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OPTICAL SPECTROSCOPY

Ultraviolet Fluorescence of Water and Highly Diluted Aqueous Media

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Abstract—Light scattering spectra at the wavelength of excitation and fluorescence spectra of water and highly diluted aqueous media were measured. Long-term (several hours and/or days) changes in the spectral parameters after shaking, ultraviolet irradiation, and other actions on the aqueous medium were detected. It was found that melt water is significantly more sensitive to physical actions and adding various compounds.

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1. INTRODUCTION

Water and many aqueous solutions feature ultraviolet luminescence [1, 2]. Its intensity usually decreases with water purification; therefore, it is explained by impurity luminescence. Two spectral ranges are distinguished: ultraviolet and blue with luminescence maxima at 300–350 and 400–450 nm, respectively. The short-wavelength band is conventionally attributed to luminescence of protein-like compounds (aromatic amino acids in proteins luminesce). The blue range is related to luminescence of dissolved organic substances, in particular, humic compounds.

Humic substances are natural organic compounds with the most complex structure. Their molecules consist of two main blocks, the aromatic skeleton and carbohydrate-peptide periphery. Due to carboxyl, hydroxyl, carbonyl, amino groups, and aromatic fragments, the spectrum of reactions with their involvement is extremely wide [3]. They are contained in all natural waters and are adsorbed on the surface of steam-air bubbles and solid inclusions. Under exposure to sunlight, humates and their complexes are transformed, which plays an important role in natural ecosystems. The use of humates in plant growing, medicine, and animal industry is continuously expanded; therefore, particular attention is paid to the study of processes with their involvement [4].

Fluorescence spectra of natural water strongly depend on the concentration of humates, the specificity of their functional groups, and the presence of various compounds capable of forming ligand complexes or chemically reacting with humates. However, it seems impossible to explain all features of fluorescence of aqueous media only by the presence of impurities.

Lobyshev et al. [5] studied fluorescence of distilled water and aqueous homeopathic preparations of sodium chloride at high degrees of dilution. In homeopathic drugs, the fluorescence intensity excited at wavelengths of 310 and 260 nm correlated with biological activity and was retained at least during several weeks after preparation. The authors of [5] assumed that the observed fluorescence reflects structural self-organization processes in the system of hydrogen bonds between water molecules and metastable state formation. They assumed that such a state can arise during the preparation of homeopathic medicines and control their biological effect.

Pershin [6] observed a broad fluorescence spectrum in the range of 300 to 600 nm in double distilled deionized water under laser excitation with $\lambda_{ex} = 266$ nm. Under experimental conditions, the intensity and peak position of Raman spectra of water (~ 290 nm) varied with the repetition rate of excitation pulses. These data allowed the conclusion that the aqueous medium is restructured under these actions.

It was detected that moderate heating [7], shaking and pouring of water [8, 9], exposure to electromagnetic radiations in a wide wavelength range at various conditions [10–12], ultrasonic treatment [13, 14], and others can increase the content of reactive oxygen species (ROSs) and long-term (for several days) changes in luminescence of aqueous media. It is

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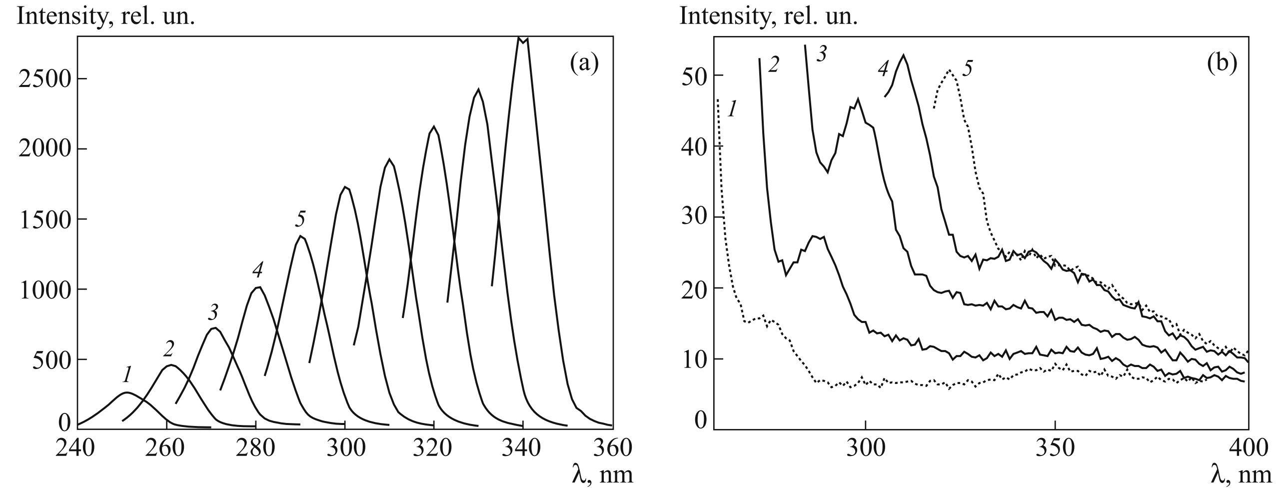

Fig. 1. Light scattering spectra at the excitation wavelength (a) and fluorescence spectra (b) of water purified using the Milli-Q system. Numerals *1–5* indicate the spectra at λ_{ex} from 260 to 290 nm. Figure 1(b) shows the corresponding fluorescence spectra.

known that ROSs in aqueous media can exist either in the form of free radicals, among which most important are the superoxide anion radical ($^{\bullet}O_2^-$) and hydroxyl radical ($^{\bullet}OH$), or in the form of compounds having no electron spin (singlet oxygen and hydrogen peroxide) [15]. ROSs enter into redox reactions with impurity molecules and can initiate radical-chain processes of the formation of organic peroxides. Some reactions involving ROSs, organic peroxides, and hardness salts existing in water are accompanied by chemiluminescence [16]. Because of its low intensity, chemiluminescence enhancers should be used [17]. They can enter into complex reactions with various medium components, thus changing properties of an initial system. Fluorescence methods do not require such additives. Experimental data on processes involving ROSs suggest that there is the strong correlation between chemiluminescence and fluorescence parameters of water spectra.

In this paper, we present the main features of fluorescence spectra of water and diluted aqueous solutions, which allow us to outline the scope of the most significant effects.

