The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization
IAEA International Atomic Energy Agency

2054-6

Structure and Dynamics of Hydrogen-Bonded Systems

26 - 27 October 2009

Concerted Proton Tunneling in Ice Ih?

Livia BOVE

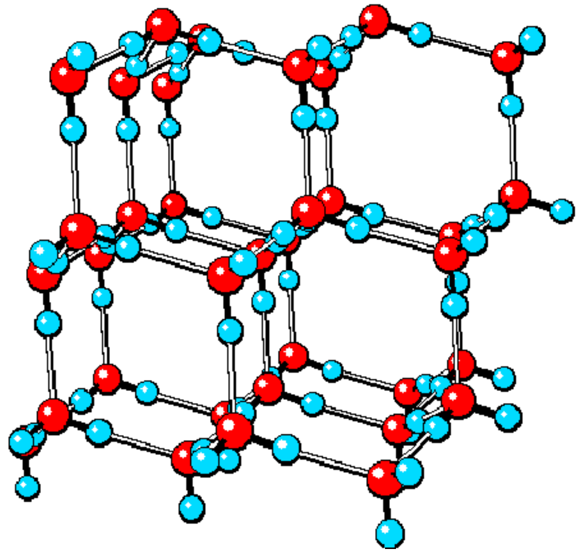
Univ. Pierre et Marie Curie Paris VI
140 rue Lourmel, 75015
Paris
FRANCE

Concerted proton tunneling in Ice Ih?

L.E.Bove[1], S. Klotz[1], A. Paciaroni[2], F. Sacchetti[2]

[1] Physique des Milieux Denses, IMPMC, Université Pierre et Marie Curie, Paris
[2] Dipartimento di Fisica, Università di Perugia, Perugia

Incoherent cross section of ice Ih



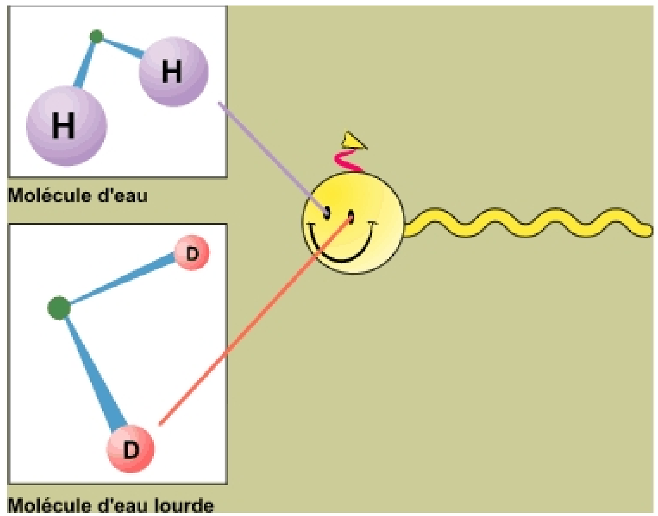
✓Hexagonal ice: the prototype of *ice disorder*

Principal building units: buckled hexagons with O at corners and 2 H-sites in between (average occupation ½)

Protons occupy randomly the two possible sites

✓Incoherent neutron scattering

High visibility of H: σ_{inc}=81 barns



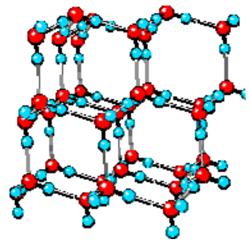
Wavelength ~ atomic distances

Measure the FT of the spatial probability density function of a single proton :
'elastic' ω~0 long time scale configurations are probed
'quasi-elastic' as a function of time (ps-ns)

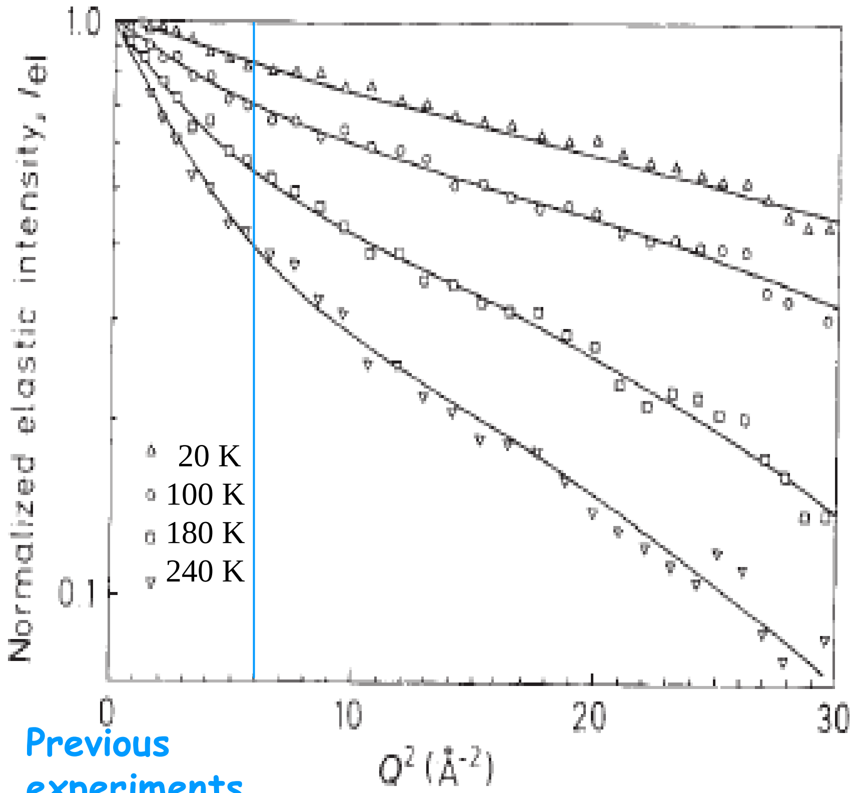
For a harmonic crystal → Debye Waller factor

$S(Q,\omega\sim 0)=\sigma_{inc}/4\pi * a_0 \exp(-Q^2\langle\Delta x^2(T)\rangle)$

Non harmonic behavior of ice Ih! [IN13-ILL]



Normalized elastic intensity

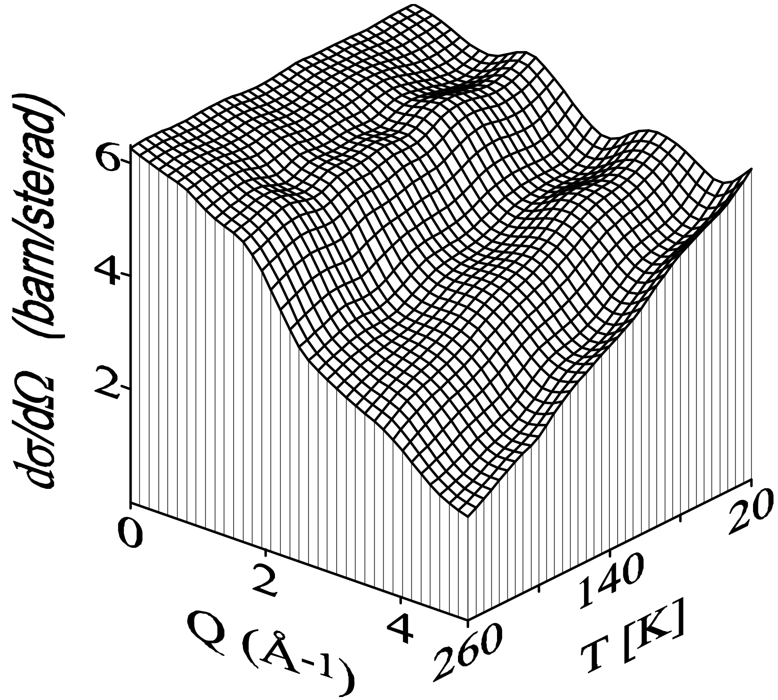


Previous experiments Q range

The elastic intensity can not be fitted by a Q- Gaussian function :

non-harmonic motion of protons!

Incoherent cross section



15 temperatures from 20 K to 260K

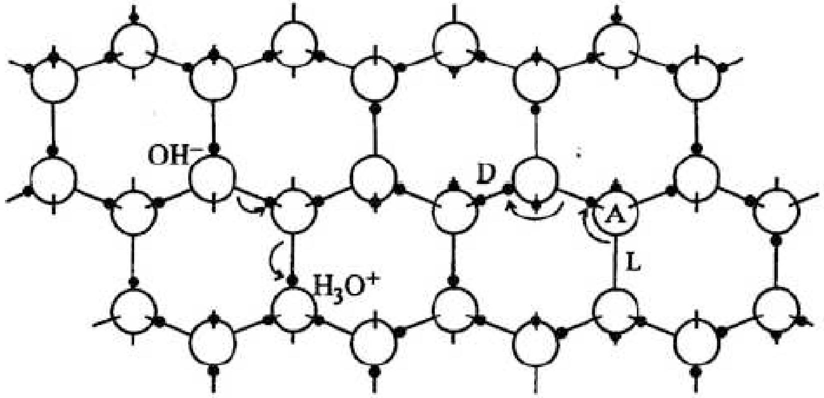
Oscillatory trend → at least one special distance in the single-proton probability density function

Coherence effects

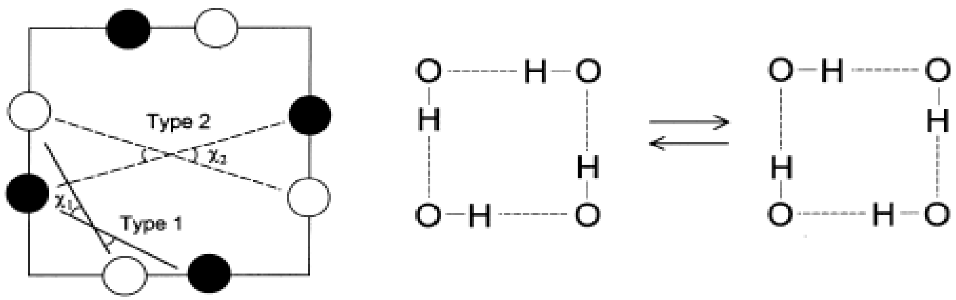
Number of protons involved ~%

L.E.B. et al, in publication

How can a proton move in a cyclic network?



