

Evolution of the spectral component of ice in the OH band of water at temperatures from 13 to 99 °C

S.M. Pershin, A.F. Bunkin, V.A. Luk'yanchenko

Abstract. It is established for the first time by Raman scattering of second-harmonic pulses of an Nd:YAG laser that there are molecular complexes with frequencies of ~ 3600 , ~ 3450 , and ~ 3200 cm^{-1} (which are characteristic of dimers, tetramers, and ice-like hexamers observed in H_2O molecular beams) in water at temperatures of 13–99 °C. The frequency of the ice hexameric component is found to shift only slightly with an increase in the water temperature, whereas its contribution decreases but remains significant, with a simultaneous increase in the contribution of small complexes.

Keywords: Raman spectroscopy of water, OH-band envelope, ice-like hexameric complexes of H_2O molecules.

The mixed two-liquid model of water suggests the existence of ice-like hydrogen-bound molecular complexes [1–3]. It has been recently established [4, 5] that, when recording a Raman spectrum of the water OH band, a decrease in the averaging time or the sampling interval up to the pulse width (10 ns) leads to significant fluctuations of the band envelope, which manifest themselves in a periodic shift of its centre by ± 50 cm^{-1} . A sample of the spectra with a centre shifted to lower frequencies yields an OH-band envelope for bulk ice [4]. This coincidence indicates the existence of ice-like complexes in water at room temperature. Recently, ice nanolayers were found to form on a graphite substrate at room temperature [6]. Small-angle synchrotron X-ray scattering spectroscopy [7] of bulk water revealed components that are characteristic of bulk ice.

Previously [8] we observed spectral components corresponding to ice and small complexes (which were also found in H_2O molecular beams [9]) in the Raman spectra of water, using the statistics of fractional moments [10] when averaging spectra over 100 laser pulses at room temperature.

However, it remained unclear how the amplitude ratio of these components should behave with a change in water temperature. Obviously, water heating must be accompanied by destruction of ice-like clusters and increase in the number of small clusters. Then, if the spectral component at

~ 3200 cm^{-1} is due to ice-like complexes, it is natural to expect it to decrease in amplitude simultaneously with an increase in the amplitude of the components of tetramers (~ 3450 cm^{-1}) and other small clusters. The purpose of this study was to establish such peculiarities.

The experiment was performed on a Raman spectrometer using 10-ns second-harmonic (532 nm) pulses of the Nd:YAG laser. The pulse energy did not exceed ~ 1 mJ, a value corresponding to the beam intensity of no more than 500 MW cm^{-2} in the focal region of a lens with a 7-cm focal length. The backscattered Raman light was focused onto the slit of an MS 260i polychromator. The Raman spectrum was amplified by a gated electro-optic Andor iStar ICCD camera (ICCD-3161) and recorded by a cooled CCD array. The spectral resolution of the instrument at a typical entrance slit width of 25 μm was 0.2 nm (5.7 cm^{-1}). The spectrograph scale in the range of the Stokes shift (600–670 nm) was calibrated to the neon lines of gas discharge.

The object of study was as-prepared distilled water. It was poured into a quartz cylindrical cell, which was then placed in a heating furnace. The temperature was measured by a precise thermometer with a resolution of 0.1 °C. The measurements were performed under the same conditions both upon heating and cooling the water. Spectra were recorded for each laser pulse at a pulse repetition rate of 5 Hz, and then summed over samples of 100, 1000, or 5000 pulses. The fluctuations of water temperature during measurements did not exceed ± 0.3 °C at temperatures close to room temperature and increased to ± 0.4 °C when approaching the boiling temperature. After reaching 99 °C the voltage across the heater was reduced discretely to make it possible to measure the OH-band spectrum upon water cooling. To obtain a higher cooling rate at temperatures close to room temperature, we used forced cooling with a fan.

The physical meaning of the approach proposed to analyse experimental data is as follows. The smoothed spectral component of the water OH band reflects the frequency distribution of OH oscillators, whose lifetime is determined by the hydrogen bond switching time (~ 100 fs) [1–3]; it is much shorter than the spectrum measurement time. Then, during the time equal to the laser pulse width (10 ns) a proton undergoes 10^4 – 10^5 jumps between molecules along the hydrogen bond direction and thus ensures time averaging of the spectrum for unstable complexes. This spectral component corresponds in the best way to the model of continuous frequency distribution of OH oscillators [1–3] and definition of ‘generalised mean’ [8, 10]. Note also that averaging is performed not only over time (i.e., the pulse width and the number pulses) when

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Received 14 July 2010

Kvantovaya Elektronika 40 (12) 1146–1148 (2010)

Translated by Yu.P. Sin'kov

recording a spectrum but also over the ensemble of molecules, the number of which ($\sim 10^{19}$) is determined by the volume of the beam waist in the lens focal region.