2. MATERIALS AND METHODS

Samples of water of various degrees of purification were used: tap water purified using the Geizer-1 filter, distilled water, and water highly purified using the Milli-Q system. In some experiments, distilled water was additionally purified using Akvafor V-300 and Akvamed 1-N membrane filters. The conductivity of such water did not exceed 0.5 μS cm^{-1}. For both additional purification and the purpose of studying the properties of melt water, we froze and defroze water samples two times and removed fractions freezing most rapidly and most slowly. In most experiments, such double refrozen distillate (DRD) samples were used. Dipeptide glycyltryptophan (Reanal, Hungary) was used without additional purification. Other used reagents were purified by the Serva Co.

Fluorescence spectra were recorded using a modified SDL-2 spectral measuring system (LOMO, Russia) in the photon counting mode. In this system, light of a 150-W xenon lamp is passed through a monochromator and is focused by a lens system to a cell into a spot ∼ 2 mm in diameter. Fluorescence and light scattering spectra excited by a 150-W xenon lamp were recorded at a right angle to exciting light using the second monochromator and an FEU-100 photomultiplier at room temperature. Samples with aqueous media in a quartz flask or a cell were placed in front of the mercury lamp SVD-120A window without heat filters. The technique is described in detail in [18].

3. RESULTS AND DISCUSSION

Figure 1(a) shows the light scattering spectra of water purified using the Milli-Q system, measured at excitation wavelengths from 250 to 340 nm. Figure 1(b) shows the fluorescence spectra at λ_{ex} from 250 to 290 nm. We can see that the observed signal intensity increases with λ_{ex}, while the broad maximum of the fluorescence spectrum near 420 nm is almost not shifted. Correction of the fluorescence spectra with allowance for the system sensitivity shows that the position of water fluorescence spectra is almost independent of the excitation wavelength in this range. The highest signal intensity is observed at

$\lambda_{ex} = 250–260$ nm. As λ_{ex} increases, the light scattering spectra at the excitation wavelength and the long-wavelength component of the Raman spectrum are superimposed on the fluorescence spectra. This often masks the spectral features in the region of 300–380 nm. The parallel study of various samples at $\lambda_{ex} = 260$ and 310 nm showed identical changes in the fluorescence spectra excited at these wavelengths.

It is known that the optical absorption maximum in the range of 250–260 nm is observed in ozonized aqueous solutions and is probably caused by OH radical excitation [19]. It was found that OH radicals and other ionized and excited products are formed under acoustic actions on aqueous media. In this case, luminescence referred to as sonoluminescence arises in gas bubbles [20]. Although the physical mechanisms of the appearance of sonoluminescence are obscure in many respects, it is undoubted that this phenomenon arises in chemiluminescence processes of recombination of free radicals and secondary products of their interactions with ambient medium. These facts provide a basis to search for common causes of chemiluminescence and fluorescence under ultraviolet excitation of aqueous media.

Figure 2 shows the uncorrected fluorescence spectra of a 10-μMol l^{-1} glycyltryptophan aqueous solution in which tryptophan fluorescence is excited (the absorption spectrum and fluorescence maxima are at ~280 and ~350 nm, respectively). As λ_{ex} increases, a long-wavelength band with a maximum near 390 nm appears. A similar band (with a maximum at 380–450 nm) also appears in highly diluted solutions of some other substances, whose fluorescence spectra (in more concentrated solutions) are outside this band. It is in pharmaceutical hydrogen peroxide solutions and in well purified water after various physical actions [9, 18, 21]. The intensity of this band can significantly vary with time. For the first time, fluorescence features in this spectral region in the diluted glycyltryptophan solutions and in distilled water were described by Lobyshev et al. [22]. The slowness, quasi-periodicity, and sensitivity to electromagnetic irradiation of the fluorescence parameters allowed these authors to assume that this fluorescence reflects the structurization of the aqueous matrix. The results we obtained show that ultraviolet fluorescence of water depends on many factors and it cannot be unambiguously associated with impurities, water structure, or other factors.

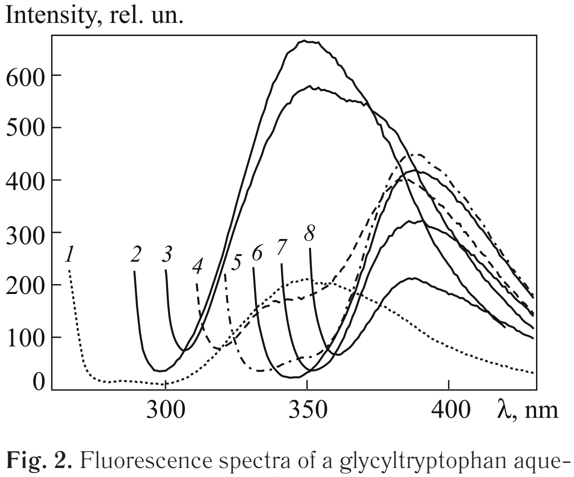

Fig. 2. Fluorescence spectra of a glycyltryptophan aqueous solution (10 μMol l^{-1}) at excitation wavelengths $\lambda_{ex} = 260$, 280, and 290–340 nm (from left to right).

Let us dwell on some features of water fluorescence spectra. It was detected that they depend strongly on water source and treatment method. As an example, Fig. 3 shows the light scattering spectra at a wavelength of 260 nm and the fluorescence spectra of various water samples. Spectra *1* correspond to tap water purified using the Geizer-1 household filter. This sample contains a relatively large amount of impurities. Tap water (including that without any purification) usually exhibits a broad spectrum with a maximum at ~410–420 nm. This spectrum is close to the fluorescence spectrum of diluted pharmaceutical hydrogen peroxide [18, 21]. With time, this spectrum, as well as the spectrum of water in sealed cells, blueshifts to ~360–380 nm. This broad peak is usually absent in distilled and higher purified waters (see spectrum *2* in Fig. 3); however, it can appear as a result of various actions, e.g., intense shaking (see Fig. 4).

Spectra *3* in Fig. 3 correspond to DRD. The corresponding fluorescence and light scattering spectra of water samples purified using the Milli-Q system are in Fig. 1. During refreezing (with removal of the fractions freezing most rapidly and most slowly) of high-purity water samples, the spectra were obtained, whose parameters were close to the similar parameters of refrozen distillate spectra. Therefore, we believe that the above water samples are finally purified almost identically using the double refreezing method.

