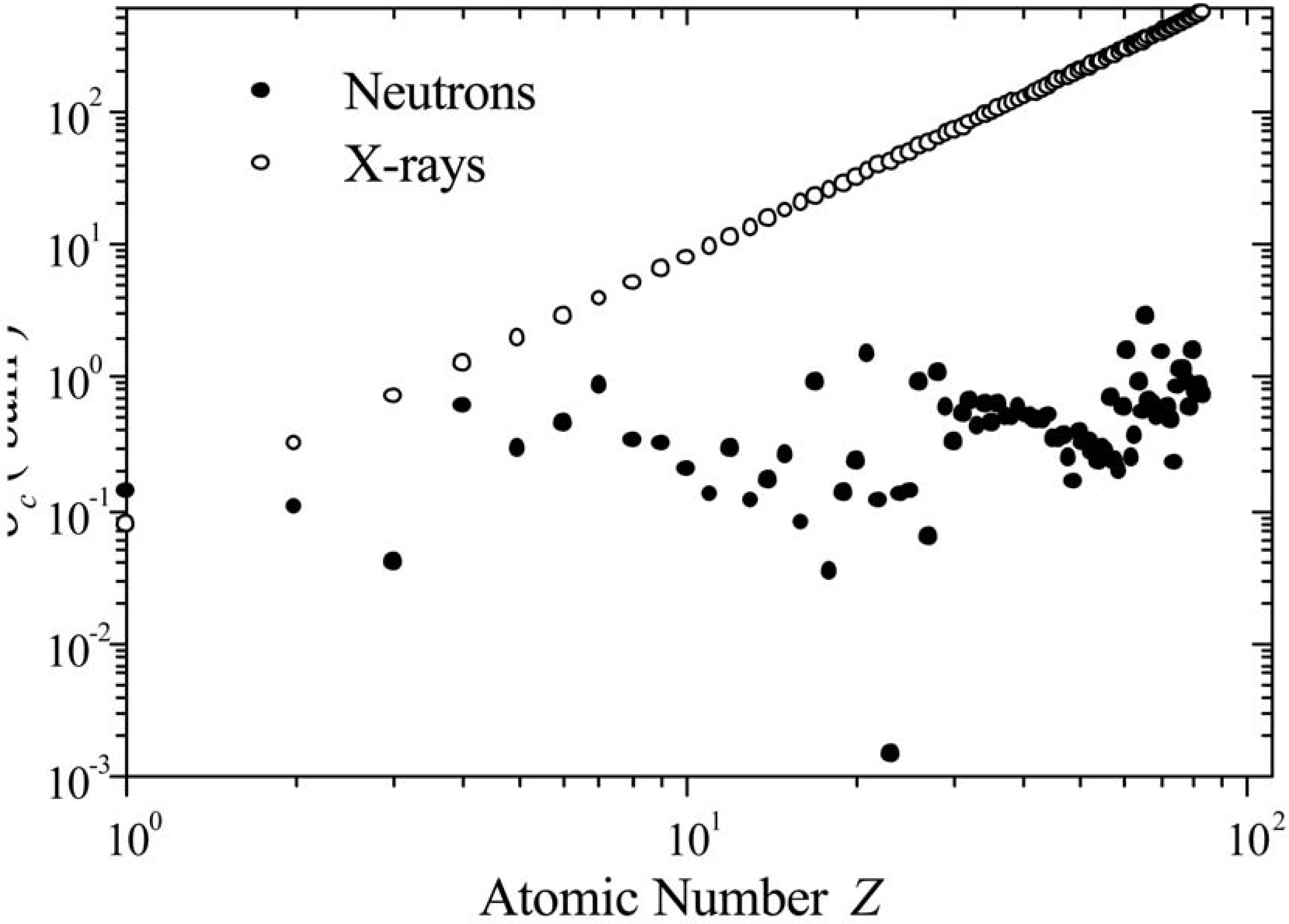
Proprietà fondamentali del neutrone

- **Relazione tra energia, impulso e lunghezza d'onda: ordini di grandezza…**

- **Elettricamente neutro**

- **Spin 1/2**

SPETTROSCOPIA DI NEUTRONI



SPETTROSCOPIA DI NEUTRONI

➢ Sezione d'urto doppio differenziale

$$\frac{d^2\sigma}{d\Omega dE} \propto \sigma_{coh} S_{coh}(Q,E) + \sigma_{inc} S_{inc}(Q,E)$$

Q : vettore d'onda scambiato tra neutroni e campione $Q \sim$ Å^{-1}

E : energia scambiata $E \sim$ meV ≡ 8 cm^{-1} ≡ 0.24 THz

➢ Fattore di struttura dinamico coerente

(correlazioni tra posizioni di *particelle diverse (jk)*, in funzione del tempo)

$$S_{coh}(Q,E) \propto \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{jk} \left\langle \exp\left[-i\vec{\mathbf{Q}}\cdot\vec{\mathbf{R}}_j(0)\right] \exp\left[i\vec{\mathbf{Q}}\cdot\vec{\mathbf{R}}_k(t)\right] \right\rangle$$

➢ Fattore di struttura dinamico incoerente

(correlazioni tra posizioni di *una stessa particella (kk)*, in funzione del tempo)

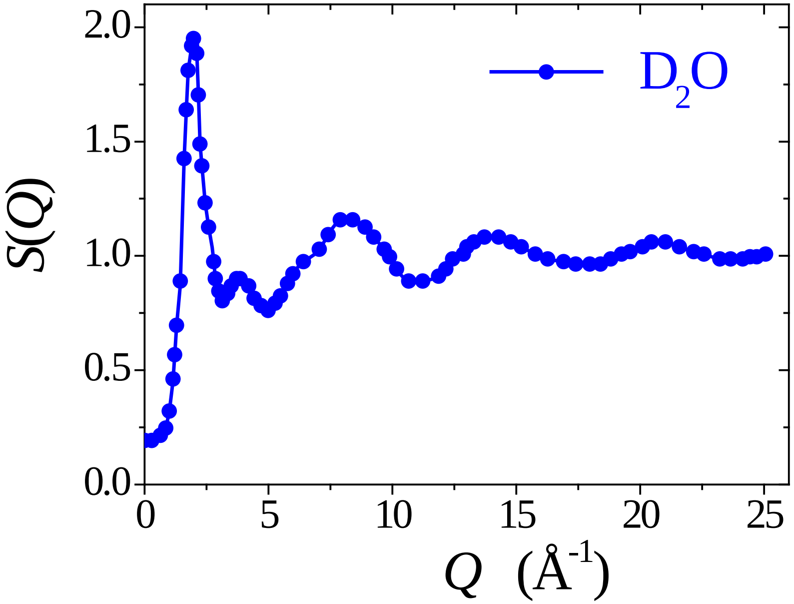
$$S_{inc}(Q,E) \propto \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{k} \left\langle \exp\left[-i\vec{\mathbf{Q}}\cdot\vec{\mathbf{R}}_k(0)\right] \exp\left[i\vec{\mathbf{Q}}\cdot\vec{\mathbf{R}}_k(t)\right] \right\rangle$$