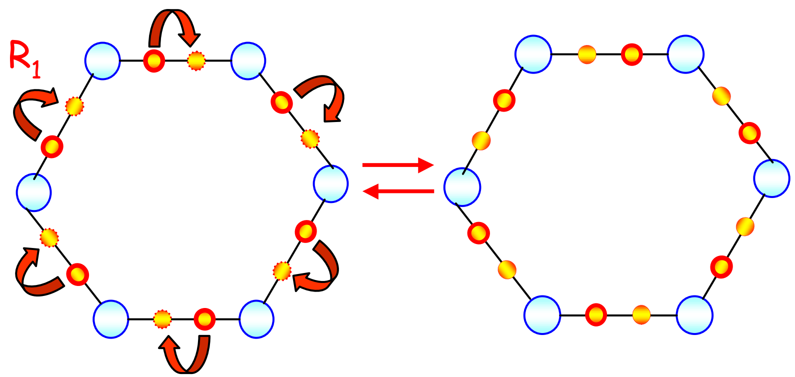
A single protons cannot jump from one site to the other without producing defects :
High activation barrier ~ →10^{-6} events



Saenger et al., Nature 296 (1992)
Flip-Flop H bonding in a partially disordered Cyclodextrin

Brougham et al., Nature 397 (1999)
Coordinated proton tunneling in cyclic array of 4 H- bonds (calix[n]arene)

Ordered hexagonal loops: the H occupies the same site in the six bonds



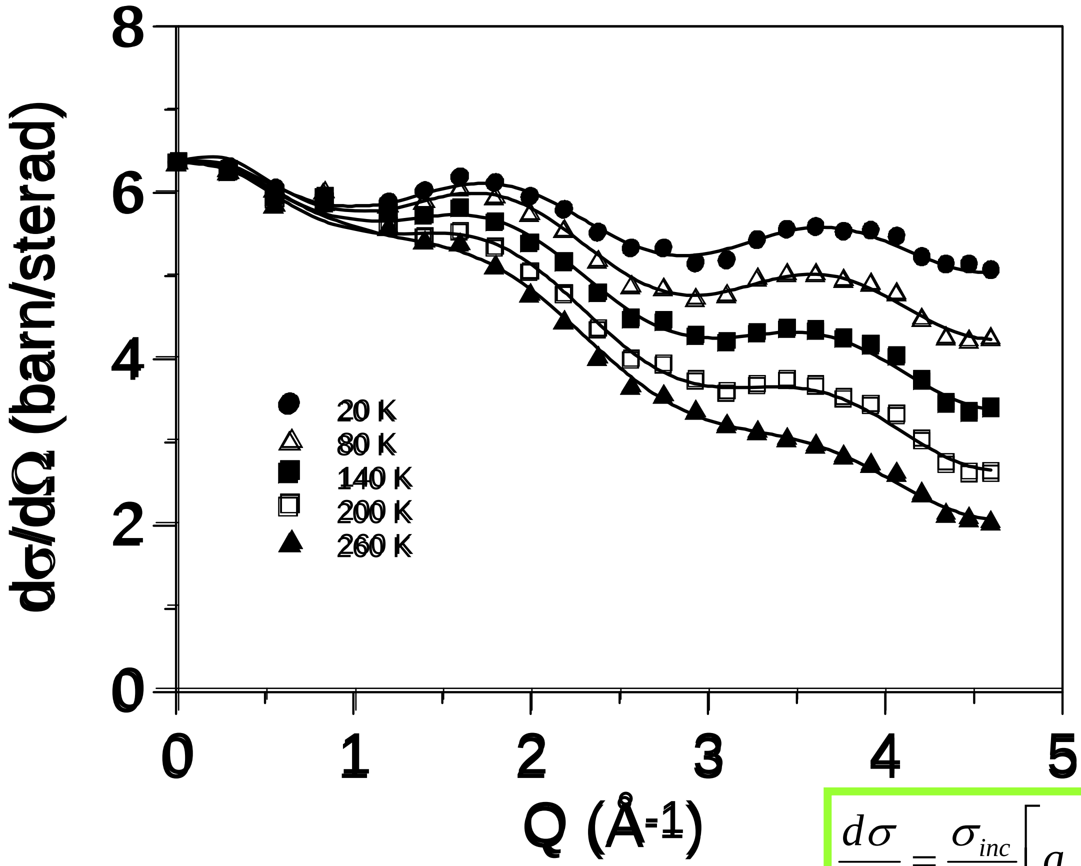
In the ordered loops 6 protons can move with no change of the total E_{crist}

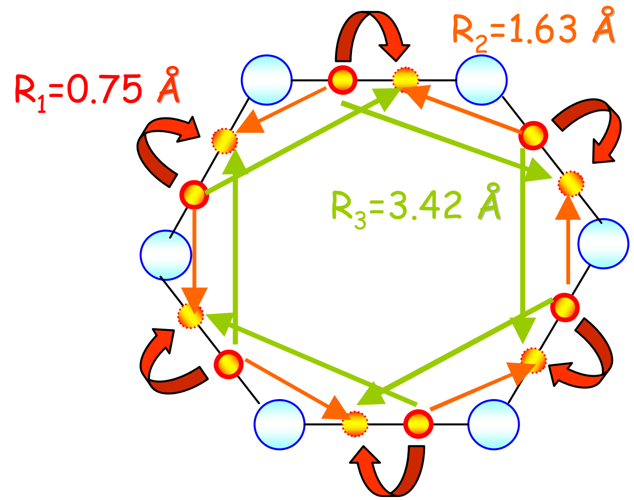
Coordinate motion highly favored:
Most likely lower activation barrier

«.. .a jump of a H atom from one position to another in ordered loops causes all the connected H bonds to change in a cooperative concerted mechanism (domino effect) »

L. Pauling, J Am. Chem. Soc. 57 (1935)

Concerted proton jump model





$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{inc}}{4\pi}\left[a_0 \exp\left[-<\Delta x^2> Q^2\right] + \sum_i^N a_i \cos(Q \cdot R_i)\right]$$

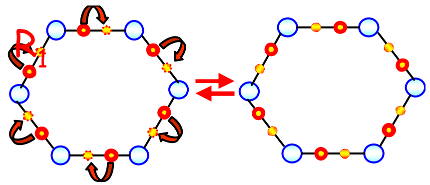
The best fit is obtained using two distances parameters only:

R_1=0.75+-0.03 Å → H sites along one O-O side; weight factor 0.9; slightly T dependent

R_{av}=3.4+-0.05 Å → average of all others distances?; weight factor 0.1, T independent

L.E.B. et al, in publication

First conclusions and new challenges:



✓Non-harmonic motion of H in ice Ih, faster than our t-window (0.5 ns)

Time scale? T-behaviour of the associated time

↓

Quasielastic Neutron Scattering experiment on a shorter time scale

✓Coherence effects in the incoherent cross section on a main distance of 0.75 Å

Which kind of motion? Associated with H-disorder?

↓

Comparison with a H-ordered ice form (Ice VIII) and with a different H-disordered form (Ice Ic)

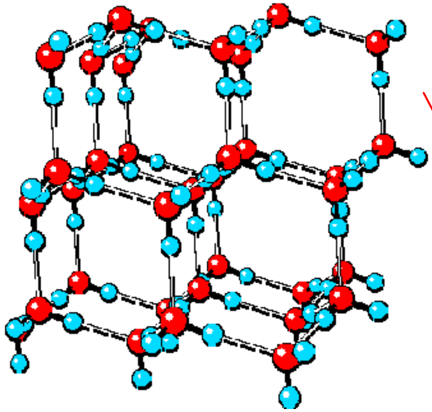
✓H involved ~% →low energy barrier

Concerted mechanism? Role of the ordered loops?

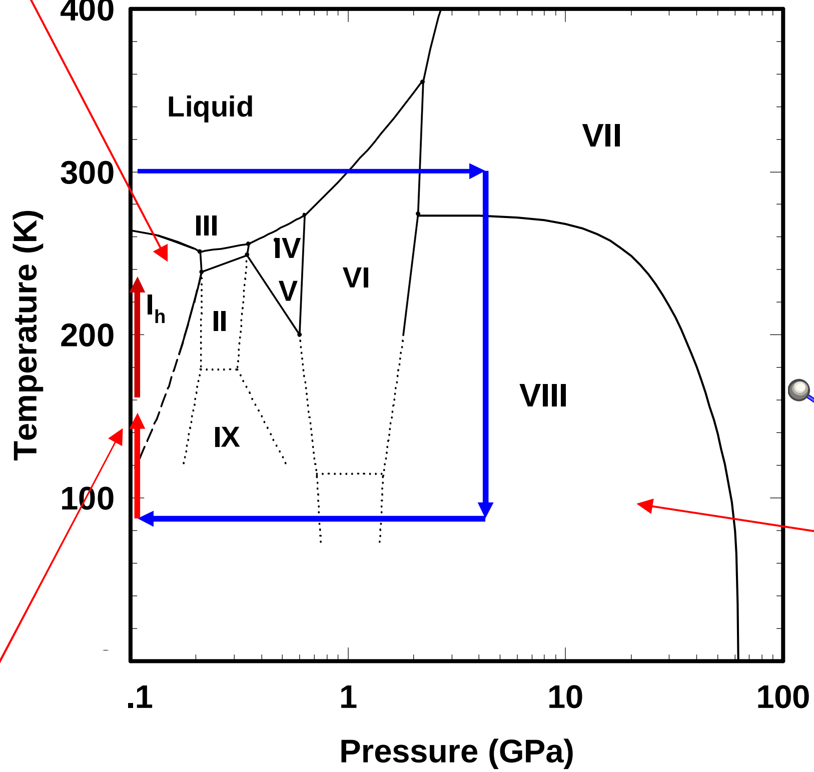
↓

Partial deuteration to broke the loop symmetry

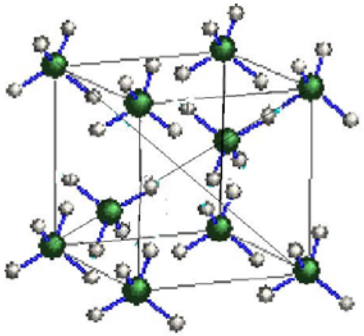
Ice ordered and disordered structures:

