

TWO-LIQUID WATER

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A new physical phenomenon in water, i.e., harmonic oscillations of the centroid of the OH stretching vibration band, was detected. It was found that the oscillation period in distilled water under standard conditions is tens (20–50) of seconds, and the oscillation damping time exceeds 16 min. The physical mechanism of the detected phenomenon is discussed using the two-liquid water model whose application is justified.

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1. Introduction

The subject of this paper is the experimental validation of the hypothesis of independent existence of two liquids in water. Both liquids consist of hydrogen-bonded complexes of H₂O molecules, which exhibit characteristic frequency distributions of OH oscillators and form an integrated envelope of the OH stretching vibration band. An impetus of this study was the fact that we detected the existence of extraordinary slow (with characteristic times of tens of seconds) weakly damping harmonic oscillations of the OH band center in comparison with orientational motions (picoseconds) and hydrogen bond switching (femtoseconds). To our knowledge, an attempt to determine the effect of the existence of two H₂O molecule states (ortho and para spin isomers) in gas on the formation of a solution of two liquids in water is undertaken for the first time.

It is known [1–3] that, in the general case, water vapor is a mixture of independent fractions of ortho and para modifications, transitions between which are strictly forbidden even at collisions

[4–7]. In equilibrium water vapor, the concentration of ortho molecules is three times higher than that of para molecules [3]. Such a difference is caused by the sum of hydrogen nuclei spins, equal to unity (ortho) at parallel and zero (para) at antiparallel hydrogen spin orientations in a molecule. This suggests that para isomers of the water molecule do not rotate in the ground state with rotational quantum number $j=0$. On the contrary, ortho isomers rotate always (and in the ground rotational state ($j=1$) with energy 23.79 cm^{-1}) [3–5].

This difference was put into the basis of the explanation of the mechanism of spin-selective adsorption of para isomers from water vapor passed through a porous material with developed surface [1, 4, 5] and upon the formation of molecular complexes, i.e., H₂O–He and H₂O–CO₂ dimers [2, 3]. Threefold [4, 5] and twofold [8] enrichment of water vapors with ortho isomer molecules at the carbon filter output, as well as above the surface of organic (lysozyme protein and others) and inorganic compounds [9], shows that continuously rotating ortho isomers of the water molecule feature

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a higher mobility, while para molecules are characterized by the higher complexing ability.

It is known that water vapors enriched with ortho spin isomers of water molecules are condensed into liquid and frozen into ice [4,5]. In view of the fact that water belongs to associated liquids with strong intermolecular interaction [10–12] provided by hydrogen bonds, it is reasonable to expect that condensation of vapors enriched with H₂O ortho spin isomers will be accompanied by the formation of hydrogen-bonded complexes. It is still unclear, how the non-equilibrium ortho/para ratio is retained in solid and liquid phases; however, it was reproduced upon repeated evaporation [4,5]. The increased probability of dimer formation from para isomer molecules of water and other gases (H₂O–He, H₂O–CO₂) [2,3] and bonding with the surface [4,5,9] give ground to expect that this selectivity will also appear upon vapor condensation. In this case, hydrogen-bonded complexes involving H₂O para isomers (of the same type or with trapping of gases and impurities from air [2–5,9]) will be formed with higher probability than those with ortho isomers.

The hypothesis of the possible formation of liquids independently from ortho and para spin isomers is supported by the existence of liquid ortho and para hydrogen. These liquids differ by the melting temperature (T) and latent heat of melting (ΔH): $T_o = -254.52^\circ\text{C}$ (ortho H₂) and $T_p = -259.27^\circ\text{C}$ (para H₂); $\Delta H_o = 0.197 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta H_p = 0.117 \text{ kJ}\cdot\text{mol}^{-1}$ [13]. We note that despite the forbiddenness, spin conversion of ortho hydrogen into para hydrogen occurs in the presence of catalyst, which is accompanied by an energy release of $1.4 \text{ kJ}\cdot\text{mol}^{-1}$. Water differs from liquid hydrogen by the existence of hydrogen bonds and a high temperature of the liquid state. Nevertheless, the above facts provide grounds to assume the existence of two independent states of liquid water with long lifetimes and two hydrogen bond types differing by energy. For example, the energy of the hydrogen bond between ortho isomers of molecules which always rotate seems to be lower than between para molecules, a part of which cannot rotate at room temperature.

The existence of strong and weak hydrogen bonds between H₂O molecules [11] also manifests itself in the study of ices. It is known that compression of ices VI/VII/VIII is accompanied by a density increase due to oxygen atom repacking so that new bonds can be formed only “through” stable tetrahedral structures [14,15] with strong hydrogen bonds. We note that the ice I–ice II structural transition was considered in [12, p.49] as a phase transition in the system of H₂O molecule spins. Another fact of the existence of strong and weak hydrogen bonds in water is an increase in the water density to $\sim 2.0 \text{ g}\cdot\text{cm}^{-3}$ under pressure [15]. In this case, it is assumed that some molecular complexes decompose while others retain tetrahedral structures without changes, as in ices [14]. It is important that an increase in the water density manifests itself in distortion of the Raman scattering (RS) spectrum. For example, the amplitude of the low-frequency wing of the OH band increases as pressure increases from 200 to 10000 atm [15]. Such a distortion was recently observed at smaller pressure variations (1–270 atm) [16]. Moreover, the OH-band center shift to the low-frequency wing was observed under water compression in a field of acoustic pulses of moderate intensity [17].

Thus, a decrease in the contribution of the high-frequency wing under water and ice compression [14–17] is a spectral manifestation of breaking of apparently weak hydrogen bonds, as well as a decrease in their concentration and complexes. On the contrary, a reverse distortion of the water OH band is observed upon heating: the contribution of the high-frequency wing increases [18,19] and the band center shifts to the high-frequency region [20]. In this case, it is considered that the hydrogen bond concentration introduced as an order parameter in [21] also decreases. This contradiction is resolved if to assume the existence of strong hydrogen bonds between water para molecules, which stabilize tetrahedral structures under compression [14,15], but are transformed (their concentrations decrease [21]) into weak hydrogen bonds as the temperature (T) increases [18–21]. Since the temperature increase is accompanied by thermal energy kT (k is the Boltzmann constant) redistribu-

tion in degrees of freedom, it is reasonable to expect an increase in the librational vibration amplitude and in the number of rotating molecules [22]. The X-ray diffraction study of water [23] detected a shoulder in the slope of the radial distribution behind the first main maximum in the region of 3.2–3.4 Å. This anomaly was attributed to the manifestation of an ensemble of weakly bound or free molecules in water, which can appear in the ortho modification state.

The possibility of H₂O molecule rotation in water was discussed in [22–25]. For example, the permittivity dispersion and Debye relaxation were calculated in [24] on the basis of the model of water consisting of two independent fractions. In this case, one of liquids in this model is enriched with rotators and features increased mobility. In [22], basing on optical measurements, it was proposed to expand the RS spectrum in two components, which reflect the existence of low- and high-temperature molecules. It was assumed [22] that the latter are uniaxial rotators. However, no reports on direct observation of rotational motion of molecules in water were published.

Recently [26, 27], rotational resonances of H₂O molecules in liquid water were detected for the first time (to our knowledge) using four-photon spectroscopy. These results confirm the hypothesis of [22, 24] about the existence of water molecule rotation under standard conditions. In spontaneous RS, the spectral manifestation of the increased mobility of hot molecules [22, 24] is apparently the high-frequency wing of the OH band, as well as a narrow peak in it in the OH vibration frequency region ($\sim 3680\text{ cm}^{-1}$) of weakly bound molecules [28]. Water heating results in an increase in the statistical weight of the high-frequency wing [18, 19] and a shift of the band center with a factor of $\sim 1\text{ cm}^{-1}\cdot^{\circ}\text{C}$ [20]. Knowing this factor, the water temperature can be measured [20] by the RS spectrum without thermometer.

