PHYSICAL REVIEW A VOLUME 26, NUMBER 6 DECEMBER 1982

Incoherent quasielastic neutron scattering from water in supercooled regime

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(Received 3 June 1982)

Measurements of the quasielastic spectra have been made with a three-axis neutron spectrometer at constant-Q mode in a temperature range from 38 °C down to -20 °C. Two energy resolutions both high ($\Delta E = 100$ μeV) and low ($\Delta E = 800$ μeV) were used to identify and separate a sharp component from a broad one. As temperature is decreased below zero the spectrum shows an increasing sharp component standing out on top of the broad one. The broad component is attributed to rotational motions of water molecules. A preliminary analysis of the linewidths gives a Q-independent relaxation time which has the same magnitude as the rotational relaxation time measured by nuclear magnetic resonance. The Q dependence of the sharp line is analyzed by a Q-dependent diffusion coefficient. A temperature-independent characteristic length $l_0 = 0.5$ Å is obtained. We then attempt to relate this length to local geometry of protons associated with hydrogen bonding.

I. INTRODUCTION

The study of the molecular dynamics of water has been made using different experimental techniques such as measurements of viscosity,[1] self-diffusion,[2] nuclear magnetic resonance (NMR),[3] dielectric relaxation time,[4] depolarized light scattering,[5] and incoherent quasielastic neutron scattering.[6] In spite of the large amount of data which have been accumulated in the last 25 years, the microscopic mechanism of molecular diffusion has not yet been clearly understood.[7] Recent progress in this direction has been made largely from the study of the supercooled region, because various thermodynamic and transport anomalies are strongly enhanced in supercooled water.[8]

Most of the techniques used to study the molecular dynamics of water give some kind of characteristic time, say τ, between 1 and 10 ps with rather anomalous temperature dependence. For example, one can make an Arrhenius plot by defining an activation energy by

$$E_A = d\log_{10}\tau / d(1/T) .$$

One then finds that E_A varies from 4.6 kcal/mol at room temperature up to 8.8 kcal/mol at -30 °C. The activation energy turns out to be almost the same for relaxation times associated with different dynamic properties. Pruppacher[2] has shown that, within an accuracy of a few percent, two simple laws, $D\eta / T = \text{const}$ and $D\tau = \text{const}$, seem to be very well verified. D, η, and τ are, respectively, the self-diffusion coefficient, shear viscosity, and dielectric relaxation time. This is an indication that one single molecular mechanism can probably explain the behavior of the different dynamic properties.

The situation is less clear for the interpretation of the linewidth of quasielastic incoherent neutron scattering, Γ. A large number of experimental results[6] have been analyzed either with a continuous diffusion picture or with a jump and wait mechanism.[7] Both interpretations are not complete in the sense that the continuous diffusion picture predicts linewidths larger than those actually observed at not too large momentum transfer Q ($Q > 0.5$ Å^{-1}), while the jump diffusion picture in its simplest form[9] predicts linewidths at large Q ($Q > 1$ Å^{-1}) much smaller than the measured ones, reported by various groups, around room temperature.[6] More complex theoretical pictures were developed with intermediate situations between these two extremes.[10] These theories can be made to fit the data perhaps at one temperature, but the temperature dependence of the characteristic times extracted from these fittings does not agree with temperature dependence of other characteristic times, such as those from dielectric relaxation and depolarized light scattering. Another puzzling point is that the Q dependent of Γ at room temperature, as given by different authors,[6] varies by a factor of as much as 2 at large Q. A possible explanation of this discrepancy may be the way the inelastic background was subtracted in the time-of-flight spectra. But it is also possible that the room temperature Γ actually contains contributions from two processes, and without proper deconvolution procedure different authors may extract different linewidths for the translational diffusion. If the latter is true, an experimental way of overcoming this difficulty may be to lower the temperature sufficiently so that the two processes contributing to the two lines are better separated in the frequency width.

A hint in this direction comes from recent experiments on depolarized light scattering[5,11] down to low temperatures. In these spectra, it is clear that there are both narrow and broad components present. In spite of the difficulty concerning the interpretation of these lines, it was conjectured that an analogous situation may also apply to incoherent quasielastic neutron spectra. Because in a typical neutron experiment the energy transfer range covered is only several times larger than the instrumental resolution, it is difficult to cover both lines in the same experiment. We decided to perform separate experiments using two different energy resolutions for the same sample. A three-axis spectrometer operated at constant Q mode is judged to be more appropriate for this purpose. This is in contrast with all other experiments on water performed so far by others using time-of-flight spectrometers.

