



Experiment title: ,
Role of the hydrogen bonding in the high frequency dynamics of NH_3 , H_2O and HF

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HS-361

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19

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Report:

We have a long term research project on the study of the high frequency dynamics in liquid water and other hydrogen bonded molecular liquids [1]. The present report gives a **first** overview on the new results obtained during the last Run in Dec. 97 on the inelastic x-ray scattering beamline. The main aim of this experiment was the determination of the temperature (T) and momentum transfer (Q) dependences of the transition from low to **fast** sound in liquid water. These measurements, continuing a previous attempt in a limited pressure (P) and T regions, show that this transition in liquid water corresponds to a structural relaxation **process** substantially similar to that typically found in glass-forming systems. Specifically, the transition between the two dynamical behavior presents a phenomenology like the one observed for the structural α -relaxation. The relevance of the result reported here **is** that the time-scale of **this** relaxation process is in the picosecond range, while, for typical glassformers, the relaxation time **is** at the nanosecond level in the melting temperature region. Moreover, contrary to glass-formers, liquid water does not have a transition to a glassy phase. Consequently, our findings generalize the physics of the α -relaxation showing that it is a specific feature of the liquid-phase in liquids with a high degree of local orientational order, and its observation is not **sufficient** to grant the formation of a glass.

In Fig. 1 we present a set of inelastic **x-ray** scattering **spectra** taken at $Q=4 \text{ nm}^{-1}$ at **different** temperature & These data were measured at constant density, $\rho=1 \text{ g/cm}^3$, using a high pressure/temperature **cell** that we developed explicitly for this experimental program. This cell stands up to 5 kbar and 400 C. Similar data were taken also at other Q values (2 and 7 nm^{-1}) in the $20 \div 300$ C T -region with a 20 C temperature grid. The data were fitted using standard procedures using a damped harmonic oscillator to represent the inelastic signal. The central frequency, $\omega_c(Q)$, obtained from the fit, is **reported** for three **different** temperatures in Fig. 2 **as** a function of Q . We observe that the transition from one **sound** velocity to the other **is** found at an increased Q value for **increasing** temperature.

Therefore, as in the α relaxation, in glass forming systems, the velocity of sound at a given Q value changes between its infinity (c_∞) and zero frequency (c_0) values at a well defined temperature: this temperature is associated to a specific value of the relaxation time $\tau(Q, T)$ by a relation approximately given by $cQ\tau=1$, with $c \approx (c_\infty + c_0)/2$. The velocities of sounds scaled to c_0 , i. e. $\omega_c(Q)/c_0Q$, are shown in Fig. 3 as a function of temperature at three different values of Q . Here, we clearly see again that the largest sound velocity dispersion is found at increasing Q values with increasing temperature. Using the relation between τ and c , we estimate a value of τ ranging from 2 ps at -30 C to 0.6 ps at 150 C. An improved data analysis is at present being developed to increase the statistical accuracy of these determinations.

The direct experimental determination of a structural relaxation time, with its temperature dependence (i) at such high frequencies, in (ii) a liquid **as** important as water, and (iii) in such an extended P , T , and Q ranges **has** two very important implications. The first point is that the structural relaxation time is very likely to correspond to the lifetime of tetrahedrally coordinated units of H_2O molecules, induced by the presence of the hydrogen bond. The dynamics is therefore very different whether the considered momentum and frequency are either higher or lower than the size and lifetime of these units. In the long wavelength case, water behaves as a continuum and its density fluctuations reflects average properties well described within the hydrodynamic picture. In the other case, when the wavelength is small compared to size of these units, the density fluctuations strongly reflects the local order among molecules, and the dynamics become like the one of solid ice. The second one is connected to the Maxwell equation relating $\tau(T)$ to the macroscopic viscosity $\eta(T)$. Consequently, this study, which relates $\tau(T)$ to the lifetime of tetrahedrally coordinated units of water molecules, implies that **the macroscopic viscosity is intimately associated with the structural relaxation of the microscopic environment.**

These results start to give a satisfactory picture on the dynamics of hydrogen bonded liquids, and on the effect of highly directional bonding on liquid properties. It will be very important, however, to continue these studies in water up and above the critical point (360 C), where kinetic effect are expected to overcome the hydrogen bond even at these high frequencies, and in other hydrogen bonded liquids (methane, methanol, ammonia and fluoridric acid), where the strength of the hydrogen bond can be effectively modified. These will be the directions where we would like to concentrate our future efforts.

[1] F. Sette, G. Ruocco, M. Krisch, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli and R. Verbeni, Phys. Rev. Lett. 75, 850 (1995). G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Signorelli and R. Verbeni, Nature 379, 521 (1996). F. Sette, F. Sette, M. Krisch, C. Masciovecchio, R. Verbeni and U. Bergmann Phys. Rev. Lett. 77, 83 (1996). M. Sampoli, G. Ruocco and F. Sette, Phys. Rev. Lett. 79, 1678 (1997).