However, the one-to-one center–temperature correspondence is violated at the ice–water phase transition and decomposition of the ice crystal structure. This manifests itself as an OH band cen-

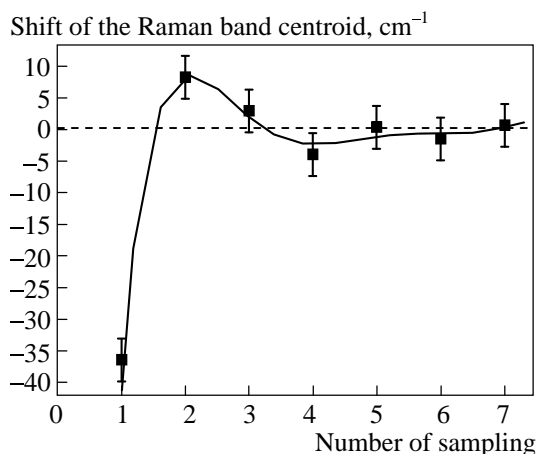


Figure 1. Oscillations of the OH band centroid in water overcooled to -1°C in relation to measurement index [29].

triod jump by $\sim 150\text{ cm}^{-1}$ due to an increase in the contribution of the high-frequency wing [18]. A similar ($\sim 40\text{ cm}^{-1}$) jump was observed in water overcooled to -1°C [29]. It is important that the band center position after this jump slowly ($\sim 6\text{ min}$), in comparison with the picosecond time of hydrogen bond switching [10–12, 22–25], evolved along the aperiodic curve “overheating by $\sim 9^{\circ}\text{C}$ (9 cm^{-1})—overcooling by $\sim 4^{\circ}\text{C}$ (-4 cm^{-1})” with respect to an equilibrium value at $\sim 0^{\circ}\text{C}$ (see Fig. 1 taken from [29]). The existence of the center jump and overshoot without change in physical state shows the dynamics of the hydrogen bond concentration [21], which can be considered to be structural heating–cooling (introduced by Samoilov, see [10, p. 86]).

To date, it still remains unclear whether this overheating–overcooling process results from an overcooled water perturbation by an optical pulse or this is a fundamental property of water, which manifests itself at any temperature. In this paper, we show that such an evolution of the band center is steadily observed in water and at room temperature. Moreover, this overheating–overcooling process is approximated by a harmonic function with a period of $35 \pm 13\text{ s}$ without noticeable damping for $\sim 16\text{ min}$.

2. Experimental

A single 10-ns pulse or a train of pulses (with an interval of 1 s) of the second harmonic of the Nd:YAG laser, backscattered in water, were measured with an RS spectrometer [20, 21, 28–30]. Laser beam was focused by a lens with focal length of 8 cm into a cell with room-temperature water. The beam caustic volume (in the cell), from which RS radiation was collected, can be approximated by a cylinder 3–4 mm long and 0.2 mm in diameter. Assuming that the unit volume of the water molecule is a cube with a $\sim 3 \cdot 10^{-8}$ -cm side, the separated fraction of the beam caustic will contain $\sim 10^{19}$ water molecules whose response forms a RS signal during the 10-ns laser pulse. The radiation intensities in experiments were 350, 35, 15, and 1–2 MW·cm⁻². The RS signal was focused on the polychromator input and was measured by a diode array with a gated brightness amplifier in front of it. The spectral resolution was 13–15 cm⁻¹ per a diode array unit. Results with low pulse intensity were obtained when measuring the signal by the cooled diode array.

We note that the pulsed RS spectrometer differs from conventional ones based on the cw argon laser with the power 100–800 mW [18, 19]. It allows (i) a significant decrease in the average power of sample irradiation (to 10⁶ times at a low repetition rate [20, 28]) and (ii) stroboscopic illumination of the process under study if it contains variable and regular components [29].

Using this scheme, RS spectra with deep modulation of the OH band envelope [28–30] were measured for scattering of short pulse trains. It was found that two spectral components dominate over others, i.e., ice-like spectra with a peak at the low-frequency wing and heated water spectra with a peak at the high-frequency wing [18, 19]. An example of such spectra measured one after another in 10–12 s upon irradiation of water by eight-pulse trains with intensity of 35 MW·cm⁻² is shown in Fig. 2 (solid lines). The dashed curve is the Gaussian approximation of the ice-like [10–12] spectrum (bold curve) for determining the position of the OH band centroid [20, 21]. Previ-

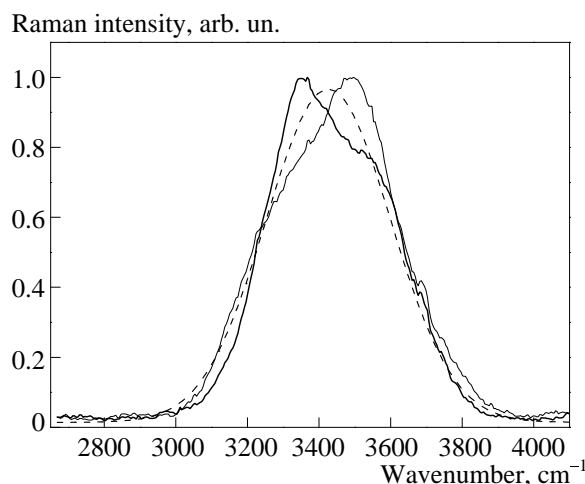


Figure 2. Two RS spectra of eight-pulse trains in water (solid curves), measured sequentially in 10 s. Dashed curve is the Gaussian approximation of the ice-like spectrum (bold curve) for determining the position of the OH band centroid.

ously [29], it was found that an increase in the number of train pulses from 2 to 128 results in a centroid shift to lower frequencies (structural overcooling and ordering), as upon thermal cooling of water [10–12, 20, 21].

3. Results and discussion

Figures 3 and 4 show the dependences of the position of the OH band centroid on the observation time for water probing by two-pulse (left panel in Fig. 3) and eight-pulse (right panel in Fig. 3) trains with intensities of 350 (Figs. 3a and 3c) and 35 MW·cm⁻² (Figs. 3b and 3d). Figure 4 shows the results of processing of spectra of two sequential measurement series with the interval 30–35 s at a pulse intensity of 15 MW·cm⁻² in two-pulse trains.

For convenience, all graphs were plotted on a comparable scale on both axes. The interval between experimental points was defined by the writing time of the data file (~ 9 –11 s) and the train duration. We note that the 3rd and 4th points in Fig. 3d reflect band centroid positions of the spectra shown in Fig. 2. It is clearly seen that the centroid of the ice-like spectrum (Fig. 2, bold curve) redshifts with respect to the average value by 8–