II. EXPERIMENTAL

We used a three-axis spectrometer at the high flux reactor of the Oak Ridge National Laboratory. Two modes of spectrometer configuration were used. For large energy transfer and low resolution measurements, we chose a constant final energy at $E_f = 14.8$ meV which is filtered with pyrolytic graphite to remove the second order. The spectrometer was operated at constant-Q mode with variable incident energy ranging from 10 to 19 meV. The energy resolution was checked by taking a vanadium rocking curve which showed that $\Delta E = 800$ μeV (full width at half maximum). For small energy transfer and high resolution measurements, we chose a constant final energy of $E_f = 4.0$ meV which is beryllium filtered. The energy transfer range was ± 0.8 meV with $\Delta E = 100$ μeV. Typical scanning time for a quasielastic peak was 12 h.

The sample container consists of a set of 150 Pyrex capillary tubes with i.d. 0.3 mm and o.d. 0.4 mm. A double layer of these capillary tubes was made which covered a beam area of 40×32 mm^2. The sample was mounted on an aluminum plate with a beam window and sealed in a helium gas container. The container was then mounted on an Air Product constant temperature refrigerator which controlled and maintained the temperature to an accuracy of 0.05 K. The water was triple distilled, deionized, and millipore filtered. Capillaries were filled within a week prior to the experiment and selectively tested for supercooling down to -25 °C. The experiments were always done starting from room temperature and cooled down slowly as they proceeded. At the very end of the experiment, the sample was cooled down to -35 °C, and an ice background was taken (we shall call this A) in order to test for the freezing of the sample and to make sure that the water remained as liquid during the run. The ice peak was always just the resolution function as obtained from the vanadium rocking curve.

For a background correction later on, we also ran the ice spectra with the analyzer rotated 5° away from the Bragg position, so that we got a smooth background without an elastic peak (we shall call this B). In all the runs we made (about 60), we never encountered a sign of sample freezing during the run. We also inspected the capillary tubes after each series of experiment, and there was no sign that any capillary was broken.

The low resolution runs were made at temperatures from 40 °C down to -5 °C, while the high resolution runs were made from 0 °C down to -20 °C in steps of 5 °C. A multiple scattering code was run to estimate the multiple scattering from the sample. It amounts to less than 5% of the signal, so no correction was made of the double scattering in the subsequent analysis.

III. RESULTS AND DATA PROCESSING

A typical example of the quasielastic peak taken at high resolution after subtraction of the background is shown in Fig. 1(a). The background subtraction was performed in the following way: First,

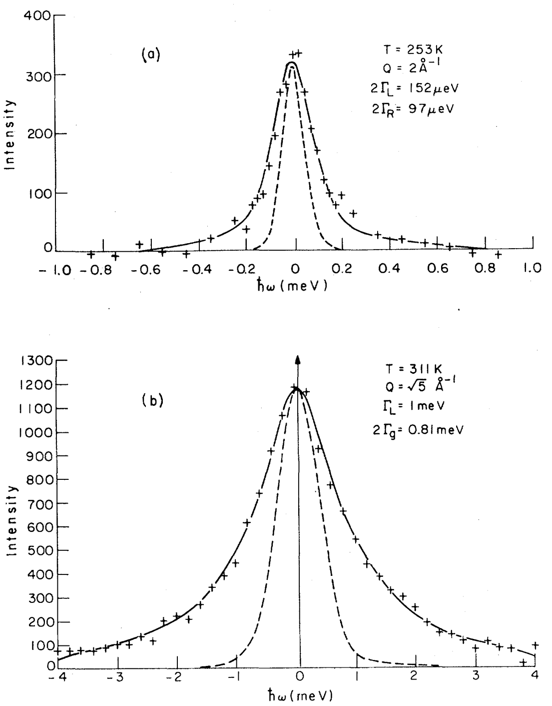

FIG. 1. Typical quasielastic spectra of water [proportional to $S_s(Q,\omega)$] taken with high and low resolutions. (a) A spectrum at $T=253$ K and $Q=2$ Å^{-1}. + indicates data and solid line is the fitted curve using a Lorentzian function convolved with the resolution function (dashed line). The resolution function is a Gaussian function with FWHM $=97$ μeV and the extracted Lorentzian function has a FWHM $=152$ μeV. (b) A spectrum at $T=311$ K and $Q=\sqrt{5}$ Å^{-1}. Dashed line is a Gaussian resolution function with FWHM $=810$ μeV. The extracted Lorentzian line has a FWHM $=2000$ μeV.

