

Dynamical structure of water: Low-frequency Raman scattering from a disordered network and aggregates

J. L. Rousset, E. Duval, and A. Boukenter

Laboratoire de Physicochimie des Matériaux Luminescents, UA 442 du CNRS—Université Lyon I, 69622 Villeurbanne, France

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Low-frequency inelastic light scattering of water is observed from a temperature equal to 80 down to -20°C in the supercooled regime. For energies higher than 3 cm^{-1} it is shown that the major part of the light scattering is Raman scattering. A broadband with a maximum at 50 cm^{-1} is interpreted as scattering from transverse acoustic modes of a disordered network. A weaker scattering which shifts towards the Rayleigh line when the temperature decreases is well explained by Raman scattering from the oscillations of water molecule aggregates which grow when the temperature decreases.

I. INTRODUCTION

The structure and dynamics of water are still a matter of numerous theoretical and experimental studies, because their knowledge is capital in chemistry, biology, geophysics, and correlatively because of the anomalous properties of this vital liquid. These so-called properties are well described in different review articles.¹ Examples of such anomalies are the density maximum above the freezing point; the minimum in the compressibility at 46°C and its rapid rise below 0°C ; the constant-pressure heat capacity which increases by about a factor 2 within the measured supercooled range; the shear viscosity which is strongly non-Arrhenius and changes rapidly with temperature.

Most of the models, in order to interpret the anomalies, assume the coexistence of two states of water. The less compact structure would develop down to a temperature lower than -35°C . The spinodal model of Speedy and Angell² and that of Stillinger of cage-like polyhedra in a random network, or that of Speedy³ of self-replicating pentagons predict a divergence of the correlation length of density fluctuation or of the size of the noncompact network at a critical temperature $T_s = -45^{\circ}\text{C}$. Stanley and Teixeira (S.T.)⁴ show in their model that water is above its bond percolation threshold. In the thermally broken percolation network, low density open structure or "patches" of four H-bonded molecules grow when the temperature decreases. The S.T. model does not predict a critical temperature. However the authors do not exclude a percolation of the species-4 oxygen atoms.

The scattering techniques (neutrons, x ray or light) would be able to show the existence of the low-density aggregates of water molecules. The obtained experimental results are not very convincing.⁵ However after examination of the experimental results from depolarized Rayleigh scattering,⁶⁻⁹ the treatment of the data and the conclusions of these experiments have to be called in question again. The problem is the discrimination between depolarized Rayleigh scattering and low-frequency Raman scattering. In the case of water it is thought that Raman scattering is non-negligible down to less than 3 cm^{-1} from the Rayleigh line.

In the work which is presented in this paper the Raman scattering of water was studied from ideas developed to in-

terpret the low-frequency scattering from nucleated glasses¹⁰ and gels.¹¹⁻¹⁴ The origin of this study by nonspecialists of liquids is the comparison between the low-frequency Raman scattering of a wet silica-gel and water. The Raman scattering of the gel was dominated by the scattering of water, and the scattering of water was not very different of the scattering of a gel. From a gel or rather an aerogel which is constituted of aggregates of noncompacted silica particles one observes the Raman scattering by the surface vibration of silica particles.^{12,13} The frequency of these vibrations is proportional to the inverse of the size of particles.¹⁰ New measurements of low-frequency Raman scattering were carried out to test the model of Raman scattering from aggregates of water molecules.

II. EXPERIMENTAL

The experimental configuration to observe Raman scattering from a sample was conventional. The incident light was emitted from an argon laser. The 5145 \AA line was principally used. The power of the beam laser varied between 100 and 300 mW. A Jobin-Yvon model U1000 double monochromator and a photon counting system were used to analyze the scattered light.

Water samples in ampoules of 2, 5, or 10 cm^3 were provided by the laboratoire Aguetant. The water for medical application, filtered and doubly distilled, was supercooled in a cryostat down to -22°C . Ampoules embedded in a copper block, were cooled with a flow of cold helium gas. The temperature was measured with a linear temperature resistance placed very close to the sample.