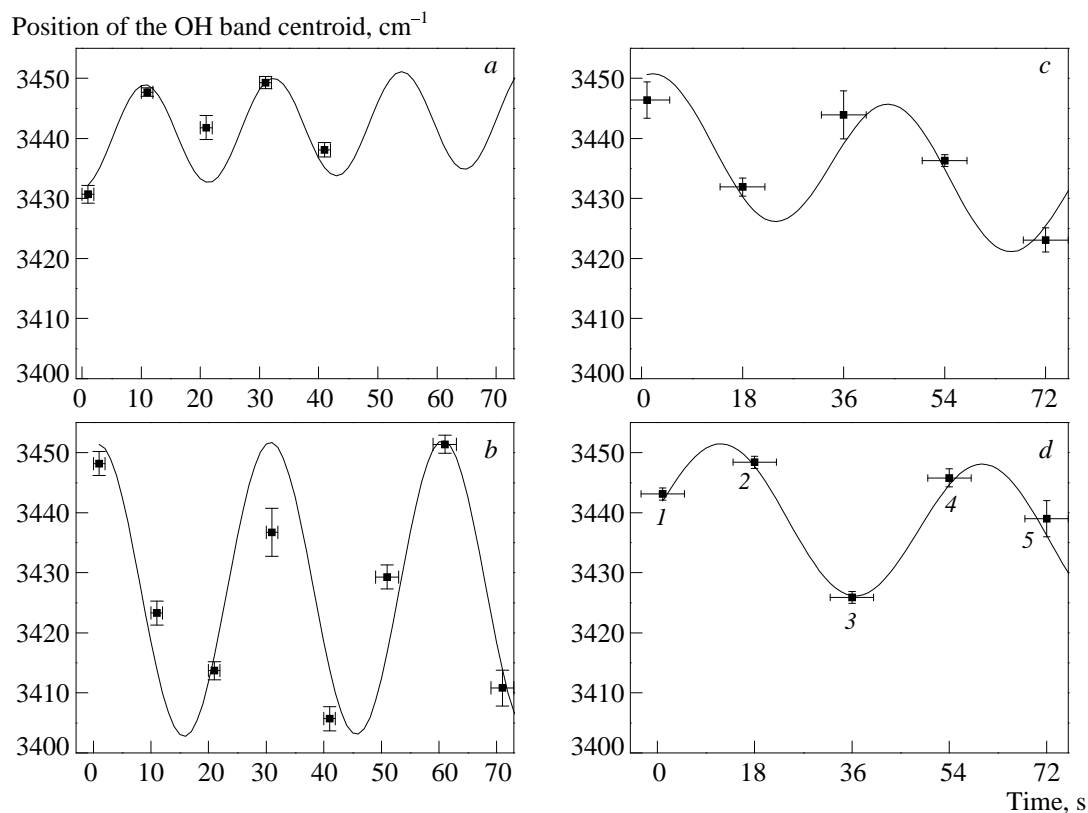


Figure 3. Temporal variation in the OH band center (■) for RS in water, measured using trains of two (left panel) and eight (right panel) pulses with an intensity of $350 \text{ MW}\cdot\text{cm}^{-2}$ (a, c) and $35 \text{ MW}\cdot\text{cm}^{-2}$ (b, d). The curves are sinusoids with periods of 22 (a), 31.5 (b); 42 (c), and 48 s (d).

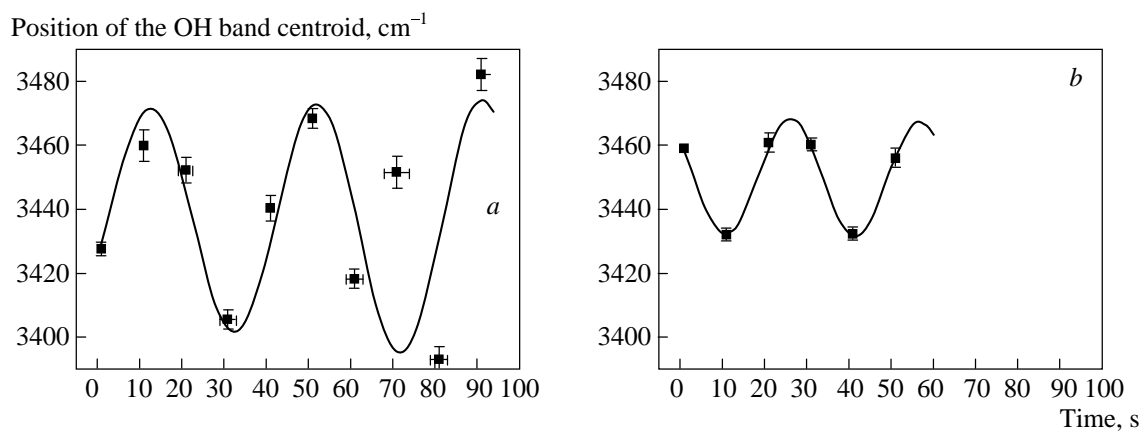


Figure 4. Time dependence of the position of the OH band centroid (■) for RS in water, measured using trains of two pulses with an intensity of $15 \text{ MW}\cdot\text{cm}^{-2}$: the first (a) and (b) second measurement series. The curves are sinusoids with periods of 39 s (Fig. 3a) and 31 s (Fig. 3b).

10 cm^{-1} (which is equivalent to cooling by $8\text{--}10^\circ\text{C}$ [20, 21] or to local overcooling); the centroid of another spectrum blueshifts (the overheating and disordering region).

The general and main indication of evolution of the position of the OH band centroid during the measurement time (t) is that experimental points of all measurement series fit the harmonic dependence

$$S = A \sin(\omega t \pm \varphi), \quad (1)$$

where A is the amplitude of the center deviation from an equilibrium average value, $\omega = 2\pi f$ is the circular frequency of centroid oscillations, f is the oscillation frequency (Hz), and φ is the oscillation phase at the measurement start point.

Another characteristic feature is the effect of laser radiation on the spectral response of water, which manifests itself in a decrease in the oscillation amplitude and period as the laser pulse intensity increases (Fig. 3). An increase in the number of train pulses from two to eight (Figs. 3*b* and 3*d*) also results in a decrease in the oscillation amplitude. A similar decrease was observed under identical irradiation conditions (Fig. 4*b*) possibly due to a total irradiation dose during the first measurement series (Fig. 4*a*). We note that the maximum centroid shift from the equilibrium position (points at the measurement end in Fig. 4*a*) was almost identical to the jump of 40 cm^{-1} during water overcooling to -1°C [28] (see Fig. 1).

3.1. Oscillations of the OH band centroid when probing water by low-intensity pulses

To decrease the effect of the optical field on water, an experiment on water irradiation by single low-intensity ($1\text{--}2\text{ MW}\cdot\text{cm}^{-2}$) pulses was carried out, as was previously proposed [28, 29]. During ~ 16 min, 100 spectra with an interval of 10 s between them were measured. The RS spectra were measured by the diode array (cooled to -20°C) with an electron-optical amplifier in front of it. Due to the low energy ($\sim 50\ \mu\text{J}$) of laser pulses, the OH band shape was somewhat extraordinary. It was

strongly irregular in comparison with the RS spectrum envelope in Fig. 2, which did not allow one to perform its Gaussian approximation. The characteristic shape of two spectra (Nos. 70 and 80), which are more similar to the spectra of small-size water clusters in molecular beams [31], is shown in Fig. 5*a*. A comparison of the spectra in Fig. 5*a* shows that spectrum No. 70 (bold curve) is enriched with high-frequency components (with respect to the band centroid indicated by an arrow in a region of $\sim 3350\text{ cm}^{-1}$, see the calculation below) in contrast to spectrum No. 80 (thin curve), in which the contribution of low-frequency components is more noticeable. Such spectral inhomogeneity of the response, as well as a decrease in the spike amplitude and probability outside the band (error bars indicate the variance $\sigma = N^{1/2}$ of the number of N counts of the RS signal), cannot be a consequence of only thermal fluctuations of the sensitivity of the brightness amplifier and receiver elements. In our opinion, these features reflect redistribution of the energy of vibrational-rotational transitions.

To calculate the OH band centroid evolution, the following procedure was proposed. First, the spectra were averaged over all 100 measurements (bold curve, Fig. 5*b*), and the band centroid position of the averaged band envelope was determined by the Gaussian approximation maximum (see Fig. 5*b*, dashed curve). Some spectra from an entire series, for example, No. 60 (thin curve in Fig. 5*b*) are more symmetric and more similar to the averaged spectrum than others (see Fig. 5*a*). We note that the envelope modulation decreases after averaging over 100 pulses, but remains larger than when averaging over eight pulses of moderate intensity (Fig. 2).

