

# Effect of microscopic NaCl impurities on clustering dynamics in liquid water: low-frequency Raman spectroscopy

A. V. Baranov, V. I. Petrov, and A. V. Fedorov

*S. I. Vavilov State Optics Institute, 199034, St. Petersburg, Russia*

G. M. Chernyakov

*S. M. Kirov Military Medical Academy, 194175, St. Petersburg, Russia*

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The temperature dependence of the characteristics of the elastic-vibration band of water clusters in the spectra of low-frequency Raman scattering of water and aqueous solutions of NaCl has been studied. The size of the clusters is estimated as a function of the temperature (0–99 °C). The NaCl has a pronounced destructive effect on the clustering process even at a concentration of  $10^{-5}$  M. This effect apparently occurs only above a threshold concentration. This threshold may be considerably lower than the concentrations used in these experiments.

Most existing models of the structure of liquid water assume that two distinct phases of the water are present simultaneously: a disordered network of weakly interacting molecules and groups of several molecules bound by hydrogen bonds. That groups are present is demonstrated by experimental data on Raman scattering. Those results reveal (a) bands at  $\sim 50$  and  $\sim 175$   $\text{cm}^{-1}$ , which are attributed to vibrations of oxygen atoms bound by hydrogen bonds, and (b) a component at  $\sim 3200$   $\text{cm}^{-1}$  of the broad band at  $3200$ – $3400$   $\text{cm}^{-1}$ , which is attributed to OH vibrations of water molecules in groups.<sup>1,2</sup> The interpretation of the two latter bands is based for the most part on the temperature dependence of their characteristics,<sup>1</sup> but the band at  $\sim 50$   $\text{cm}^{-1}$  has essentially no temperature dependence.<sup>2,3</sup> There has also been active research on how impurities of various salts affect the positions, widths, and amplitudes of these bands. However, real changes in the characteristics of the lines at 175 and 3200  $\text{cm}^{-1}$  have been detected only at extremely high salt concentrations: 0.1–3.0 M in Raman spectra<sup>4</sup> and  $\sim 0.05$  M in the spectra of polarized Raman group scattering of the band at<sup>5</sup> 3200  $\text{cm}^{-1}$ .

Rousset *et al.*<sup>3</sup> have recently shown that the 50- $\text{cm}^{-1}$  band has a slight low-frequency knee which shrinks linearly with decreasing temperature. By analogy with the low-frequency Raman spectra of glasses and gels, this low-frequency knee has been attributed to transverse acoustic vibrations of dynamic molecular clusters of water, whose size increases with decreasing temperature. The 50- $\text{cm}^{-1}$  band has been interpreted as the upper limit of a transverse acoustic mode of a disordered network of hydrogen bonds corresponding to a correlation length equal to the distance between neighboring O–O atoms.

Our purpose in the present study was to find the temperature dependence of the

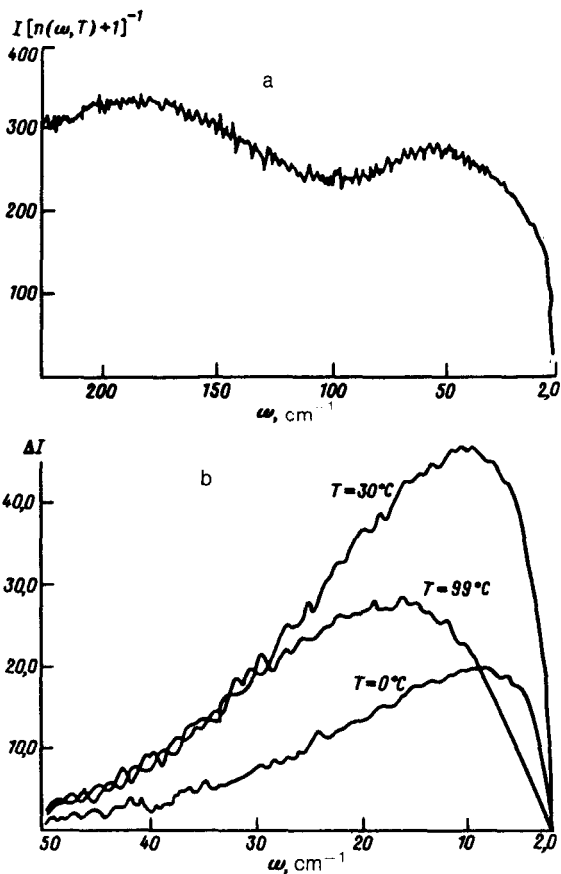


FIG. 1. a—Fragment of a Raman spectrum of water normalized by the Bose-Einstein factor; b—difference Raman spectra corresponding to the elastic-vibration band of water clusters at  $T = 0, 30,$  and  $99^\circ\text{C}$ .

