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HAL Id: jpa-00209627
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Submitted on 1 Jan 1983

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Hydrogen bond dynamics in water studied by depolarized Rayleigh scattering

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(Reçu le 17 novembre 1982, accepté le 21 décembre 1982)

Résumé. — Nous avons mesuré le spectre de diffusion Rayleigh dépolarisée de l'eau, entre 80 °C et −17 °C. L'analyse spectrale a permis une décomposition en deux raies de largeurs très différentes. A partir de la raie étroite nous avons déduit un temps de relaxation qui peut être interprété comme un temps de réorientation dû aux rotations. La raie large donne un temps de relaxation dont la dépendance en température suit une loi d'Arrhenius avec une énergie d'activation $E = 2.7$ kcal/mole. Ce temps plus court peut être associé au temps de vie des liaisons hydrogène dans l'eau et $E$ représente alors l'énergie d'activation associée au processus de formation des liaisons hydrogène. Cette interprétation est en accord avec des résultats récents de diffraction quasi élastique de neutrons et peut se justifier également si l'on tient compte des fréquences de libration déterminées par spectroscopie Raman.

Abstract. — We measured the depolarized Rayleigh light scattering by water from 80 °C down to −17 °C. The spectra obtained could be analysed into two lines, a broad and a sharp one. From the sharp line we deduced a relaxation time which can be interpreted as a reorientational time due to rotations. The broad line gives a relaxation time which is Arrhenius temperature dependent, with an activation energy $E = 2.7$ kcal/mole. This shorter time can be associated with the mean lifetime of H-bonds in water and $E$ is the activation energy of the formation and breaking of H-bonds process. This interpretation can be supported by recent measurements on quasi-elastic neutron scattering and by taking into account the librational frequencies from Raman spectroscopy.

1. Introduction. — A considerable amount of experimental work has been done in last years concerning the reorientation motion of water molecules in liquid state [1, 2]. Data are available on different dynamical properties such as viscosity $\eta$, [3], self-diffusion coefficient $D_s$ [4, 5], dielectric $\tau_d$ [6, 7] and nuclear magnetic $\tau_n$ [8, 9] relaxation times. All of them have strong temperature dependences and from Arrhenius plots one can deduce analogous activation energies which become strongly temperature dependent below the melting point.

At low temperatures the quantities $D_s \eta/T$ and $D_s \tau_d$ are nearly constant with temperature. This feature was interpreted by Pruppacher [4] as evidence for one single mechanism explaining dynamical properties.

In liquids composed of non-spherically symmetric molecules, depolarized Rayleigh light scattering has proven to be a powerful technique of studying molecular reorientation. However the interpretation of the spectral distributions is usually not easy since the various models for reorientational motions which have been proposed predict often very similar line-shapes which are difficult to distinguish experimentally [10]. But for nearly spherical molecules it has been observed that in the low frequency region, say below 50 cm$^{-1}$, the spectra are approximately Lorentzian and a jump diffusion mechanism for reorientation seems to be well adapted to the interpretation of the data.

Experimental studies of the quasi-elastic depolarized light scattering in liquid water have been carried out [11, 12] above the melting point. Montrose et al. [11], for $T < 20$ °C, fitted the spectra with two Lorentzians whose half-widths differ by a factor of about four. The sharp line gives a relaxation time $\tau_A$ of the same order of magnitude as $\tau_n$ or $\tau_d$ and was then interpreted as reflecting the dynamics of a rotational diffusion process. On the other hand, from the broad line, which was the only one detectable at higher temperatures, they deduced a relaxation time $\tau_B$ lower than the picosecond. $\tau_n$ shows an Arrhenius temperature dependence, a rather unexpected result for H$_2$O [1]. The activation energy which

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Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:01983004404052500
is deduced, $E_B = 3.0$ kcal/mole, is interpreted by Montrose et al. [11] as corresponding to the formation and breaking of hydrogen bonds and $\tau_B$ as the average lifetime of a hydrogen bond.

In this paper we present new measurements of the depolarized Rayleigh light scattering down to $-17^\circ C$ and we give further support to the previous interpretation of $\tau_B$.

2. Experimental. — Depolarized Rayleigh light scattering experiments were carried out in water from $80^\circ C$ down to $-17^\circ C$. In order to cover a large enough temperature range in the supercooled region, we used the capillary (i.d. = 2 mm) technique described elsewhere [13].