Under laser excitation at a wavelength of ~260 nm, well resolved rather narrow bands with a maximum at ~280–290 nm are attributed to Raman scattering of light on stretching vibrations of water molecule protons. In our experiments, the shift of these bands with varying the fluorescence excitation wavelength can be seen in Fig. 1(b).

It is known that the continuum in the range of 270–290 nm in sonoluminescence spectra is attributed to emission of excited water molecules,

$$H_2O^*(^3B_1) \rightarrow H_2O(^1A_1) + h\nu. \qquad (1)$$

It is believed that such continuums can be caused by transitions between states, among which at least

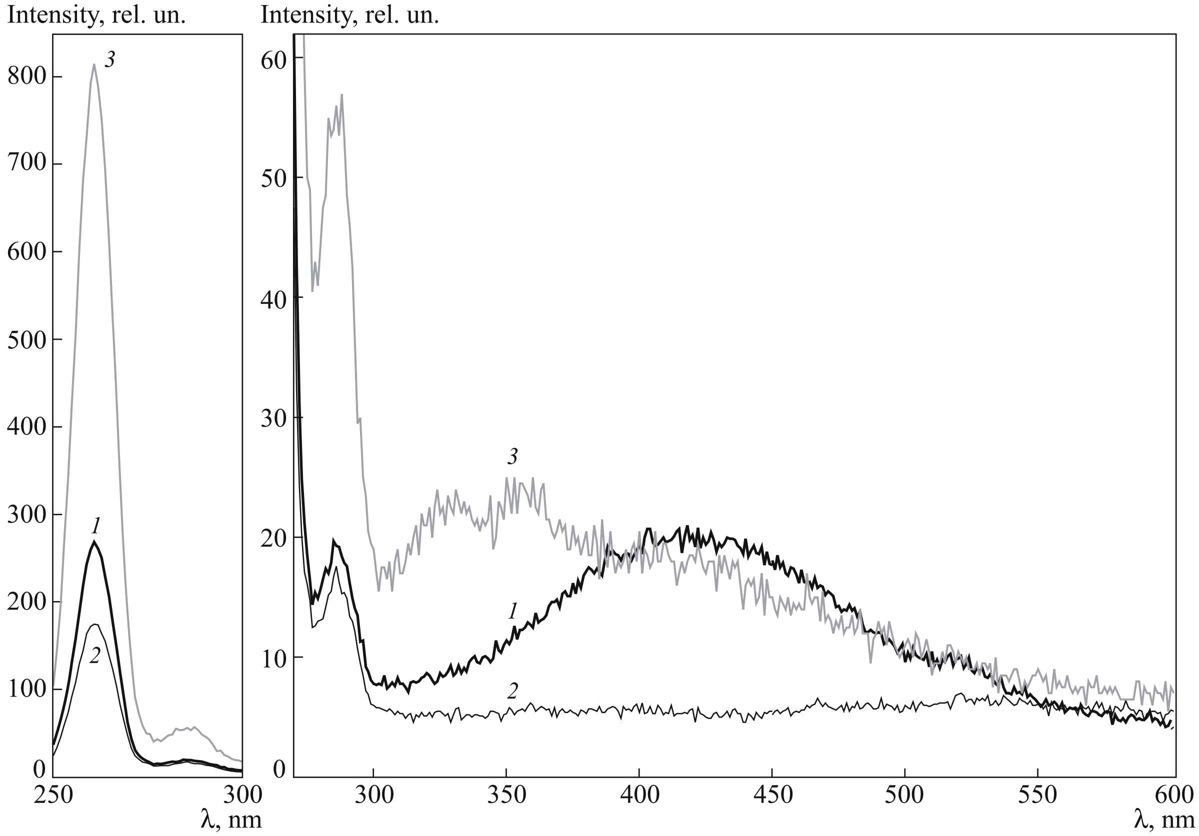

Fig. 3. Fluorescence spectra (right) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\mathrm{ex}} = 260$ nm (left) for various water samples: (*1*) tap water after purification using the Geizer filter, (*2*) distilled water without additional treatment, and (*3*) distilled water after double refreezing.

