

Collective Dynamics in Water by High Energy Resolution Inelastic X-Ray Scattering

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A propagating excitation with a velocity of sound of 3200 ± 100 m/s is measured in H₂O at 294 K between 4 and 14 nm⁻¹, using inelastic x-ray scattering with 5 meV energy resolution. The existence of *fast sound* is therefore demonstrated in an energy-momentum region much wider than that of previous neutron measurements on D₂O. The equivalence of the *fast sound* velocity in H₂O and in D₂O rules out models where this mode propagates only on the hydrogen network. These results show the ability of inelastic x-ray scattering to study the collective dynamics of liquids.

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In 1974 Rahman and Stillinger [1], interpreting their molecular dynamics (MD) simulations of the dynamical structure factor $S(q, \omega)$ of liquid water, proposed the existence of high frequency collective excitations which propagate with a velocity much higher than that of ordinary sound (fast sound). These excitations would coexist with the ordinary sound, and propagate up to momentum transfer comparable with the inverse of the single molecule size. This work stimulated various studies, justified by the practical importance of a liquid like water, and by the implications associated with the possible coexistence of different kinds of acousticlike excitations in molecular liquids, similar to those proposed for binary mixtures [2]. In the water case, these excitations would be those associated with the center-of-mass translational dynamics, and those related to the dynamics of hydrogen atoms.

The first experimental verification came in 1985 from Teixeira, Bellissent-Funel, Chen, and Dorner (TBCD) [3], who performed inelastic neutron scattering experiments in heavy water at q values between 3.5 and 6 nm⁻¹. Their results show strong evidence of collective excitations propagating with a speed of sound of 3300 m/s, a value comparable with the speed of sound of ice, and 2 times larger than the ordinary sound of water. TBCD argued on the basis of their data that this mode was highly overdamped, and it was hard to separate it from the tails of the intense central peak at q values larger than 6 nm⁻¹. They also interpreted this fast mode as excitations propagating on the hydrogen-bond network. Since then, many theoretical and MD simulation studies have tried to clarify the origin of these excitations [4–11]. In those studies, the properties of the hydrogen bonding have been investigated by using more refined intermolecular interaction potentials. An increased infinite-frequency velocity has also been suggested from the analysis of Brillouin light scattering in supercooled water [12]. Despite those efforts, however, the matter is not yet settled, mainly because neutron data are available only in a limited q - ω region. Moreover, in a second re-

cent neutron experiment, Bermejo *et al.* interpreted their results opposite to TBCD, claiming that there is no fast sound in heavy water [13].

In this Letter we present the experimental determination of $S(q, \omega)$ of water using inelastic *x-ray* scattering. This method offers important advantages with respect to *neutrons* on this specific water problem; the most important are the possibility to investigate a much larger q - ω region, the absence of the incoherent contribution to the spectrum, and the possibility to study light water directly. We found acousticlike excitations in the q region between 4 and 14 nm⁻¹, which disperse with a slope of 3200 ± 100 m/s up to $q = 10$ nm⁻¹. Our experimental results confirm those of TBCD in D₂O in a much wider q - ω region, and give precise values for the H₂O fast sound and its damping at high frequencies. From the comparison of our results with those of TBCD, we deduce the absence of a hydrogen isotopic dependence of the fast sound velocity; this has direct implications on the theoretical models so far proposed. We also show that the damping is comparable to the average excitation frequency, and, for q values larger than 6 nm⁻¹, it is always much smaller than that expected from the q^2 dependence found by TBCD. Finally, our results demonstrate that inelastic scattering using x rays from the new third generation undulator synchrotron radiation sources is an important complementary technique to neutrons in the study of liquids and disordered systems.