The light from an Ar$^+$ laser (514.5 nm, about 250 mW), polarized perpendicularly to the scattering plane, was incident along the axis of the capillary and focused in its centre. The light scattered at 90$^\circ$, polarized in the scattering plane, was analysed by a single monochromator with a 150 $\mu$m slit width and for frequency shifts up to 50 cm$^{-1}$. The detection system consisted of a photomultiplier tube connected to a standard photon counter and a digital-analog converter.

The polarization of the incident and scattered light was selected by two Glan-Thompson prisms with an extinction ratio of $10^{-7}$ placed just before and after the scattering cell.

Thermal equilibrium was obtained by regulation of a methanol or water bath according with the temperature region covered. For all measurements the temperature stability was better than 0.05 °C.

3. Results and discussion. — The experimental depolarized spectrum, $I_{VH}$, is the convolution of the instrument function, $I_0$, and the true spectrum. $I_0$ was determined from the polarized spectrum of a milk sample and we obtained a very good fitting with a Gaussian function $G(\omega)$, characterized by a half-width at half maximum (HWHM) equal to 1.1 cm$^{-1}$, where $\omega$ refers to frequency shifts from the excitation line.

The depolarized Rayleigh spectrum is composed of two components corresponding to the orientation and the collision-induced contributions.

In spite of the high quality of the Glan-Thompson polarizers we used, there is always polarized leakage since the depolarized spectrum is much weaker than the intense polarized scattering [14]. We took it into account by super imposing a $\delta$ function to the depolarized spectrum.

The collision wing is a very broad distribution decreasing roughly exponentially with frequency [15], but on the lower frequency region of the spectrum it can be considered as a constant background [11].

The depolarized orientational line is assumed to have a Lorentzian shape and $I_{VH}$ was computed by

Fig. 1. — Depolarized Rayleigh spectra of water at $\langle a \rangle$: $-14.7^\circ C$, $\langle b \rangle$: $59.2^\circ C$ and $\langle c \rangle$: $9.7^\circ C$. --- is the extrapolation to low frequency shifts of the collision-induced scattering; --- represents the best fit obtained with eq. (1) to the data points *. In $\langle a \rangle$ and $\langle b \rangle$ the solid curve is the Lorentzian component. In $\langle c \rangle$ the dotted curve represents the two-Lorentzian fit which better takes into account the accuracy of the experimental points.
an equation of the form:

\[ I_{\text{VH}}(\omega) = C + G(\omega) \cdot \left( D\delta(\omega) + B \frac{1}{\pi \omega^2 + \Gamma_B^2} \right) \]  

(1)

where \( C, D \) and \( B \) are constants. \( \delta(\omega) \) as previously described takes into account the spurious polarized contribution.

We used the following method to fit our experimental spectra: the convoluted function \( I_{\text{VH}} \) was calculated for a given value of the parameter \( \Gamma_B \) and fitted by a least-squares procedure to the data. \( \Gamma_B \) was then varied until a good agreement between the computed curve and the data points is obtained, as evaluated by \( \chi^2 \) test.

In figure 1 (a, b) we give examples of experimental spectra obtained at two temperatures, \(-14.7^\circ\text{C}\) and \(59.2^\circ\text{C}\), and their fitting by one Lorentzian and a constant background. Both the Lorentzian line and the total fit by equation (1) are represented.

From the HWHM, \( \Gamma_B \) of this Lorentzian, a relaxation time \( \tau_B \) can be deduced

\[ \tau_B = (2\pi \Gamma_B)^{-1}. \]  

(2)

In figure 2 we present a semi-log plot of \( \tau_B \) as a function of the reciprocal temperature. As can be seen, the experimental data can be very well fitted by a straight line in this type of diagram indicating that the mechanism responsible for the scattering process is thermally activated. From the slope we deduced an activation energy \( E_B = 2.7 \text{ kcal.mole}^{-1} \) and from the intercept a pre-exponential factor equal to \( 5.6 \times 10^{-15} \text{ s} \). Our results agree quite well with those previously reported in the normal temperature range, i.e., above the melting point, by Montrose et al. [11] and Danninger and Zundel [12]. These authors have obtained respectively activation energies of 3.0 kcal.

mole\(^{-1}\) and 2.5 kcal.mole\(^{-1}\). The main differences come from the value of the pre-exponential factor but we think that this arises mainly from the deconvolution procedure used.