Fattore di struttura dinamico coerente

(correlazioni tra posizioni di *particelle diverse*, in funzione del tempo)

- Elastico → Fattore di struttura statico → Struttura

$$S_{coh}(Q) = \int S_{coh}(Q,E)\,dE$$



- Anelastico → Fluttuazioni di densità, onde "sonore" (THz !)
  → Curve di dispersione → Velocità del "suono"
  → Fattori di smorzamento → Libero cammino medio

$$S_{coh+1}(\mathbf{Q},E) \propto \sum_{s}\sum_{\mathbf{G}} (\mathbf{Q}\cdot\boldsymbol{\varepsilon}_s)^2\,[n(E)+1]\cdot\delta(E-E_s)\cdot\delta(\mathbf{Q}-[\mathbf{G}+\mathbf{q}])$$

Fattore di struttura dinamico incoerente

(correlazioni tra posizioni di *una stessa particella*, in funzione del tempo)

- Quasielastico → Dinamica "diffusiva" e coefficienti di diffusione D

  Ad esempio:

$$S_{inc}(Q,E) \propto \frac{\Gamma}{E^2+\Gamma^2} \quad \text{con} \quad \Gamma \propto D$$

- Anelastico → Densità degli stati vibrazionali $G(E)$ ⟺ $< u^2 >$

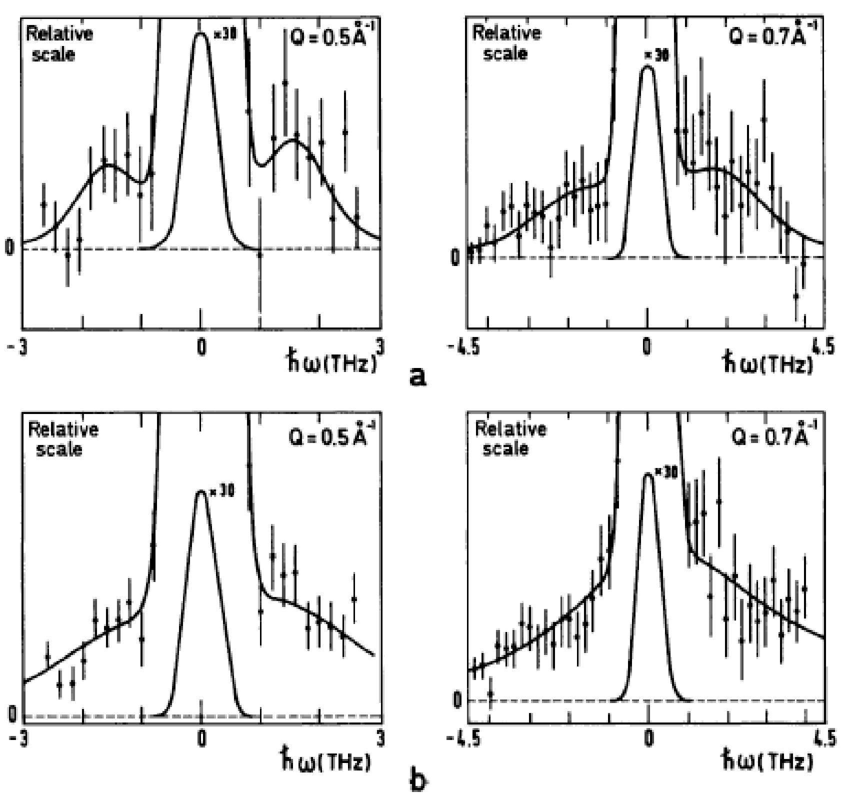
$$S_{inc}(Q,E) \propto \frac{Q^2}{E^2} G(E) \quad \text{e} \quad \langle u^2 \rangle \propto \int_0^{E_{\max}} dE \frac{1}{E^2} G(E)$$

The first neutron Brillouin spectra of a biological sample…

Biophys. J. © Biophysical Society
Volume 56 October 1989 713–716

Low-frequency collective modes in dry and hydrated proteins

M-C. Bellissent-Funel,* J. Teixeira,* S. H. Chen,‡ B. Dorner,§ H.D. Middendorf,| and H. L. Crespi¶

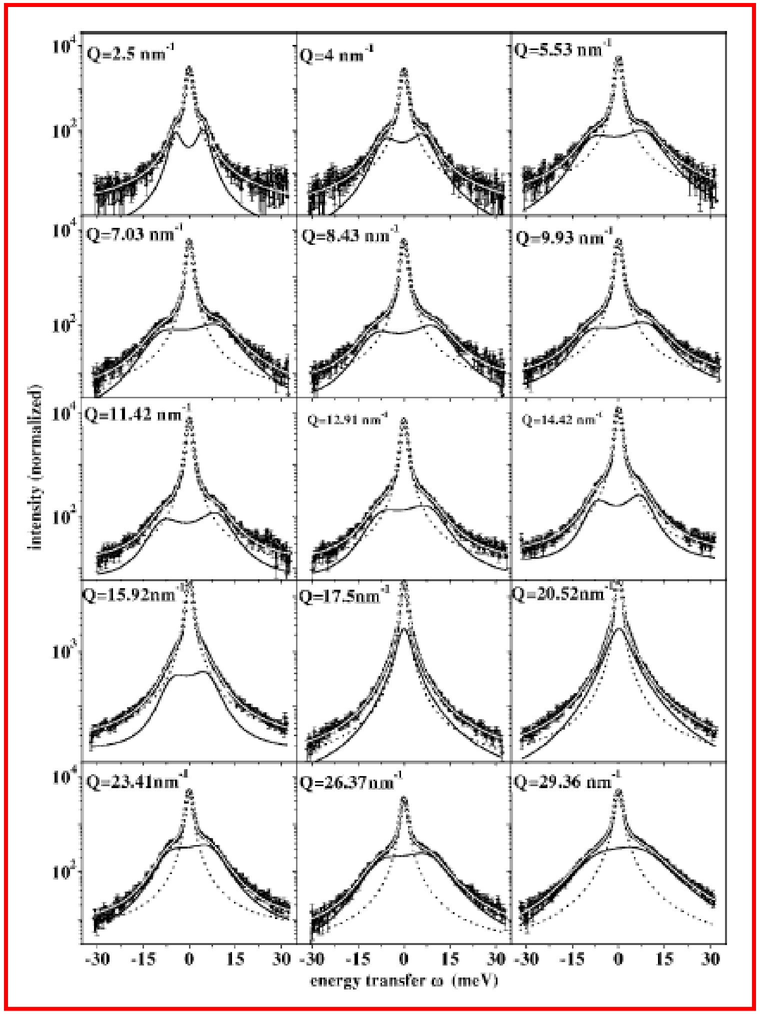


- Fully deuterated C-Phycocyanin in D_2O.
- «These modes are tentatively interpreted as due to short-lived coherent excitations propagating with velocities between 2000 and 4000 m/s… »
- «A detailed quantitative interpretation of the data presented here is hardly possible because of the poor statistics…»