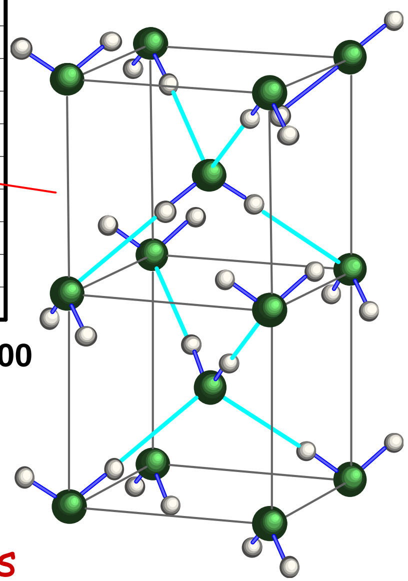


At 190K->Ice Ih
H-disordered



At 145K→Ice Ic
metastable
H-disordered



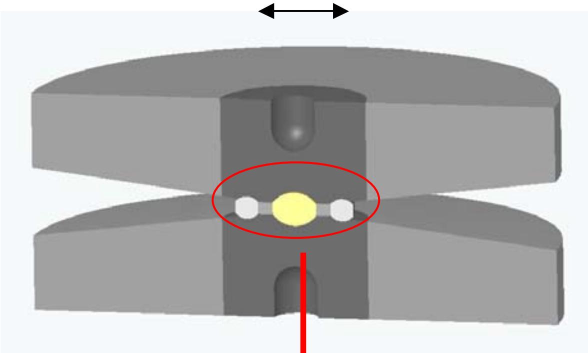


Ice VIII
H- ordered

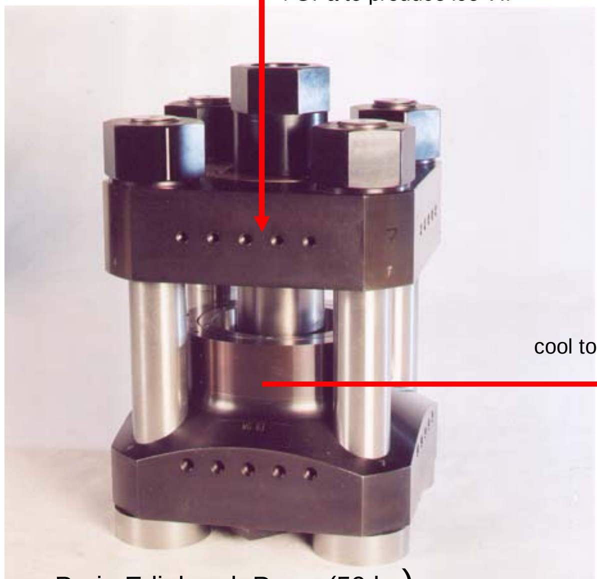
Mutual transformation of the 3 phases
Minimize the possible spurious differences

Making large quantities of H2O ice VIII

10 mm

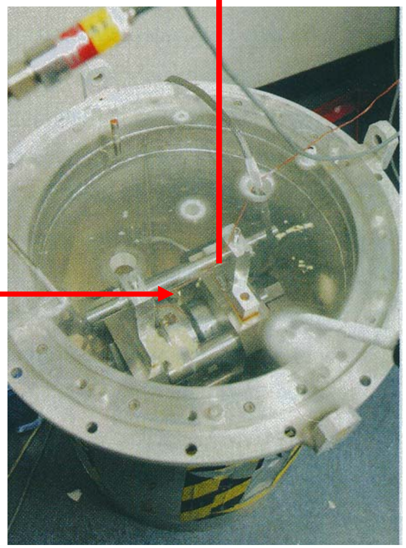


Increase load to
4 GPa to produce ice VII

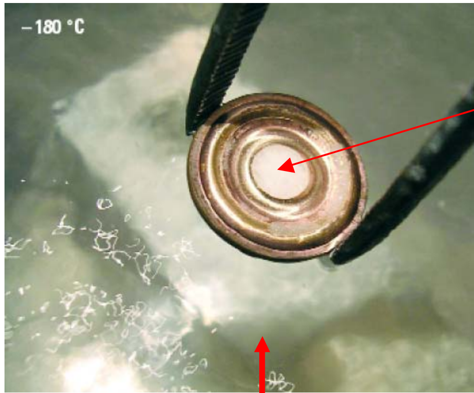


Paris-Edinburgh Press (50 kg)

cool to 77 K

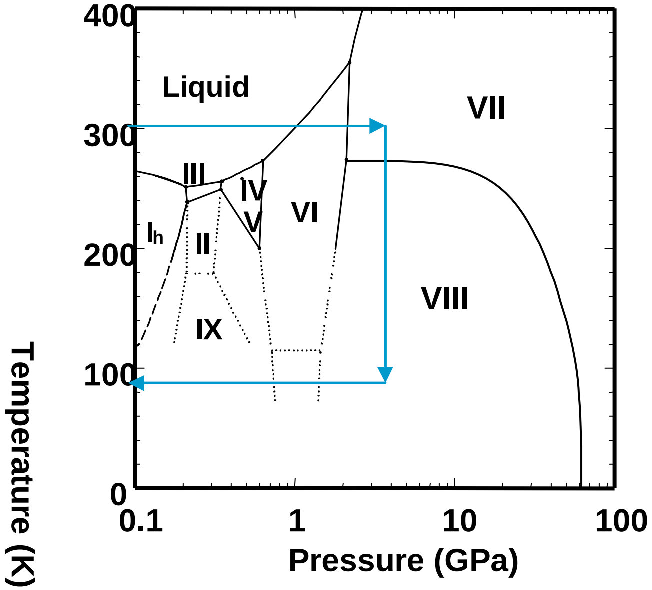


Decrease load
and recover



Ice VIII

40 mm^3/loading
1 loading/day
25 loadings:
1 cm^3/month



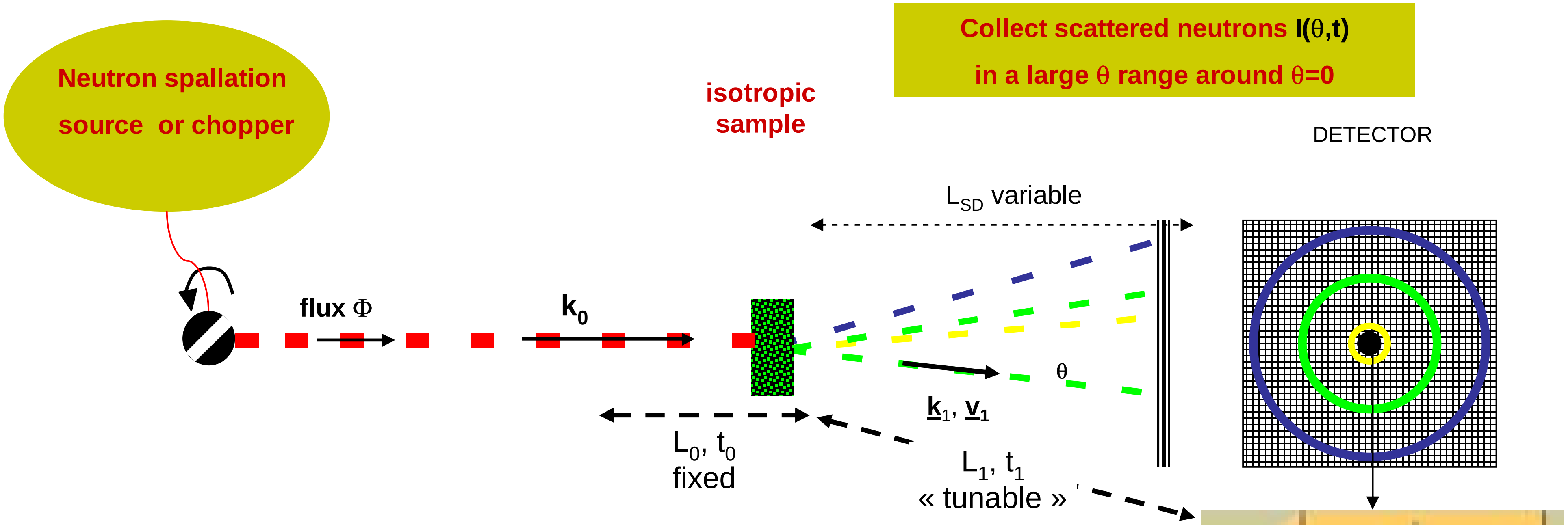
S.Klotz, L.E.B. et al. Nature Materials 8, 405 (2009)