The other (difference) spectral OH-band component after subtraction of the smoothed component has an envelope modulated by amplitude fluctuations of OH oscillators and receiver noises. As our preliminary results showed [8], the amplitude fluctuations of OH oscillators are not random. The fundamental difference of the approach under consideration to analysis of experimental data is the rejection of statistical hypotheses about the character of the signal studied [10]. The rejection of these assumptions significantly expands the class of problems to be solved and simplifies the analysis of experimental results.

Figure 1a shows the spectra of the water OH band, averaged over 100 pulses, at temperatures of 13, 45, and 99 °C. It can clearly be seen that an increase in the water temperature from 13 to 99 °C leads to an almost twofold decrease in the Raman signal amplitude and an asymmetric distortion of the band profile. For each averaged spectrum we obtained (using the median smoothing technique [8]) the profile of generalised mean [10], which was then subtracted from the experimental OH-band envelope. In our case the number of median smoothing points ($k = 20 - 23$) was substantiated previously [8].

Figure 1b shows the spectrum of the water OH band at a temperature of 13 °C and the OH-band envelope after median smoothing with $k = 20$. It can be seen that in the profile wings the smoothed envelope is above the experimental spectrum, which has a small bending radius. This difference leads to the formation of portions with a

negative amplitude in the difference spectrum, which are due to the subtraction procedure. Obviously, these negative spectral amplitudes do not have a physical meaning, but the change in the dip shape indicates a change in the contribution of OH oscillators (enrichment, suppression, or depletion) on the wings of the OH-band envelope.

Figure 2a shows the difference spectra of the OH band at temperatures of 13 and 99 °C. The difference spectrum (3), recorded by the same technique as in analysis of the Raman spectrum of bulk ice (symmetry group 1h) [11], is given for comparison. For convenience the water spectra are shifted by a constant value along the ordinate axis. According to the data in Fig. 2a, the dominant component in the bulk ice spectrum has a frequency of 3200 cm^{-1} , which is consistent with the spectrum of hexameric ice-like clusters in H_2O molecular beams [9]. One can also see from Fig. 2a that the amplitude and area of this component decrease with an increase in temperature, but its contribution remains large even at 99 °C. On the contrary, the amplitudes of the components related to small complexes (trimers and dimers) increase. In this case, the high-frequency wing of the OH band is enriched with new components, and its extremum shifts to higher frequencies (vertical bars in Fig. 2a). In addition, the shape and position of the dip minimum in the low-frequency spectral region ($3050 - 3100 \text{ cm}^{-1}$) change with an increase in temperature and at the ice–water transition, which indicates a smaller contribution of low-frequency OH oscillators to the band envelope.

The temperature dependence of the positions of the maxima of ice spectral components (3200 cm^{-1}) and tetra-

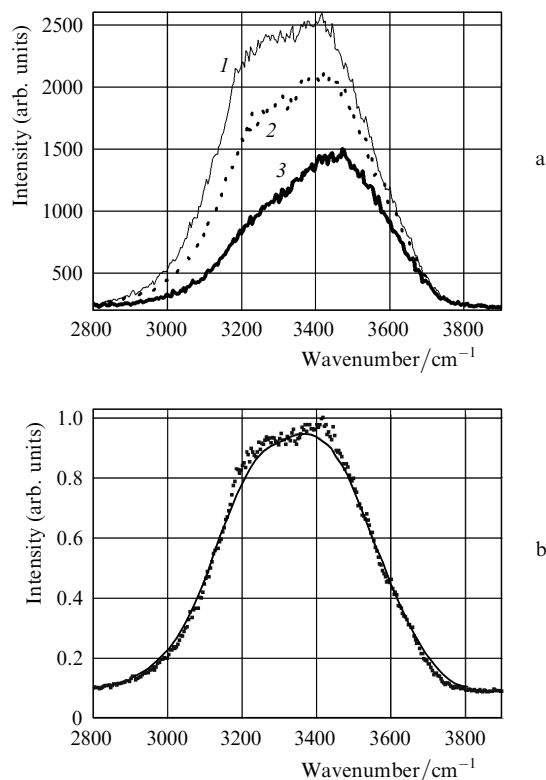


Figure 1. (a) Evolution of the spectrum of the water OH band [measurements at temperatures of (1) 13, (2) 45, and (3) 99 °C] and (b) the experimental (circles) and smoothed (solid line) spectra of the OH band at 13 °C. The data were collected for 100 laser pulses.