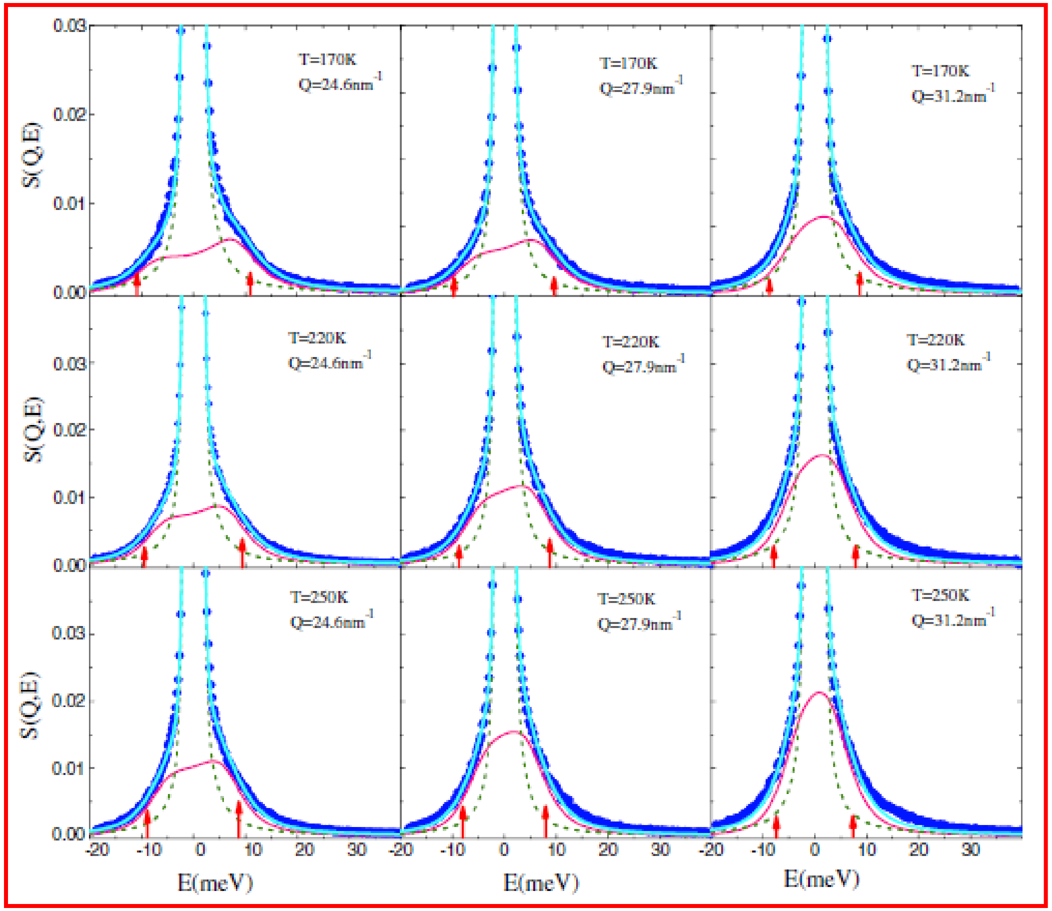
Nowadays X-rays can provide a powerful tool…

Oriented Fibers of DNA

Globular protein BSA



Krisch et al., PRE 73, 061909 (2006)



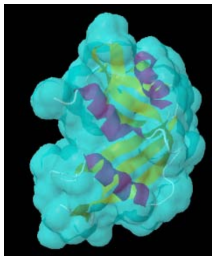
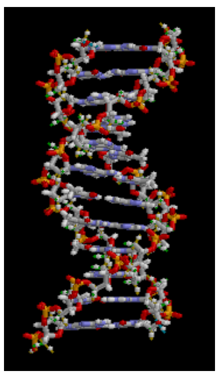
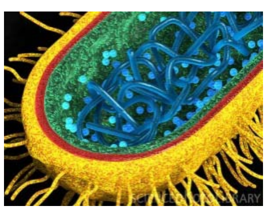
Liu et al., PRL 101, 135501 (2009)

… but do not allow <u>contrast methods</u>…

…(and may induce radiation damages on biological samples?)…

Samples & Measurements

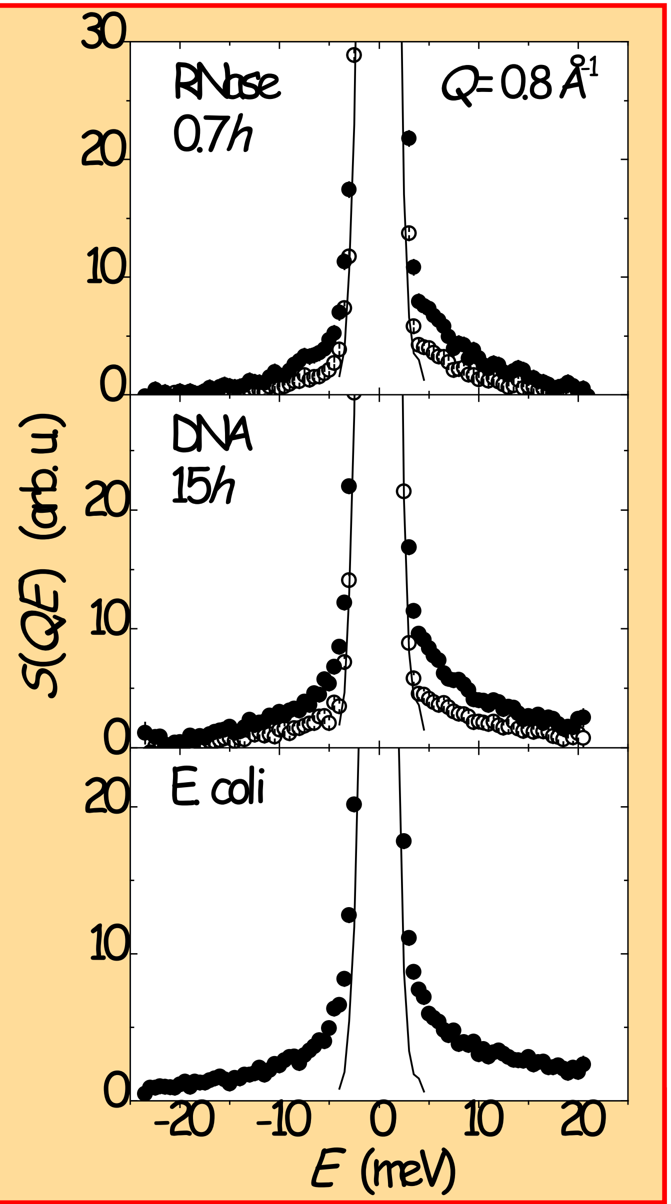
BRISP spectrometer @ ILL - E_i = 83.7 meV, δE = 2.7 meV, T = 300 K

	Sample	*Hydration Level*
	Hydrogenated RiboNuclease + D_2O (m ~ 6 g)	dry h = 0.0
		wet h = 0.7
	Hydrogenated DNA + D_2O (m ~ 6 g)	dry h = 0.0
		wet h = 1.0
		wet h = 15.0
	Deuterated *Escherichia coli* (m ~ 7.5 g)	*Natural* $h \approx 3$