the room background B was taken from the ice background A. We then estimated the inelastic and rotational background by fitting the ice background with an expression

$$A+B\omega+C\omega^2+DG(\omega)\ ,$$

where $G(\omega)$ is a Gaussian function representing the instrumental resolution function. The constants A, B, C, and D are determined. This expression is then used to subtract the inelastic and rotational contribution from the quasielastic peak. We assume that the corrected peak represents the translational diffusion peak and fitted it with an expression

$$I(Q,\omega)=KG(\omega)*\left[\frac{1}{\pi}\frac{\Gamma_s(Q)}{\omega^2+\Gamma_s(Q)^2}\right]\ , \qquad (1)$$

where the asterisk means a convolution and K is a normalization constant. The width of the Lorentzian $\Gamma_s(Q)$ is then extracted from each spectrum. We also tried to fit $I(Q,\omega)$ with two Lorentzians without being able to improve the quality of the fit. Figure 1(a) shows the quasielastic peak at $-20\,^\circ$C and $Q=2$ Å^{-1}. The resolution function, also indicated, has a full width at half maximum (FWHM) equal to 97 μeV, and the best fitted Lorentzian has a FWHM, $2\Gamma_s=152$ μeV.

Figure 1(b) gives a typical result taken with low resolution $\Delta E=800$ meV. The fit was done with the expression

$$I(Q,\omega)=A+B\omega+G(\omega)*[\alpha\delta(\omega)+\beta L(\omega)]\ , \qquad (2)$$

where $A+B\omega$ represents the inelastic background, $\alpha\delta(\omega)$ the sharp line as in Fig. 1(a), and $\beta L(\omega)$ the broad Lorentzian line representing the rotational motion. At $T=38\,^\circ$C and $Q=\sqrt{5}$Å^{-1}, the resolution width of $G(\omega)$ is 810 μeV, and the best estimate of the width of the broad Lorentzian line is

$$2\Gamma_b=2.0\text{ meV}\ .$$

In Fig. 2(a) we plot the linewidth Γ_s of the sharp component from the high resolution experiments versus Q^2 showing that separation from the continuous diffusion line starts approximately at $Q=1$ Å^{-1}. Fig. 2(b) is a similar plot for the broad line from the low resolution experiments. We note that the difference in scale in Figs. 2(a) and 2(b) is about 5.

IV. INTERPRETATION OF THE LINEWIDTHS

If we remember that the two resolutions used in the low and high resolution experiments were 100 and 800 μeV, respectively, it is clear from inspection of Figs. 2(a) and 2(b) that at all temperatures measured there are two lines present which we shall call "sharp" and "broad." At the scale of the broad line, the sharp line is seen like a δ function (essentially, the resolution function), and at the scale of the sharp line, the broad line looks like a constant background. The procedure of deconvolution given in the previous section reflects this assumption. We also note that the high-resolution data cannot be fitted with two Lorentzian components with an improved agreement.

In this paper we shall focus our attention mainly on interpretation of the sharp component. But it suffices to say here that the broad component is certainly connected with the rotational motion of wa-

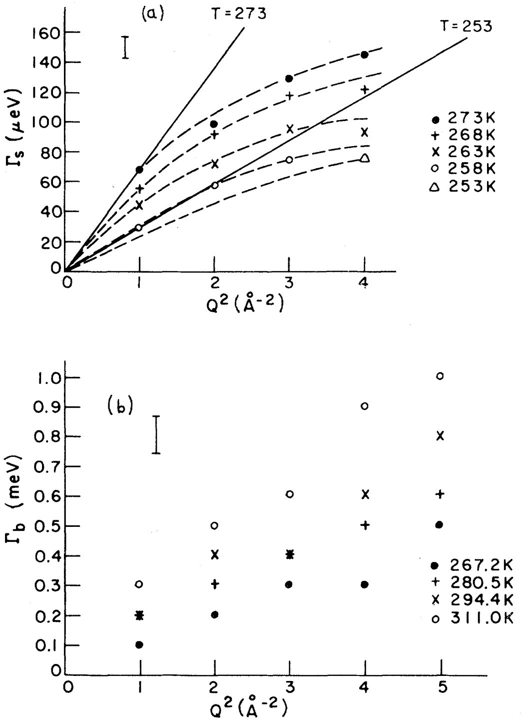

FIG. 2. Half widths of the sharp Lorentzian line Γ_s and the broad line Γ_B plotted as a function of Q^2. (a) Γ_s in μeV at five temperatures. Dashed lines are put through data points to guide the eyes. Solid line is the diffusion line DQ^2. (b) Γ_B in meV. If one puts $\Gamma_B=\Gamma_s+D_R$, then D_R thus extracted shows little Q dependence and $\tau_R=D_R^{-1}$ agrees with NMR rotational relaxation time.