III. RESULTS AND DISCUSSION

The problem with the inelastic low-frequency scattering is to discriminate the Raman scattering from the depolarized Rayleigh scattering. In other words sometimes it can be difficult to know if the motion which is responsible of the inelastic scattering is quantified or not. The problem can be simplified when the Raman scattering is polarized. In this case the low-frequency depolarized scattering can be considered as a Rayleigh scattering. It is certainly not true for water.⁶⁻⁹ Indeed in the Raman spectrum of water there exists a broad

band with a maximum at 50 cm^{-1} which spreads down to the foot of the Rayleigh line. The intensity $I(\omega)$ of Raman scattering is proportional to the Bose factor $n(\omega)$ for anti-Stokes and $n(\omega) + 1$ for Stokes scattering. In Fig. 1 the reduced intensity $I(\omega)/n(\omega) + 1$ at low energy ($3\text{--}180 \text{ cm}^{-1}$) is represented, for different temperatures, between 80 and -20°C . One observes that the broad band at 50 cm^{-1} is roughly temperature independent. On the contrary, a bump on the low-energy wing of the broadband shifts towards the Rayleigh line when the temperature decreases. Below -10°C it appears as a broadening of the Rayleigh line.

not change with temperature, the position of the less intense band, which is temperature dependent, is obtained by subtracting the broadband at -20°C without the broadening at the foot of the Rayleigh line. From the evolution of the reduced intensity with temperature it is clear that the principal part of this very low-energy broadening at -20°C comes from the high-energy wing of the weak temperature dependent band. This justifies the used procedure. It was impossible to determine with precision the position of the temperature dependent band at temperatures less than -5°C , although the shift of this band was observed below -5°C (Fig. 1).

The position of the temperature dependent band is plotted in Fig. 2 against the temperature $T(^{\circ}\text{C})$. It appears linear in temperature. By extrapolation, the band would be at $\omega = 0$ for $T \approx -30^\circ\text{C}$.

Before to interpret the experimental results, our analysis of the inelastic low-frequency light scattering has to be justified, in particular because it is different from that used by other authors.⁶⁻⁹ In the previous works the low frequency depolarized scattering was decomposed into a constant signal and two Lorentzian broadenings of the Rayleigh line. The narrower broadening, with a correlation time larger than one picosecond, was attributed to the orientational motion of water molecules. The water broadening, with a correlation time shorter than 1 ps , was assigned to fluctuations in the anisotropy of the molecular polarizability associated with the formation (and breaking) of hydrogen bonds between water molecules. The shorter correlation time which would correspond to the lifetime of hydrogen bonds had an Arrhenius temperature variation: $\exp -E/kt$ with $E \approx 3$ or 2.5 kcal/mol . The energy E would be the energy of the hydrogen bond.

Our experiments show that such an analysis is not correct. (1) As the depolarized Rayleigh scattering, the Raman broadband at 50 cm^{-1} is depolarized. Therefore the Raman scattering is not eliminated in the depolarized scattering. (2) The Raman broadband (50 cm^{-1}) spreads down to the Rayleigh line as seen in Fig. 1. This behavior is confirmed by the inelastic low-frequency neutron scattering.⁵ Consequently the Rayleigh broadening is not obtained by subtracting a constant signal. (3) The temperature dependent band does not correspond to Lorentzian broadening of the Rayleigh line. In Fig. 3 the scattered intensity at 20°C is compared to the reduced intensity at -20°C without the broadening at the foot of the Rayleigh line (seen on the reduced intensity) multiplied by the Bose factor $n(\omega) + 1$. The dif-