→ The H/D contrast highlights the coherent signal of water against the incoherent signal of the biomolecule

Data Treatment

- Corrections for:
  - background and cell scattering
  - detector efficiency
  - sample self-absorption
  - multiple scattering



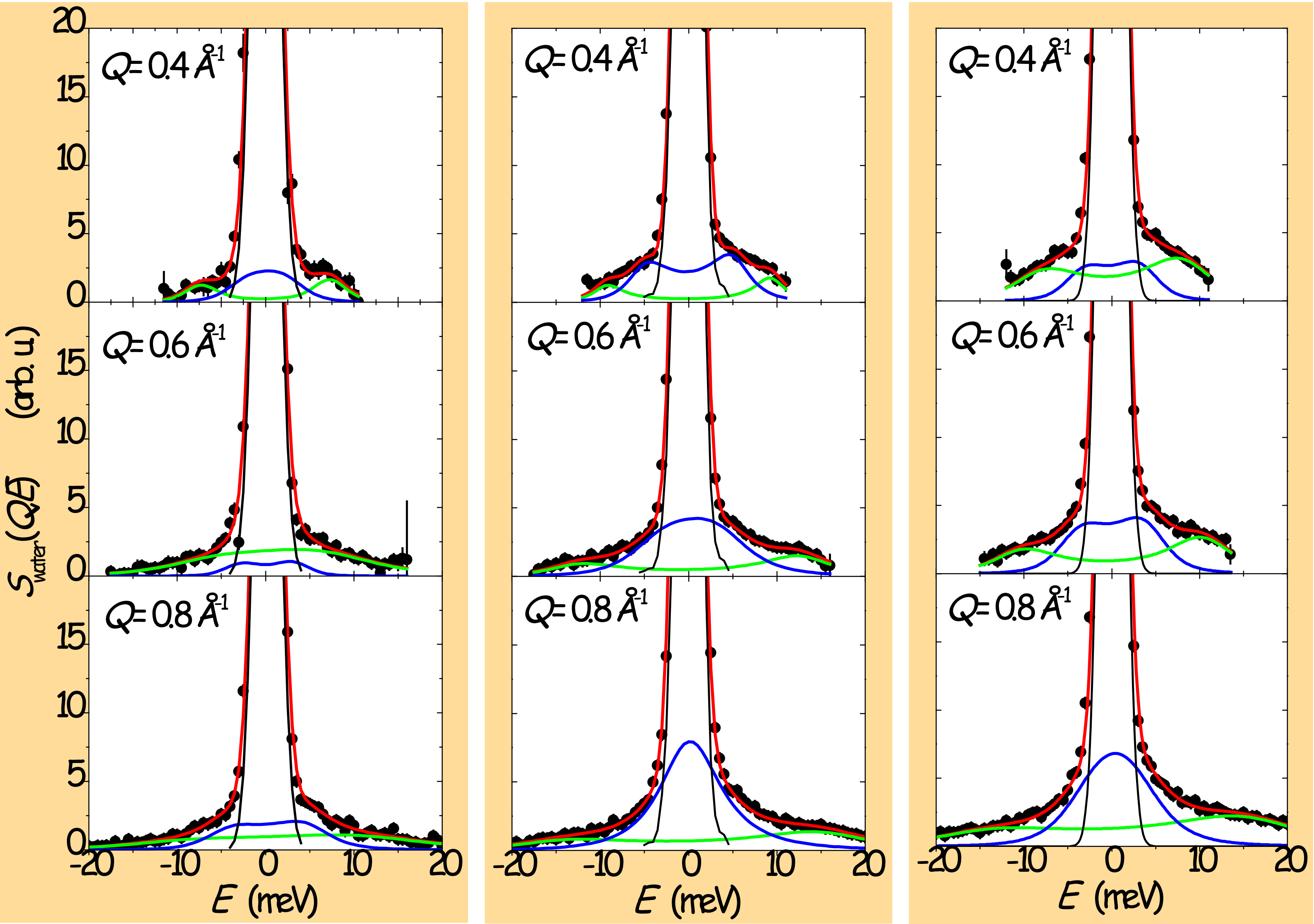
- Water contribution:

$$I_{water}(Q,E) = I_{wet}(Q,E) - I_{dry}(Q,E)$$

- Model: elastic delta function + double DHO

$$S(Q,E) = a_{QE}(Q)\,\delta(E) + \\ + [n(E)+1]\left\{ a_H(Q)\frac{\Gamma_H(Q)\,E}{[E^2 - E_H^2(Q)]^2 + [\Gamma_H(Q)\,E]^2} + a_L(Q)\frac{\Gamma_L(Q)\,E}{[E^2 - E_L^2(Q)]^2 + [\Gamma_L(Q)\,E]^2} \right\}$$