Then the values for each spectrum in the frequency range 2800 to 4000 cm^{-1} were separated into high-frequency (blue) and low-frequency (red) OH band wings with respect to the measured frequency of the centroid. The amplitudes of the spectral components of the blue and red wings were summed. The sums Σ_{blue} and Σ_{red} of the numbers of counts of each spectrum were statistically significant and varied from 6000 to 18000. This made it

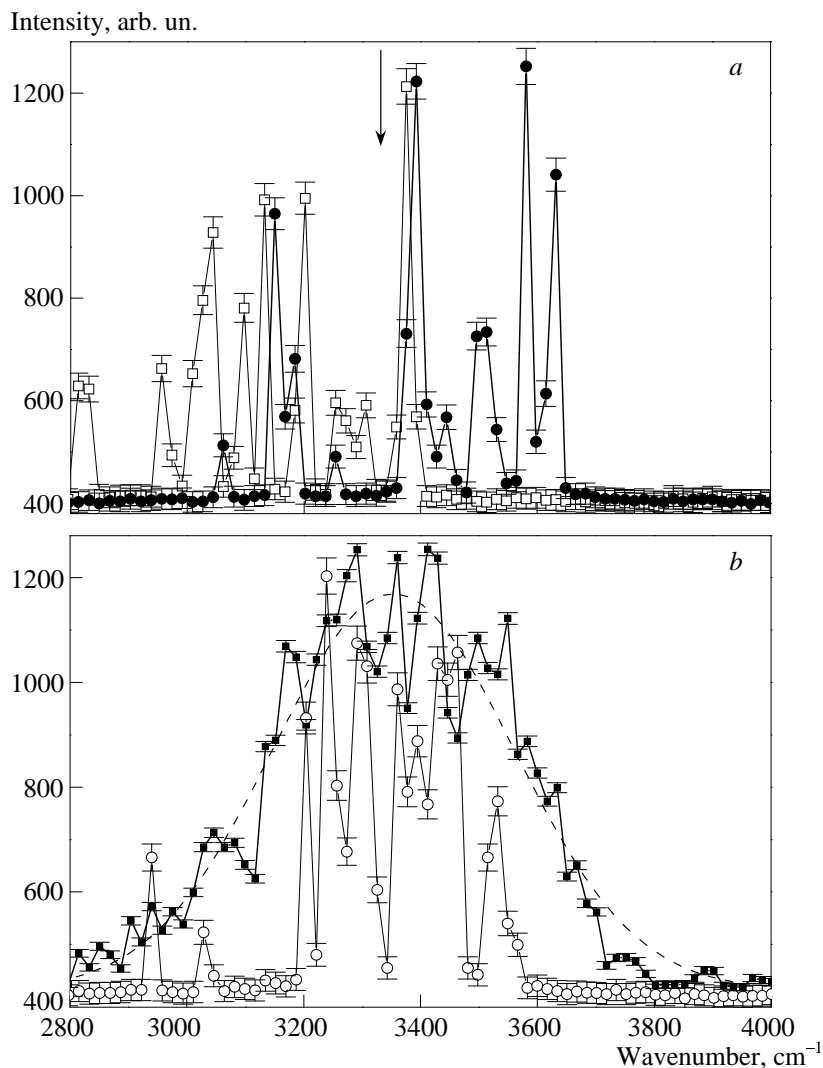


Figure 5. RS spectra in water from a series of 100 spectra measured with an interval of 10–11 s: (a) spectra No. 70 (bold curve) and No. 80 (thin curve); (b) spectrum No. 60 (thin curve) and the spectrum averaged over 100 pulses (bold curve) and its Gaussian approximation (dashed curve).

possible to study the evolution of the OH band centroid position by the ratio

$$R = \frac{\Sigma_{\text{blue}}}{\Sigma_{\text{red}}}. \quad (2)$$

In the case under consideration, i.e., strong modulation of the OH band, such an approach is more statistically representative than the ratio of amplitudes of two components selected in the Stokes and anti-Stokes wings of the band, which

was applied to analyze the temperature distortion of the band [32].

The dependence of R on the number of measurement is shown in Fig. 6a (squares) together with the harmonic oscillation curve (thin curve). The sinusoid is smoothed during its calculation with a smaller argument step after passing to the dependence on the measurement time (Figs. 6b and 6c). Figures 6b and 6c show the first 25 (b) and the last 25 (c) among 100 spectrum measurements (Fig. 6a).

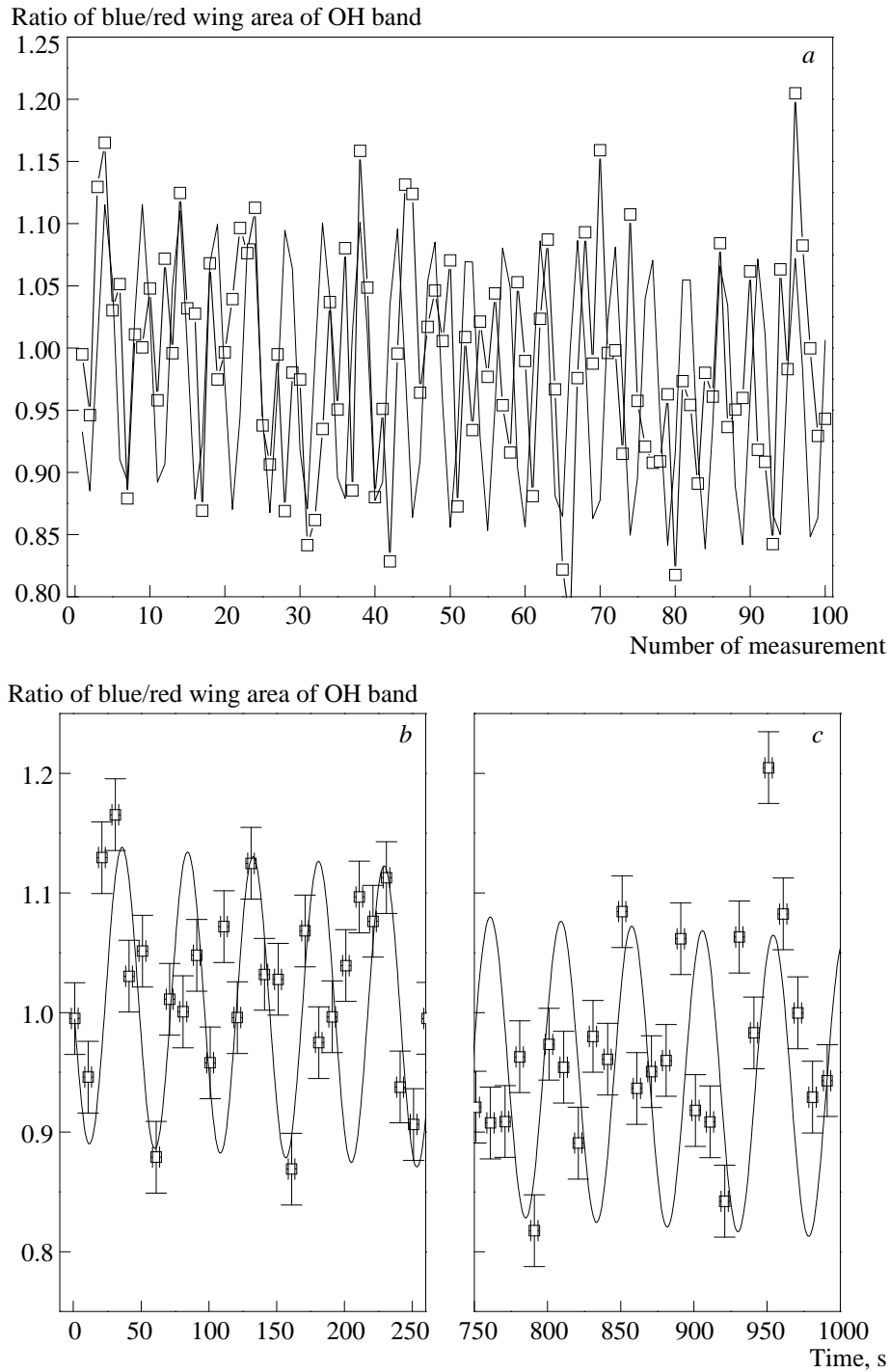


Figure 6. Dependence of the ratio of high- and low-frequency wings of the OH bands for a RS pulse with an intensity of $2 \text{ MW}\cdot\text{cm}^{-2}$ in water: (a) on the measurement index and (b, c) on the measurement (\square); the latter dependence is approximated by a sinusoid with a period of 48 s (curve).

