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Hydrogen-Bond Spectroscopy of Water by Neutron Scattering

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We obtain a series of incoherent-inelastic-neutron-scattering spectra covering the complete frequency range of vibrations of hydrogen atoms in water over a temperature range of −15 to 80°C and also in ice at 20 K for reference. Comparison of these frequency spectra with those generated by computer molecular dynamics with flexible water molecules indicates that the proton motion in a free water molecule is substantially affected by formation of hydrogen bonds in the condensed phases.

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As a result of the existence of spin incoherence in neutron scattering from protons, neutrons are uniquely suited for probing the single-particle motions of protons in hydrogen-containing substances. This feature is particularly valuable for the case of water because of the fact that the hydrogen motion is sensitively affected by the formation of hydrogen bonds which is so characteristic of this substance. Although traditionally Raman scattering has been used extensively to study the hydrogen-bond dynamics in water,[1-4] the quantitative theoretical prediction of the resulting Raman spectra of water has been difficult. This is due to the fact that the intensity of the Raman bands is related to the fluctuation spectra of the polarizability tensor of the molecules which is difficult to calculate when every molecule is interconnected to its neighbors by the hydrogen-bond network.[5] On the other hand, the incoherent neutron scattering spectrum singles out the vibrational and diffusive motions of the hydrogen atoms which can be directly simulated on a computer with molecular dynamics.[6] The analysis of the neutron spectrum in terms of a computer molecular dynamics (CMD) simulation serves the valuable purpose of refining the intramolecular and intermolecular potential model for water.[7]

In this paper we report for the first time measurements of incoherent neutron scattering spectra of water extending to an energy transfer of 600 meV at reasonably small momentum transfer and at a range of temperatures including that of a supercooled state.[8] Such measurements have become possible because of the high intensities of epithermal neutrons produced by a pulsed spallation source. In parallel with the neutron experiments we have developed a new series of CMD simulations of water taking into account the internal vibrational motion of the molecule. Previous CMD studies of water used mainly potential models applicable to rigid molecules; thus the results give little information on the intramolecular part of the spectra.[6,9] The combination of experiment and simulation allows us to unambiguously identify and understand the features of the vibrational spectrum in the 50–500-meV range. We must qualify that although the neutron spectra are easier to interpret in terms of the proton motion, the Raman scattering is still superior in its energy resolution compared with the present stage of development of the neutron scattering technique.

The experiment was carried out at the intense pulsed neutron source (IPNS) at the Argonne National Laboratory. We used the time-of-flight spectrometer HRMECS (high-resolution medium-energy chopper spectrometer) with incident neutron energies E_0 of 800 and 500 meV. HRMECS has 120 detectors distributed over an angular range from 3.5° to 20° covering a wave-vector transfer ($|\vec{Q}|$) range of 1.5 $\mathrm{\AA}^{-1}$ to 8 $\mathrm{\AA}^{-1}$ depending on the energy transfer E. The energy resolution $\Delta E/E_0$ is approximately 3% at the higher end of the energy transfer. A major advantage of this spectrometer is the availability of high incident energy E_0 coupled with low scattering angle θ, which results in a low

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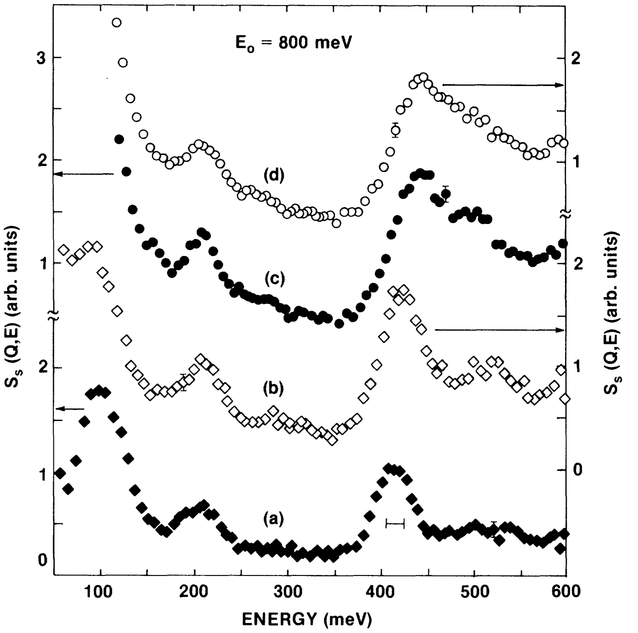

FIG. 1. Dynamic structure factor $S_s(Q,E)$ at a scattering angle $\theta = 8°$ for ice (20 K) and water at three different temperatures, $-15\,°C$, $40\,°C$, and $80\,°C$. Peak shift and broadening of the stretch band E_S with an increasing temperature is clearly displayed.

wave-vector transfer Q at a given energy transfer E. This is particularly crucial for measurements of excitations in liquids where the Doppler broadening of the excitation peaks depends on Q^2.