Hydration Water Spectra

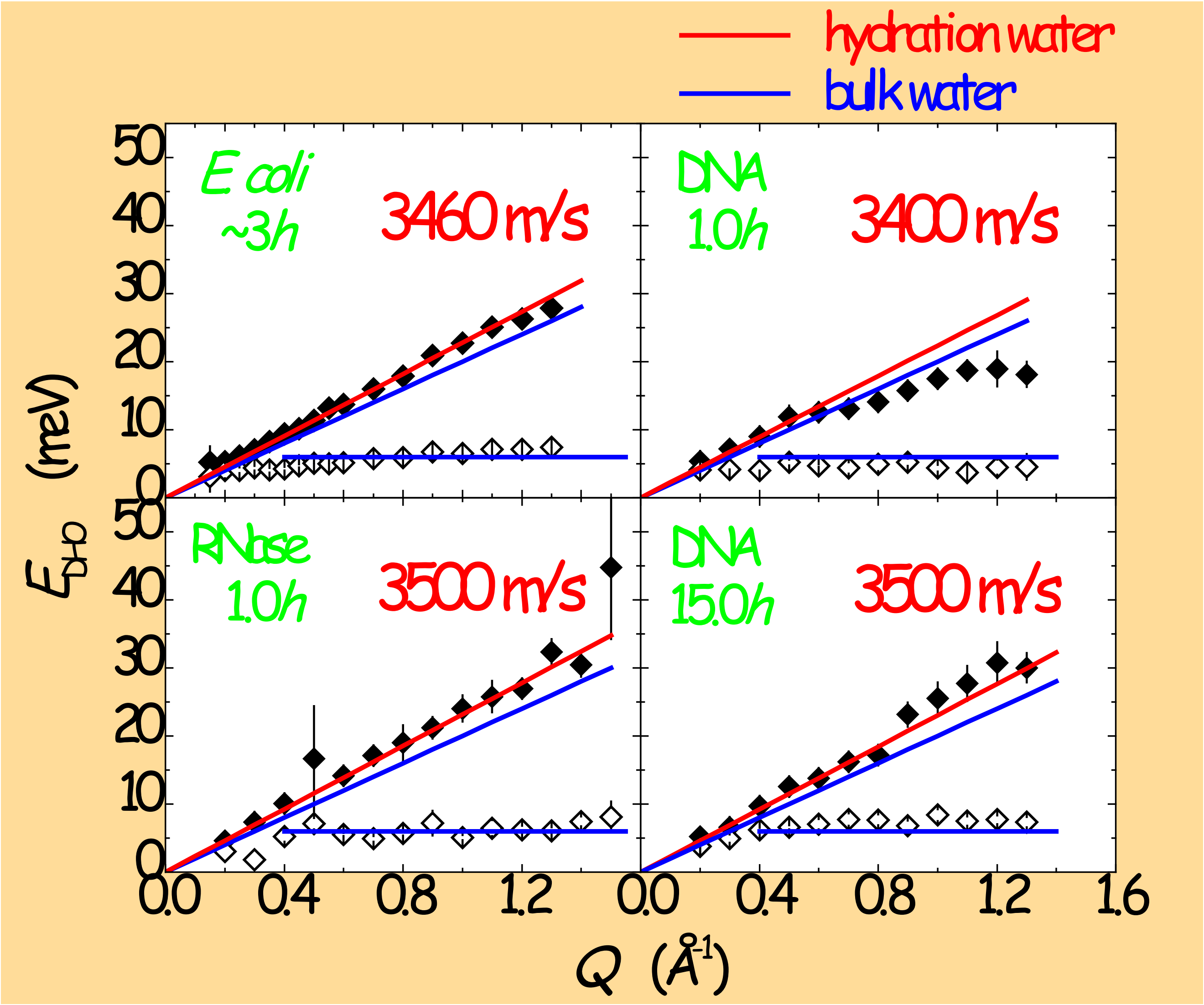


RNase
h = 0.7

DNA
h = 15

E. coli
h ≈ 3

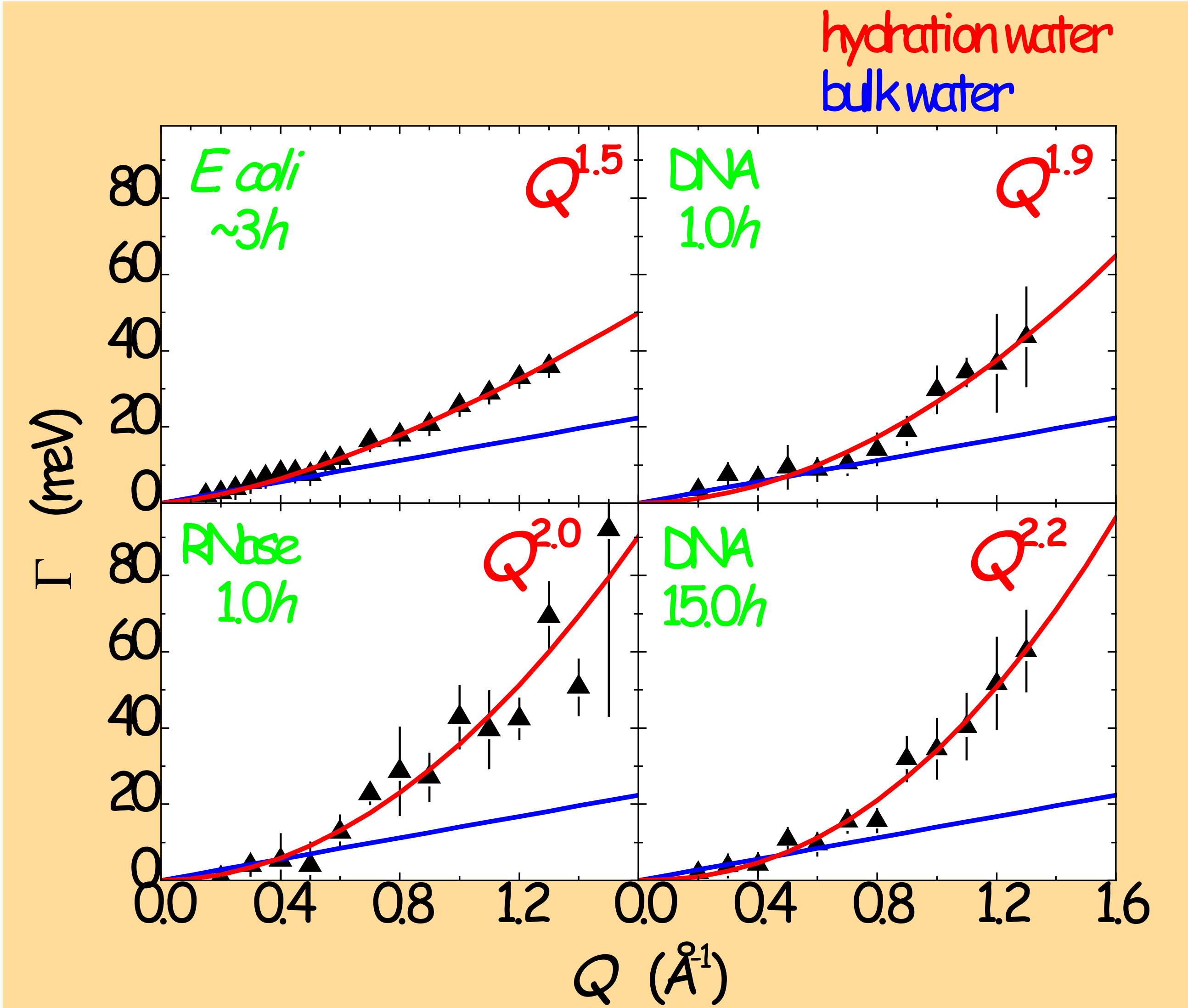
Dispersion Curves



- Close similarity between hydration water and bulk water

→ the biomolecule has small effect on the vibrational frequencies

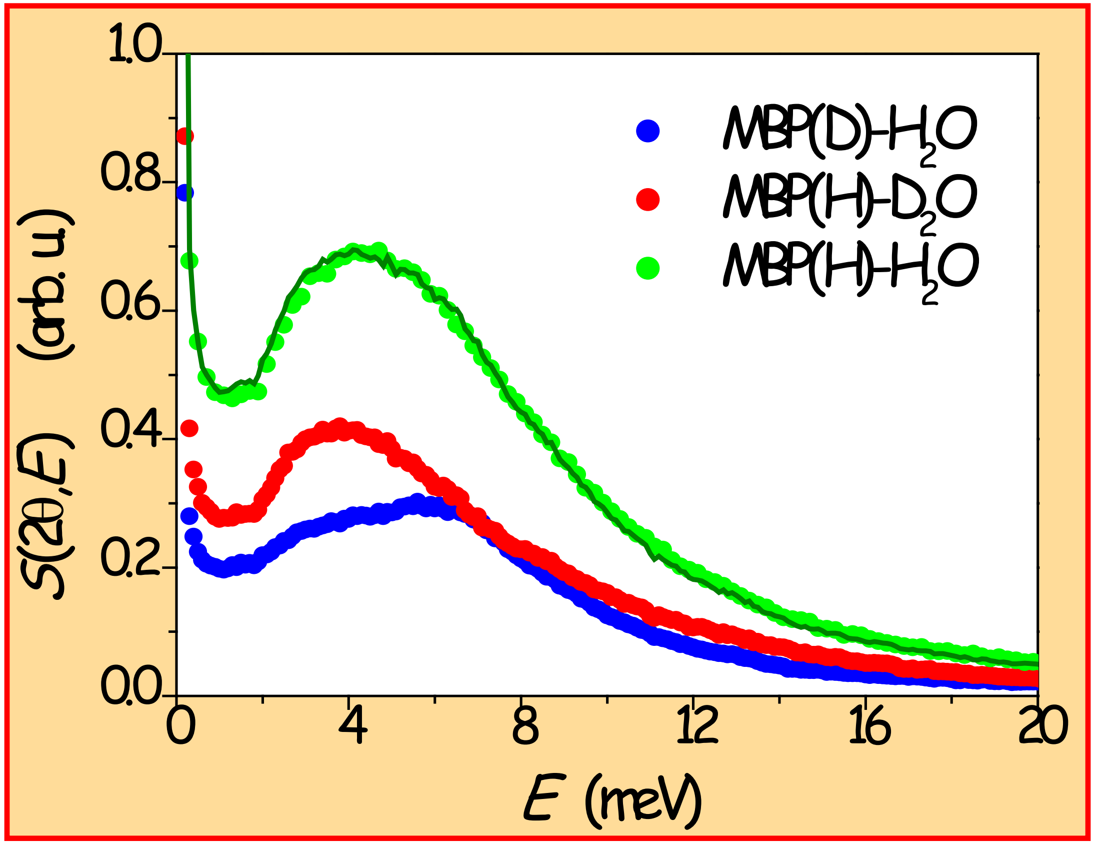
Damping Factors



- Larger damping than in bulk water → a "glassy" dynamical behavior?