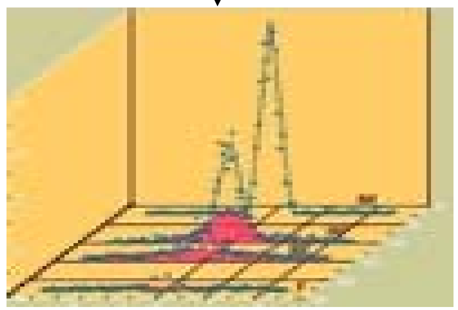
Ice VIII→Ice Ih conversion

movie

Incoherent Quasi-Elastic Neutron Scattering [IRIS-ISIS]:

Probes motions of single proton: ΔE=15 μeV→ dynamics faster than 100 ps





FWHM QENS signal→ t scale

FWHM Q-dependence→ which kind of motion

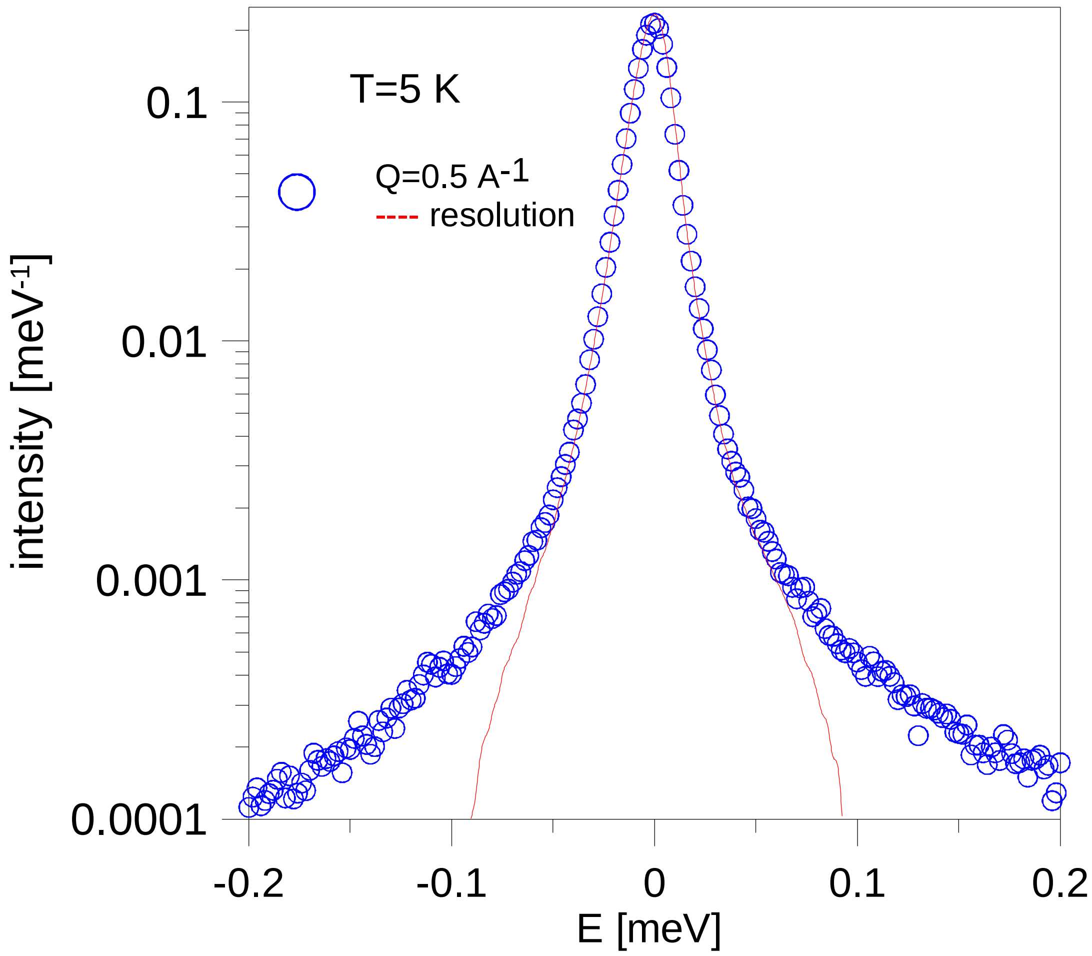
EISF high Q limit→ number of protons involved

QISF Q-bevavior→ distances involved

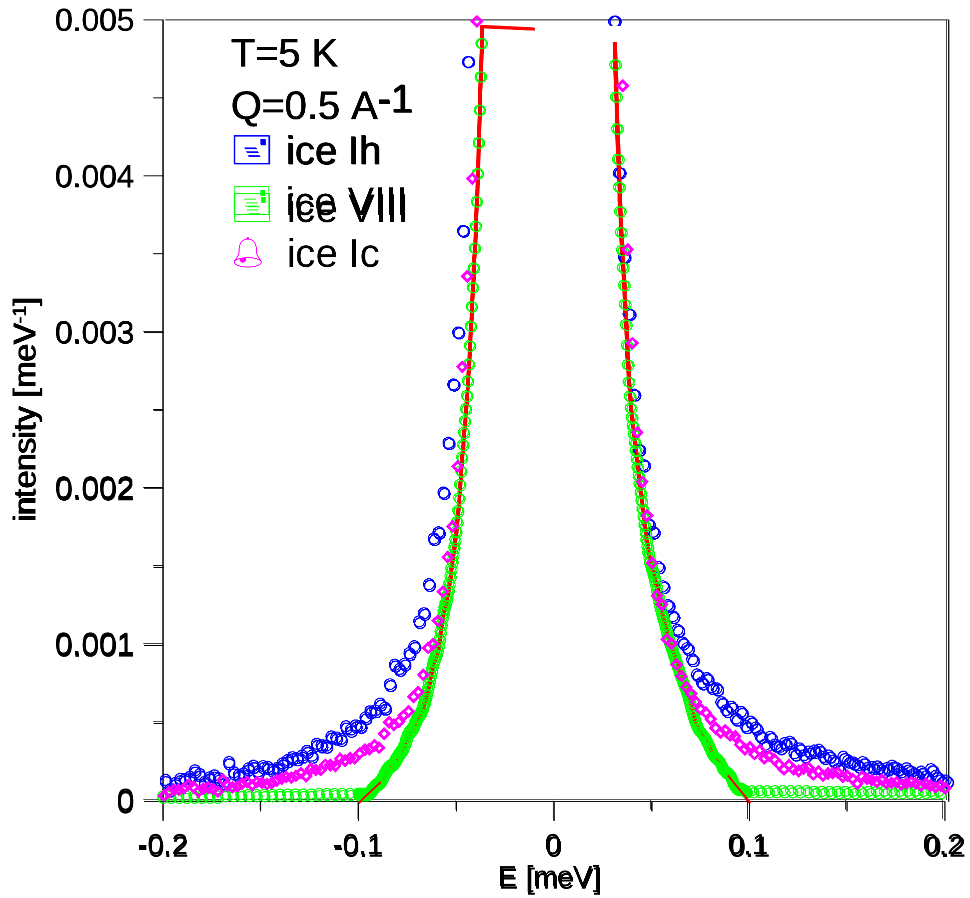
QISF T-behaviour→E barrier

$$I(\theta,E)=\Phi N \varepsilon(k_1)\frac{k_1}{k_0}\tilde{S}(Q,E)$$

Quasi-elastic contribution in H-disordered ice down to 5K!



Quasi-elastic contribution in H-disordered ice down to 5K!



✓Proton dynamics in ice Ih active at 5K

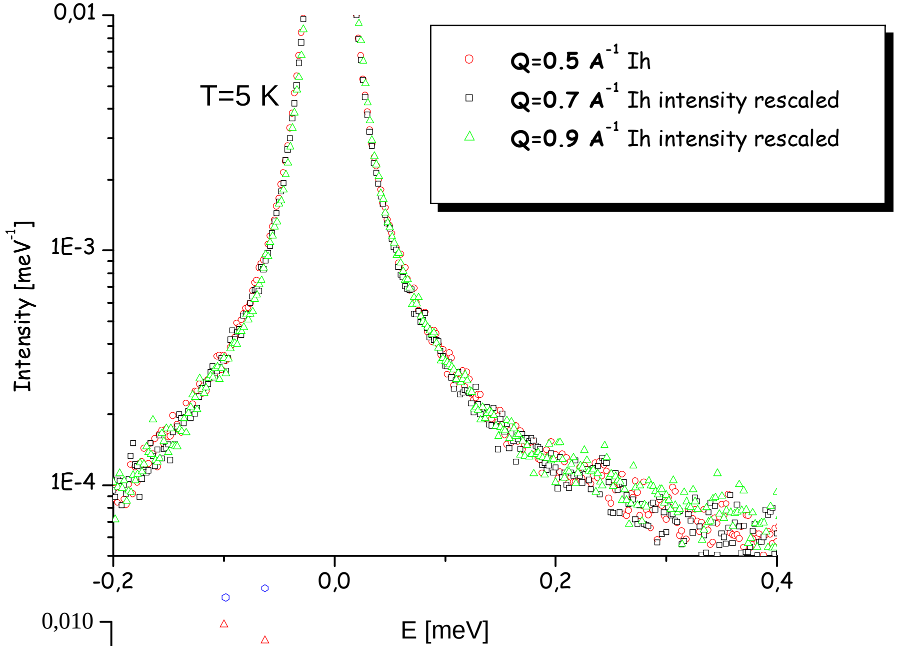
✓The dynamics is absent in the H-ordered phase Ice VIII