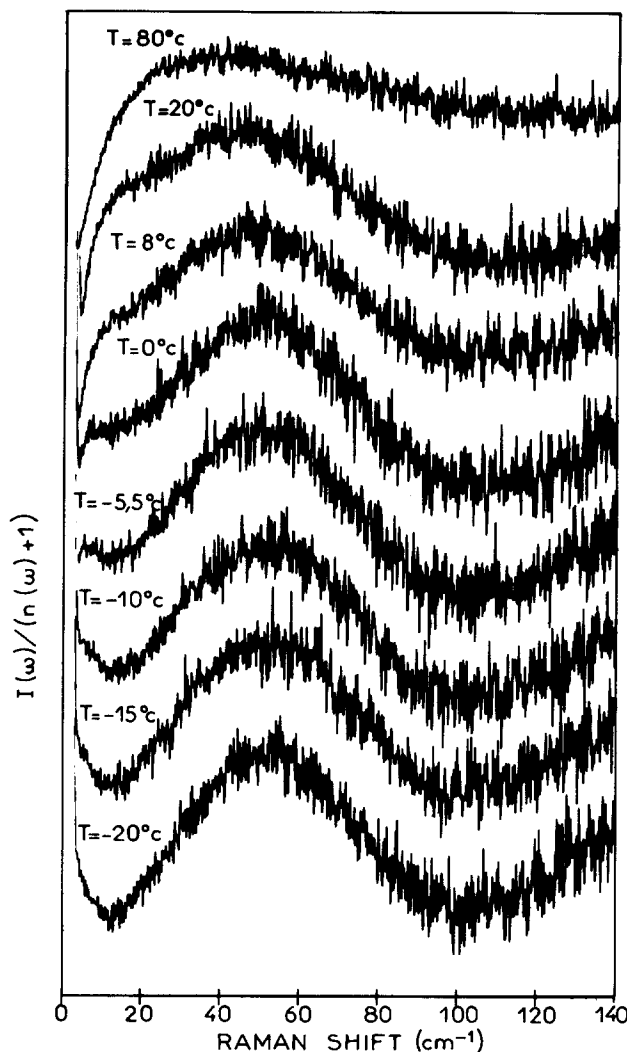


FIG. 1. Reduced intensities $I(\omega)/n(\omega) + 1$ of low frequency Raman scattering from water at different temperatures.

ference between these two spectra gives the nonreduced intensity of the temperature dependent band. From Fig. 3, it is clear that the spectrum resulting from the difference is not a Lorentzian broadening of the Rayleigh line, since it presents a maximum at about 7 cm^{-1} . This maximum is an indica-

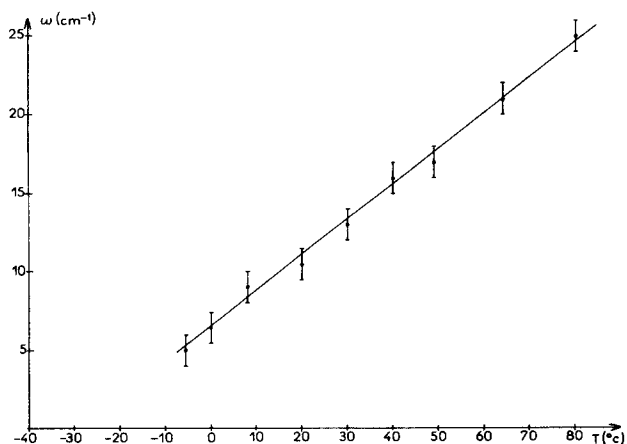


FIG. 2. Energy of the less intense Raman scattering band against the temperature T .

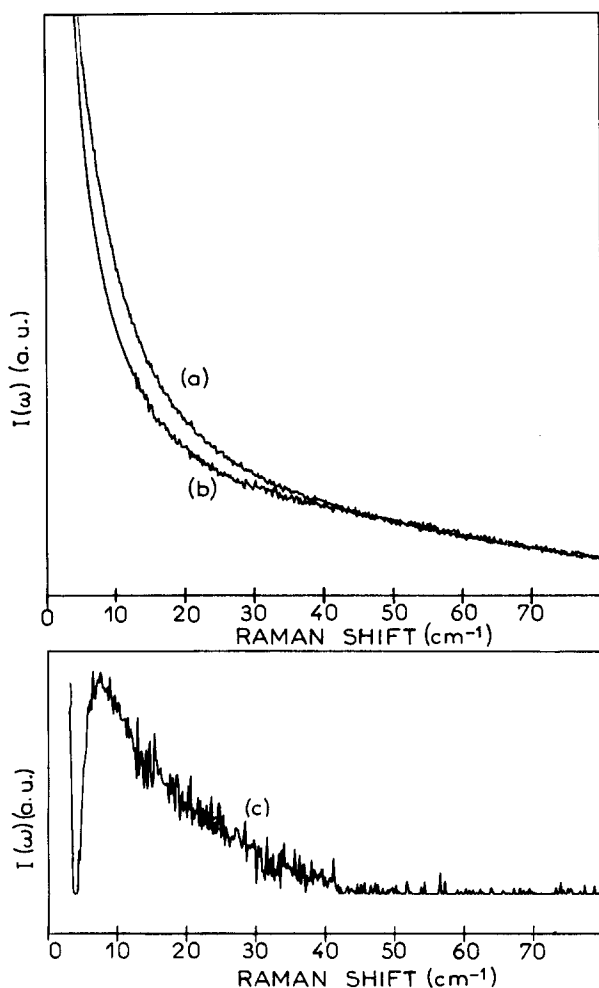


FIG. 3. Comparison between the Raman scattering intensity (nonreduced) at 20 °C (a), and the temperature independent broadband (b). Curve (b) is obtained by multiplying the reduced intensity at -20 °C minus the broadening at the foot of the Rayleigh line (Fig. 1) by the Bose factor $n(\omega) + 1$. Curve (c) which is the difference between (a) and (b) corresponds to the temperature dependent Raman band (nonreduced).

tion that the temperature dependent scattering is a Raman scattering.