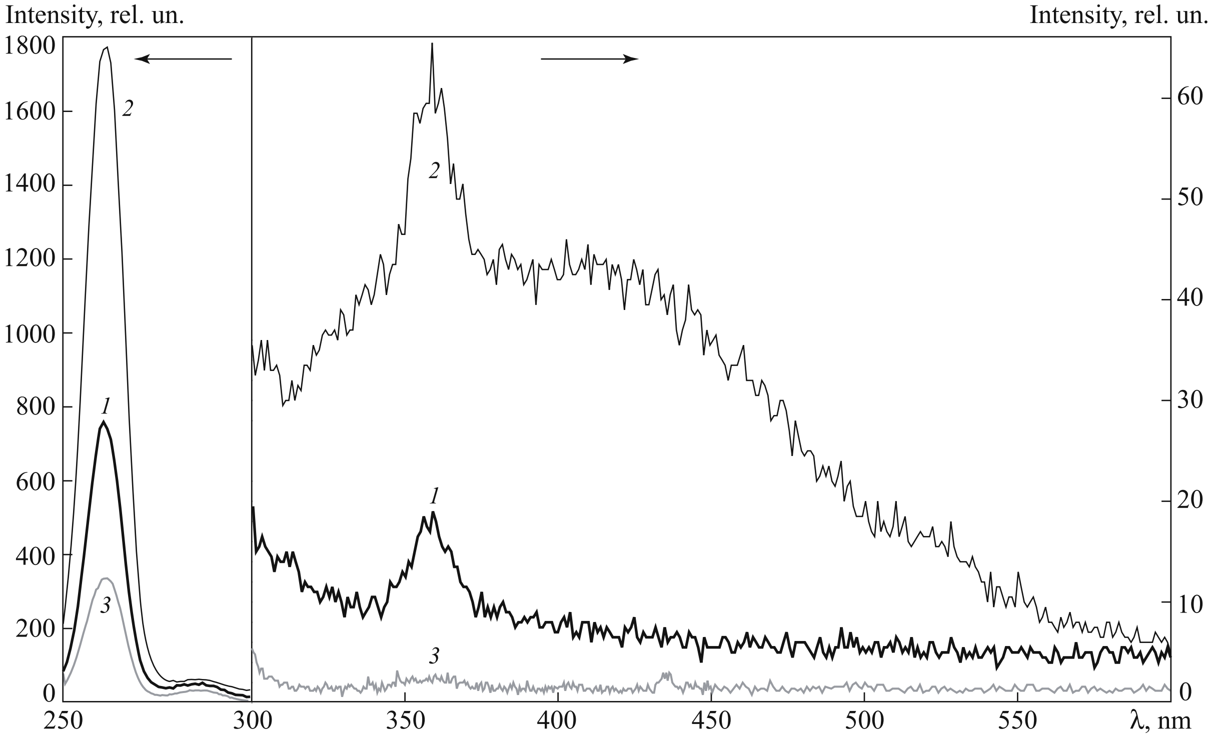

Fig. 4. Fluorescence spectra (right) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\mathrm{ex}} = 260$ nm (left) of distilled water: (*1*) initial water, (*2*) water after intense shaking, and (*3*) water after 35-min ultraviolet irradiation.

one is not quantized [20]. Such processes can be radical recombination, electron–ion recombination, bremsstrahlung, and some processes involving excited molecules. It can be assumed that the superposition of absorption and fluorescence spectra of some ROSs [16] and excited water molecules can have a significant effect on the properties of an aqueous system and compounds dissolved in it.

It was found that various physical actions (shaking, pouring, ultraviolet irradiation, heating, activation by electrolysis, and others) for all water samples can affect the parameters of light scattering and fluorescence spectra in the range of ∼310 to 650 nm. Figure 4 shows the typical light scattering and fluorescence spectra of distilled water immediately after distillation (*1*), after shaking in a test tube (*2*), and after long-term (35 min) ultraviolet irradiation (*3*).

Ultraviolet irradiation for 35 min leads to almost complete disappearance of the spectrum and a sharp decrease in the light scattering intensity. Ultraviolet irradiation for shorter times yields complex kinetics of spectral parameter variation, which is associated with oxidation process reversibility. After distillate shaking, a sharp increase in the light scattering intensity and the appearance of a broad band with a maximum near 400 nm is observed.

The shaking effect is even more pronounced for DRD samples. Figure 5 shows the spectra of initial distillate and distillate after refreezing (for 4 days) with impurity removal. The refreezing procedure itself results in an approximately twofold increase in the light scattering intensity, although it is known that water saturation with air gases decreases during refreezing [23]. Light scattering is controlled by both the number and nature of inhomogeneities; therefore, we can suggest that the increase in the light scattering intensity in this case is induced by the formation of an icelike water structure around gas bubbles [24]. We can see in Fig. 5 that the signal in a wide spectral range of 270 to 600 nm also slightly increases after refreezing.

It was found that distilled water gained high sensitivity to various actions after refreezing and additional purification from impurities. Initial distilled or highly purified waters have no such property.

Figure 6 shows the fluorescence and light scattering spectra of refrozen distillate before and after multiple shakings and pourings similarly as it was done for initial distillate (Fig. 4). A comparison of Figs. 4 and 6 shows that changes in the spectra and the light scattering intensity are more pronounced in the refrozen water sample. Changes in the DRD spectra after shaking continue at least for 3 days. In this case, the light scattering intensity increases by a factor of more than five and remains constant (within ±10%) for several days.

It should be emphasized that significant changes in the fluorescence spectra during shakings, pourings, irradiations with nitrogen laser, ultraviolet, Chizhevsky chandelier, and others in refrozen distillate and well purified water samples have usually long-term kinetics. In many cases, changes in the spectra become appreciable only in a few hours after an action and can be retained for a long time (at least, several days). Then against the background of slow variations in spectral parameters, their relatively sharp jumps can be observed. Such jumps are generally observed in a day and more after actions under the conditions when the fluorescence peak with a maximum near 400–420 nm is clearly distinct.

For many water samples initially exhibiting a detectable signal in the region of 360 to 380 nm (see Fig. 7), the fluorescence spectrum recording itself results in a blueshift of the fluorescence spectrum maximum. In this case, the light scattering intensity increases. Such changes are observed immediately after recording and are retained at least for a day. Therefore, a new sample was taken from a common closed vessel for each spectrum recording in most experiments described in this paper.

Figure 8 shows the changes in DRD spectra, observed immediately after opening a bottle with refrozen water and in two days after several openings of the bottle for sampling. We can see that not only the fluorescence spectra, but also the light scattering spectrum intensity change with time.

We can see in Figs. 4–7 that the changes in the water fluorescence and light scattering parameters are most pronounced for DRD samples. The ratio of spectral intensities at two wavelengths (light scattering intensities at $\lambda_{\rm ex} = 260$ and 310 nm were usually compared) can exhibit significant variations. In photon counting measurements in Rayleigh scattering, the signal intensity is proportional to the cubic light frequency ($I \sim \nu^3$). For initial DRD samples and these samples after intense shaking, the light scattering intensity for corrected spectra obeyed (within 10% of the experimental error) the Rayleigh dependence. The same effect was observed for initial distilled water (Fig. 4). However, after shaking of distilled water, the dependence of the light scattering intensity on the excitation wavelength sharply weakened. The same effect was observed when surfactants (e.g., sodium dodecyl sulfate) were added to initial samples with concentrations lower than the critical concentration of micelle formation. These data show the different nature of inhomogeneities in DRD and distillate after shaking. In DRD, the characteristic size α of inhomogeneities is much smaller than the excitation wavelength λ (i.e., $\alpha \ll \lambda$) and is unchanged after shaking. In distillate, the size