The fitting of some spectra obtained between \(10^\circ\text{C}\) and \(30^\circ\text{C}\) was very poor and a great improvement was found by adding a second Lorentzian \( A \left( \frac{\Gamma_A}{\pi \omega^2 + \Gamma_A^2} \right) \) inside the parentheses of expression (1), as is shown in figure 1 (c) for \( T = 9.7^\circ\text{C} \). \( \Gamma_A \) increases with temperature from roughly \( 1.8 \text{ cm}^{-1} \) at \( 10^\circ\text{C} \) to \( 2.7 \text{ cm}^{-1} \) at \( 29^\circ\text{C} \), but it remains very small when compared with \( \Gamma_B \).

This second relaxing process was already put in evidence by Montrose et al. [11] for \( T < 20^\circ\text{C} \). From intensity measurements they concluded that its intensity is lowered when temperature increases which explains that it cannot be seen at higher temperatures. In fact we could see this narrower line only in a specific intermediate temperature range, the reasons for it being absent on the two extreme temperature sides being of a different nature. At higher temperatures we point out the same argument as in reference [11]. But in the lower range, in spite of the increase of the total intensity, its half-width decreases and rapidly becomes equal to the instrumental resolution. The deconvoluting technique does not allow in such cases the separa-

![Fig. 2.](image-url)  
Relaxation time, \( \tau_B \), versus the reciprocal temperature. ● this work, ○ ref. [12] and △ taken from Fig. 4 in ref. [11]. The solid line is the best Arrhenius fit to our data.

![Fig. 3.](image-url)  
Variation with the reciprocal temperature of (a) \( \tau_B \), this work, (b) \( \tau_B \) from ref. [11], (c) \( \tau_B \) from ref. [12], (d) \( \tau_\alpha \) from refs. [6, 7], (e) \( \tau_B \) from refs. [8, 9], (f) \( \eta_B/T \) (\( \eta_B \) from ref. [3]), (g) \( \nu_B^{-1} \) from refs. [4, 5]. ● represents \( \tau_A \) (this work) and ▲ \( \tau_\alpha \) from ref. [11].
tion in two lines and the Lorentzian line is hidden by the instrumental Gaussian function.

The relaxation times $\tau_A$ deduced from $\Gamma_A$ are very close to the determination of the rotational relaxation time $\tau_r$ from NMR [8, 9] or $\tau_d$ from complex dielectric constant [6, 7]. Taking into account the few results we obtained for $\tau_A$, we did not try any specific temperature dependence of $\tau_A$ but if we look at the ensemble of experimental values measured by Montrose et al. and by us it is possible to attribute to $\tau_A$ the same behaviour with temperature as $\tau_r$ or $\tau_d$. This is illustrated in figure 3 where the ensemble of the different data are shown together.

Given the magnitude and the particular behaviour of $\tau_A$, Montrose et al. [11] interpreted it as related to a molecular reorientational motion of rotational diffusion type.

On the other hand, $\tau_B$ looks to be uncorrelated with this kind of motion, in particular because of its temperature dependence. There are several comments which can be made [11, 12] to support this argument:

- $\tau_B$ describes a much faster process than others which are determined by NMR or dielectrics.
- $\tau_B$ can be analysed by an Arrhenius equation in all the temperature range studied extending from 80 °C to the supercooled regime until $-17$ °C. The activation energy deduced is temperature independent, while all the other transport processes in water are characterized by a "pseudo" activation energy which is strongly temperature dependent.
- If $\tau_B$ was a correlation time determined by a diffusional process then the Stokes-Einstein-Debye relation would apply and $\tau_B$ would be linear in $\eta_s/T$. This argument does not necessary apply to a strongly associated liquid like water, but is still expected to be valid because different relaxation times are proportional to $\eta_s/T$, at low temperatures, as mentioned above. From figure 4 it can be seen that such a linear relation holds only in the high temperature range.

We evaluated the activation energy of the orientational kinetics reflected in the broad Lorentzian component of the depolarized spectra to be 2.7 kcal. mole$^{-1}$. The corresponding values given by Montrose et al. [11] and Danninger and Zundel [12] are, respectively, 3.0 and 2.5 kcal. mole$^{-1}$. These values are in very good agreement with that quoted by Walrafen [16], 2.55 kcal. mole$^{-1}$, for the formation and breaking of hydrogen bonds between water molecules. Therefore, taking this agreement as a decisive factor, Montrose et al. ascribed this fast Lorentzian to the dynamics of the formation of H-bonds and identified the relaxation time $\tau_B$ with the lifetime of a hydrogen bond in water.