- Intermediate damping in *E. coli* → a "mixture" of waters → ***h* = 0.9**

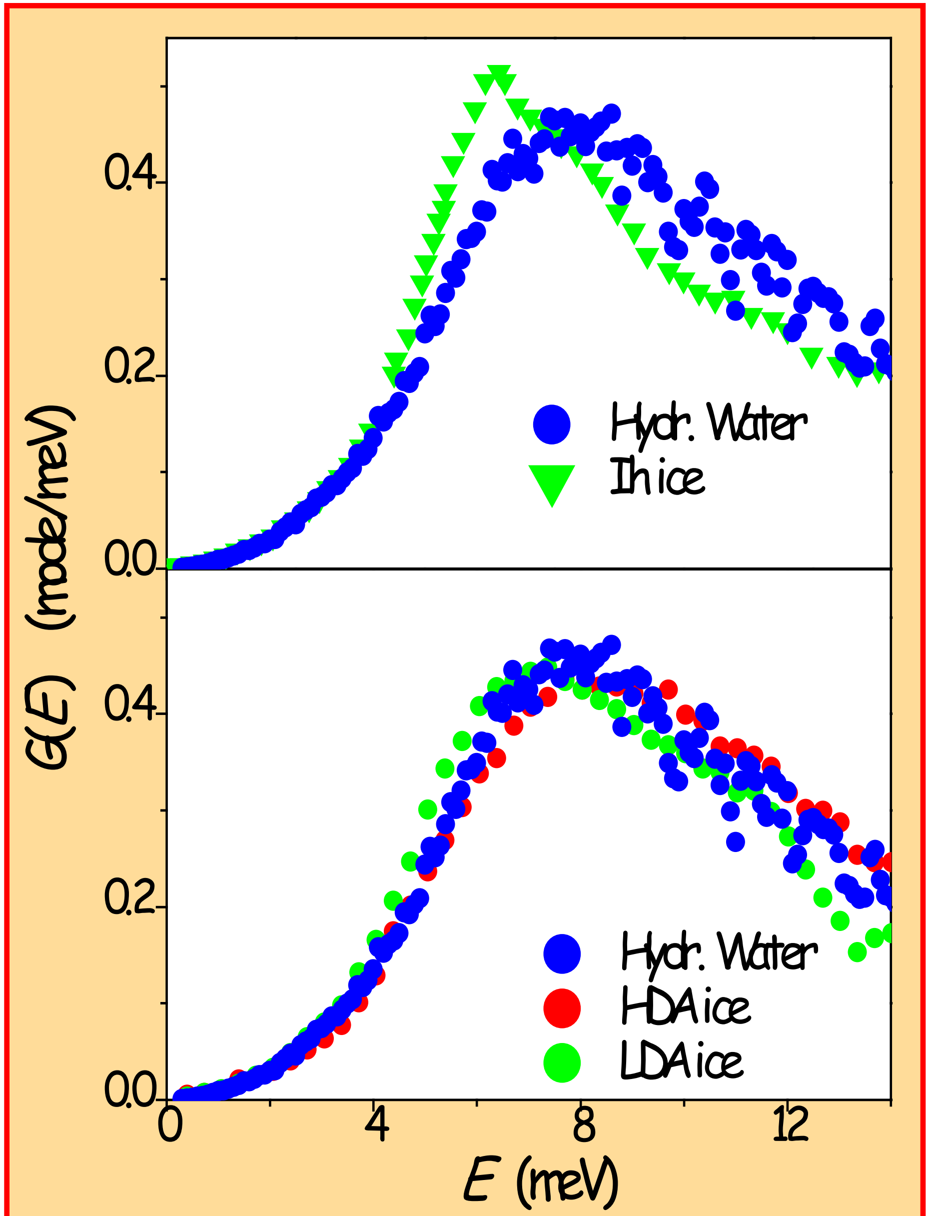
More about the "glassy" dynamics of hydration water…

- A <u>perdeuterated protein</u> by the ILL Deuteration Lab: D-MBP
- …hydrated with <u>hydrogenated water</u>…
- …allows a reliable measurement of the hydration water incoherent dynamic structure factor