We can see in Fig. 6 that the time position of the OH band centroid is described by the harmonic function within the measurement accuracy. We note that the centroid of spectra Nos. 60, 70, and 80 shown in Fig. 5, as expected, are near the average value (No. 60) and are oppositely shifted from it (Nos. 70 and 80). The oscillation period distinctly increases to 48 s and the average equilibrium value of the centroid slowly redshifts. The trend observed in Fig. 6a indicates another previously unknown phenomenon, i.e., the nontrivial overcooling–ordering effect which reflects an entropy decrease [10–12] without change in the water temperature in a field of low-power ($1\text{--}2\text{ MW}\cdot\text{cm}^{-2}$) laser pulses with repetition rate of $\sim 0.1\text{ Hz}$.

The band centroid shift was also observed in previous experiments at short time intervals (see Figs. 3b–d and Fig. 4). We note that this freezing of hot molecules [24] is more efficient than water heating due to insignificant [10–12], but finite radiation energy losses which are absent only in superconductors. A weak centroid blueshift is observed in a strong field (Fig. 3a). Previously [33], we showed that an increase in the average power (pulse repetition rates are from 1 to 8 Hz) of water irradiation, as well as of ice, is accompanied by a band centroid blueshift almost by 20 cm^{-1} . This blueshift was interpreted as a result of structural overheating due to hydrogen bond breaking without ice melting, since the absorbed radiation energy was insufficient to heat water by degree fractions when calculating the temperature in the adiabatic approximation neglecting losses.

The observed trend of spectrum enrichment with low-frequency components can result from molecule rotation slowing-down by a combined effect of two mechanisms: (i) alignment of dipole molecules in a linearly polarized laser field [34] and (ii) striction pressure in the optical beam. We note that an increase in the dynamic pressure in water in a field of acoustic pulses [17] and static pressure [15, 16, 25] is exactly accompanied by a band centroid redshift.

Analyzing periodic oscillations of the band centroid (Fig. 6), it is reasonable to expect that the RS spectra at the points of maximum deviation from

the equilibrium position will have a shape most typical of overcooled and overheated water. To verify this assumption, several spectra were sampled among 100 ones with upward (Nos. 22, 44, 68, 70, 74, 86, 94, 96) and downward (Nos. 17, 31, 32, 42, 61, 66, 80) shifted centroids. The spectra averaged over these samples are shown in Fig. 7 by dots and a thin curve, respectively. It is noteworthy that the overcooled water spectrum (thin curve) is quite similar to the ice spectrum (bold curve) [10, 12, 15, 20, 25, 29] with a characteristic peak at 3200 cm^{-1} , in which the contribution of OH vibrations of free molecules in the region of 3650 cm^{-1} is imperceptible. On the contrary, these vibrations mainly contribute to the spectrum of overheated water (bold curve). We note that a less pronounced peak in this region was previously observed at the beginning of series of measurements of scattering spectra of moderate-intensity pulses [28, 30]. In Fig. 2, the contribution of OH vibrations to the formation of the band envelope is also distinguishable.

A comparison of Figs. 2 and 7 shows that the sample of spectra of a separated state (overcool-

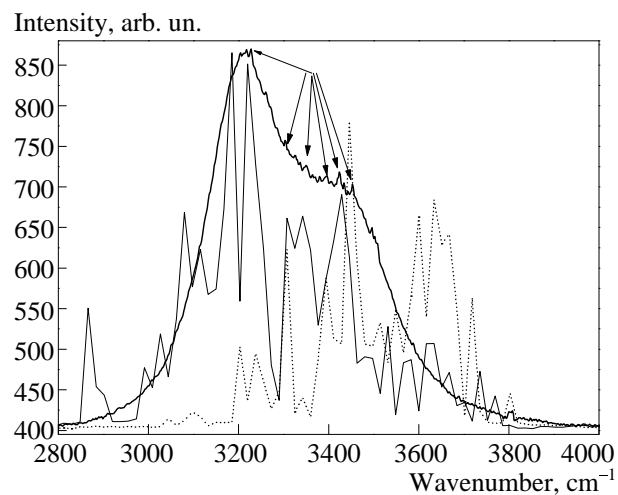


Figure 7. RS spectra of single pulses in water from a series of 100 spectra, averaged over a sample of seven and eight spectra, whose OH band centroid red- (thin curve) and blueshifts (dots). The RS spectrum of a 32-pulse train in ice I_h (bold curve) from [20]; arrows indicate spectrum envelope features with frequencies identical to those of RS components in water (thin curve and dots).

ing–overheating) at identical averaging numbers emphasizes characteristic features of the spectral response of water in these states. Moreover, the envelope of the RS spectrum in ice (measured in 1997 [20] using a pulsed RS spectrometer, averaging over 32 pulses) was almost identical to the water spectrum recently measured at room temperature (thin line in Fig. 7) even in details indicated by a set of arrows in Fig. 7. It follows from this identity that ice-like structures such as in crystalline ice [10] actually exist in a water macrovolume confined by the laser probe beam not only at -1°C [29], but also at room temperature. At time points of deep overcooling, these structures can be centers of spontaneous crystallization according to the homogeneous model. Subsequent decomposition of hydrogen-bonded ice-like structure complexes in water is accompanied by an increase in the concentration of free and weakly bound molecules, which manifests itself in the resonance appearance at a frequency of 3650 cm^{-1} (dots in Fig. 7).

3.2. Band center oscillation damping

The physical mechanism of the initial deviation of the RS spectrum centroid from the equilibrium position is not yet entirely clear. Its oscillations show that water (as a physical object) can be unstable for 10 seconds and requires a long time for averaging of measured parameters. A remarkable fact is also the absence of appreciable damping of the oscillation amplitude of the OH band centroid for both 100 s (Figs. 3 and 4) and 16 min (Fig. 6).

This feature suggests that oscillations are stimulated and supported by an energy inflow as in open nonequilibrium systems [35]. This is probably the case. Since oscillations are periodic, they cannot be considered to be manifestation of only thermal fluctuations in the hydrogen bond concentration [21] without external modulation source. In the presence of such a source, this process can be considered to be a physical clock by analogy with the Belousov–Zhabotinskii chemical clock [36]. The clock stability allows one to implement stroboscopic illumination conditions, under which RS spectra are measured in a time interval equal or multiple to the oscillation period. In this case, the

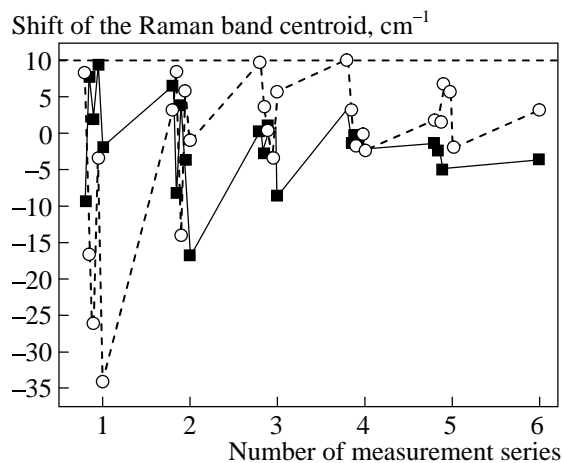


Figure 8. Evolution of the OH band centroid position in relation to the measurement series index for RS of trains of 2, 8, 16, 32, 64, and 128 pulses with intensities of $35\text{ (}\circ\text{)}$ and $350\text{ MW}\cdot\text{cm}^{-2}\text{ (}\blacksquare\text{)}$.

band centroid shift reflecting the water state will have a fixed value. We observed such a stroboscopic effect previously [28] when studying the dependence of the OH band centroid position on the irradiation intensity and dose, shown in Fig. 8. We can see that water was in an overheated state at the beginning of the first four measurement series, since the OH band centroid blueshifted as much as possible (indicated by dashed line). We note that the interval between measurement series was 30–35 s [28]. This value is consistent with a 31.5-s period of harmonic oscillations of the OH band centroid in Fig. 3b, which we experimentally measured later under the same conditions. Such an agreement counts in favor of the clock hypothesis and makes it possible to perform an interesting experiment with parametric pumping of the oscillatory process at the instant of maximum overcooling to enhance the tendency to the centroid redshift (see Fig. 6) and to achieve maximum overcooling.