The experiment was carried out at the new very high energy resolution inelastic x-ray scattering beam line (BL21-ID16) at the European Synchrotron Radiation Facility (ESRF). Given the uniqueness of the setup, the experimental aspects will be discussed in some detail. The source, a high- β undulator with a period of 42 mm, was used in fifth harmonic, where it produces x rays of ≈ 18 keV. This x-ray beam, with angular divergence 24 vertical \times 40 horizontal μ rad² full width at half maximum (FWHM), is premonochromatized to a bandwidth of 2×10^{-4} by a cryogenically cooled Si(111)

double crystal monochromator. The premonochromatized beam impinges on another silicon crystal, which operates at the (999) reflection (intrinsic energy resolution of 1.1×10^{-7}), and is positioned at a Bragg angle of 89.98° . This backscattering geometry allows us to match the source divergence and maximize the reflected intensity [14–17]. The beam from the Si(999) has an energy of 17794 eV, an energy resolution of 2 meV, an intensity of 10^9 photon/s, and is focused on the sample to a spot size of $150 \times 350 \mu\text{m}^2$ by a toroidal mirror. The scattered photons are collected by a spherical silicon crystal analyzer operating at the Si(999) and at a Bragg angle of 89.97° , in Rowland geometry. This analyzer has been constructed at the ESRF by gluing ≈ 7500 silicon crystal cubes of 1 mm size on a spherical glass blanket. The resulting focusing system is designed to collect a solid angle up to 600 mrad^2 , while maintaining the perfect crystal properties of the Si(999) reflection, essential to keep the high energy resolution. This *spherical perfect crystal*, with a curvature of 2500 mm, yields an energy resolution of $4.0 \pm 0.5 \text{ meV}$. This is a factor of 2 worse than the Si(999) theoretical value, due to residual distortions from the construction method and to the scattering geometry.

The total energy resolution function was measured by filling the water cell with krypton gas, and it is approximated by a Lorentzian of $2\Gamma_R = 5.0 \text{ meV}$ FWHM (2.8×10^{-7} resolving power). Contrary to neutrons, in inelastic x-ray scattering with meV resolution, the momentum transfer is dictated only by the scattering angle θ_s [$q = 2k \sin(\theta_s/2)$, where k is the wave vector of the incident photon, and is practically identical to that of the scattered photon]. The scattering angle for momentum transfers between 4 and 14 nm^{-1} was selected by rotating the analyzer arm in the vertical scattering plane. The q resolution was set to 0.7 nm^{-1} by an aperture in front of the analyzer. Energy scans were done by varying the relative temperature between the monochromator and analyzer crystals with millikelvin precision. The temperature scans were done keeping the analyzer at 292 K, and scanning the monochromator temperature from 293 to 290.5 K with a step of -0.015 K , corresponding to an energy step of 0.7 meV. Each scan took about 2.5 h, and each q point was obtained by averaging eight spectra. The data were normalized to the intensity of the incident beam. The water sample was high purity H_2O , kept at 294 K, and confined in a stainless-steel cell 15 mm long. The cell windows were two silicon single crystals of $20 \mu\text{m}$ thickness, chosen to limit undesired sources of scattering signal. A long flush of water in the cell ensured the sample cleanness. Empty cell measurements gave the flat electronic background of the Peltier cooled Si diode detector (Eurisy-Mesures EPX-R) of 3 counts/min at any of the q transfer investigated here. In this geometry, where the cell length is comparable to the x-ray photoabsorption length, multiple scattering is negligible.

Inelastic x-ray scattering spectra at selected q values, and the corresponding fits discussed in the following, are shown in Fig. 1. The data are normalized to the peak intensity. The inset shows the count rate at the central peak maximum. The curve aligned with the central peak is the resolution function used in the fitting procedure, and it is reported to indicate the presence of scattered intensity at the two sides of the central line. This inelastic intensity is due to collective excitations in water. In order to determine the energy positions and the damping of these excitations at each q , the spectra have been modeled by the function $F(q, \omega)$, consisting of a Lorentzian for the central peak, and a damped oscillator [18] for the two side peaks:

$$F(q, \omega) = I_0(q) \frac{\Gamma_0(q)^2}{\Gamma_0(q)^2 + \omega^2} + [n(\omega) + 1] I(q) \frac{\omega \Gamma(q)^2 \Omega(q)}{[\Omega(q)^2 - \omega^2]^2 + \Gamma(q)^2 \omega^2}. \quad (1)$$

