Sonoluminescence of terbium chloride in an H_2O—D_2O mixture

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The effect of solvent deuteration on the multibubble sonoluminescence (SL) of an aqueous solution of terbium chloride was studied. The dependence of the intensity of the characteristic SL of the Tb^{III} ion on the composition of an H_2O—D_2O mixture is similar to an analogous dependence of its photoluminescence (PL) but with a much smaller isotope effect. In pure D_2O, the SL intensity increases by 4 times only compared to the SL in water, while the PL intensity increases by 10 times. The mechanism of inner-bubble excitation of lanthanide ions is considered. According to this mechanism, an additional "heterogeneous" channel of quenching of excited Tb^{III} ions appears, which is absent for PL. The proposed model satisfactorily describes the experimental data on the effect of solvent deuteration on the SL intensity.

Key words: sonoluminescence, photoluminescence, terbium(III), isotope effect, decay time, photoluminescence yield, H_2O—D_2O mixture.

An intense ultrasonic irradiation produces in liquids pulsatory vapor-gaseous bubbles emitting a weak glow, so-called sonoluminescence (SL). As a result of heating of the content of the bubbles, electron-excited particles appear in the compression phase inside the bubbles upon collisions of "hot particles." [1]

The multibubble SL of water and aqueous solutions was studied in most detail. Primary elementary processes that occur inside cavitation bubbles result in the formation of excited water molecules[2] and radicals $^{\bullet}H$ and $^{\bullet}OH$ [3] and in the excitation of bubbles of dissolved particles, in particular, metal ions,[4,5] and gases[6] that are present in the system and penetrate into the gas cavity. In the case when electron-excited species have no time to luminesce in the gas phase, they can transfer to the solution and be consumed *via* several routes: decomposition to radicals, excitation energy transfer to other molecules, or nonradiative deactivation due to the interaction with the solvent or dissolved substances.

In this work, we used a Tb^{III} ion as the luminescent probe for studying these processes. This choice is caused by several factors. First, it has been found[5,7] that terbium(III) is excited upon sonolysis of aqueous solutions. Second, the mechanisms of influence of different additives, in particular, the effect of solvent deuteration, on photoluminescence (PL) of Tb^{III} are well known.[8,9] Third, the luminescent state of this ion $^5D_4$ is characterized by a long lifetime exceeding the lifetime of the bubbles.

In the present work, we studied the effect of solvent deuteration on the spectrum and SL intensity of an aqueous solution of terbium chloride. It has previously been shown that the Tb^{III} ion is excited upon sonolysis mainly *via* the mechanism of collisions with "hot" particles inside the bubbles ("inner-bubble mechanism").[5] This study would make it possible to obtain additional proves for this mechanism and elucidate the influence of such a possible process as the transition of an excited ion through the gas—liquid interface on the luminescence yield.

Experimental

Bidistilled H_2O and D_2O (the latter with 99.8% enrichment) were used. Sonoluminescence spectra were recorded on an AMINCO-BOWMAN spectrofluorimetric attachment with a HAMAMATSU 1P28 photomultiplier without corrections to the spectral sensitivity of the detector. Photoluminescence spectra were obtained on a spectrometric setup based on an MDR-23 monochromator.

To obtain acoustic oscillations, we used an ACE GLASS ultrasonic generator with a titanium waveguide 130 mm long, 6 mm in diameter, and with a working frequency of 20 kHz. The generator was equipped with an acoustic power detector. Experiments on SL detection of solutions of terbium chloride (reagent grade) were carried out at an ultrasonic radiation power of ~26 W. Sonoirradiation was performed in a steel 20-mL temperature-controlled reactor with a lateral quartz window. The distances from the axis of the waveguide immersed into the solution and from the center of cluster of luminescing bubbles to the window were 6 mm. This distance for the used concentration of $TbCl_3$ (0.1 mol L^{-1}) provided the practical absence of the UV sonoluminescence absorption of the solvent by the Tb^{III} ions in the solution bulk and induced noticeable sonophotoluminescence (re-emission of the absorbed light) for solutions in neither

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D_2O (PL quantum yield $\varphi \approx 0.8$) nor H_2O ($\varphi \approx 0.08$).[10] Sonoluminescence spectra were recorded with the spectral resolution $\Delta\lambda = 20$ nm. During recording of the spectra, the temperature of all air-saturated solutions was maintained at a level of 4±2 °C. The time of recording of one spectrum was ~1 min.