This suggests that water exhibits periodic oscillations of the OH band centroid, which reflect the exchange between two water states. The small coefficient of oscillation amplitude damping gives grounds to assume that such an exchange can be accompanied by a transformation of the hydrogen bond structure in a fraction of molecules without

change in the internal energy of the entire ensemble of molecules in a solution of two liquids as at the second-order phase transition. In this case, different oscillation phases at the beginning of various measurements (see Figs. 3–6) also indicate that oscillations existed before water probing by laser pulses. Nevertheless, there is a certain effect of nonresonant optical radiation (532 nm) on the spectral response of water. This effect manifests itself in a change in the oscillation period, as well as in the centroid shift trend.

At the same time, the detected spectrum of molecule rotation in water [26, 27] gives us grounds to permit the existence of penetrating low-frequency radiation from an external energy source which is a necessary attribute of open nonequilibrium systems [35, 36]. Such a source of resonant pumping of librational and rotational motions in water is coherent radiation of galactic masers at rotational transitions of H₂O and OH molecules in the tera- and subterahertz frequency region. For example, radiation from the giant hydroxyl cloud in space at a frequency of 1.667 GHz (the wavelength is ~ 18 cm, the power is $\sim 10^{30}$ erg·s⁻¹) [6] penetrates into a laboratory similarly to radiation of the carrier frequency of mobile phones. Apparently, namely the diurnal variation in the intensity of this radiation maintained the diurnal cyclicality of the intensity modulation of both spontaneous and induced luminescence of aqueous solutions of glycyltryptophan,

$$r(T, t, I, f) = r_e(T) \pm \Delta r_e(T, t, I, f) \pm \delta(T, I, f)t, \quad (3)$$

$$1 - r(T, t, I, f) = 1 - [r_e(T) \pm \Delta r_e(T, t, I, f) \pm \delta(T, I, f)t]. \quad (4)$$

It follows from relations (3) and (4) that the ratio $r_e(T)/(1-r_e(T))$ of equilibrium values is similar to the ratio of hydrogen bond concentrations [21] and describes the observed [20] OH band centroid shift. Previously [38], the temperature shift of the OH band centroid was calculated by the evolution of the ratio $r_e(T)/(1-r_e(T))$, which can be presented as two overlapping levels with the Boltzmann distribution of populations (the representation of the OH band as a sum of two Gaussians appeared also convenient when studying water properties under

detected by the authors of [37]. It is noteworthy that the modulation amplitude damping almost does not manifest itself during the measurement time within 20 days.

3.3. Two-level approximation

The period of harmonic oscillations (overheating–overcooling) of the OH band centroid (35 ± 13 s) exceeds the characteristic times of proton hopping along the hydrogen bond line and orientational relaxation of dipoles by a factor of $\sim 10^{12}$ – 10^{13} [10–12, 22–25]. Such a difference indicates the existence of two dominant states of hydrogen-bonded complexes or two liquids with a longer lifetime in water, which differ by distributions of the vibration-rotational energy over oscillators in each state (see Fig. 2). Let us denote as r the relative fraction of the first state, controlled by the contribution of the high-frequency wing of the OH band. Then the fraction of the lower state (low-frequency wing) will be $(1-r)$. It follows from the experimental dependences that at a given temperature T , these quantities can be presented as a sum of the equilibrium $r_e(T)$ value and its variable part $\Delta r_e(T, t, I, f)$. The time trend of the band centroid shift is defined by the coefficient $\delta(T, t, I, f)$, which takes into account the laser radiation effect on water and depends on probing pulse parameters (intensity I and repetition rate f),

pressure [15, 25]). The calculated coefficient satisfactorily agreed with the blueshift of the observed OH band centroid as temperature increases [20, 21]. This suggests that an increase in the thermal energy kT is a determining factor of an increase in the upper level population or fraction of one of two liquids in water, whose values are described by Boltzmann statistics.

It is reasonable to expect that as water temperature approaches the boiling point, the ratio of upper and lower level populations $r_e(T)/(1-r_e(T))$ will

tend to a certain value. Most likely, this value will be close to the ratio 3:1 defined by the equilibrium concentration of ortho/para spin-isomers of H_2O molecules in the gas phase. Measurements of narrow resonances in liquid water, attributed to rotational transitions ($3_{03}-3_{12}$, 36.5 cm^{-1} and $0_{00}-1_{11}$, 37.1 cm^{-1}) of ortho/para H_2O molecules [39], allows one to carry out the experimental verification of this hypothesis by varying the water temperature.

3.4. Energy barrier between two states

An analysis of the evolution of the OH band envelope in the two-level approximation was allowed

by the possibility of its approximation by two Gaussians with shifted centroids [15, 25, 38]. The characteristic shoulder in the low-frequency wing of the band (see Fig. 2, thin curve) allowed such a two-profile and more complex approximation [10, 12, 23]. Relatively recently, more distinct splitting of the OH band into two spectral components with a deep minimum between them (~ 0.6 of a maximum value) was observed in some RS spectra (see Figs. 2*a* and 3*b* in [30]) for scattering of two pulses of moderate power ($35\text{ MW}\cdot\text{cm}^{-2}$). Such a minimum value satisfies the Rayleigh criterion in spectral resolution of the doublet and indicates that a molecule ensemble with a two-humped distribution over oscillators exists in the probed water volume at certain time