frequency and the integral intensity of the low-frequency knee in the Raman spectra of pure water and of aqueous solutions of NaCl with concentrations of  $10^{-1}$  and  $10^{-5}$  M.

We studied gas-free doubly distilled water. The NaCl used to prepare the solutions was graded "for spectral analysis." A hermetically sealed cell holding the water was placed in a constant-temperature chamber. The temperature could be adjusted over the range  $0\text{--}99^\circ\text{C}$  within  $0.1^\circ\text{C}$ .

The depolarized component of the linearly polarized light at  $514.5$  nm from a  $70\text{-mW}$  argon laser, scattered through  $90^\circ$ , was analyzed. We used a DFS-52 spectral instrument with a  $2\text{-cm}^{-1}$  slit. The spectra were recorded under repeated-scanning conditions (20 scans). The time taken to record a spectrum was  $\sim 1$  h.

Figure 1a illustrates the results with a fragment ( $2\text{--}225\text{ cm}^{-1}$ ) of the Raman spectrum of water at  $10^\circ\text{C}$ , normalized by the Bose-Einstein factor:  $[n(\omega, T) + 1]$ , where  $n(\omega, T) = [\exp(\hbar\omega/T) - 1]^{-1}$ ,  $\omega$  is the Stokes frequency, and  $T$  is the absolute temperature. This spectrum agrees qualitatively with the corresponding spectra reported in Ref. 3: Against the background of the wing of the  $175\text{-cm}^{-1}$  band there is a

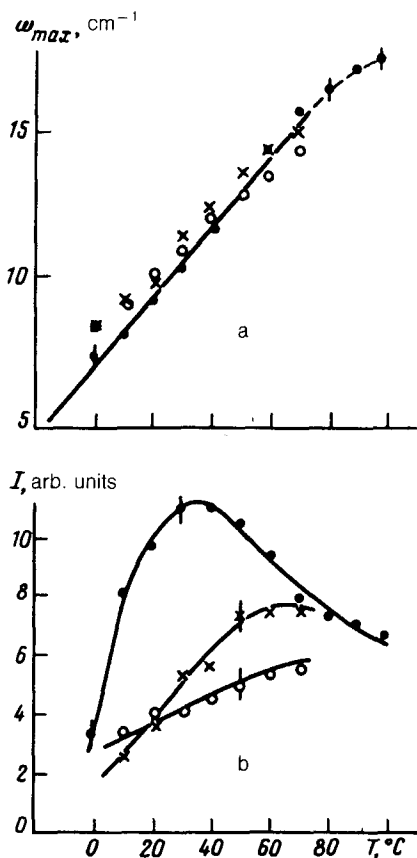


FIG. 2. Temperature dependence of (a) the position of the peak of the low-frequency knee ( $\omega_{max}$ ) and (b) the integral intensity  $I$  of this knee. Filled circles—Pure water; crosses—NaCl solution with  $C=10^{-5}$  M; open circles—NaCl solution with  $C=10^{-1}$  M. The curves are drawn to aid the eye.

broad band at  $50 \text{ cm}^{-1}$ . On the low-frequency side of this band is the low-frequency knee corresponding to transverse acoustic vibrations of water clusters. Similar spectra were found for the water and for the NaCl solutions at other temperatures.

To single out the low-frequency knee, we subtracted from the experimental spectra a theoretical spectrum whose band near  $50 \text{ cm}^{-1}$  was approximated by a damped Lorentzian:

$$I(\omega) = \omega_0^2 \omega \Gamma / [(\omega^2 - \omega_0^2)^2 + \omega^2 \Gamma^2], \quad (1)$$

where  $\omega_0 = 60 \text{ cm}^{-1}$  and  $\Gamma = 70 \text{ cm}^{-1}$ , and whose band at  $175 \text{ cm}^{-1}$  was approximated by a Gaussian with temperature-dependent parameters. These parameters and also the relative amplitudes of the lines were found by fitting calculated spectra to the experimental spectra in the region  $60\text{--}250 \text{ cm}^{-1}$ .