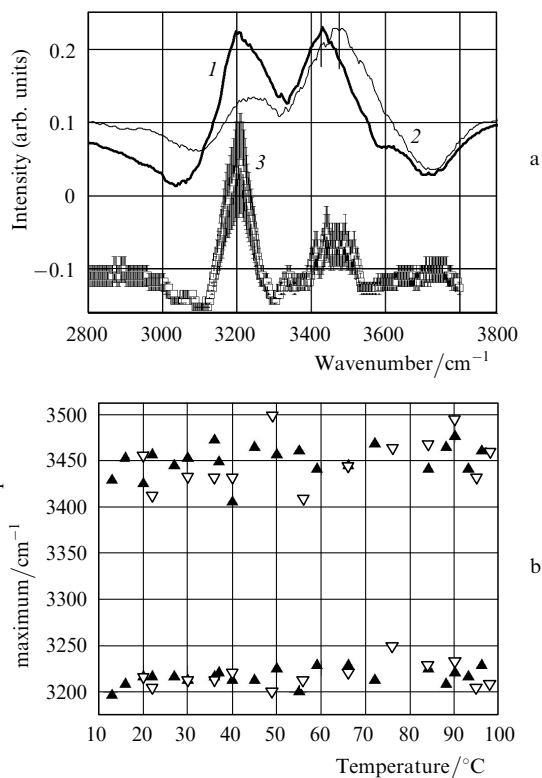


Figure 2. (a) Difference spectra of the OH band (1, 2) for water at temperatures of (1) 13 and (2) 99 °C and (3) for bulk ice and (b) the dependences of the positions of the centres of ice-like (bottom) and tetrameric (top) components upon (\blacktriangle) heating and (∇) cooling.

meric complexes (3450 cm^{-1}) upon water heating and cooling are illustrated in Fig. 2b. Note that water heating and cooling yield similar results. At the same time, the spread in the positions of the component with a frequency of 3450 cm^{-1} significantly exceeds that of the ice component at 3200 cm^{-1} . This is apparently caused by the lower stability of tetrameric complexes and the formation of trimeric ones with a characteristic frequency of 3533 cm^{-1} [9], whose contribution blurs the local minimum (Fig. 2b) in the envelope at a frequency of 3570 cm^{-1} upon heating. It can also be seen that the small-complex component (3450 cm^{-1}) shifts to higher frequencies more rapidly than the ice component. This behaviour is in good agreement with the similar difference observed in the small-angle X-ray scattering (SAXS) experiments [7]. Hence, upon destruction of ice-like hexamers small complexes (trimers and dimers) are formed with a higher probability than tetrameric ones.

To make sure that the features observed are not instrumental [i.e., related to the nonuniform sensitivity of the detector (diode array), short sample (small number of averaging pulses), and high optical field intensity in the lens focus [5]], we guided the spectral signal to another array point by slightly rotating the diffraction grating, increased the sample by a factor of 10–50, and reduced the pump intensity by a factor of 10 (to $2\text{--}5\text{ MW cm}^{-2}$) [5]. In this case, the Raman signal reduced to the noise level (about 200 photocounts per array column), as a result of which spectra with a signal-to-noise ratio $S/N \approx 1$ could be recorded.

The measurements were performed at room temperature of water. The Raman spectra were analysed using the same method of subtracting the generalised mean. Figure 3 shows the difference spectra recorded at sample lengths of 100, 1000, and 5000 pulses (with a repetition rate of 5 Hz). It can be seen that the previously found spectral components are present at all sample lengths. In addition, one can clearly see that at an S/N ratio reduced to unity noise spikes arise in the spectra (peak at a frequency of 3020 cm^{-1} upon averaging over 100 pulses; these spikes were absent at $S/N = 10$ (see Fig. 1). The increase in the number of averaging pulses to 1000 and 5000 leads, as one would expect, to smoothing the noise spikes [for example, the peak at 3020 cm^{-1} ; see Fig. 3, spectrum (3)], which was observed upon averaging over 100 pulses. It is of importance that the position and amplitude ratio of the spectral components did not change in this case.