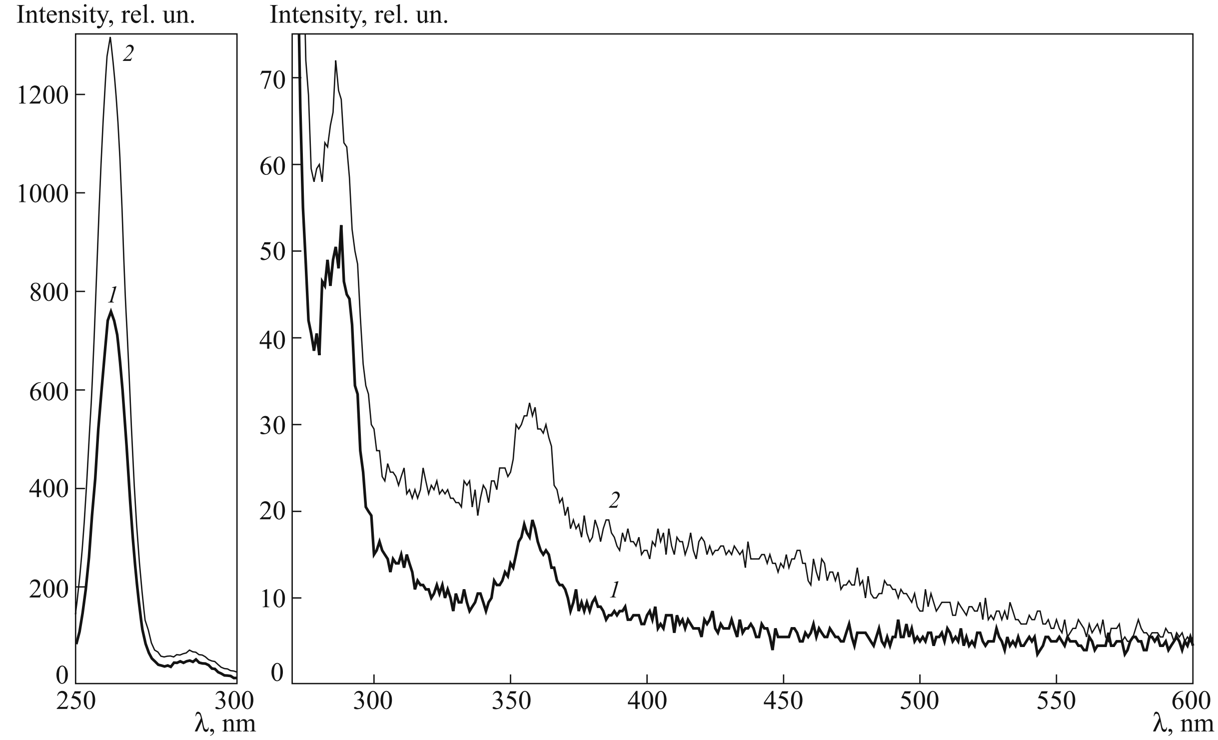

Fig. 5. Fluorescence spectra (right) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\mathrm{ex}} = 260$ nm (left) of (*1*) initial distillate and (*2*) distillate after double refreezing with impurity removal (DRD).

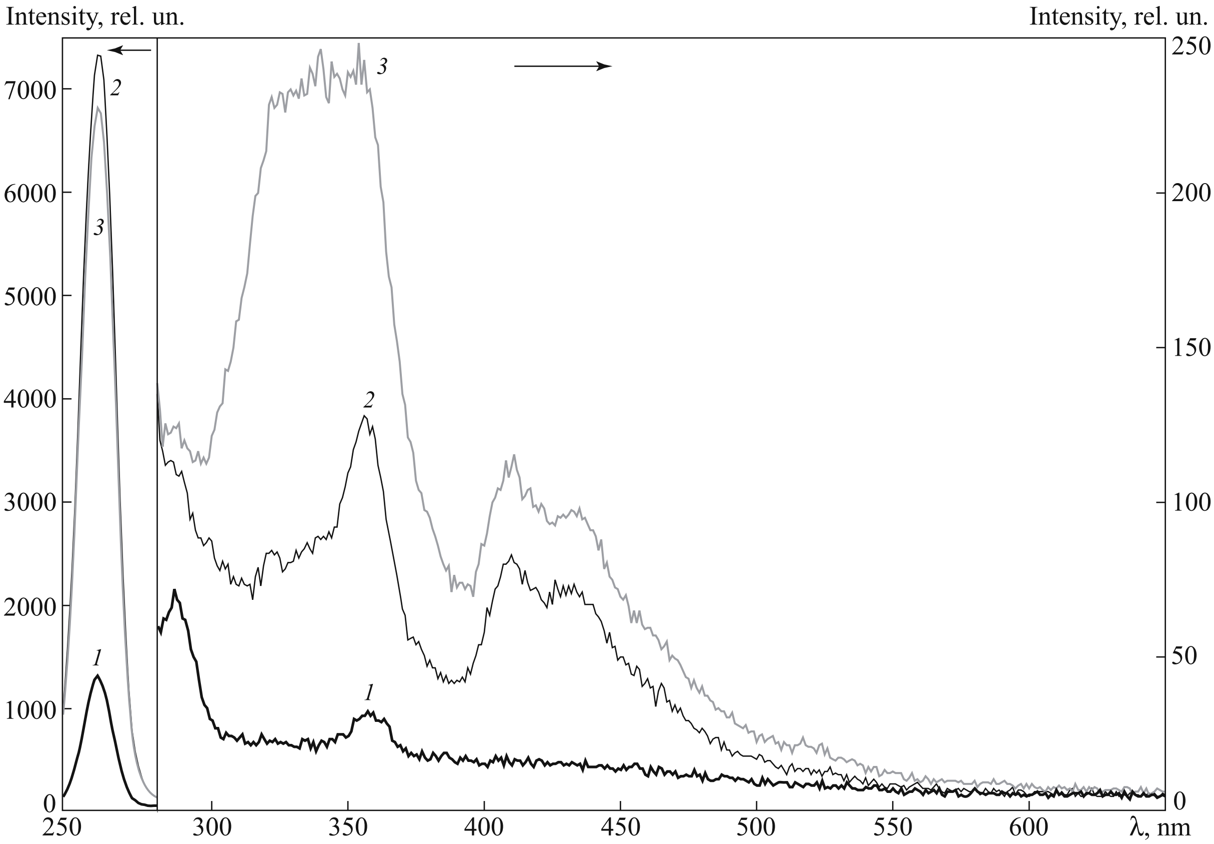

Fig. 6. Fluorescence spectra (right) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\mathrm{ex}} = 260$ nm (left) of (*1*) initial DRD, (*2*) after intense shaking, and (*3*) in three days after shaking.

