Observation of New Short-Wavelength Collective Excitations in Heavy Water by Coherent Inelastic Neutron Scattering

J. Teixeira and M. C. Bellissent-Funel
Laboratoire Léon Brillouin, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette Cedex, France

and

S. H. Chen
Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

B. Dorner
Institut Laue-Langevin, 38042 Grenoble Cedex, France
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A coherent-inelastic-neutron-scattering experiment was performed on liquid D_2O at room temperature. We observe for the first time the collective high-frequency sound mode as predicted by computer molecular-dynamics simulations. We interpret the excitation to be a mode propagating within the hydrogen-bonded patches existing in liquid water, and distinct from the ordinary sound wave.

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Short-wavelength collective excitations in dense atomic liquids are in general difficult to observe by coherent inelastic neutron scattering. We may define the evidence of the collective excitations by the existence of a peak or a shoulder in the dynamic structure factor $S(Q,\omega)$ on each side of the central line, in the Q range of, say, $0 < Q < 1.2$ Å^{-1}. The neutron-scattering experiments performed so far indicate that, for neon at a liquid density 1.2 g cm^{-3} and $T = 26.5$ K, the excitation exists up to $Q\sigma \leq 1.0$,[1] and for liquid rubidium and lead near their melting points up to $Q\sigma \leq 4.0$,[2,3] where σ is the effective hard-core diameter of the atoms. From the computer molecular-dynamics simulations of hard spheres by Alley and coworkers,[4] it was established that the collective excitation exists up to $Q\sigma \leq 0.5$. It was generally believed that the damping of the short-wavelength excitations depends critically on both the steepness of the repulsive part and the depth of the attractive part of the potential. For liquid metals, the repulsive part is generally softer and the attractive well deeper. This may be the reason why the excitation is observable up to higher Q. More recently, the existence of a collective mode in simple fluids has been discussed explicitly in terms of the kinetic theory of dense fluids.[5] These authors claimed that collective excitations can be defined in dense fluids up to $Q\sigma \leq 30$ and that the behavior of $S(Q,\omega)$ is dominated by these modes for all Q in which they exist.[5]

In this paper we report for the first time an observation of new collective modes in a molecular fluid: water. From a point of view of the intermolecular interaction, water is a rather special case. Take, for instance, the ST2 model potential which has been shown to be successful in predicting various properties of water.[6] This potential consists of superposition of a Lennard-Jones potential between the molecular centers and directional electrostatic interactions which mimic the hydrogen bonding. A new feature of this potential, as compared with that of the simpler liquids, is the presence of a directional and strong attraction between molecules. Our experimental results lead us to conjecture the existence of a new collective mode which we shall call schematically the "high-frequency mode," which is different from the ordinary sound wave in water. This kind of mode was already predicted in an earlier computer molecular-dynamics simulation (CMD) of Rahman and Stillinger[7] and more recently also by Impey, Madden, and McDonald.[8] We shall, in the following, compare our experimental results with these CMD predictions.

The experiment was performed on the three-axis spectrometer IN8 at the Institut Laue-Langevin. The experiment poses some problems because the collective excitations in water can be observed only in a very narrow window of the (Q,ω) space. To reach the energy transfer at small momentum transfer, one has to use high-energy incident neutrons. In order to improve the performance of the instrument at small scattering angles, the distances monochromator-sample and sample-analyzer have been increased. A He-filled box 1.5 m both before and after the sample eliminated air-scattering contributions to the background.

The sample was D_2O (99.95% isotopic purity). It was contained in a rectangular cell of 5 (width) × 6 (height) × 0.7 (thickness) cm^3 in aluminum. The windows had 0.1-mm thickness. In order to reduce the

multiple scattering, a set of sixty horizontal plates was inserted inside the container.[9] Each plate was made from 0.1-mm-thickness aluminum coated on both sides with 50-μm thickness of cadmium. The separation between the plates was 1 mm. Previous calculations of Söderström *et al.*[3] show that this geometry reduces substantially the double scattering.

A fixed incident energy of 80 meV (corresponding to an incident wave vector of 6.2 Å^{-1}) was selected by Bragg reflection of a Cu(220) monochromator crystal and pyrolitic graphite (004) was used as analyzer. The collimation arrangement was open, 40′-40′-40′. Besides the sample runs, empty-cell and vanadium runs were made for the purpose of data correction. The instrumental resolution (measured with vanadium) can be well represented by a Gaussian with FWHM (full width at half maximum) equal to 1.15 THz. The scattered intensity from the empty cell represents less than 5% of the water signal. We used the constant-Q mode in all measurements and the intensity at each point was summed from different scans typically 50 min altogether.