Here $\Gamma_0(q)$ and $I_0(q)$ are the width and intensity of the central peak, $\Gamma(q)$ and $I(q)$ are the damping and intensity of the side peaks with central frequency $\Omega(q)$, and $n(\omega)$ is the Bose factor. $F(q, \omega)$, adopted as a model for the $S(q, \omega)$ of water, is used here to determine the spectroscopic parameters independently from a specific theory, and to allow for a direct comparison of our results with those from the neutron data [3,13], obtained using

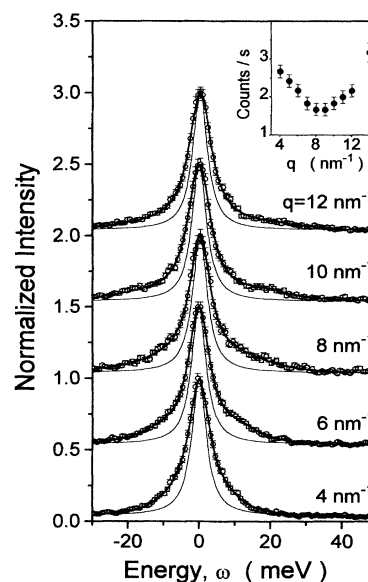


FIG. 1. Inelastic x-ray scattering spectra of H_2O at 294 K, taken at the indicated q values. The experimental data are normalized to the intensity of the central peak maximum, reported in the inset in counts/s. The data (\circ), shown with the error bars, are superimposed to the fit (solid line) as explained in the text. The line under the central peaks is the resolution function, shown to emphasize the q -dependent intensity on the sides of the central peak.

the same model. The convolution of $F(q, \omega)$ with the Lorentzian representing the resolution function has been fitted to the experimental data, after subtraction of the detector dark counts. The fit has been performed by standard χ^2 minimization, using the MINUIT routine [19]. The χ^2 values were always within 1 standard deviation from the expected value. As an example, the individual contributions to two typical fits ($q = 6, 10 \text{ nm}^{-1}$) are shown separately in Fig. 2. We find that the central peak has a width $2\Gamma_0 = 2.0 \pm 0.5 \text{ meV}$ at the investigated q values.

The derived values of $\Omega(q)$ are shown in Fig. 3. The $\Omega(q)$ values follow a linear behavior characterized by a speed of sound of $3200 \pm 100 \text{ m/s}$ up to $q = 10 \text{ nm}^{-1}$. For higher q values there is indication of a speed reduction. This value of the velocity of sound is identical, within the error bars, to that of $3300 \pm 250 \text{ m/s}$ found by TBCD in heavy water.

The values of $\Gamma(q)$ are shown in Fig. 4. The damping is constant up to $q = 10 \text{ nm}^{-1}$, and then it starts to increase. In the q region between 4 and 6 nm^{-1} , there is agreement, within the error bars, with the values found by TBCD, although they found a q^2 dependence. At large q , however, the damping values measured here are up to an order of magnitude lower than those extrapolated from such a q^2 dependence. This behavior of Γ at large q reflects the relaxation of the longitudinal viscosity [2].

The results shown in Fig. 3 and their comparison with those of TBCD allow for two firm conclusions: (i) The fast sound exists in water in the q region between 4 and 14 nm^{-1} . (ii) The identical value of the fast sound velocity in H_2O and D_2O rules out that these modes propagate in an atomic network constituted primarily by the hydrogen atoms, and indicates that the whole molecule is involved in this kind of motion. The isotopic shift expected for the whole molecule is, in fact, $\approx 5\%$, well within the error bars, while for the individual hydrogen atoms would be $\approx 40\%$.