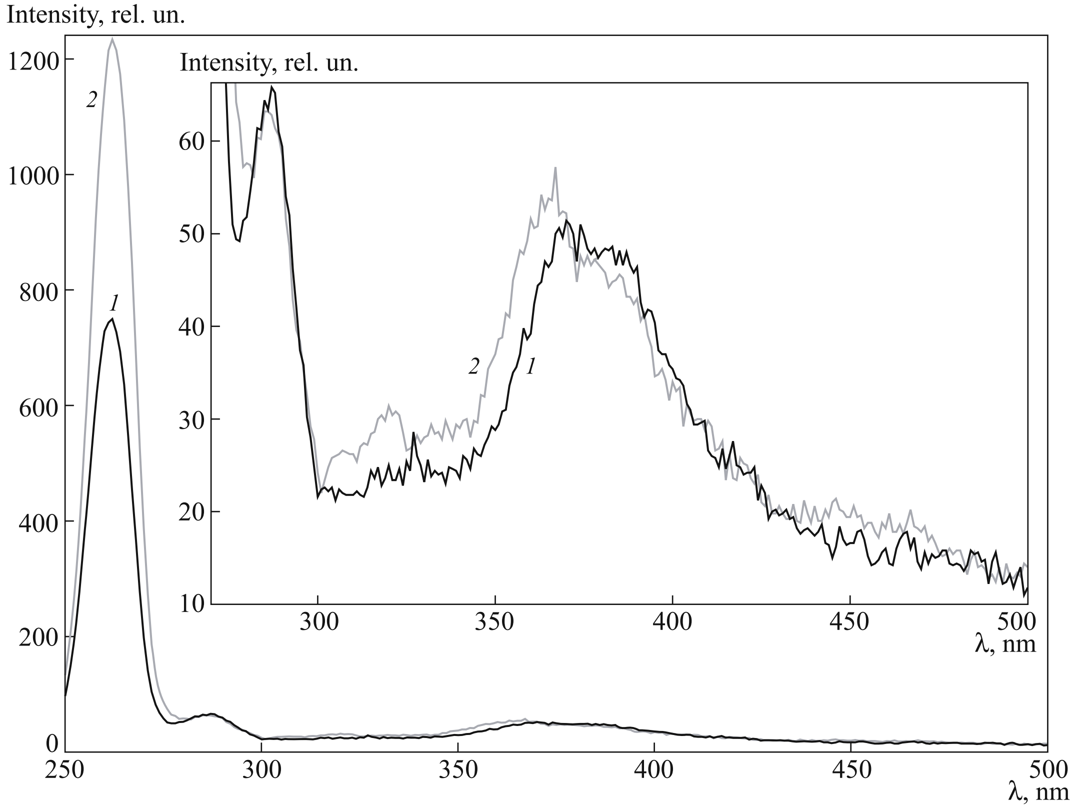

Fig. 7. Fluorescence spectra (inset) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\text{ex}} = 260$ nm (left) of (*1*) freshly purified water with a conductivity of 0.4 μS cm^{-1} at the first spectrum recording and (*2*) at further recordings for the same sample.

of inhomogeneities sharply increases and becomes comparable to the wavelength ($\alpha \sim \lambda$).

A comparison of the light scattering intensities at various wavelengths for various purified water samples showed that this parameter can significantly vary depending on the presence of small additives and actions on an aqueous medium. This is due to variations in the number and size of inhomogeneities in an aqueous medium. It can be supposed that this effect primarily depends on characteristics of steam-air bubbles always existing in water. Shaking of water or an aqueous solution, despite the apparent simplicity, is a complex physical process which leads to dispersion of steam-air bubbles in an aqueous medium, the generation of flows and shock waves, the formation of a developed interface and associated redistribution of molecules of dissolved substances and ions. It is known that the equilibrium with an air is reached in a long time after such actions, i.e., of the order of a few hours or even days [25].

The experiments we performed show that the broad band with a maximum at 360–380 nm in water and highly diluted aqueous media is as a rule associated with fluorescence of reduced organic impurities. The data on a decrease in or total disappearance of this band in oxidation by potassium permanganate or under long-term exposure to ultraviolet argue in favor of this conclusion (see Fig. 4). An increase in pH or an addition of reducer (ascorbic acid) result in an increase in the intensity of this band. However, weak fluorescence in this region is also observed after some actions on pure water, when the introduction of organic impurities is excluded. Probably, processes involving excited and ionized water states, as well as gases and ROSs existing in water, also contribute to observed fluorescence. In [26], the peak with a maximum near 370 nm is attributed to the OH-radical emission in the $^2\Sigma^+$ state. According to the data by Margulis [20], the continuum extending from 250 to 700 nm in the spectra of sonoluminescence of water saturated with argon is also associated with emission of the excited OH radical. Lines near 310 nm (strong) and 280 and 340 nm (weaker) are superimposed on this spectrum.

These experiments showed that the medium pH and carbonic acid content affect the fluorescence spectrum parameters.

It is known that air carbon dioxide dissolved in an aqueous solution is in equilibrium with carbonic acid,