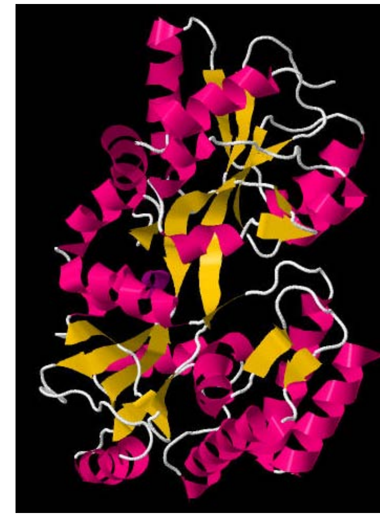


Measured on IN5 @ 100 K

Hydration Water Density of States…



…in the MBP protein

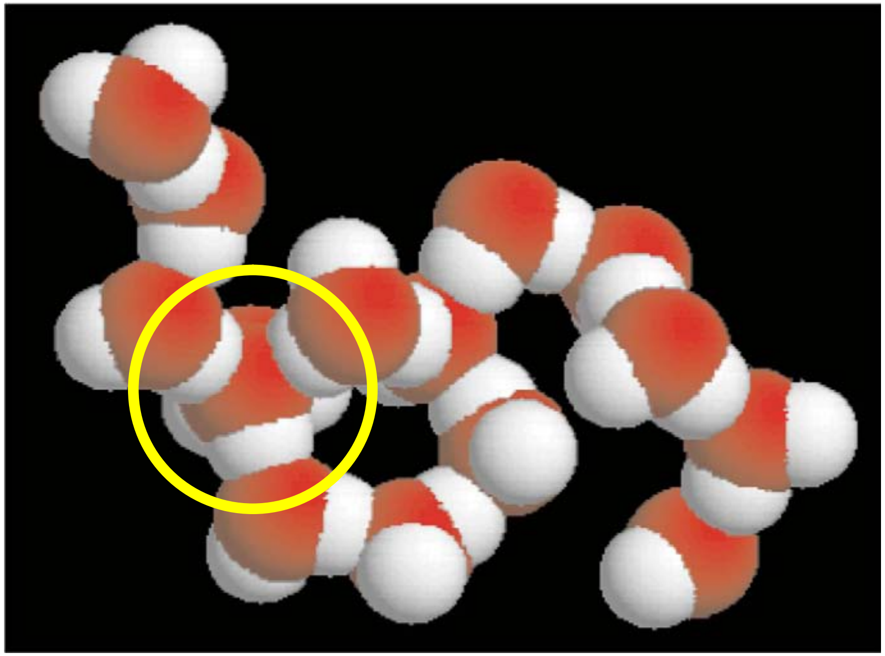


- The DoS of hydration water is correctly reproduced only by a linear combination of the DoS of Low-Density and High-Density Amorphous Ice.

A general dynamical property of <u>interacting water</u> ?...

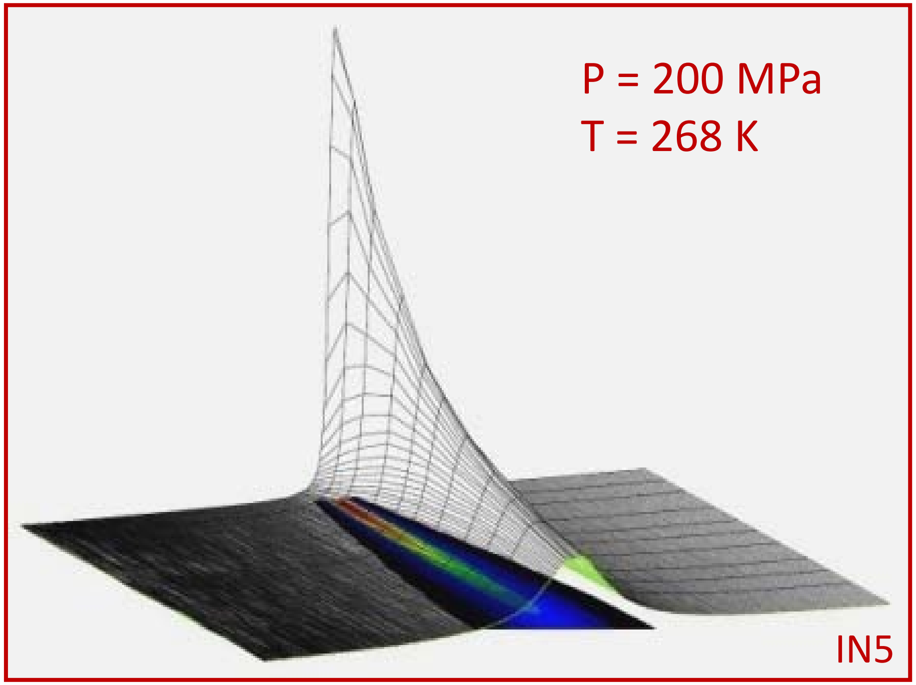
- Interaction with a hydrophilic molecule…
  (globular protein, DNA helix, whole *E. coli* cell, nanoparticle…)

- Distortion of locally ordered tetrahedra…

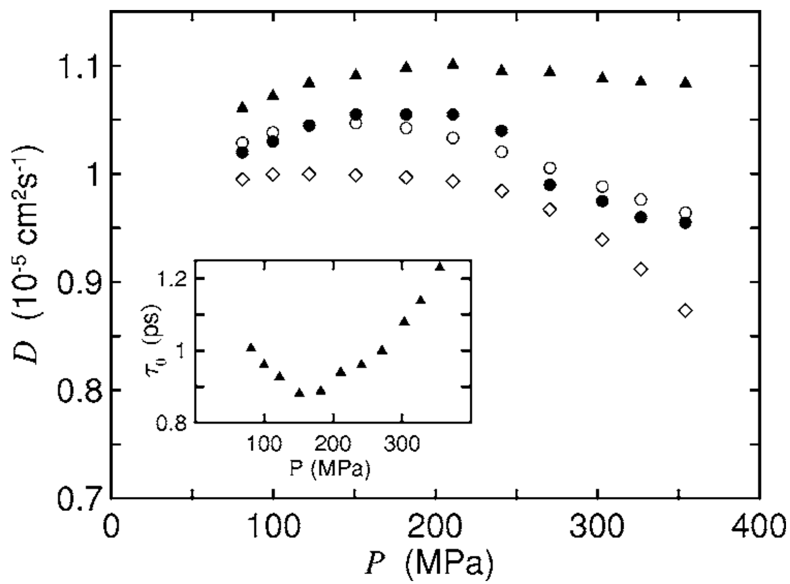


- Role of the hydrogen bond network…

An alternative way to distort hydrogen bonds…



- Pure water under pressure
- Diffusive dynamics *vs.* P and T



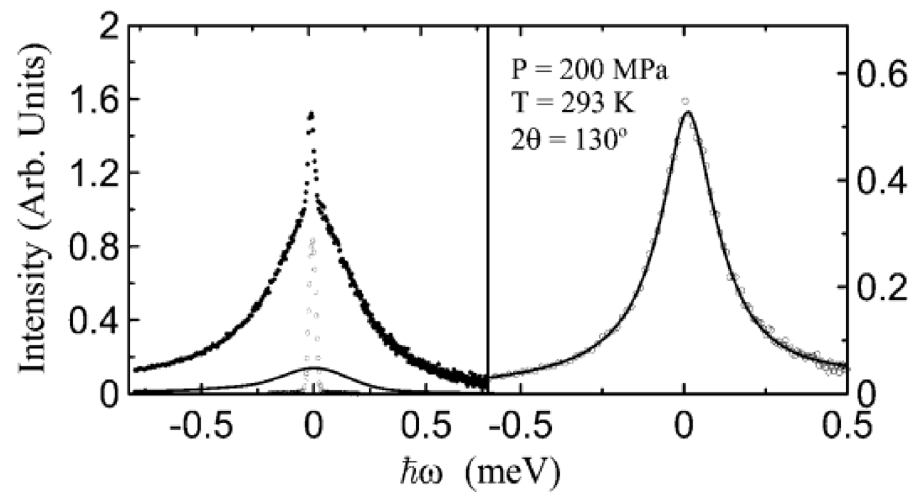


Figure 1. Left panel, typical experimental data (full circles) as compared to the multiple scattering contribution (full line) and the instrument resolution (empty circles). Right panel, corrected intensity (empty circles) and model fit (full line) described in the text.