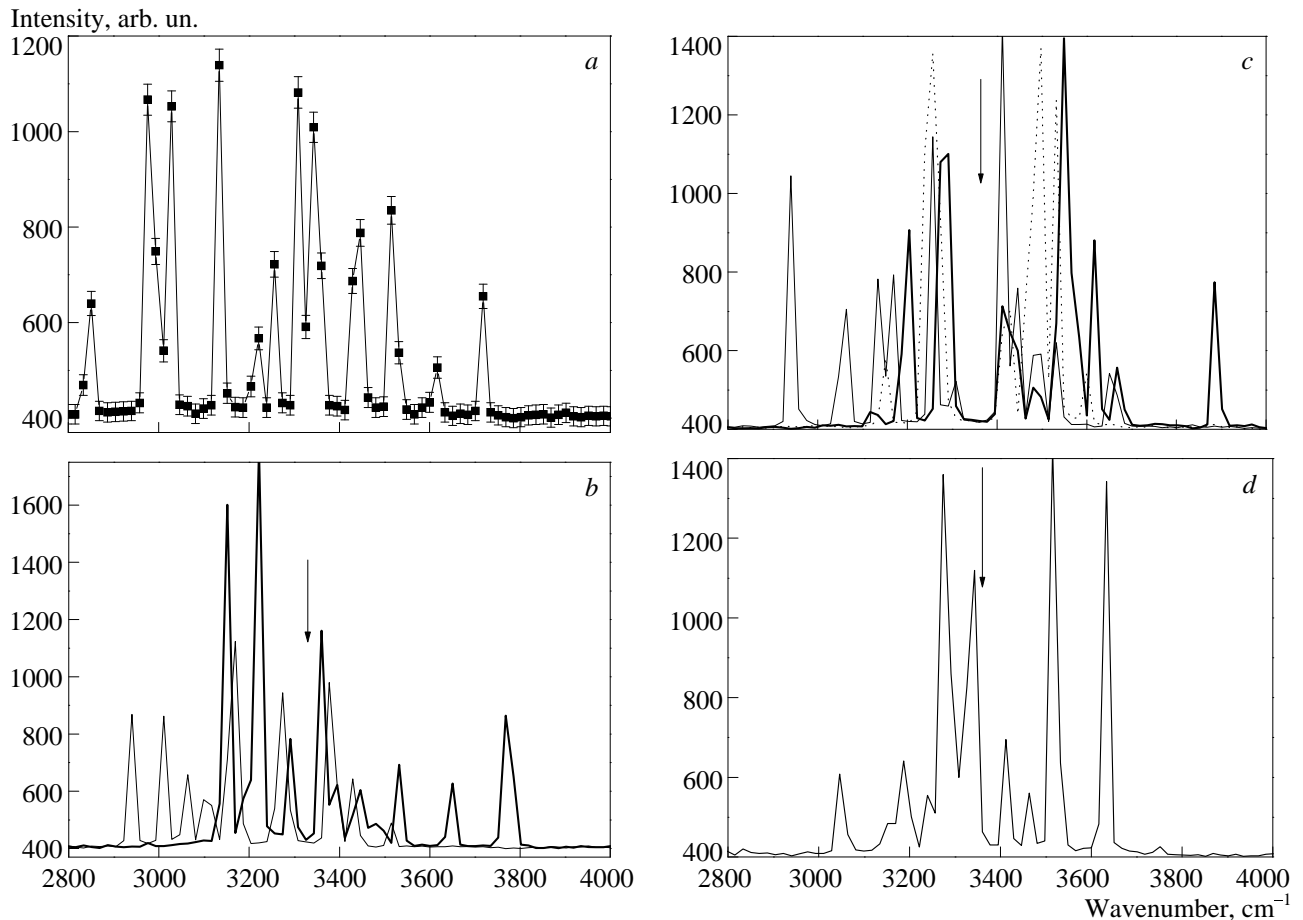


Figure 9. Series of RS spectra of a single pulse in sequential measurements Nos. 31–37 repeating in 10 s: (a) No. 31, (b) No. 32 (thin curve) and No. 33 (bold curve); (c) Nos. 34–36 (dotted, thin, and bold curves, respectively); and (d) No. 37. The arrow indicates the energy gap position.

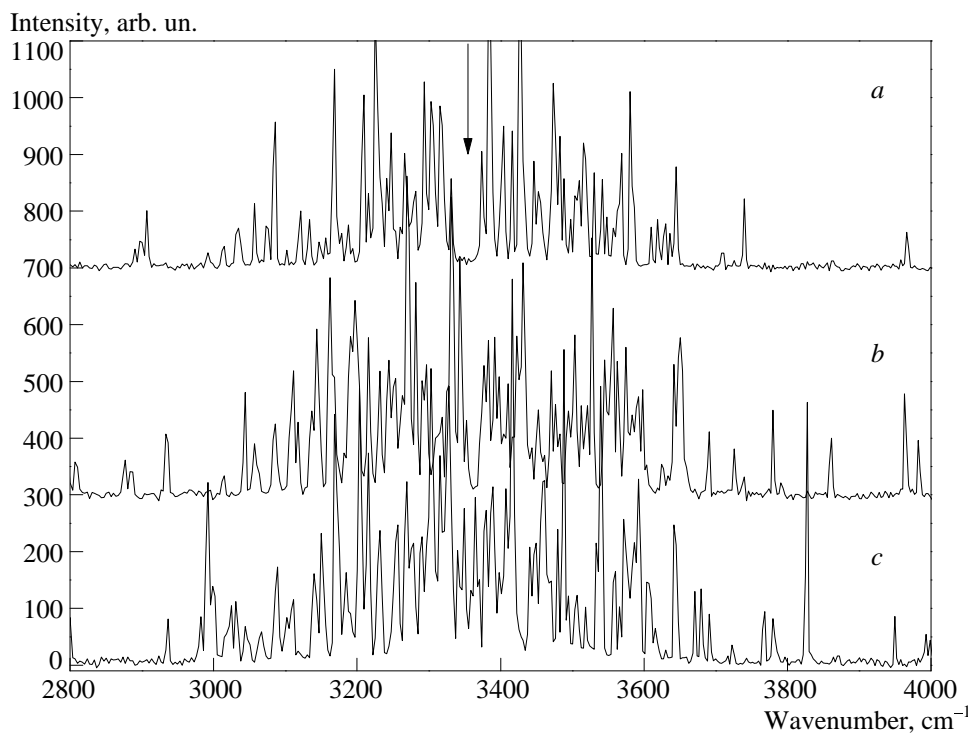


Figure 10. RS spectra of trains of pulses repeating with a second interval and 10 s between trains: (a) seven, (b) nine, and (c) nine pulses.

intervals; these humps are noticeably narrower than the OH band at these time intervals.

It is important that a further decrease in the power and number of probing pulses allows us to observe RS spectra (Fig. 5a) with a clearly detected energy gap between two levels. An analysis of the series of 100 spectra showed that such states can be very stable and are reproduced not only in single (Fig. 5a), but also in several sequential measurements. Figure 9 shows seven RS spectra (Nos. 31–37) sequentially measured in ~ 10 s one after another. Five (for ~ 40 s) of them (Nos. 32–36) contain a distinct minimum at the OH band centroid. In three sequential spectra (Nos. 34–36, Fig. 9c), the energy gap is a noticeable value (~ 100 cm^{-1}) remaining almost unchanged despite variations in spectral components in the OH band wing. The formation of spectral components with comparable amplitudes in place of the gap at the band centroid (see Figs. 9a and 9d) shows that diode array and brightness amplifier elements do not differ in sensitivity within experimental error.

It is reasonable to assume that if the observed energy gap or barrier is a spectral manifestation of the actual physical distribution of the vibrational–rotational energy in two water states with large lifetimes, it can be detected by scattering a train of several (3–5) low-intensity pulses. Such measurements were performed in a few days using the same scheme. Figures 10a–c show the spectra sequentially measured during scattering of a train of seven (Fig. 10a) and nine pulses (Figs. 10b, c), respectively. Train pulses were separated by a second interval. The pause between spectra was ~ 10 s. We can see in Fig. 10a that two states separated by an energy barrier were observed in water during the first six seconds, despite the integration over a rather large volume when probing by pulses of ~ 10 ns. During a 10-s pause before the next measurement and during the measurement (8 s), these states were apparently still separated (Fig. 10b). Then (Fig. 10c), in ~ 34 s from the measurement start, the distribution functions of each state begin to broaden, the energy barrier decreases, and states mix.

3.5. Overheated nonequilibrium water with long lifetime

Relatively recently [40], we detected a long-lived (no shorter than a year) water state in which the fraction of the high-frequency wing of the OH band was larger than in a test sample of distilled water. It was found that the OH band centroid of distilled water after its evaporation in a cavitation fountain followed by condensation blueshifts by $10\text{--}12\text{ cm}^{-1}$. Such a shift was also observed in commercial Penta water, which was subjected to cavitation treatment in a chamber after distillation, and then was cooled to 4°C [41]. Such a shift indicates water overheating by $10\text{--}12^\circ\text{C}$ and an increase in the liquid fraction with higher mobility (dots in Fig. 7), enriched with rotators [22, 24]. It is reasonable to expect that an increase in the molecule mobility should manifest itself in an increase in the water solvency as upon thermal heating. This property was identified by an increase in the dissolution rate of calcium oxalate crystals (major component of nephroliths) in cavitation treated water [42]. Moreover, such water treatment resulted in a decrease in its resistivity to $4\text{--}6\text{ M}\Omega\cdot\text{cm}$ without change in the parameter pH [43], as at dissolved gas removal [44].