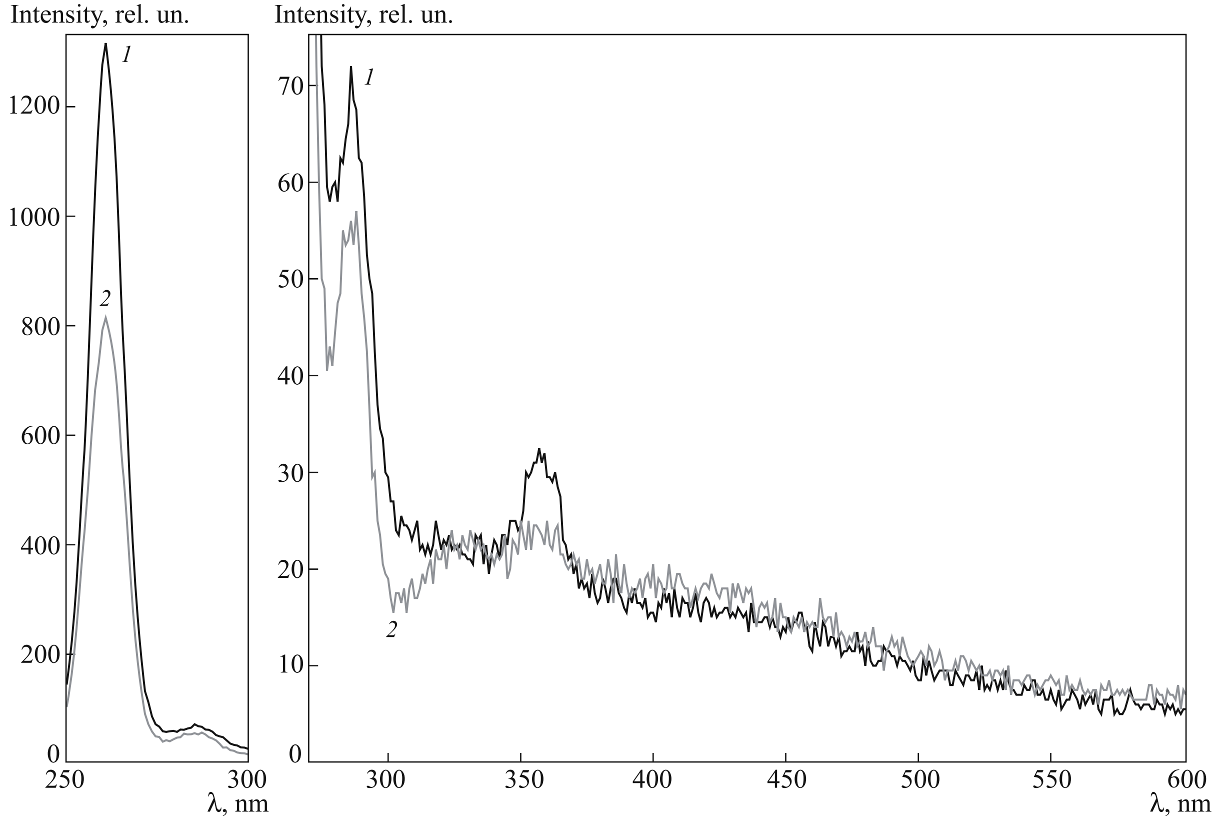

Fig. 8. Fluorescence spectra (right) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\text{ex}} = 260$ nm (left) of DRD (*1*) immediately after refreezing and (*2*) in two days.

$$\begin{aligned} CO_2(\text{gas}) &\leftrightarrow CO_2 + H_2O \\ &\leftrightarrow H_2CO_3 \to H^+ + HCO_3^-. \end{aligned} \tag{2}$$

The dissociation constant of carbonic acid ($pK_1 = 6.1$) controls buffer properties of the system. When water is exposed to ultraviolet, ROSs are formed, in particular, hydroxyl radicals [19]. Their concentration, hence, the medium redox potential depend on the presence of HCO_3^- ions. These ions can be interceptors of hydroxyl radicals, which results in the formation of carbonyl radicals [27] being good reducers [28],

$$OH^\bullet + HCO_3^- \to H_2O + HCO_3^\bullet. \tag{3}$$

Thus, the effect of carbonic acid on both the redox state of organic impurities and on the interaction between various ROSs types is possible. Modeling of the effect of carbonic acid on water using $NaHCO_3$ additives allowed us to detect the very complex effect of the pH and HCO_3^- ion on the spectral parameters.

Figure 9 shows the spectra freshly purified (distillation, membrane filters) water at pH 5.5 and 11.3. We can see that the intensity of the band with a maximum at 360–370 nm increased about twice in an alkali solution without soda additives. In the presence of $NaHCO_3$ (pH 11.3), the spectrum intensity is close to that at pH 5.5. Exposure of water to ultraviolet in the presence of $NaHCO_3$ almost quenches fluorescence, while exposure of a similar alkali solution leads to a significant increase in the signal intensity.

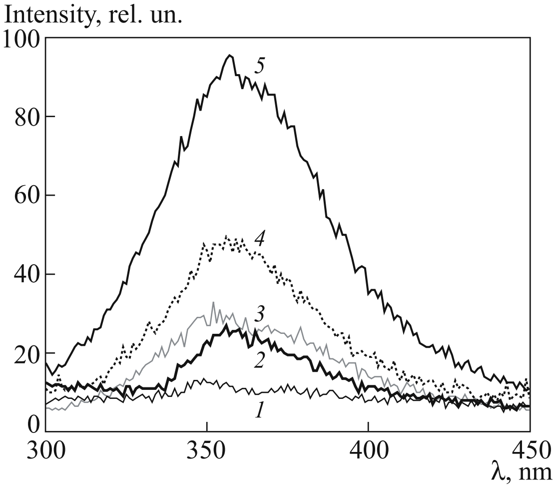

Fig. 9. Fluorescence spectra of freshly purified water at the excitation wavelength $\lambda_{\text{ex}} = 260$ nm: (*1*) water with $NaHCO_3$ after 30-s ultraviolet treatment, (*2*) initial water with pH 5.5, (*3*) water with $NaHCO_3$, (*4*) water with pH 11.3 (brought by KOH), and (*5*) water with pH 11.3 after 30-s ultraviolet treatment.