Mazzacurati and Benassi¹⁶ observed the light scattering at very low energy by using a Fabry-Pérot interferometer. There is a good agreement between their and our experimental results. Furthermore with their data a maximum at $2.5 \pm 0.5 \text{ cm}^{-1}$ is evinced for the Raman reduced intensity at the temperature of -14 °C. This supplementary experimental point is very well situated on the straight line drawn in Fig. 2. However, Mazzacurati and Benassi fitted the low-frequency light scattering with two Lorentzian lines, one which is temperature dependent and the other nondependent, plus a flat background which decreases with the energy. Such a fitting is qualitatively not very different from that used by other authors,⁶⁻⁹ although the interpretations differ.

Aliotta *et al.*¹⁷ fit their observed low-energy light scattering with two Lorentzian curves plus a Raman contribution reflecting the low-energy vibrational spectral density. The Raman contribution is constituted not only of two broad bands centered at about 60 and 190 cm^{-1} but also of a low-frequency Raman scattering which is reminiscent of our

temperature dependent low-frequency Raman scattering.

An experimental confirmation of the low-frequency vibrational band is the presence of a shoulder around 10 cm^{-1} at 20 °C in the far-infrared absorption observed by Hasted *et al.*¹⁸ Recent measurements by millimeter laser spectroscopy confirmed the presence of this low-energy absorption.¹⁹

However, it is likely that it exists, in addition to the two low-frequency Raman bands (temperature dependent and independent), a narrower broadening of the Rayleigh line corresponding to the molecular motion, as assumed in the previous light scattering experiments^{6-9,16,17} and observed in quasielastic incoherent neutron scattering.²⁰ This broadening is too narrow to be measured with sufficient precision (correlation time larger than 1 ps).

After subtraction of a background, which would be due to the collision-induced light scattering, Walrafen *et al.*²¹ fitted the low-frequency Raman scattering, up to 300 cm^{-1} , with three Gaussian broadbands at 50, 70, and 180 cm^{-1} , respectively. Our experimental results (Fig. 1) can be fitted without the broad band at 70 cm^{-1} .

IV. INTERPRETATION OF THE LOW-FREQUENCY RAMAN SCATTERING

The interpretation of the temperature independent broadband has to be consistent with that of the temperature dependent weaker band.

A. Raman broadband at 50 cm^{-1}

The maximum at 50 cm^{-1} was often attributed to the flexing motion of the 0-0-0 units.²² It is not possible to interpret the broadband as a broadening of a peak at 50 cm^{-1} broadened by a distribution of the 0-0-0 angles. Now if we consider the infrared or Raman spectra of disordered ice crystals,²³ and the inelastic neutron scattering from normal ice,²⁴ a band appears in the vibrational spectrum with a maximum at 50 cm^{-1} . This band is attributed to transverse acoustic modes.²³ The local structure of liquid water is close to that of hexagonal ice⁵ and it is likely that the upper limit of the transverse acoustic modes corresponds to the flexing motion of the 0-0-0 units.

In Sec. I, the similarity of the low frequency Raman scattering of water and a glass or a gel was noticed. In our opinion this similarity is not accidental. At a given time the disordered network of liquid water is related to the crystal of ice in a similar manner as the network of a glass to the corresponding crystal. Obviously the disordered network of water transforms in an approximate time of 1 ps (at room temperature). As in a glass (or a gel),²⁵ in water the light is Raman scattered from acoustic modes localized by the disorder. This explains why, in the Raman scattering of water, there exists a broad band which spreads down to the Rayleigh line. The maximum at 50 cm^{-1} corresponds to the upper frequency limit of the transverse acoustic modes. As already noticed this broad band is well confirmed by low-frequency neutron scattering,⁵ and also by infrared absorption.¹⁶

The interpretation of the low frequency light scattering by a Raman scattering is very realistic after the calculation of Madden and Impey.²⁶ The simulation given by these authors of the Raman scattering associated with the motion of

the molecular center of mass through the polarizability induced by dipole-dipole interaction between the water molecules account for the Raman broadband at 50 cm^{-1} . The mechanism of dipole-induced-dipole has been much developed by the Italian specialists of water²⁷⁻²⁹ to interpret the Raman light scattering.