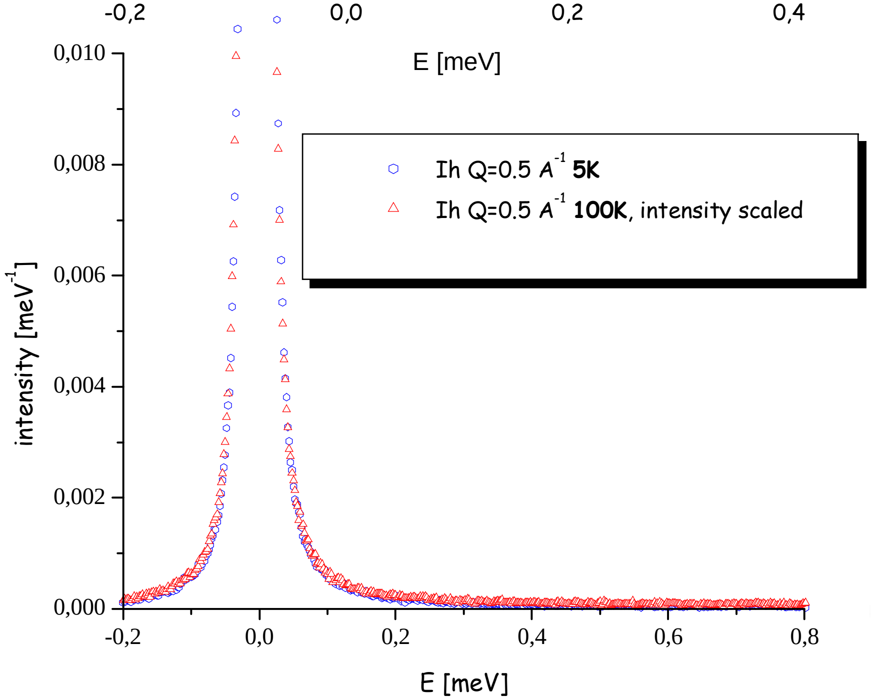
✓The dynamics is present in the other H-disordered phase Ice Ic

Dynamics connected to H-disordered structure!

L.E.B. et al, PRL 103, 165901 (2009)

Temperature and wavevector characterization

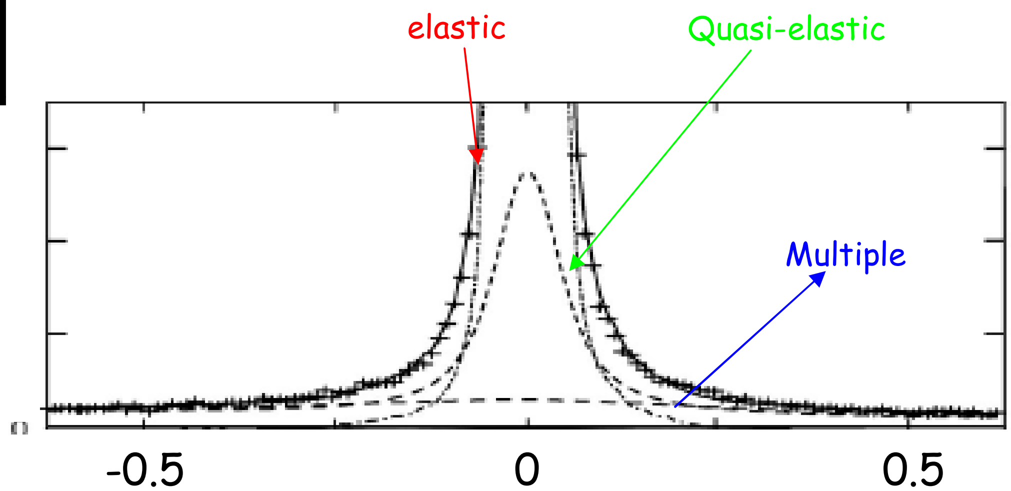




✓T independent FWHM→ non Arrhenius

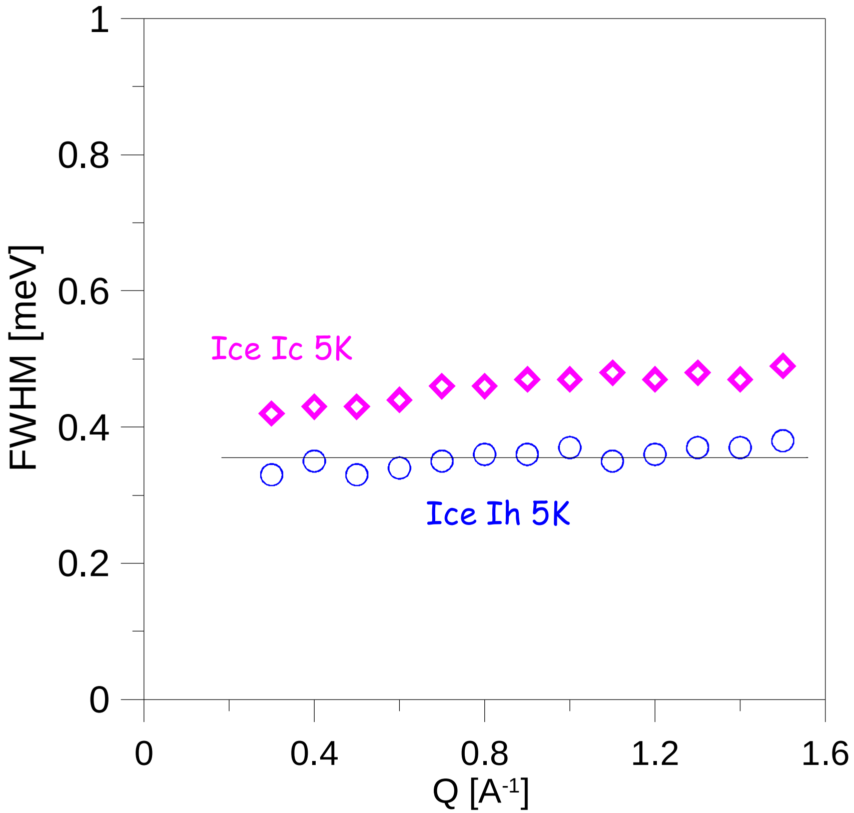
✓Q-independent FWHM : localized mode

$$S(Q,\omega)=e^{-2/3\langle\Delta x^2(T)\rangle Q^2}\,[S_0\delta(\omega)+S_1\tau_c/\pi(1+\omega^2\tau_c^2)]$$



Time scales:

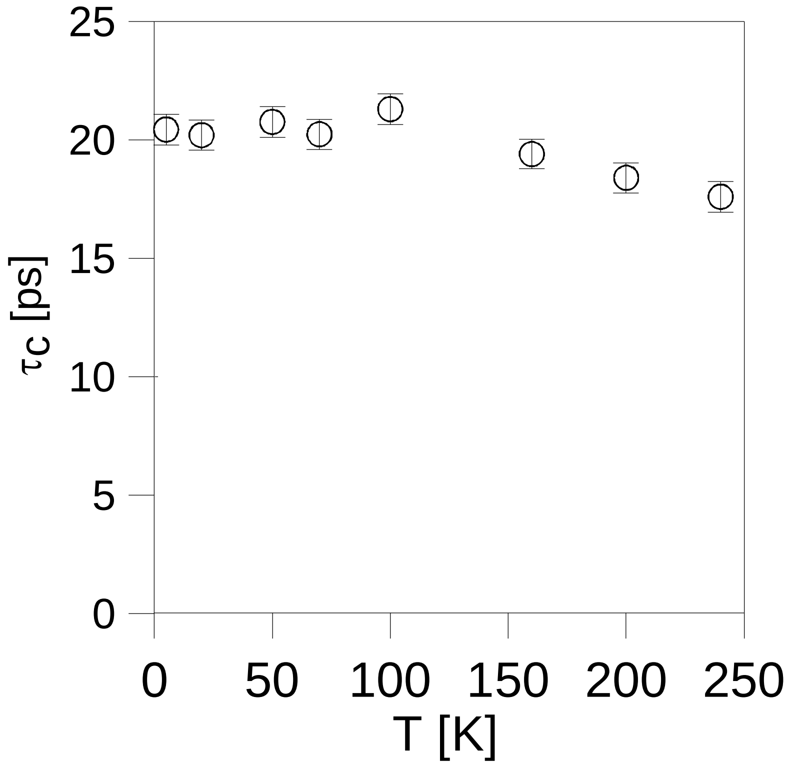
✓Q independent FWHM



τ_c ~3.6+-0.3 ps in ice Ih
τ_c ~2.9+-0.3 ps i ice Ic

The inverse correlation time in the low T limit determines the hopping rate k_0

✓FWHM (T)→ non Arrhenius



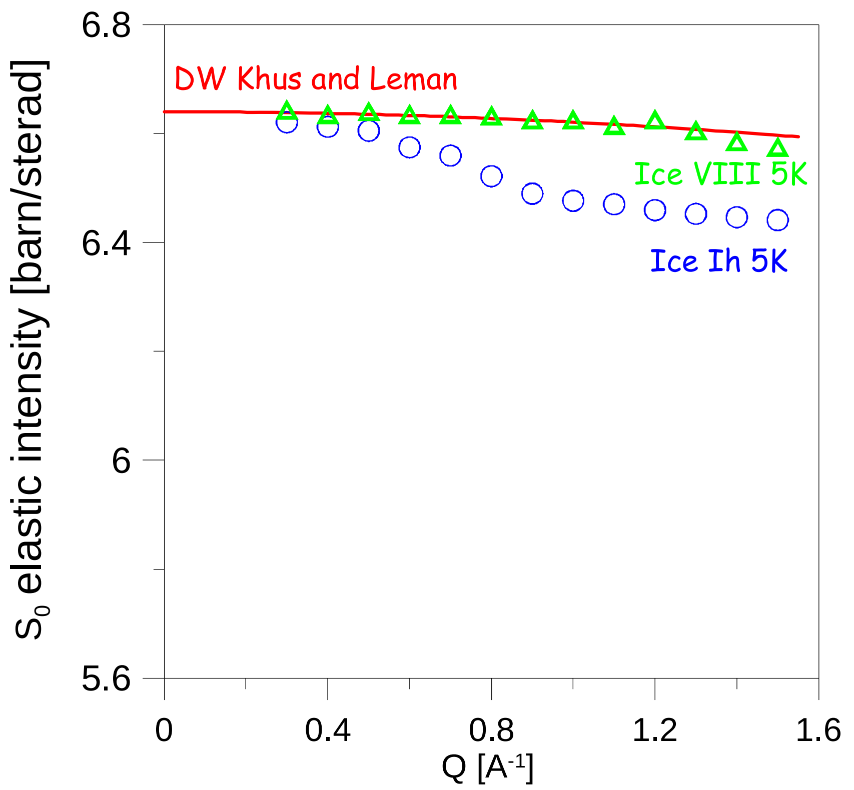
k_0~2.7x10^{11} s^{-1} T independent in 5-100 K range