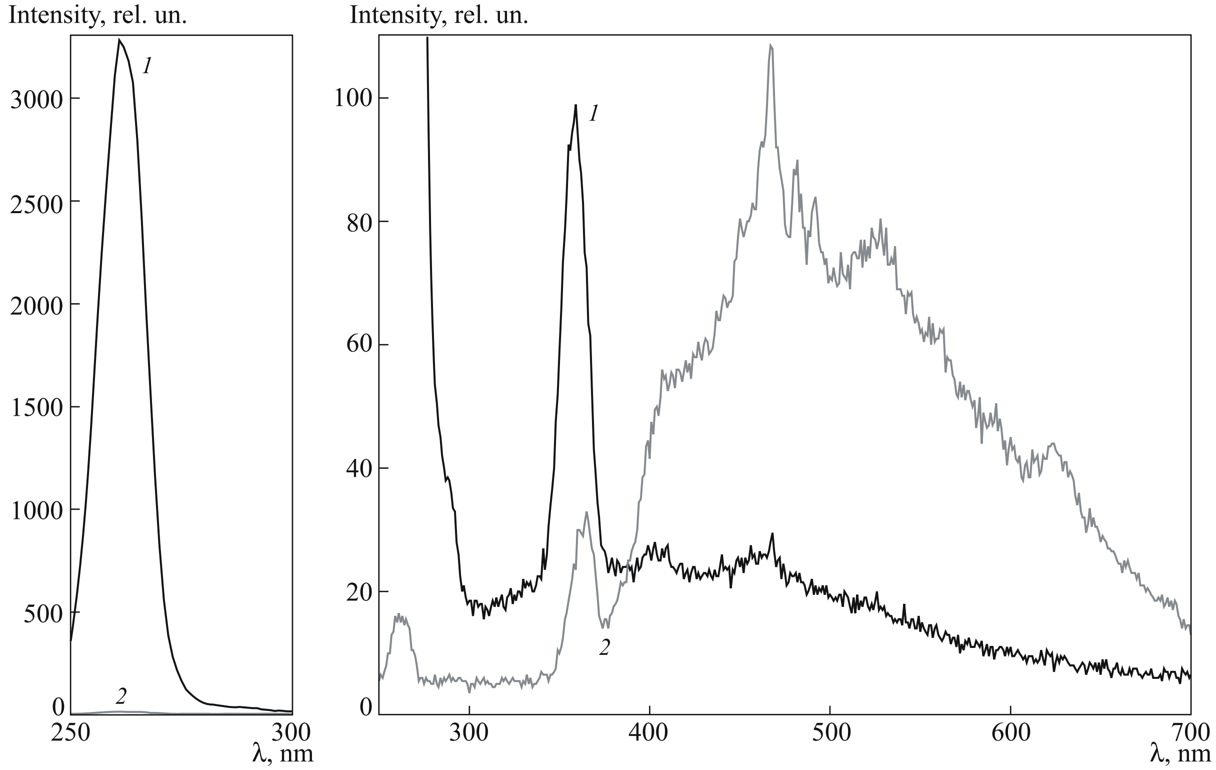

Fig. 10. Fluorescence spectra (right) and light scattering spectra at the fluorescence excitation wavelength $\lambda_{\mathrm{ex}} = 260$ nm (left) of (*1*) DRD with $FeSO_4$ ($\sim$1 mMol l^{-1}) and (*2*) with hydrogen peroxide addition (0.015%) to the previous sample.

A similar exposure of water at pH 5.5 has a negligible effect. In contrast to long-term variations in the spectra of neutral solutions (hours), the intensity in alkali solutions rapidly decreases after UV exposure. After only 10 min, its intensity decreases by $\sim 30\%$. As under sonolysis, CO_2, NO, N_2O gases, and substances leading to their formation in aqueous media have a significant effect on the spectral parameters. The mechanisms of their effect on luminescence characteristics of water require further study.

The broad chemiluminescence maximum in the range of 400 to 450 nm, observed under acoustic actions on water–organic systems is assigned to emission of triplet-excited molecules of carbonyl chromophores formed in radical-chain reactions of hydrocarbon oxidation [29, 30]. Another product of these reactions is excited (singlet) oxygen.

The data we obtained are in agreement with the literature data and allow us to attribute the broad fluorescence peak with a maximum at 400–450 nm to emission of excited carbonyl compounds. Probably, they are formed upon decomposition of organic peroxides adsorbed on the surface of steam-air bubbles [18]. It was found that small amounts of organic impurities at the interface are oriented by the interface and enter into radical-chain reactions under the action of the OH radical or other ROS types. Such reactions are reversible and can be controlled by macroscopic characteristics of a medium (pH, redox potential, temperature, and others). Sharp intensity jumps of the emission band of excited carbonyl radicals against the background of significantly slower variations can be associated with the radical-chain mechanism of the formation and decomposition of organic peroxides. However, in addition to these processes generally prevailing in the presence of organic additives, there exist phenomena not associated with organic impurities. They are most appreciable in refrozen water (DRD). For such water, the effect of additives of small amounts (mMol l^{-1} and lower) of metal ions (iron, copper, calcium, and others) is most pronounced). For example, an addition of Fe_2SO_4 to DRD (see Fig. 10) results in a sharp broadening of the narrow band with a maximum at 360 nm and a further increase in the light scattering intensity. An additional introduction of hydrogen peroxide in the presence of iron (Fenton reaction [31]) gives rise to a wide, but certainly structured spectrum in the range of 400 to 700 nm [9]. The position of the maxima in this spectrum is close to the known emission wavelengths of processes involving singlet oxygen [32] in the gas phase. We can see in Fig. 10 that the light scattering intensity in the Fenton reaction decreases almost to zero. Probably, under these conditions, gas bubbles completely collapse, and molecular products of the reaction become incorporated into the water matrix without the formation of noticeable (comparable to the wavelength) inhomogeneities.

4. CONCLUSIONS

The results presented demonstrate the complex dependence of the fluorescence and light scattering spectra at the excitation wavelength on the presence of small additives, the degree of purification, and preliminary treatment of water and highly diluted aqueous solutions. Even the best currently available systems of the water purification do not release air gases, heavy water impurity, and ROSs. It seems that reactions between organic impurities, hardness salts, and ROSs always existing in tap water and natural waters due to natural factors (background radiation of the Earth; light, electromagnetic, and acoustic actions) occur continuously. These reactions proceeds via the radical-chain mechanisms; therefore, the role of ROSs can consist in the initiation of the formation or decomposition of organic peroxides. Various physical actions on such systems, perturbing the bubble surface, affect the redox state of adsorbed molecules. Changes in surface parameters, in turn, can cause bubble growth or decrease and a change in the state of water surface layers. Due to the unique features of the hydrogen bond network, local actions can be prolonged to significant distances from the surface. It can be supposed that the numerous published data on the water memory or the formation of ROSs under low-energy actions are associated with the above features of water systems.

It is important to note that well purified melt water is more sensitive to small additives of biologically important substances, as well as to shaking, ultraviolet and laser irradiation, and other actions. The surface of such bubbles almost does not contain organic impurities which can store energy in the form of peroxide compounds. In our opinion, the specific properties of such water are caused by a change in the bubble type in this case. The absence of salts stabilizing small gas bubbles can lead to an increase in the number of clathrate cavities in the hydrogen bond network. As is known, gas molecules stabilize clathrate cavities continuously appearing in water. Such cavities are well inscribed into the water structure and can have a significant effect on its properties.

Moreover, the heavy water (D_2O) content decreases in refrozen water, which probably has a significant effect on the efficiency of collective processes in water [33, 34].

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