It is important that the band centroid shift by $10\text{--}12\text{ cm}^{-1}$ was also observed in Penta water in a year of storage under normal conditions without vessel opening (a commercial plastic bottle of 0.5 l). This example shows one of the methods for preparing nonequilibrium overheated water with long lifetime. It is possible that cavitation microexplosions induced by an acoustic field are accompanied by hydrogen bond breaking, molecule overheating over rotational states, and generation of ortho spin isomers of molecules under supercritical conditions followed by condensation into a liquid enriched with rotators and depleted by dissolved gases. Long-term conservation of such a state without contact with air suggests that the role of dissolved gases (bubbles) in the formation of water properties and the light scattering spectrum is still unclear. For example, in [19] a drastic decrease in the sensitivity of degasified water to electromagnetic exposure which is measured by a decrease in

Rayleigh light scattering by (20–30)% in water before degassing.

Of most interest is broadening of the Rayleigh wing in water by a factor of 1.5–2 after its cavitation treatment in an ultrasonic fountain, which we experimentally detected in [45] (see Fig. 11). We interpreted this broadening of the four-photon scattering signal as an increase in the orientational relaxation rate with the rotator concentration, as was shown in [24]. We note that the formation of additional maxima in the Rayleigh wing (bold curve in Fig. 11) in the range $0.4\text{--}0.9\text{ cm}^{-1}$ in comparison with the scattering spectrum in Milli-Q water (thin curve in Fig. 11) correlates within the response function width of 0.1 cm^{-1} [45] with resonances of rotational transitions ($4_{23}\text{--}3_{30}$, 0.4 cm^{-1} ; $6_{16}\text{--}5_{23}$, 0.74 cm^{-1} ; and $5_{32}\text{--}4_{41}$, 0.89 cm^{-1}) in H_2O ortho isomer molecules, whose frequencies are indicated by arrows in Fig. 11. The para isomer line ($4_{22}\text{--}5_{15}$, 0.072 cm^{-1}) indicated by a dashed arrow does not notably contribute to the spectral distortion. The observed selective enrichment of water with ortho isomer rotators after cavitation treatment correlates with an increase in its solvency [42] and electrical conductivity [43], as well as with the band centroid blueshift [40].

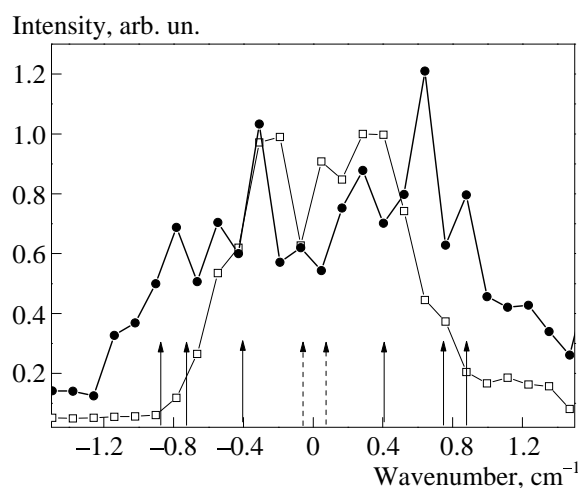


Figure 11. Four-photon scattering spectrum in the Rayleigh wing from [45] in Milli-Q water (thin curve) and water after cavitation treatment (bold curve). Arrows indicate rotational resonances of ortho isomers (solid arrows) and para isomers (dashed arrows) of H_2O molecules.

In the two-liquid water approximation, this is equivalent to an increase in the mobile component fraction.

3.6. Analogy to helium II

Despite the fundamental difference between liquid helium II and water, some processes in them are qualitatively analogous, apart from the even number of elementary particles. The thermal energy kT is the major factor controlling the ratio of superfluid and normal components of helium II, as well as OH band distortion in water (the ratio of fractions of two liquids, one of which features larger mobility). Of most interest is the analogy between the weakly damping harmonic wave “crystallization–melt” at the crystal–liquid interface in helium II [46] and the observed harmonic process overcooling–overheating in water. In this case, oscillation damping is insignificant as in helium II. As an example, we also note the discussion of the face rounding mechanism in the helium crystal [47] and growth of the lysozyme crystal with rounded terraces in an aqueous solution [41] enriched with a mobile component after cavitation treatment. The lysozyme crystal grows as a spiral induced by a screw dislocation [41], with an increased terrace roughness, which also manifests itself in helium crystals [48].

It is important that the crystallization–melt wave period (~ 100 s) in helium II [48] has the same order of magnitude as the oscillation period of the OH band centroid (35 ± 13 s) in water. From this it can be concluded that centroid oscillations in water most likely reflect slow processes of the formation–decomposition of the crystalline ice-like structure (see Fig. 7) as in helium II [48]. These facts do not contradict the two-liquid model of water, which can be considered to be a mixture of states with high and low densities under normal conditions [49].

4. Conclusions

Thus, a new physical phenomenon was detected, which manifests itself as (i) spontaneous weakly damping harmonic oscillations of the OH band

centroid in water with an amplitude up to 50 cm^{-1} and a period of 35 ± 13 s, which decrease as the intensity of laser probe pulses increases; (ii) the laser-induced redshift of the equilibrium position of the band centroid (cooling) when water is exposed to pulses of the second harmonic of the Nd:YAG laser with moderate intensity ($< 30 \text{ MW}\cdot\text{cm}^{-2}$) and a repetition rate of 1 and 0.1 Hz. The mechanism of the initial deviation of the band centroid from the equilibrium position is still unclear.

It was found that a decrease to $1 \text{ MW}\cdot\text{cm}^{-2}$ in the intensity of probe pulses with a repetition rate of 0.1 Hz allows us to measure spectra whose averaged envelope fits the RS spectrum profile for ice even in details. Moreover, an energy gap as wide as 100 cm^{-1} at the OH band centroid ($\sim 3300\text{--}3400 \text{ cm}^{-1}$) is clearly observed in several sequentially measured spectra. The room-temperature lifetime of such states in water is comparable with the band centroid oscillation period equal to 30–40 s.

The observed phenomenon was interpreted on the basis of the proposed model of two-liquid water as a solution of two mixed liquids consisting of hydrogen-bonded molecule complexes differing by the hydrogen bond concentration and structure. The distribution functions of oscillators over vibrational–rotational degrees of freedom in these liquids form the right and left OH band wings. An energy gap at the band centroid, whose energy is comparable to the thermal energy of translational and rotational motions of ortho/para molecules, was detected for the first time in a series of sequential RS spectra. This gap indicates the possibility of tunnel exchange between states of a fraction of molecules of these liquids, which manifests itself as band centroid oscillations at a given temperature.

Band centroid oscillations with a period of 35 ± 13 s can be a consequence of lowering the strict forbiddenness of the transition between ortho and para spin isomers of water molecules due to local fluctuations of magnetic fields in liquid, caused by density fluctuations in ortho isomers with summed magnetic spin. Periodic water overcooling with an amplitude of about 10°C can be an actuating mechanism of spontaneous crystallization of water and aqueous solutions of salts.

The observed OH band centroid shift to the side of heating in water subjected to cavitation treatment in an ultrasonic fountain [40], which features higher solvency [42] and longer lifetime, can be considered to be an example of water capable to accumulate and conserve the energy.

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