We measured at six different Q values between 0.35 and 0.6 Å^{-1} as given in Fig. 1. It is clear from the spectra that a shoulder is present on each side of the intense central line. We tried to fit these curves by adjusting different kinds of profiles, convoluted with the instrumental resolution. Essentially, we used Gaussian, Lorentzian, or damped harmonic-oscillator-type functions. The analysis shows that the last one gives the best results within a χ^2 criterion. This form is consistent with the form predicted by generalized hydrodynamics.[10] The expression used to fit the side bands was then

$$F_{\pm}(\omega) = \frac{\omega}{1-\exp(-\hbar\omega/kT)} \frac{\Gamma}{(\omega^2-\omega_s^2)^2+\omega^2\Gamma^2}, \quad (1)$$

where ω_s represents the harmonic frequency and Γ their damping. The χ^2 test gives values close to 1.2. The results of the fit are represented in Fig. 2 for $Q=0.5$ Å^{-1}. For comparison, we fitted the data as well with a Lorentzian centered at $\omega=0$ and convoluted with the instrumental resolution; χ^2 came out to be around 2.0. For $Q=0.55$ and 0.6 Å^{-1}, the shoulder is not very pronounced anymore.

As seen from Fig. 3(a), the side peaks at different Q values can be interpreted as the manifestation of collective excitations propagating at a speed c given by

$$c=\omega_s/Q. \quad (2)$$

The data can be represented by a straight line passing through the origin with a slope $c=3310\pm250$ m s^{-1}. The linear Q dependence of ω_s is again an indication

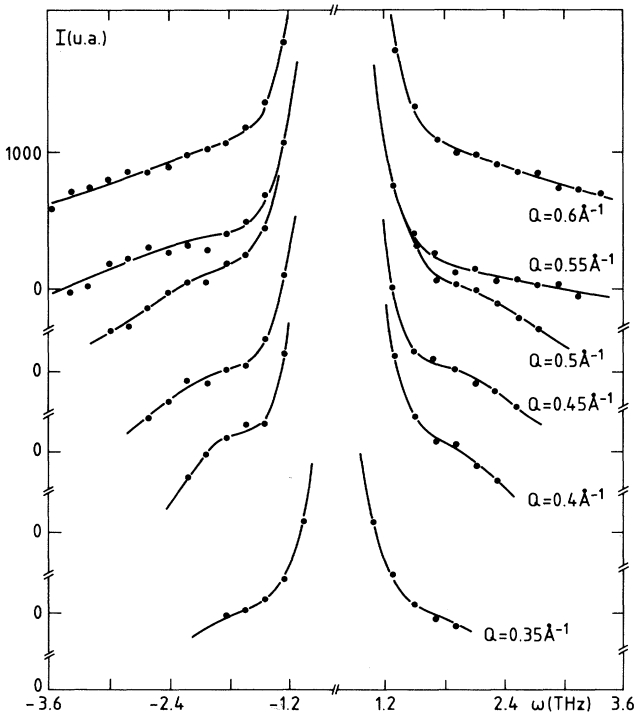

FIG. 1. Scattered intensity, I, plotted against the energy transfer, ω, for all the measured wave vectors Q. The solid lines represent the best fits with damped harmonic-oscillator-type functions. The curves are shifted in the vertical direction.

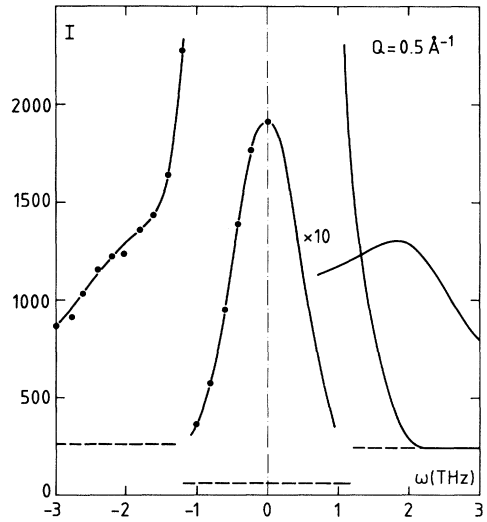

FIG. 2. Scattered intensity, I, plotted against the energy transfer, ω, for the wave vector $Q=0.5$ Å^{-1}. The left-hand side shows the experimental data (dots) and the best fit (solid line) using Eq. (1). The right-hand side shows one harmonic oscillator peak after deconvolution and suppression of the thermal corrections. The central peak has the width of the instrumental resolution. The dashed line represents the constant background.