ter molecules. It is evident from Fig. 2(b) that the order of magnitude of Γ_b is consistent with the rotational relaxation time as measured by NMR.[3] Indeed, if we roughly equate $\Gamma_b \simeq \Gamma_s + D_R$,[12] then D_R is approximately Q independent, increasing with increasing temperature. For example, for room temperature ($T=294.4$ K), $D_R \simeq 0.20$ meV, which gives

$$\tau_R = D_R^{-1} = 3.3 \text{ ps}$$

to be compared with NMR rotational correlation time 3.2 ps, as given by Krynicki[13] and Sposito.[14]

We would like to argue that the sharp line is associated with the translational diffusion of the water molecule. From the way we analyzed the data, it is clear that the broad component, which lies beneath the sharp line, has been completely removed before the one Lorentzian fit was made. We first note that this sharp line seems to increase rapidly in intensity, besides its narrowing, as temperature is reduced into the supercooled region. This is a fortunate circumstance from the experimental point of view because this allowed subtraction of the broad component much more easily and completely. This may be part of the source of the discrepancy of the linewidth data at room temperature given by previous authors (as discussed in the Introduction).

To interpret the width of the sharp line, we shall take a phenomenological approach. Since at small Q, Γ_s is proportional to DQ^2, where D is the self-diffusion coefficient and, at large Q, Γ_s falls below the diffusion line, we shall postulate an expression

$$\Gamma_s(Q,T) = \frac{DQ^2}{1+Q^2 l_0^2} \ . \tag{3}$$

This expression is consistent with a picture that, as Q increases, neutrons see more of the local motions of the diffusing protons and, consequently, the diffusion coefficient obtained by fitting the quasielastic line should become a Q-dependent quantity, $D(Q)$. The small Q expansion of $D(Q)$ should go like

$$D(Q) = D(1 - l_0^2 Q^2 + \cdots) \ , \tag{4}$$

which is consistent with Eq. (3) if $l_0^2 Q^2$ is small compared to unity.

If we were to identify Eq. (3) with a random jump diffusion model,[7] then

$$D = l_0^2/\tau_0 \ , \tag{5}$$

where τ_0 is a residence time between jumps and l_0 is a characteristic jump distance in a distribution of jump lengths

$$P(l)dl = \frac{l}{l^2} e^{-l/l_0} dl \ . \tag{6}$$

The purpose of introducing a Q-dependent diffusion constant in (3) is to test whether the characteristic length l_0 extracted from the experimental data is temperature dependent or not. We therefore plotted in Fig. 3 Γ_s/Q^2 vs Q^2 together with the value of the macroscopic self-diffusion coefficient D, at $Q=0$. We see that, for each temperature, Γ_s/Q^2 is almost linear in Q^2. Moreover, the straight lines extrapolate correctly to the $Q=0$ limit except for one intermediate temperature (268 K), for which the systematic deviation is likely a temperature error. The slope of the different straight lines decreases with decreasing temperature. This behavior suggests use of an alternate representation where the effective diffusion constant Γ_s/Q^2 is normalized by the macroscopic self-diffusion coefficient D at the corresponding temperature. This plot

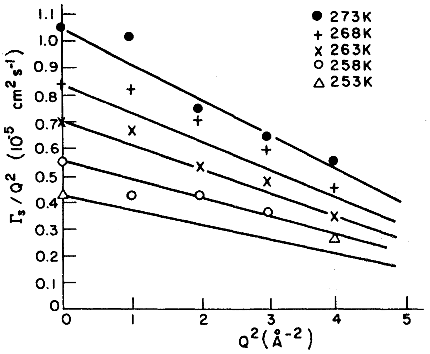

FIG. 3. Γ_s/Q^2 vs Q^2 plot for the sharp line. Note that experimental points for a same temperature extrapolate correctly to D at that temperature indicated by points at $Q=0$. Note the slopes of lines changes with T.

is shown in Fig. 4 and we see that, within the experimental accuracy, all points lie in a single straight line obeying Eq. (3). Actually, this plot shows that the deviations from the linear fit are qualitatively different for each temperature and, taking into account the experimental error, which can be evaluated to be around 12%, this is probably the best possible fit of the data. The l_0 value extracted from the slope is

$$l_0=0.5\pm0.06\ \text{Å}\ ,$$

which is temperature independent. This characteristic length gives, using Eq. (6), values of

$$\langle l\rangle=2l_0=1.0\ \text{Å}$$

and

$$\langle l^2\rangle^{1/2}=\sqrt{6}l_0=1.23\ \text{Å}\ ,$$

which are lengths of an average diffusion step.