Figure 1 shows difference spectra corresponding to the elastic-vibration band of clusters in pure water for 0, 30, and  $99^{\circ}\text{C}$ . Figure 2 shows the temperature dependence of the position of the peak ( $\omega_{max}$ ) and the integral intensity  $I$  of the low-frequency knee for pure water and the NaCl solutions, respectively.

The plot of  $\omega_{\max}(T)$  for water at  $T < 80^\circ\text{C}$  is approximately linear. This result agrees with the data of Ref. 3, although in our case the slope of the straight line is smaller by a factor of about 1.5. At  $T > 80^\circ\text{C}$ , saturation sets in with  $\omega_{\max} \approx 18 \text{ cm}^{-1}$  at  $T = 99^\circ\text{C}$ . As in Ref. 3, we compare the change in  $\omega_{\max}$  with the change in the size of the water clusters by using the relation  $\omega_{\max} = Sv/2\bar{a}$ , where  $v$  is the transverse sound velocity,  $\bar{a}$  is the average size, and the coefficient  $S$  depends on the shape of the clusters. The product  $Sv$  can be estimated by working from measurements<sup>3</sup> of the size of the inhomogeneities ( $2\bar{a} = 36 \text{ \AA}$ ) in supercooled ( $-20^\circ\text{C}$ ) water found by small-angle x-ray scattering, under the assumption of a linear  $\omega_{\max}(T)$  dependence at low temperatures and under the further assumption that the scattering centers are of the same nature. In this case it follows from our data that the sizes of the water clusters range from  $24 \text{ \AA}$  at  $0^\circ\text{C}$  to  $10 \text{ \AA}$  at  $99^\circ\text{C}$ . As the temperature is raised to the boiling point, the clusters do not disappear; they tend toward a minimum size corresponding to two or three O—O bonds — possibly five-molecule bonds.<sup>1</sup> This conclusion agrees with the presence of a fairly intense component at  $\sim 3200 \text{ cm}^{-1}$ , which is associated with OH vibrations of associated water at high temperatures.<sup>1</sup> The  $\omega_{\max}(T)$  dependence for the solutions varies only slightly with their concentration and is approximately the same as  $\omega_{\max}(T)$  for the pure water; there is some tendency for the slope of the straight line to decrease with increasing concentration. On the other hand, the magnitude and shape of  $I(T)$  for pure water are sharply different from those for the solutions. The presence of the peak in  $I(T)$  for water is evidence that the concentration of dynamic clusters has an extremum at  $30\text{--}40^\circ\text{C}$ . When the temperature is raised further, the size of the clusters decreases, and there is furthermore a decrease in the fraction of the volume of the water which these clusters represent.

The ions in the aqueous solutions cause sharp changes in the dynamics of the clustering: The intensity increases monotonically, with some tendency toward saturation at high temperatures. The decrease in the integral intensity upon the addition of the salt shows that the ions destroy the clusters which form in pure water; *i.e.*, the ions act in the same direction as a temperature increase. At low temperatures, where the clusters are stablest, the destructive effect of the ions is at its greatest. As the temperature is raised, the ion component of the destruction decreases, explaining why the intensities of the low-frequency knee in pure water and the solutions move closer together at high temperatures. The observed effect was detected at a salt concentration  $\sim 10^{-5}\text{M}$  (one molecule of NaCl per  $\sim 5.5 \times 10^6$  molecules of  $\text{H}_2\text{O}$ ). An increase in the concentration does not lead to a corresponding change in the scattering intensity, nor does it cause any qualitative change in the temperature dependence of this intensity. The effect apparently requires a threshold concentration. We do not rule out the possibility that the threshold NaCl concentration is much lower than the concentrations used in the present experiments.

At this stage of the study it is difficult to suggest a well-grounded mechanism for the effect of the ions on the dynamics of clustering in pure water. There is the possibility that the picture will be clarified by research which we are presently carrying out on the concentration dependence of the Raman spectra of aqueous solutions with lower salt concentrations and on how these spectra are affected by particular anions and cations.

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