Excludes classical hopping or cage motion of the proton and stepwise tunneling

L.E.B. et al, PRL 103, 165901 (2009)

Length scales and number of protons involved:

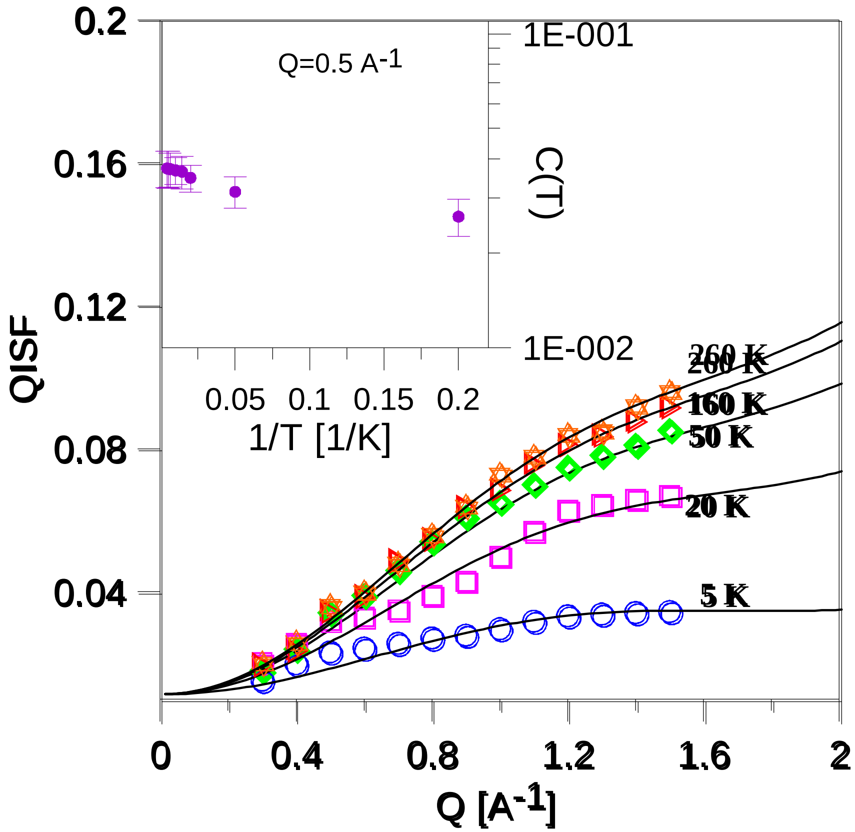
✓EISF anomalous decay



EISF: energy integrated elastic contribution

~3% H involved in ice Ih
~2% H involved in ice Ic

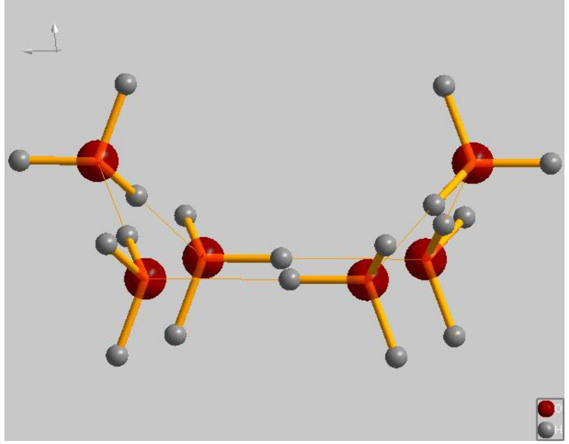
✓QISF wavevector evolution

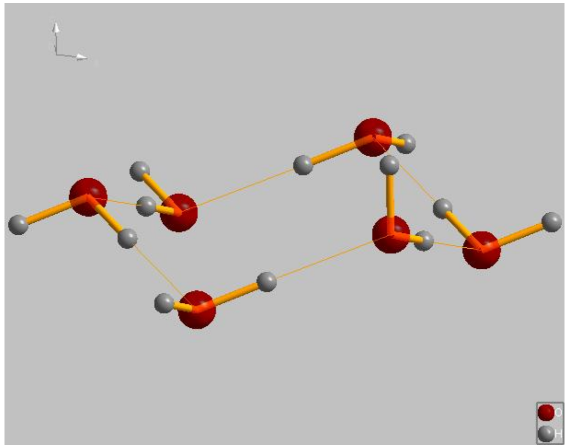


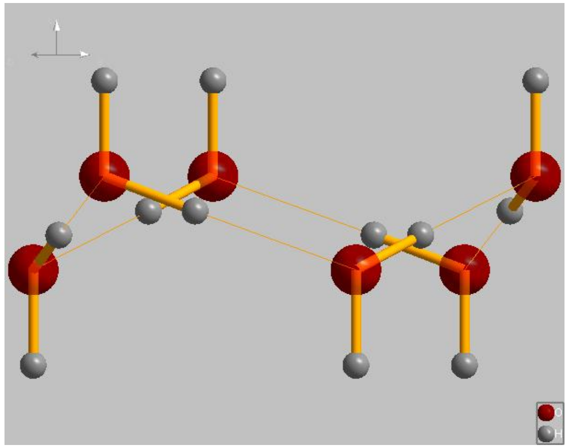
Double well model: 2C(T)[1-sin(Qd)/Qd]

Low $E_{barrier}$~meV
Distance d= 0.75+-0.05 Å

L.E.B. et al, PRL 103, 165901 (2009)





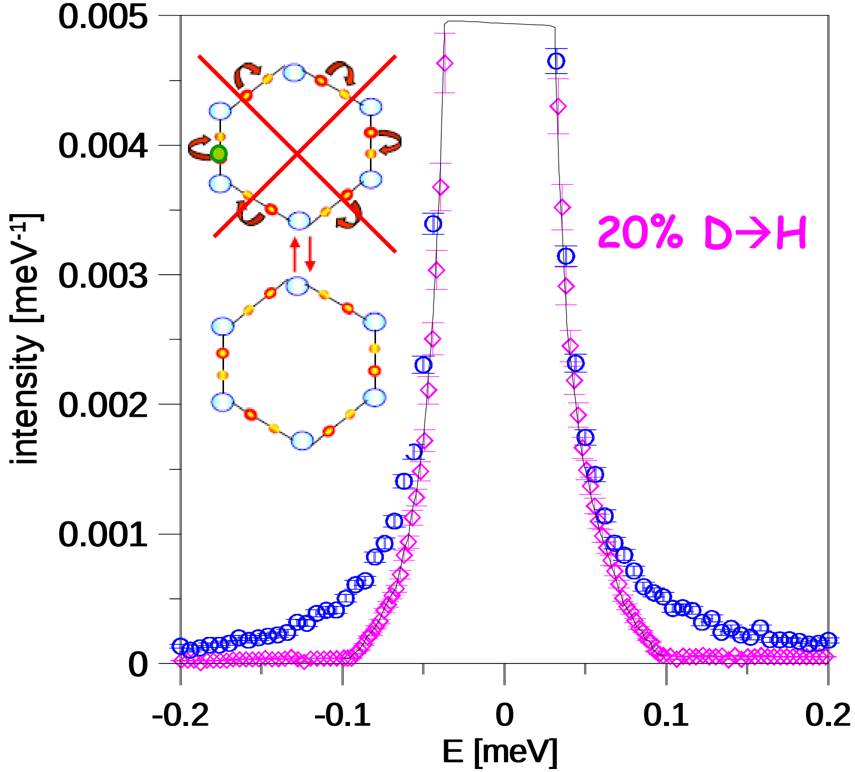


The results obtained so far are inconsistent with any known sequential or stepwise motion of the protons, a mechanism that would have an E-barrier at least one order of magnitude higher:

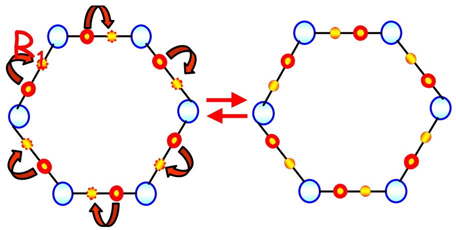
Ordered loops→ 1/32 of total loops~ number of H involved

6 protons can move with no change of the total E_{cryst}→lower E barrier

What happens if we break the symmetry? → DEUTERATION!