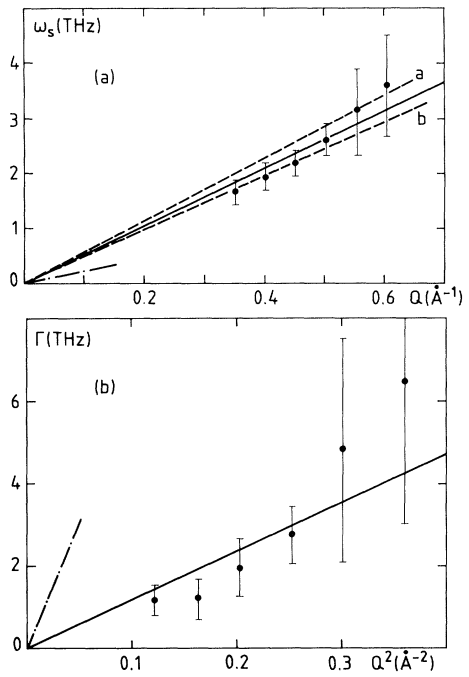

FIG. 3. (a) Representation of the dispersion curve, which gives a velocity equal to 3310 m s^{-1}. Dots: experimental points. Solid line: best linear fit by Eq. (2). Dashed lines: predictions of CMD from Ref. 7 (*a*) and from Ref. 8 (*b*). Dot-dashed line: dispersion curve of the ordinary sound wave. The corresponding velocity (1390 m s^{-1}) is measured up to 5 GHz by Brillouin light scattering (Ref. 11). (b) Linewidth, Γ, plotted against Q^2. Dots: experimental points. Solid line: best linear fit. Dot-dashed line: corresponding line for the normal sound wave, as measured by Brillouin light scattering (Ref. 11).

that our fitting procedure is not affected by the multiple scattering. This velocity is in good agreement with predictions of CMD simulations both by Rahman and Stillinger[7] and by Impey, Madden, and McDonald.[8] It is about two times the low-frequency adiabatic sound velocity as measured by Brillouin light scattering[11] [Fig. 3(a)].

The two possible interpretations of the "high-frequency sound" cannot be completely tested in the present experiment. However, it is clear from the Q dependence of the absorption of the normal sound mode that its observation is unlikely at high Q.

We believe that this high-frequency sound mode cannot be interpreted as the high-Q limit of the ordinary sound wave as it was the case in similar experiments with neon,[1] rubidium,[2] or lead.[3] Experimentally the observed excitation has a solidlike character and we interpret it as a collective excitation propagating in the local hydrogen-bond structure likely to exist in water. We can give the following arguments in support of this interpretation: (a) The wavelength associated with the observed Q range is around 20 Å, comparable with the extension of the patches of hydrogen-bonded molecules.[12] (b) The damping Γ of the modes as obtained from the fitting procedure is proportional to Q^2 [Fig. 3(b)] and much smaller than the equivalent damping of the ordinary sound extrapolated to this Q range.[11] (c) The observed velocity of the collective excitations is similar to the velocity of sound in ice.

It is striking that our experimental observation agrees so well with what has been predicted by CMD simulations. The energy of the mode as a function of Q agrees numerically quite well with the CMD of Impey, Madden, and McDonald,[8] while agreement with Rahman and Stillinger[7] is within the statistical error of the simulation. On the other hand, Impey, Madden, and McDonald[8] predicted heavy damping beyond $Q \gtrsim 0.5$ Å^{-1} while Rahman and Stillinger[7] predicted much lower damping up to $Q = 1$ Å^{-1}. Our results [Fig. 3(b)] show that the damping increases at least as Q^2. For $Q > 0.5$ Å^{-1}, the damping increases dramatically but the error bars are very large as well. The large error bars on frequency and damping for the two larger values of Q reflect the fact that the shoulder is less pronounced. The signal-to-noise ratio was so high that in the future experiments we may improve the resolution further.

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