



ESRF

Experiment title: .

Study on the origin of the transition from normal to fast sound in liquid water

Experiment number:

HS-208

Beamline:

ID16

Date of Experiment:

from: 12/5/97

to: 21/5/96

Date of Report:

27/8/97

Shifts:

21

Local contact(s):

C. Masciovecchio

Received at ESRF:

28 AOUT 1997

Names and affiliations of applicants (*indicates experimentalists):

F. Sette, ESRF

G. Ruocco, Universita' di L'Aquila

A. Cunsolo, ESRF

M. Krisch, ESRF

C. Masciovecchio

Report:

The present experiment addresses the high frequency dynamics in water. Using IXS, we showed previously: 1) the existence of propagating collective modes in liquid water in the whole $1 - 14 \text{ nm}^{-1}$ Q-transfer region [1]. The absence of a relevant isotope shifts between H_2O and D_2O demonstrated that these sound modes involve the whole molecule [1,2]. We also confirmed the results previously obtained with molecular dynamics simulations [3-5] and with neutrons [2] that the velocity of sound is $\approx 3,200 \text{ m/s}$ in the whole $4-14 \text{ nm}^{-1}$ Q-region (fast-sound), a value larger by more than a factor of two the hydrodynamic velocity of sound of $\approx 1,500 \text{ m/s}$ [1]. 2) We found that in the high frequency limit the collective dynamics in liquid water is very similar to that of ice in its I_h crystal form [6]. 3) We observed a gradual change of the velocity of sound from $2,000 \text{ m/s}$ at $Q=1 \text{ nm}^{-1}$ to its high frequency value of $3,200 \text{ m/s}$ at $Q=4 \text{ nm}^{-1}$ [1]. This transition from a value approaching the hydrodynamic limit to the fast sound is observed at the crossing between the fast-sound dispersion and a second weakly dispersing mode at $\approx 4 \text{ meV}$. These second mode has been identified with a localized transverse-like dynamics reminiscent of the transverse optical phonon branch in ice, as recently confirmed by a molecular dynamics simulation [8].

On the basis of these experimental results, one could have envisioned two possible scenarios. In the first one, a lengthscale λ , probably associated to the strong tetrahedral local order induced by the hydrogen bond, separates two different dynamical regimes. If the wavelength of the acoustic-like excitations is large compared to λ , the associated density fluctuation reflects average properties and therefore the hydrodynamic picture holds. In the opposite case, when the wavelength is small compared to λ , the density fluctuations strongly reflects the local order among molecules, and the dynamics become like the one of solid ice. This picture may explain the observed disappearance of the transverse-like mode at small Q, and relate the Q region of the transition to the inverse of the average size of water aggregates. Such picture reflects local structural properties, and therefore it should depend little on temperature.

In the second scenario, the transition is due to the coupling of the propagating dynamics to the typical relaxation processes in the system. Similarly to what is referred to as the α relaxation in glasses, when the excitation energy $\Omega(Q)$ becomes comparable to the inverse of the time τ_R required to the system to relax to its ground state, the modes are strongly affected: they change their velocity reaching an higher value whenever the frequency is larger than $1/\tau_R$. The time scale τ_R reflects the dissipation mechanisms of the system and can vary by large amounts for relatively small temperature variations. We took IXS data in liquid water with 1.5 meV energy resolution at $Q=1.2, 2$ and 4 nm^{-1} at pressures of ≈ 0 and 2 kbar in the 250-370 K range. A special high-pressure cell has been developed in our group, and used in this experiment to keep the liquid state stable down to -20 C. In spite of the limited number of investigated thermodynamic points, we observe a strong temperature and Q dependence of the sound velocity, while the pressure effect is small. Specifically, at $Q = 1.2$ and 4 nm^{-1} , the velocity of sound is basically temperature independent, with values of ≈ 2000 and 3500 m/s respectively. On the contrary, at $Q=2 \text{ nm}^{-1}$, the sound velocity changes between these two values. This behaviour, emphasized by the dotted lines, is qualitatively consistent with the results of a molecular dynamic simulation [9], also reported in the figure. These results seem to indicate that the underlying mechanism responsible for the fast sound is a relaxation process with a characteristic time $\tau_R \approx 0.6 \text{ ps}$ at room temperature. The present data, due to the limited temperature region, do not allow to determine the temperature dependence of τ_R , and therefore to asses whether the water behaviour could be assimilated to that of other glass forming systems. We hope to be able to obtain further data points at higher temperatures, and to show whether the transition from fast to slow sound takes place also at higher Q values.

- [1] F. Sette, G. Ruocco, M. Krisch, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli and R. Verbeni, Phys. Rev. Lett. 75, 850 (1995).
 [2] J. Teixeira, M. C. Bellissant-Funel, S. H. Chen and B. Dorner, Phys. Rev. Lett. 54, 2681 (1985).
 [3] A. Rahman and F. H. Stlinger, Phys. Rev. A10, 368 (1974).
 [4] U. Balucani, G. Ruocco, A. Torcini and R. Vallauri, Phys. Rev. E47, 1677 (1993).
 [5] F. Sciortino and S. Sastry, J. Chem. Phys. 100, 3881 (1994).
 [6] G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Signorelli and R. Verbeni, Nature 379, 521 (1996).
 [7] F. Sette, F. Sette, M. Krisch, C. Masciovecchio, R. Verbeni and U. Bergmann Phys. Rev. Lett. 77, 83 (1996).
 (8) M. Sampoli, G. Ruocco and F. Sette, Phys. Rev. Lett. 78, 0000 (1997).
 [9] F. Sciortino, private communication.