Conclusions II and future work:



Elastic experiment:

✓Non-harmonic motion of H in ice Ih

✓Main distance involved of 0.75 Å

✓Number of protons involved: ~ %

QENS experiment:

✓time scale → ~3 ps; localized motion~0.75 Å
✓Non-Arrhenius time rate→ no classical hopping, neither cage motion
✓It occurs in the proton disordered phases only →linked to proton disorder
✓High time rate (2.7 10^{11} s^{-1}), low E-barrier ~meV→quantum concerted proton tunnelling
✓Disappears with partial deuteration →most likely associated with ordered loops

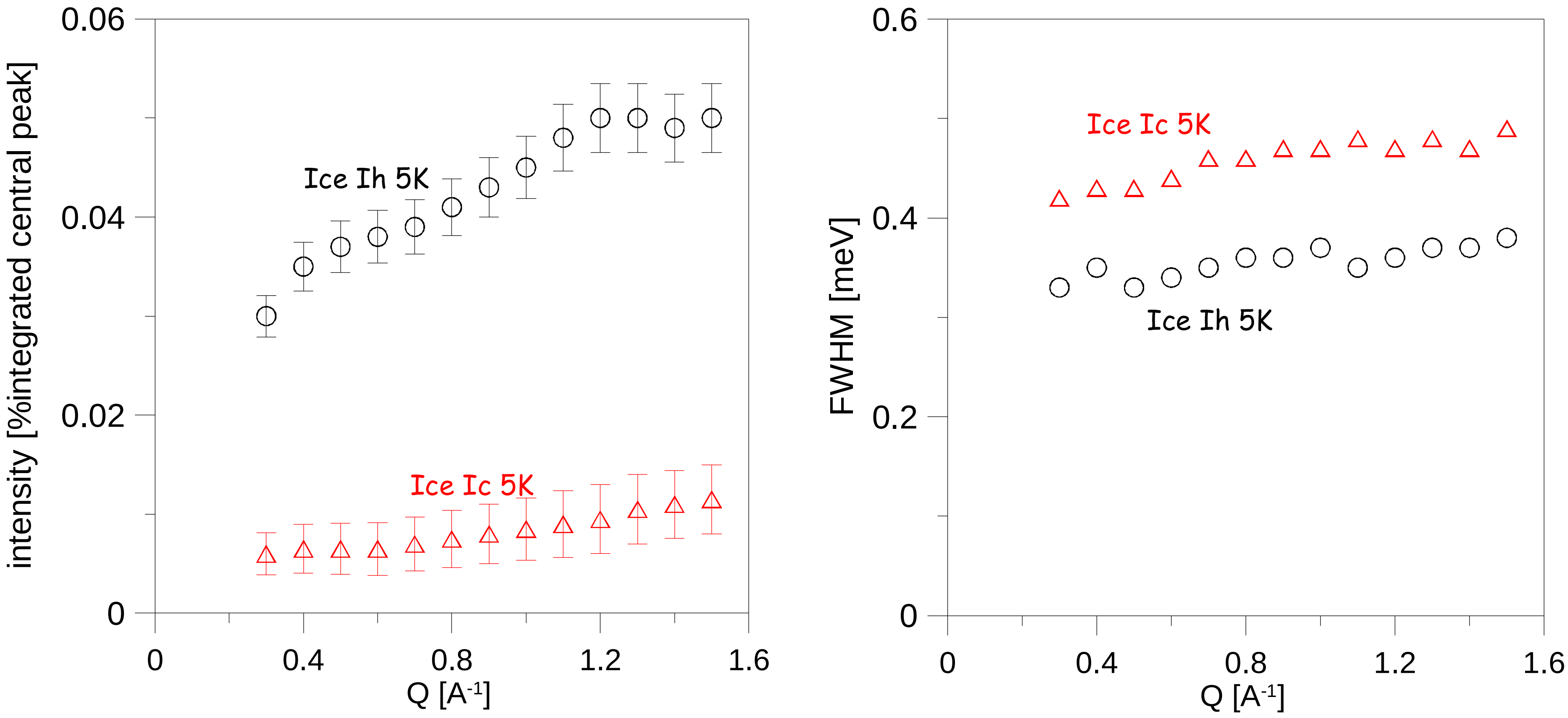
.. Work in progress

✓Detailed characterization at low temperatures (1-20 K) → $E_{barrier}$
✓Higher resolution measurements →check if the process is really stochastic
✓Measurements on a single crystal →better definition of the geometry

..we need full path integral calculations!!!

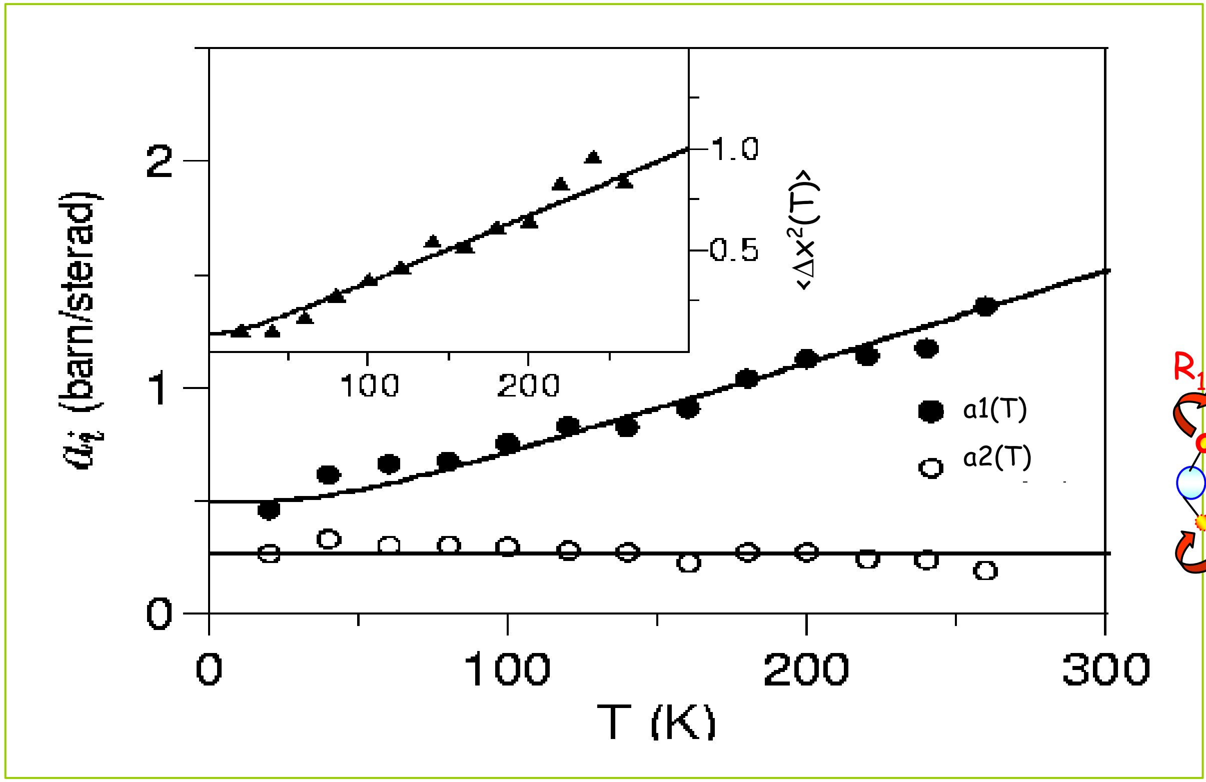
Thank you!

What about ice Ic?

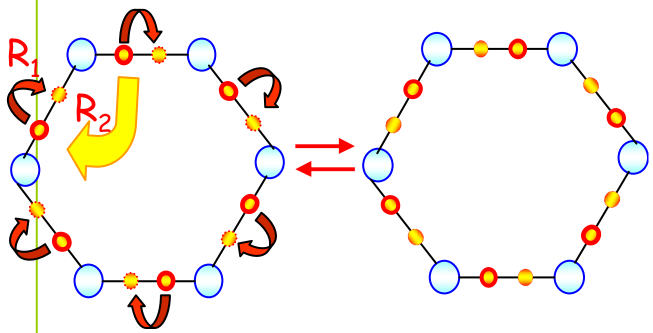


Two oscillators model:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{inc}}{4\pi}\left[a_0 \exp\left[- < \Delta x^2(T) > Q^2\right] + a_1 \cos(Q \cdot R_1) + a_2 \cos(Q \cdot R_2)\right]$$



a_i proportional to $p_a p_b$ (equilibrium population of the two tautomeres)