The water sample was made of an ensemble of 150 thin Pyrex capillary tubes covering an area of 7.2×6.6 cm^2 in planar geometry. The capillary tubes have an inside diameter of 0.8 mm and an outside diameter of 1.0 mm and were filled with triply distilled deionized water and sealed on both ends. The transmission of the water sample was 84%. The use of Pyrex capillary tubes made it possible to substantially supercool the water. The temperature of the sample was controlled to within 0.5 °C.

Measurements were made on ice at 20 K and on supercooled water at $-15\,°C$ with both 800- and 500-meV incident energies. Runs were made at higher temperatures (40 °C and 80 °C) at 800 meV only. To confirm that the sample at $-15\,°C$ was indeed liquid, a separate measurement was performed under identical conditions with the crystal analyzer spectrometer at IPNS, where the quasielastic peak could be measured with much higher resolution. In the case of ice, the width of this peak corresponded to the instrumental resolution (135 μeV), whereas at $-15\,°C$ it was appreciably broader (~ 230 μeV) indicating the characteristic diffusion of the liquid state; the value obtained for the width agrees well with results of a triple-axis measurement on supercooled water.[10] A series of spectra showing the dynamic structure factor $S_s(Q,E)$ for a scattering angle $\theta = 8°$ are shown in Fig. 1. The proton scattering density function $G(Q,E)$ given by

$$G(Q,E) = (E^2/Q^2) S_s(Q,E) \tag{1}$$

for supercooled water at $-15\,°C$ is plotted in Fig. 2.

Figure 1(a) gives the proton density fluctuation spectrum for ice at 20 K. The corresponding figures for water at $-15\,°C$, 40 °C, and 80 °C, respectively, are given in Figs. 1(b)–1(d). As we can see from the figure, density fluctuation spectra in the energy range from 50 to 600 meV consist of three major bands. Starting from the low-frequency side, one has a librational band around 80 meV due to intermolecular coupling, a bending vibrational band

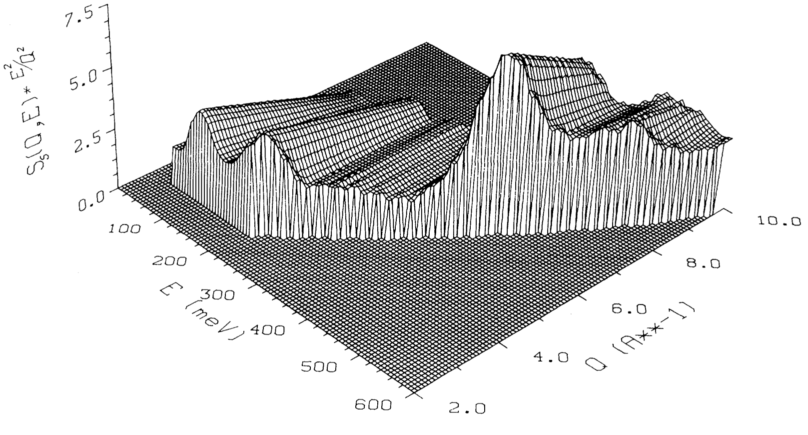

FIG. 2. Proton scattering density function $G(Q,E)$ for supercooled water at $-15\,°C$ plotted in (Q,E) space. A fourth peak at 525 meV probably due to a mode coupling process is clearly evident.

of intramolecular nature centered around 200 meV, and a stretch vibrational band of intramolecular nature centered around 425 meV. Table I summarizes the centroid and the width of the bands at the appropriate Q values at which they are observed. Also listed are the gas-phase Raman frequencies at room temperature.[11] The following observations can be made:

(1) Significant temperature dependence is observed for the bands E_L and E_S while E_B is nearly temperature independent. The band energy E_L decreases as the structure changes from ice to water. The opposite behavior is observed for the band energy E_S.

(2) The width of the band E_S which can be more reliably estimated increases with temperature. The energy resolution at the stretch band is 16 meV which means that the symmetric and asymmetric stretch vibrations in the free molecule cannot be resolved in the present experiment.