The lifetime of the excited terbium ion $\tau(Tb^{III*})$ was measured on a setup in which an LGI-21 nitrogen laser (λ = 337.1 nm) was used for PL excitation.

Results and Discussion

Figure 1 presents the SL spectra of solutions of terbium chloride in H_2O and D_2O. The spectra consist of a broad (250—700 nm) continuum glow of water (excited molecules H_2O^*, D_2O^* and radicals OH^*, OD^*) superimposed with the characteristic luminescence lines of the Tb^{III} ion with maxima at 488 nm ($^5D_4 \rightarrow {}^7F_6$) and 545 nm ($^5D_4 \rightarrow {}^7F_5$). It is seen that the spectrum and intensity of the continuum glow of the solvent remain unchanged when H_2O is replaced by D_2O. This indicates that the excitation conditions in the bubbles in H_2O and D_2O media are the same and the influence of deuteration on the characteristic luminescence of terbium upon both sonolysis and photoexcitation[8] is related to the nonradiative deactivation of the electron-excited state.

It is found that in D_2O the yield of the characteristic luminescence of terbium increases by 4 times compared to the SL intensity of terbium in an aqueous solution, while its PL intensity increases by 10 times. The plots of the $I_{H,D}/I_H$ ratio ($I_{H,D}$ is the luminescence intensity at λ = 545 nm in an H_2O—D_2O mixture, and I_H is the luminescence intensity in H_2O) *vs.* content of D_2O for SL and PL of the terbium(III) ion are presented in Figs 2 and 3, respectively. The plot of the $\tau_{H,D}/\tau_H$ ratio *vs.* D_2O content for PL of terbium is shown in Fig. 4.

According to the developed concepts,[5] the inner-bubble mechanism of excitation during sonolysis can be described as follows. In concentrated solutions Ln^{III} ions are transferred in part from the liquid layer (adjacent to the cavitation bubble) to the gas phase and are excited in the bubble bulk upon collisions with other "hot" particles. Lanthanide ions in a thin layer of the solution directly

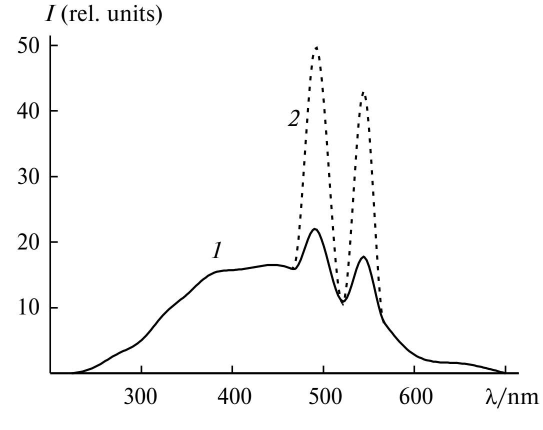

Fig. 1. SL spectra of aqueous (*1*) and deuterated (*2*) solutions of terbium chloride (C = 0.1 mol L^{-1}).