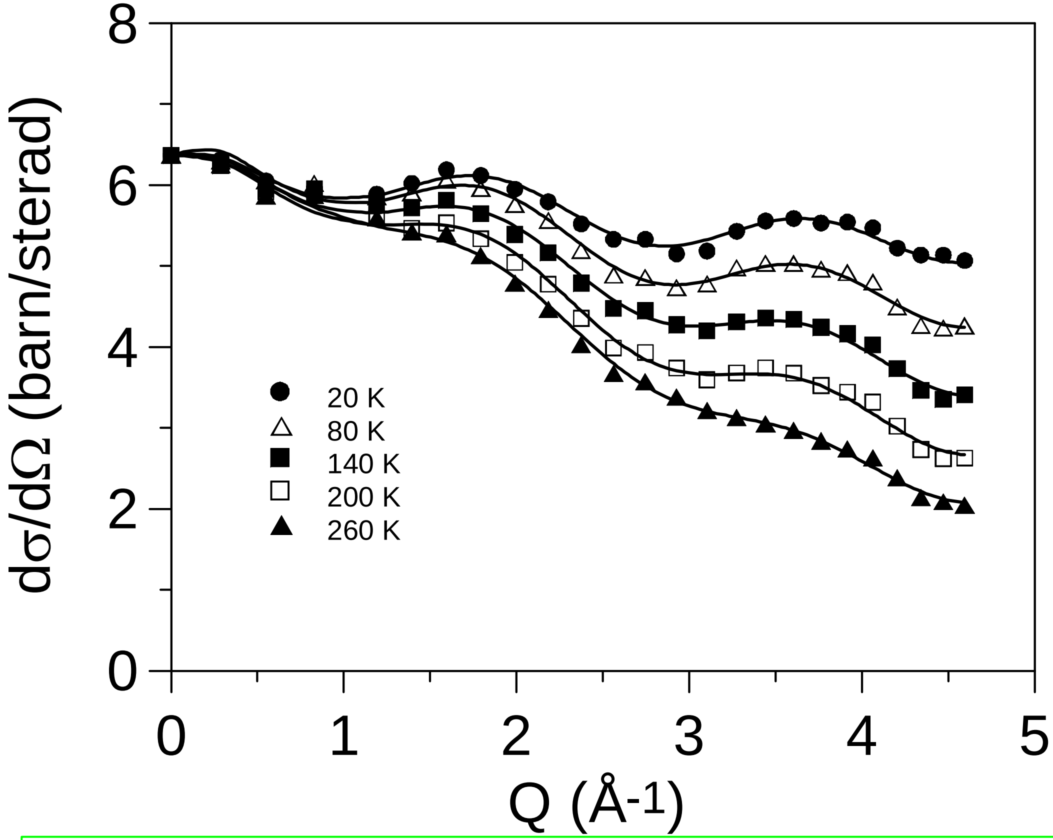


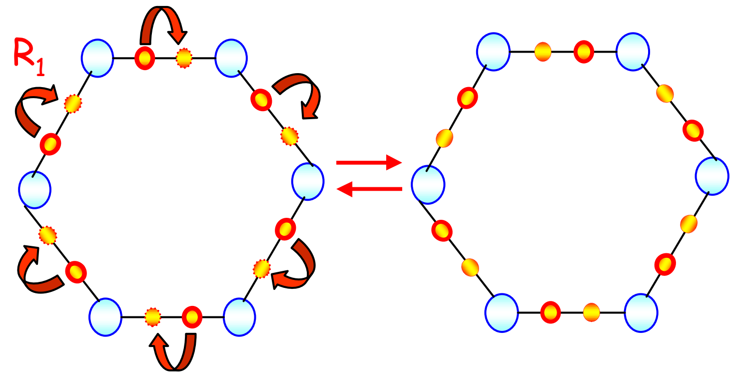
✓a1 increases with T, fitted by a Bose factor at fixed energy of 10.3+-0.5 meV:
phonon assisted process

✓a2 ~ T independent: intrinsic feature of the ground-state H wavefunction

✓$\langle \Delta x^2(T) \rangle$ in agreement with diffraction data (Kuhs and Lehmann, J. Phys. C 48 (1987))
Fitted with 2 isolated oscillators at 10.6 and 4.3 meV

Fitting with a coordinated proton jump model



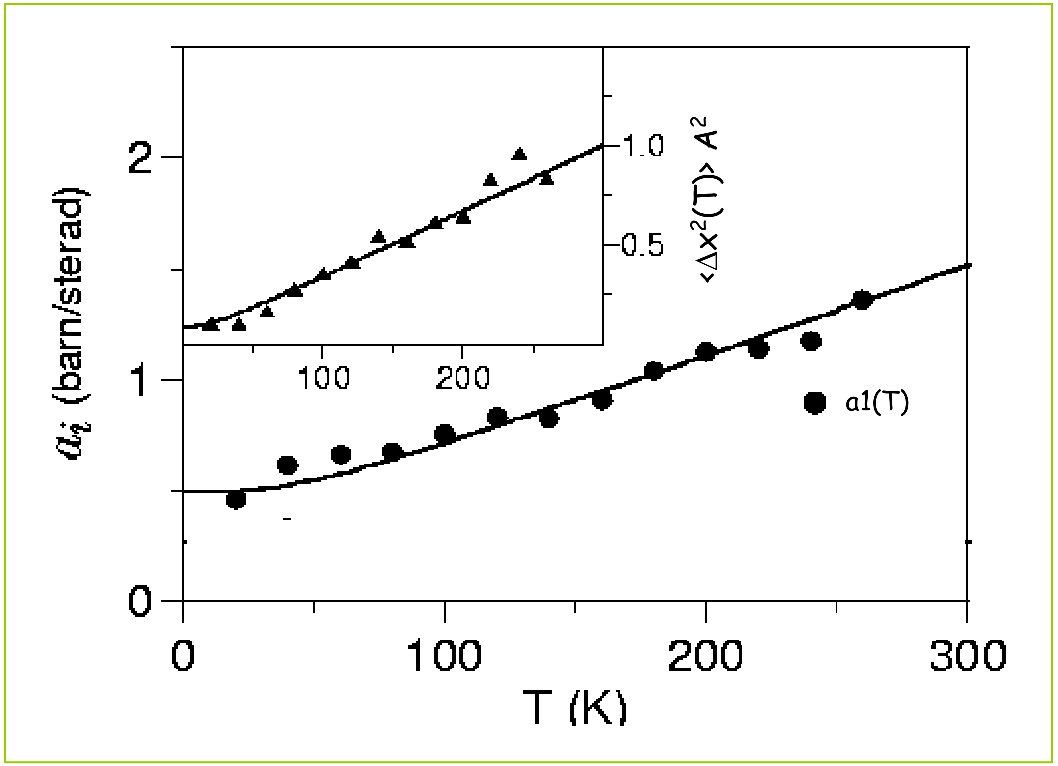


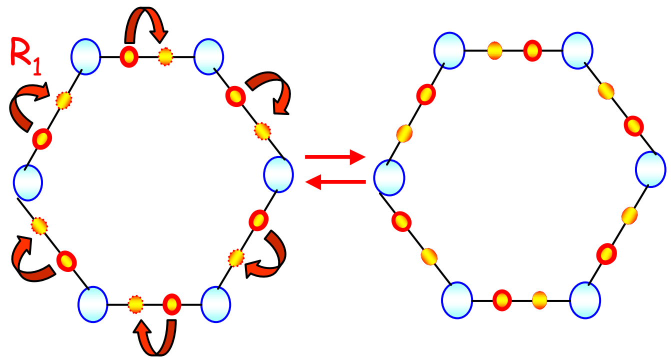
$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{inc}}{4\pi} e^{-<\Delta x^2>Q^2} [1 - 2 p_1 p_2 (1 - sin(Qd)/(Qd))]$$

The best fit is obtained with a distance of d=0.75+-0.05 Å (H sites along one O-O bond R1=0.78 Å)

Two oscillators model:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{inc}}{4\pi} e^{-<\Delta x^2>Q^2}[1-2p_1p_2(1-\sin(Qd)/(Qd))]$$

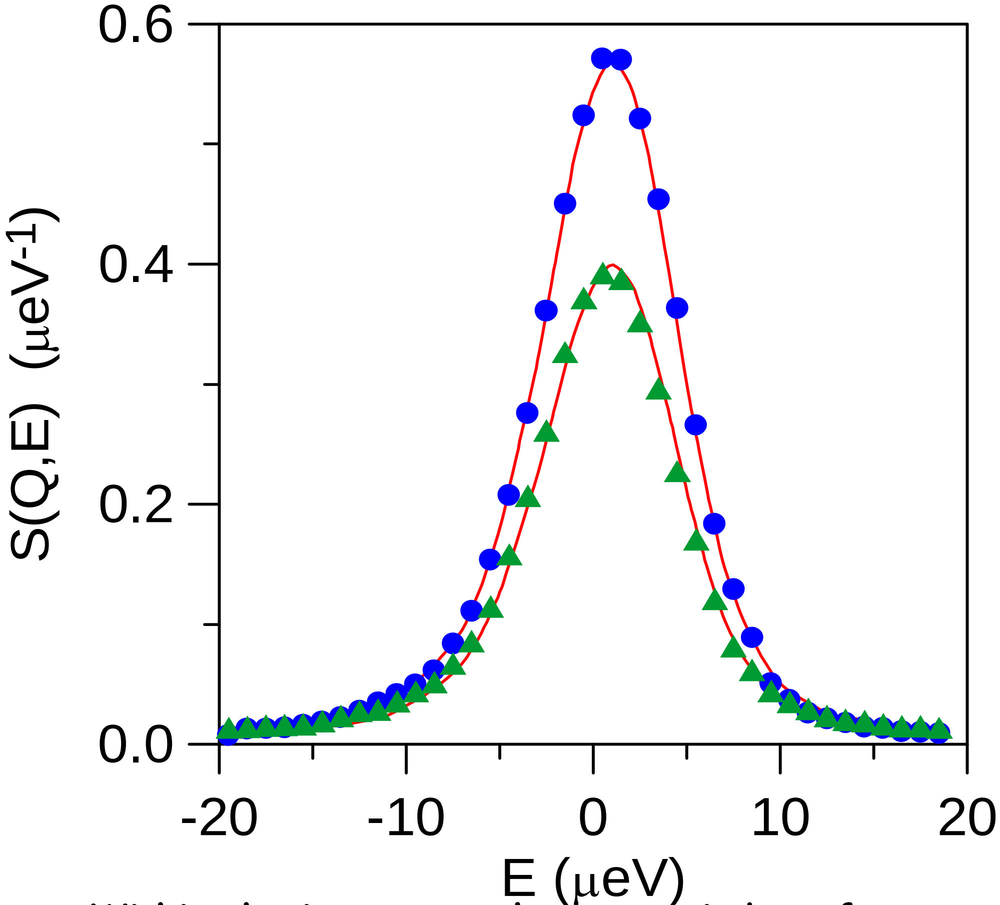




p_1, p_2 → equilibrium population of the two tautomeres

•a1=$2p_1p_2$ increases with T, fitted by a Bose factor at fixed energy of 10.3 meV: phonon assisted process

•<$\Delta x^2(T)$> was fitted by a *two isolated oscillators* model: best fit energies→ 4.3 meV and 10.6 meV in agreement with diffraction data (Khuss and Lemann,.....)



Within the instrumental energy window of IN13 (ILL) the scattered intensity is produced by an elastic process (resolution 9 μeV)