In order to understand physically the relation between the measured vibrational frequency bands in the condensed phases and that of a free water molecule, we performed CMD studies of water molecules in vapor and liquid states. We use the simple-point-charge (SPC) potential model proposed by Berendsen *et al.*[12] as a basis for our simulation. The potential is a pairwise Lennard-Jones interaction between the oxygen sites in a rigid molecular structure, together with Coulomb interactions between suitable point charges situated at the oxygen and hydrogen sites. For this calculation the SPC model has been modified to allow for flexible molecules. The system studied consisted of 100 molecules in a constant-volume simulation cell with periodic boundary conditions. CMD runs of 3000 time steps each were carried out to probe the proton and oxygen dynamics in water. The full technical details will be reported elsewhere,[13] but here we report some results which are relevant to the neutron data.

TABLE I. Experimental vibrational energies in water and ice. Data are for 800-meV incident neutron energy except for E_L which are given for 500 meV because of better resolution.

	T (°C)	E_L (meV)	E_B (meV)	E_S (meV)
Ice	−253	82	207	407(49)
H_2O	−15	74	207	418(49)
H_2O	40	⋯	207	441(66)
H_2O	80	⋯	207	443(70)
Gas (Raman)			198	454, 465
Q (Å^{-1})		2.6	3.5	6.6

The frequency spectrum of the proton and oxygen motions are derived from Fourier transforms of the normalized velocity autocorrelation functions. We generally find that the frequency spectra of hydrogen and oxygen contain major peaks at the same energy values though the intensity of those peaks are more pronounced in hydrogen compared to those of oxygen. The proton frequency spectrum $f_p(E)$ is related to $G(Q,E)$ defined in Eq. (1) by

$$f_p(E)=\lim_{Q\to 0} G(Q,E). \qquad (2)$$

The $Q\to 0$ limit is practically satisfied whenever $Q\sim 1$ Å^{-1}. The frequency spectrum $f_p(E)$ exhibits two modes, E_B and E_S, where in the gas phase E_B can be identified with the bending vibrational band and E_S with the stretch vibrational band observed in the Raman spectra.[11] The stretch band is split into two bands separated by 15 meV corresponding to the asymmetric and symmetric stretch vibrations. In the liquid phase the stretch bands shift more or less uniformly to a lower energy by 42 meV. The bending band shifts up in energy by 23 meV and an additional vibrational band appears due to the intermolecular hydrogen bonding at 65 meV. A summary of a series of runs to study both the gas and the liquid spectra is presented in Table II. The main points to note are as follows:

(1) The intramolecular OH bond length in the liquid is greater by 2% as compared to that of the gas phase. This elongation leads to a weakening of the OH bonds and hence to mode softening of the stretch vibration as evidenced by the experimental data.

(2) The formation of hydrogen bonds in the liquid phase leads to further softening of the OH stretch vibrational mode. As the temperature of the system is decreased, more intact hydrogen bonds are formed leading to a decrease in the stretch vibrational band energy. Our experimental

TABLE II. Vibrational energies in water derived from CMD simulation using the SPC model.

	T (K)	E_L (meV)	E_B (meV)	E_S (meV)
Liquid	325	65	228	429, 448
Gas	⋯	⋯	205	475, 490

data as depicted in Fig. 1 clearly show such a behavior. This trend is closely associated with an increase in the librational band energy.

In conclusion, we have demonstrated by an incoherent-inelastic-neutron-scattering experiment combined with an improved CMD simulation of water the possibility of a systematic study of hydrogen-bond dynamics in water at elevated temperatures as well as in the supercooled state. The comparison of the water data at different temperatures and that of ice clearly indicates that as far as the hydrogen bonding of neighboring water molecules is concerned, the supercooled water at −15 °C is essentially similar to ice. This is expected because the number of intact hydrogen bonds is greater than 90%.[14] Thus the various thermodynamic and transport anomalies of the supercooled water[15] are intimately related to the rapid completion of the hydrogen-bond network at low temperatures. As can be seen from Table I, the main difference between the spectra of supercooled water and that of ice exists at the low-frequency librational band E_L. Since this librational motion of the hydrogen atom is transverse to the direction of hydrogen bonding, the downshift in E_L in the supercooled state as compared to that of ice would indicate that on the average the hydrogen bond in the liquid state is more distorted from linearity than that in the solid state.[16] This trend is more pronounced as the temperature increases in water as is also evidenced by the broadening of the stretch band E_S. That the main temperature effect is in the librational band proves that a strong temperature dependence of liquid properties is more related with the breaking of bonds provided by librational motion than with the number of bonds itself.

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