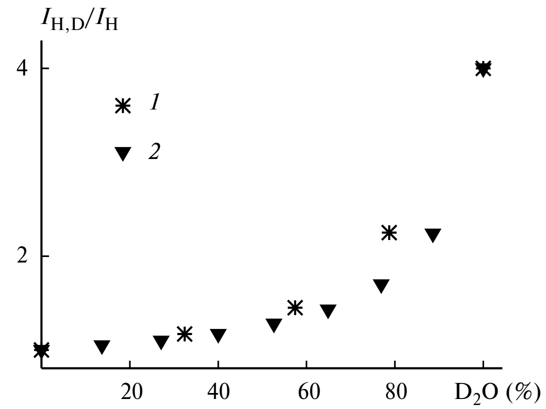

Fig. 2. Plot of the $I_{H,D}/I_H$ ratio *vs.* D_2O content in H_2O for SL of Tb^{III}: (*1*) experimental data and (*2*) calculation.

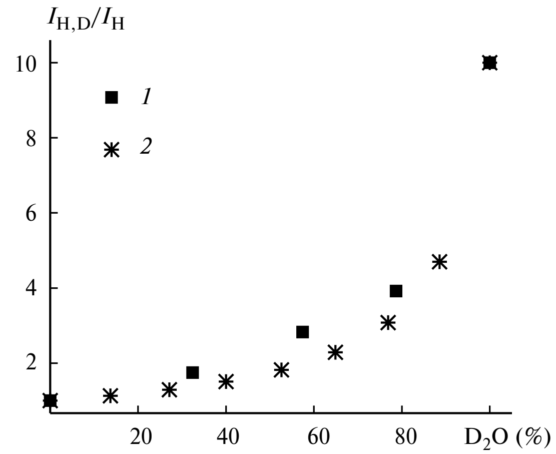

Fig. 3. Plot of the $I_{H,D}/I_H$ ratio *vs.* D_2O content in H_2O for PL of Tb^{III} (λ_{exc} = 365 nm): (*1*) experimental data and (*2*) calculation.

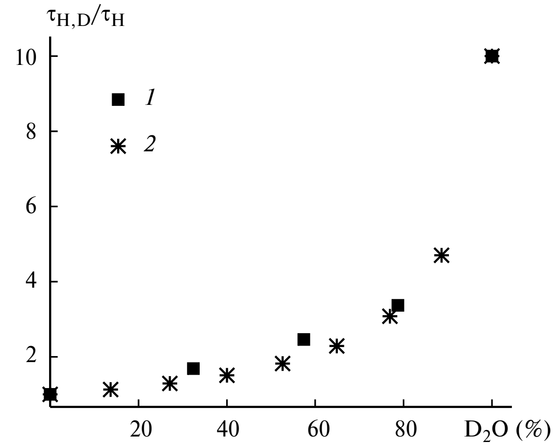

Fig. 4. Plot of the $\tau_{H,D}/\tau_H$ ratio *vs.* D_2O content in H_2O for PL of Tb^{III}: (*1*) experimental data and (*2*) calculation.

adjacent to the "bubble—liquid" interface can also be excited upon collisions.

For the solvated Tb^{III} ion, the characteristic lifetime τ of the luminescent excited state $^5D_4$ in H_2O is 400—450 μs, and in D_2O the lifetime increases by 10 times and reaches 4.0—4.5 ms, approaching the natural limit determined by the rate constant of the radiation transition.[11] In H_2O—D_2O mixtures τ has intermediate values. This increase is related to the fact that the efficiency of nonradiative deactivation (distribution of the energy of the "large" electron quantum of the excited state of the terbium ion to "small" quanta of vibrations of the OH or OD groups of solvent molecules surrounding the ion[11]) decreases upon solvent deuteration. For the formation of the Tb^{III*} ion in the gas phase of bubbles with a smaller density than that of the liquid phase of the solvent, the τ value should be higher than the values characteristic of the solvated ion in solution.

Thus, the discussed lifetimes exceed the period of bubble oscillations (50 μs at a frequency of 20 kHz) by an order of magnitude and more. Since the final collapse and cleavage of a bubble occur, on the average, after approximately five—six oscillations,[12] *i.e.*, in 300 μs, the excited ions inevitably get into the liquid phase of the solvent, which can result in the substantial jumpwise quenching of some of these ions and shortening of the potentially possible τ value for the excited ions "survived" upon the gas→liquid transition. Therefore, the decay kinetics of sonoexcited luminescence of terbium will not be exponential, unlike the usually observed exponential PL kinetics of aqua ions.