From the molecular geometry of hydrogen bonded water dimer, there are only two distances between protons which are comparable with these distances. The first one involves an angular jump across the tetrahedral angle. This is a mechanism often proposed in the interpretation of dielectric relaxation data,[15] which is pictured as a rotation of the molecule changing its hydrogen bonding from one to another next neighbors. The other possible distance involves the possibility for the proton to jump along the hydrogen bond from one to another equilibrium position. This possibility arises because it was shown recently by Kuhs and Lehmann[16] that the barrier between the two positions in the cubic ice is as low as 12 meV, which is lower than k_BT. However, this latter process seems to be hard to relate to macroscopic self-diffusion of the molecule.

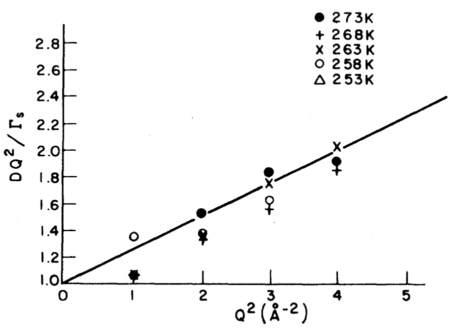

FIG. 4. Universal plot of $(\Gamma_s/DQ^2)^{-1}$ vs Q^2. Note that all data lie on one straight line with a slope $l_0^2=0.25\pm0.03$ Å^2.

From Eq. (5), we immediately deduce

$$D\tau_0=l_0^2=\text{const}\ ,$$

which, as we mentioned in the Introduction, is known to apply to various transport coefficients. At room temperature ($T=298$ K), taking $D=2.30\times10^{-5}$ cm^{2}s^{-1} (Ref. 2) one obtains $\tau_0=1.1$ ps and at -20 °C, taking

$$D=0.44\times10^{-5}\ \text{cm}^2\text{s}^{-1}\ ,$$

one obtains $\tau_0=5.7$ ps. These values lie between two time constants τ_R and τ_{HB}, where τ_{HB} is the time obtained from the analysis of the broad line in the depolarized light scattering spectrum and was attributed to the process of hydrogen bond breaking.[5] The temperature dependence of τ_0 of course follows τ_R, as measured, for example, by NMR.

V. CONCLUSION

We measured incoherent quasielastic neutron scattering of water, using a three-axis spectrometer in a Q range extending from 1 to $\sqrt{5}$ Å^{-1} and at several temperatures ranging from room temperature down to -20 °C in the supercooled region.

Two series of studies with high and low resolutions of $\Delta E=100$ μeV and $\Delta E=800$ μeV revealed that the quasielastic spectrum consists of at least two lines, a sharp one and a broad one. A similar independent study at room temperature performed by M.-C. Bellissent[17] confirms our analysis, and her results are in good agreement with ours.

The broad line is associated with the rotational motions of water molecules. A preliminary analysis of the linewidth gives a rotational relaxation time τ_R which agrees with that measured by NMR.

The sharp line is identified with the translational diffusion of the molecule. Analysis with a Q-dependent diffusion constant shows that there is a characteristic length l_0 which is temperature independent (within the temperature range we studied). We attempted to associate this characteristic length with local geometry of protons involved in the hydrogen bonding. The length l_0 can be associated either with the distance between the two possible proton positions in a hydrogen bond or with the distance between the proton positions in two adjacent hydrogen bonds.

If we further interpret this Q-dependent diffusion process with a random jump model, we can extract a residence time $\tau_0 = l_0^2/D$ that has the same temperature dependence as other transport properties and has a magnitude around 5.7 ps at $-20\,^{\circ}\mathrm{C}$.

ACKNOWLEDGMENTS

This work was supported by the U. S. National Science Foundation and Centre National de la Recherché Scientifique of France. We are grateful to the Solid State Division of Oak Ridge National Laboratory for generous allocation of the spectrometer.

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