An alternative way to distort hydrogen bonds…

$$I^{\exp}(Q,\omega) = \frac{k}{k_0}\frac{1}{2\pi\hbar}A(Q) \times \int_{-\infty}^{+\infty} e^{i\omega t} F_{\mathrm{mod}}(Q,t)\, \mathscr{R}(t)\, \mathrm{d}t$$

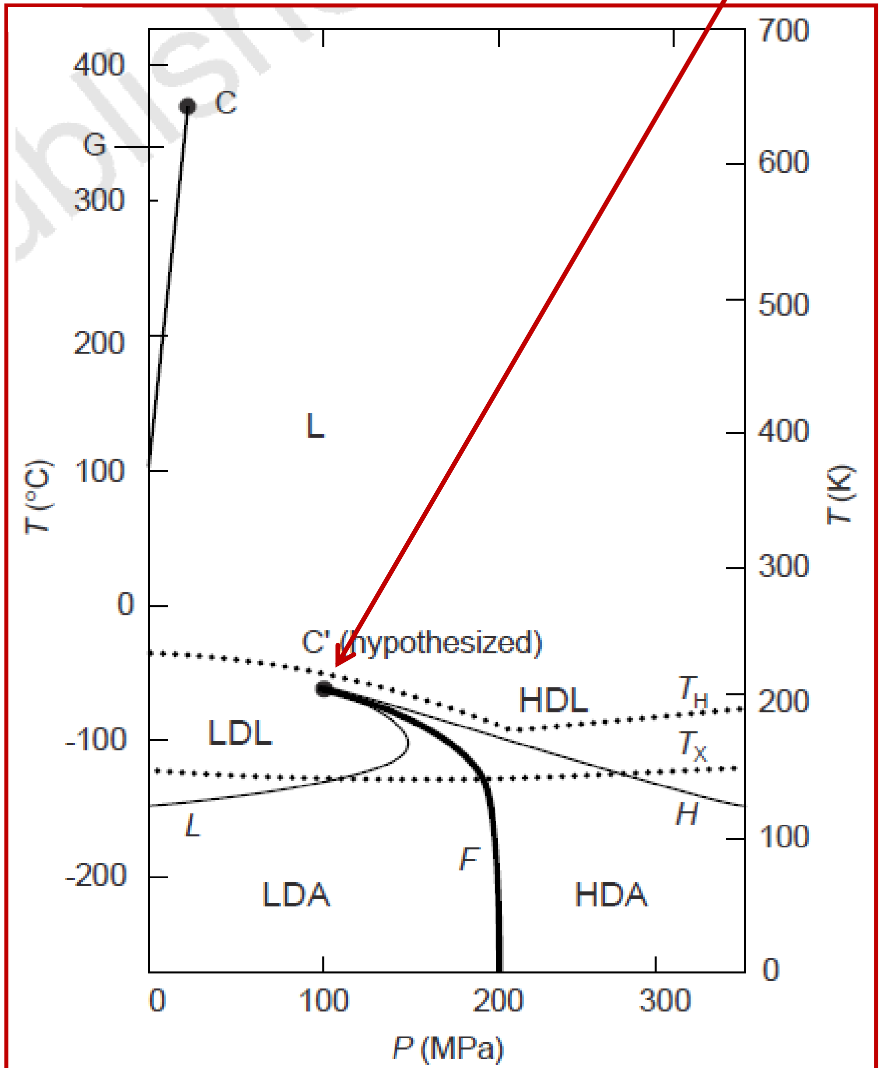
$$F_{\mathrm{mod}}(Q,t) = \exp\left\{-\left[\frac{t}{\tau_T(Q)}\right]^{\beta_T(Q)}\right\} \times \sum_{l=0}^{l_{\max}} (2l+1) j_l^2(Qd) \exp\left\{-\frac{l(l+1)}{2}\left[\frac{t}{\tau_R(Q)}\right]^{\beta_R(Q)}\right\}$$

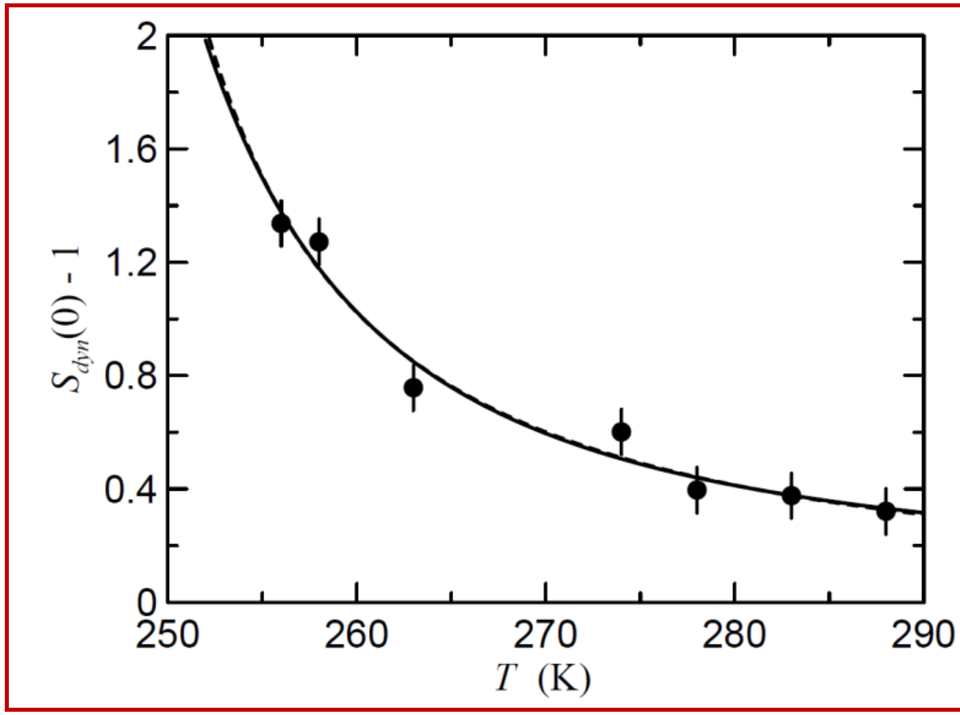
$$\tau_{\mathrm{av}}(Q) = \int_0^{\infty} \mathrm{d}t \exp\left\{-\left[\frac{t}{\tau_T(Q)}\right]^{\beta_T(Q)}\right\}$$

$$S_{\mathrm{dyn}}(Q) = \tau_{\mathrm{av}}(Q)/\tau_{\mathrm{av}}^{\mathrm{SD}}(Q) = \tau_{\mathrm{av}}(Q)/DQ^2$$

An alternative way to distort hydrogen bonds…

Divergenza del tempo di residenza a T_c = 218 ± 5 K





- Further dynamical anomalies, again at $Q \sim 0.3 - 0.5$ Å^{-1} …
- …which diverge toward the elusive second critical point (Widom line)…