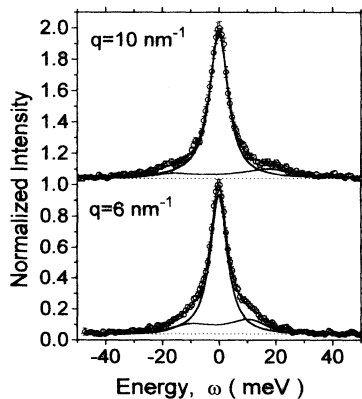


FIG. 2. Examples of fits to the data. The experimental data (\circ) are superimposed to the fit (solid line). The contribution of the central peak and the side peaks, due to the two terms in Eq. (1), are individually shown.

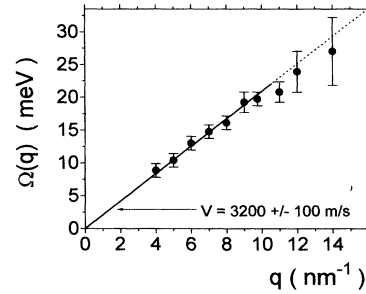


FIG. 3. Dispersion relation in water as obtained from the fit. The solid line indicates the best linear fit up to 10 nm^{-1} , and the slope corresponds to the indicated speed of sound.

This last point strongly favors those theoretical approaches to the water dynamics which explain the fast sound by an anomalously high bend up in the dispersion relation of the acousticlike excitations [5,9,11]. The physical origin of this high dispersion, observed to a much less extent in simple liquids as Ar and Cs [2], is mostly due to the interplay between the different contributions to the intermolecular potential, namely, the electrostatic and Lennard-Jones-like terms [9].

In conclusion, we summarize in Fig. 5 the present understanding on the transition from the hydrodynamic to the kinetic limit of the velocity of sound in water at room temperature. We compare the velocities derived from our H_2O data at each q point as $v(q) = \Omega(q)/q$, the analogous quantities from the D_2O data of TBCD, and those calculated from MD simulation of D_2O [10], and of H_2O [11]. In the figure are also reported the q -dependent infinite- and zero-frequency sound velocities for H_2O [9]. There is a satisfactory agreement between experiments and the considered MD simulations. The figure further emphasizes the independence of the fast sound from the hydrogen isotopes. The calculations from Ref. [10] agree well with the almost flat experimental values, which at large q turn toward the infinite-frequency limit. The absence in the experimental data of any q dependence in the low q region of this plot, and, in particular, the absence of a turn toward the zero-frequency limit, however, implies that the spanned q - ω region is still

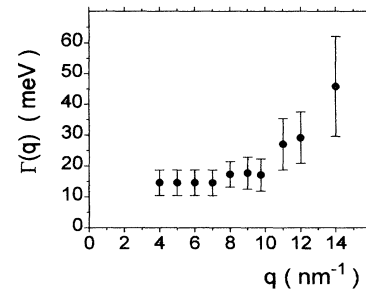


FIG. 4. Damping parameters $\Gamma(q)$ as obtained from the fit.

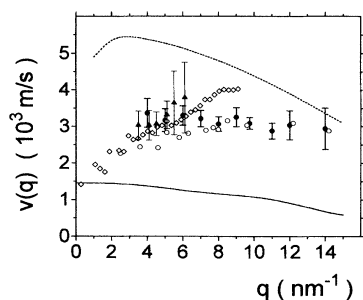


FIG. 5. Wave-vector dependence of different experimental and theoretical velocities of sound in water. \bullet , this work on H_2O ; \blacktriangle , neutron data on D_2O [3]; \circ , MD data on D_2O [10]; \diamond , MD data on H_2O [11]; solid (dashed) line, zero (infinite) frequency limit in H_2O [9].

not sufficient to show experimentally the transition from the ordinary sound to the fast sound.

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