B. Temperature dependent low-frequency Raman scattering

In the disordered network, responsible of the Raman broadband with a maximum at 50 cm^{-1} , there exists species which vibrate at a frequency which decrease with the temperature. For researchers who study the Raman scattering from the global oscillations of nuclei in glasses¹⁰ or of silica particles in aerogels,^{12,13} the first hypothesis which occurs is that the low-frequency temperature dependent Raman scattering comes from oscillations of transient water aggregates with a structure which is different from that of the disordered network. It was shown^{10,14} that the frequency ω_o of the surface vibrations of heterogeneities is correlated to the size $2a$ of scattering species:

$$\omega_o = S \frac{v}{2a} \quad (1)$$

where v is the sound velocity in the material of heterogeneities and S a shape factor.

Obviously the frequency decreases as the size $2a$ increases. It is difficult to deduce this size, because we do not know the sound velocity v and the shape factor S . However, a crude estimation can be obtained by the following simple argument. The frequency ω_o of the surface vibration modes depends directly on the strength of the hydrogen bond. As suggested above the maximum at 50 cm^{-1} corresponds to the upper limit of the transverse acoustic modes. Then, it is assumed that the frequency $\omega_o = 50\text{ cm}^{-1}$ is related to a size $2a$ which is equal to the distance between nearest neighbor oxygen O-O, i.e., 2.7 \AA . According to the expression (1), the size $2a$ is inversely proportional to the frequency ω_o . From this consideration the size of the aggregates would increase from 11 \AA at $20\text{ }^\circ\text{C}$ up to 27 \AA at $-5.5\text{ }^\circ\text{C}$.

From small angle x-ray scattering (SAXS) Bosio *et al.*³⁰ deduced, using the Orstein-Zernike theory, a correlation length equal to about 8 \AA at $-20\text{ }^\circ\text{C}$. In the case of monodisperse clusters the relation between the diameter $2a$ and the Orstein-Zernike correlation length ξ would be $2a = 2\sqrt{5}\xi$.³¹ Therefore from SAXS it would be found $2a = 36\text{ \AA}$ at $-20\text{ }^\circ\text{C}$. It is very satisfying to find such an agreement between SAXS and Raman scattering.

Figure 1 shows that the maximum ω_o continue to shift towards the Rayleigh line between -5 and $-20\text{ }^\circ\text{C}$. At the lowest temperature at which water is still in a supercooled state ω_o is less than 3 cm^{-1} and the size $2a$ of the aggregates would be larger than 45 \AA . However the Raman experiments do not allow to conclude that the size diverges at a lower critical temperature,² although the results do not disagree with such a possibility.

V. CONCLUSION

The low frequency inelastic light scattering from water, in the supercooled regime, down to 3 cm^{-1} is a Raman scat-

tering. The broadband with a maximum at 50 cm^{-1} corresponds to the scattering from transverse acoustical modes in a disordered network of hydrogen bonded water molecules. The less intense temperature dependent band corresponds to the scattering from oscillations of water aggregates with a lower density than that of the disordered network. The position of this band is linear with temperature T and shifts towards the Rayleigh line. In the frame of this interpretation the frequency of this band is inversely proportional to the aggregate size. In the temperature domain of observation the size of aggregates would vary as $1/T - T_0$, with T_0 close to $-30\text{ }^\circ\text{C}$. But our experiments do not allow to claim that T_0 is a critical temperature at which the size diverges, all the more if this critical temperature exists, it would be closer to $-45\text{ }^\circ\text{C}$.^{2,3} Obviously the disordered network and the aggregates are transient, and transform by exchange of water molecules to give a new identical structure.

Our experimental results show clearly the double structure of water. They are in agreement with the models in which the coexistence of two transient states of water is postulated.^{2,3,4,32} More precise results in the supercooled regime will be obtained with a monochromator of better resolution. Very low Raman scattering and depolarized broadening of the Rayleigh line will be observed at energies less than 3 cm^{-1} .

Note added in proof: A recent analysis of G. E. WaPrafen [to be published in *Hydrogen-Bonded Liquids*, NATO ASI, edited by J. C. Dore and J. Teixeira (Kluwer Academic, Dordrecht, 1990)] based on elasticity, results in the transverse acoustic character of the band at 50 cm^{-1} , in agreement with our interpretation.

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