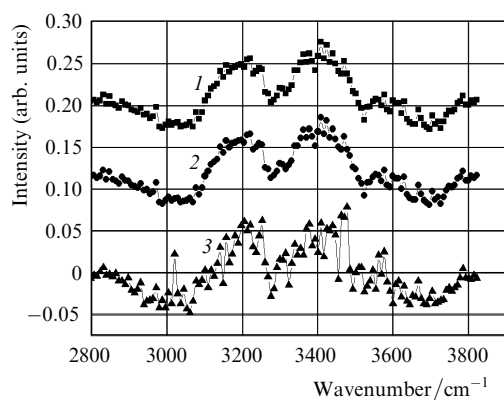


Figure 3. Difference spectra of the OH band at (1) 5000, (2) 1000, and (3) 100 averaging pulses.

Thus, the body of the data obtained suggest that the OH-band spectral components at ~ 3600 , ~ 3450 , and $\sim 3200\text{ cm}^{-1}$ were revealed for the first time by Raman spectroscopy in water; these frequencies are characteristic of, respectively, dimers, tetramers, and ice-like hexamers in H_2O molecular beams. It was established that an increase in the water temperature to 99°C is accompanied by a redistribution of the component amplitudes: a decrease in the amplitude of the ice component at $\sim 3200\text{ cm}^{-1}$ which nevertheless remains significant, with a simultaneous increase in the amplitudes of small-complex components and enrichment of their spectrum. It is of importance that these features are in agreement with the SAXS data for water [7]. The observed components of stable structural forms of the hydrogen-bonded complexes are in dynamic equilibrium at a fixed temperature, when some part of their hydrogen bonds break and recover during measurements, with conservation of the characteristic frequency of OH vibrations.

To the best of our knowledge, we established for the first time that the collective microscopic dynamics (formation and break of hydrogen bonds) of hydrogen-bonded ice-like structures in liquid water manifests itself in Raman spectra in the form of stable spectral components with a frequency of 3200 cm^{-1} , which is related to stretching OH vibrations.

Acknowledgements. This study was supported in part by the Russian Foundation for Basic Research (Grant Nos 07-02-12209, 08-02-00008, and 10-02-90301-V'et_a).

References

1. Franks F. (Ed.) *Water – A Comprehensive Treatise* (New York: Plenum Press, 1972); Eisenberg D., Kausman W. (Eds) *The Structure and Properties of Water* (Oxford: University Press, 1969); Franks F. (Ed.) *Water Science Reviews* (Cambridge: Cambridge University Press, 1985); Frank H.S., Evans M.W. *J. Chem. Phys.*, **13**, 507 (1945).
2. Samoilov O.Ya. *Struktura vodnykh rastvorov elektrolitov* (Structure of Aqueous Electrolyte Solutions) (Moscow: Izd-vo AN SSSR, 1957).
3. Zatsepina G.N. *Fizicheskie svoystva i struktura vody* (Physical Properties and Structure of Water) (Moscow: Izd-vo MGU, 1998).
4. Pershin S. *Phys. Wave Phenomena*, **13** (4), 192 (2005).
5. Pershin S.M. *Laser Phys.*, **16** (7), 1 (2006).
6. Linesh K.B., Frenken J.W.M. *Appl. Phys. Lett.*, **101**, 036101 (2008).
7. Huang C., Wikfeldt K.T., Tokushima T., Nordlund D., Harada Y., Bergmann U., Niebuhr M., Weiss T.M., Horikawa Y., Leetmaa M., Ljungberg M.P., Takahashi O., Lenz A., Ojamae L., Lyubartsev A.P., Shin S., et al. *Proc. Natl. Acad. Sci. USA*, **106** (36), 15214 (2009).
8. Pershin S.M., Bunkin A.F., Luk'yanchenko V.A., Nigmatullin R.R. *Laser Phys. Lett.*, **4** (11), 808 (2007).
9. Buck U., Huiskens F. *Chem. Rev.*, **100**, 3863 (2000).
10. Nigmatullin R.R. *J. Signal Process*, **86**, 2529 (2006).
11. Pershin S.M., Bunkin A.F. *Opt. Spektrosk.*, **85** (2), 209 (1998).