These facts should decrease the isotope effect (the increase in τ and the luminescence yield) upon terbium sonoluminescence compared to these values for photoexcitation. Let us construct a more detailed model for the phenomenon under discussion and make quantitative estimates.

The qualitative patterns of the luminescence decay of an ensemble of terbium(III) ions excited in a bubble for ultimate cases of aqueous (H) and completely deuterated D) solutions are presented in Fig. 5. At the first stage from 0 (moment of excitation upon immediate collapse; the possibility of additional excitation upon subsequent collapses is ignored for simplification of the model) to t_b (lifetime of a bubble until its final disappearance), the exponential luminescence is observed with the lifetime $\tau_g{}^H$ or $\tau_g{}^D$ characteristic of the gaseous phase of the solvent. Sharp quenching (intensity jump) is possible on going to the liquid phase through the gas—liquid interface, and then exponential luminescence occurs with the lifetime $\tau_{liq}{}^H$ or $\tau_{liq}{}^D$ characteristic of the liquid phase of the solvent.

Thus, the decay kinetics of a characteristic SL glow of terbium(III) in water, D_2O, or an H_2O—D_2O mixture can be presented as the following superposition of two exponents:

$$I^{gl}_{SL} = \begin{cases} I_0 \exp(-t/\tau_g),\ 0 < t < t_b \\ \chi I'_0 \exp\left(-\dfrac{t-t_b}{\tau_{liq}}\right) = \chi I_0 \exp(-t_b/t_g)\exp\left(-\dfrac{t-t_b}{\tau_{liq}}\right),\ t \geq t_b. \end{cases}$$

Here $I^{gl}{}_{SL}$ is the intensity of a sonoluminescence glow, I'_0 is the intensity at $t = t_b$, and χ is the quenching ("surviv-

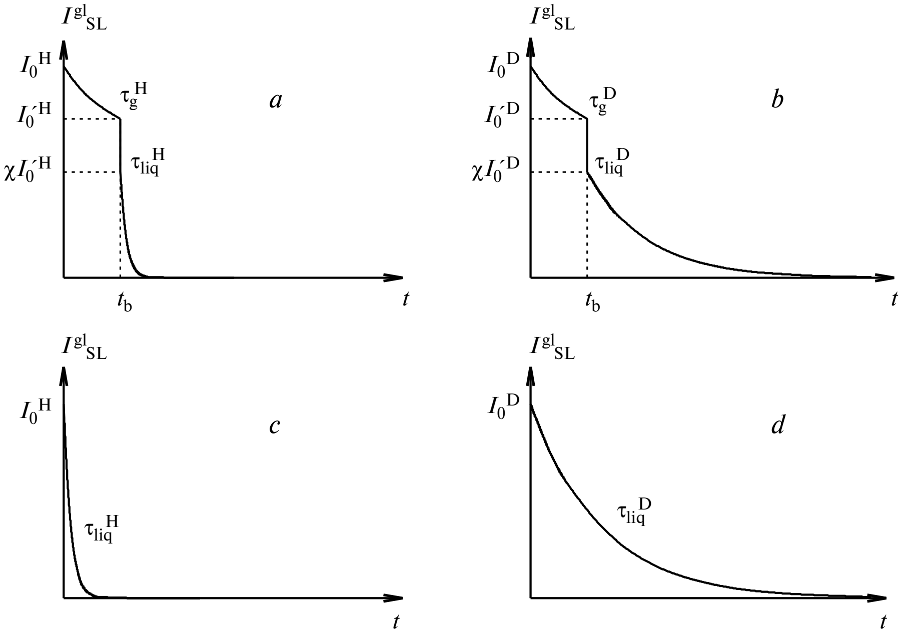

Fig. 5. Nonexponential SL decay kinetics of Tb^{III} in H_2O (*a*) and D_2O (*b*); exponential PL decay kinetics of Tb^{III} in H_2O (*c*) and D_2O (*d*).

ing") coefficient of excited ions on going through the gas—liquid interface.