More evidence in support of this interpretation can be considered from a recent calculation of Bertolini et al. [7]. From their results on the dielectric relaxation time and following the percolation model [17], these authors evaluated a H-bond lifetime which agrees quite satisfactorily with our results for $\tau_B$ in the supercooled region.

It is interesting to compare the value of the pre-
exponential factor $\tau_B^0$ in the Arrhenius equation

$$\tau_B = \tau_B^0 \exp\left(\frac{E_B}{RT}\right)$$

with characteristic lines in the Raman spectrum of liquid water. As mentioned above, by fitting our $\tau_B$ data to equation (3), we obtained $\tau_B^0 = 5.6 \times 10^{-15}$ s. From this value we deduced a corresponding frequency which lies within the librational band of H$_2$O molecules. This means that each molecule is vibrating over periods of order $\tau_B$. When the O-H ... O angle is too large the bonding energy falls below the cutoff value and the hydrogen bond is broken. In this sense $\tau_B$ is then a measure of the hydrogen bond lifetime. It can be assumed moreover that when a sufficient number of hydrogen bonds are simultaneously broken, the molecule will jump to a new position in a diffusional process strongly correlated with angular jumps of the protons across the tetrahedral angle. This interpretation justifies why translational diffusion and molecular rotations are strongly related [4] and the temperature dependences of the two measured times $\tau_A$ and $\tau_B$ are so different [17].

This mechanism was already considered by Chen et al. [18] to interpret their results on incoherent quasi-elastic neutron scattering. These authors found a temperature independent characteristic length $l_0$ and, considering the local geometry of protons involved in the hydrogen bonding, they associated $l_0$ with the distance between the proton positions in two adjacent hydrogen bonds.

![Fig. 4. — Relaxation time $\tau_B$ as a function of the shear viscosity $\eta_s$ [3] over temperature.](image-url)
4. Conclusion. — We measured the depolarized light scattering of water in a temperature range extending from 80 °C down to −17 °C, in the supercooled region. The depolarized spectra were analysed for frequency shifts up to 50 cm⁻¹ from the excitation line.

In this frequency range, three main contributions were considered to give the best fit of the experimental spectra. A constant background which is the extrapolation to low frequency of the collision-induced scattering and two Lorentzian lines whose half-widths differ by a factor about four.

Owing to limitations imposed by the experimental technique the narrow line was detectable only in a small temperature range around room temperature. From its HWHM we deduced a relaxation time $\tau_A$ which agrees well with those obtained in dielectric on NMR experiments [6-9]. Our values of $\tau_A$ are also in good agreement with those previously reported by Montrose et al. [11]. This narrow line can then be associated with the rotational motions of water molecules and $\tau_A$ is a rotational diffusion time.

The analysis of the broad line in all the temperature range studied (80 → −17 °C) revealed a faster process with a characteristic time $\tau_B$ which shows an Arrhenius temperature dependence. We deduced an activation energy $E_B = 2.7$ kcal/mole which is in good agreement with the values 3.0 and 2.5 kcal/mole given, respectively, by Montrose et al. [11] and Danninger and Zundel [12], in the normal temperature range. Moreover, those values agree with the value obtained by Walrafen [16], from Raman spectroscopy, for the formation and breaking of hydrogen bonds between water molecules.

Therefore, this broad Lorentzian component can be associated with the fluctuations in the anisotropy of the polarizability arising from the breaking and formation of the H-bonds. In this case $\tau_B$ is the average lifetime of H-bonds in water.

Further support to this interpretation is given by the feature that $\tau_B$ extrapolates at infinite temperature to the characteristic time of librational motions in water. A simple mechanism of angular jump across the tetrahedral angle can be foreseen, which is supported by recent measurements on incoherent quasielastic neutron scattering [18].

Acknowledgments. — We are very grateful to C.A. Angell for his suggestions and fruitful discussions. We would like to thank J. Rouch for giving us some facilities which made possible this experiment. One of us (O.C.) wishes to express thanks to the Instituto Nacional de Investigação Científica, Lisbon, for a maintenance grant.

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