The total luminescence emitted within a glow (*S*) is

$$S = \int_0^\infty I_{\mathrm{SL}}^{\mathrm{gl}}\mathrm{d}t = I_0\left[\tau_g + \left(\chi\tau_{\mathrm{liq}} - \tau_{\mathrm{g}}\right)\exp\left(-t_{\mathrm{b}}/t_g\right)\right].$$

Using this formula for the estimation of the total SL intensity $I_{\mathrm{SL}} = NS$ (*N* is the number of glows per time unit), the ratio of the SL intensity of the partially or completely deuterated solution to the SL intensity of an aqueous solution can be presented as

$$\left(\frac{I_{\mathrm{H,D}}}{I_{\mathrm{H}}}\right)_{\mathrm{SL}} = \frac{\tau_{\mathrm{g}}^{\mathrm{H,D}} + \left(\chi\tau_{\mathrm{liq}}^{\mathrm{H,D}} - \tau_{\mathrm{g}}^{\mathrm{H,D}}\right)\exp(-t_{\mathrm{b}}/\tau_{\mathrm{g}}^{\mathrm{H,D}})}{\tau_{\mathrm{g}}^{\mathrm{H}} + \left(\chi\tau_{\mathrm{liq}}^{\mathrm{H}} - \tau_{\mathrm{g}}^{\mathrm{H}}\right)\exp(-t_{\mathrm{b}}/\tau_{\mathrm{g}}^{\mathrm{H}})}, \qquad (1)$$

where ${\tau_{\mathrm{liq}}}^{\mathrm{H}}$ and ${\tau_{\mathrm{liq}}}^{\mathrm{H,D}}$ are the lifetimes of excited $\mathrm{Tb^{III}}$ ions in the liquid medium, *i.e.*, in water or an H_2O—D_2O mixture, respectively; ${\tau_{\mathrm{g}}}^{\mathrm{H}}$ and ${\tau_{\mathrm{g}}}^{\mathrm{H,D}}$ are the lifetimes in the gaseous phase of bubbles in the corresponding solvents.

To estimate the τ values in this formula, let us use the published data on the influence of deuteration on the PL of solutions of terbium chloride.

The lifetime of any excited state can be determined as

$$\tau = (k_{\mathrm{e}} + k_{\mathrm{nr}})^{-1},$$

where k_{e} and k_{nr} are the rate constants of radiation and radiationless transitions from this excited state to the ground state.

According to data,[8,11] the effect of solvent deuteration on the intensity (quantum yield) and lifetime τ of photoluminescence of an aqueous solution of terbium(III) are due to a decrease in k_{nr} when H_2O is replaced by D_2O. It is most likely that the mechanism of nonradiative deactivation can be reduced to the inductive-resonance transfer of the electron-excitation energy to overtones of high-frequency stretching vibrations of solvent molecules. In the case of the O—H bond (${\nu_3}^{\mathrm{H}} \approx 3400\ \mathrm{cm^{-1}}$), the transfer is more efficient than that for the O—D bond (${\nu_3}^{\mathrm{D}} \approx 2250\ \mathrm{cm^{-1}}$), because a less number of quanta are required in water to achieve resonance with the electron-excitation energy[13] and the corresponding integral of overlapping of the wave functions is greater than that in the case of D_2O. It has been found[14—16] that k_{nr} for $\mathrm{Ln^{III}}$ ions depends linearly on the mole fraction of H_2O in an H_2O—D_2O mixture. This fact shows that the quenching action of each (O—H)-oscillator localized near the $\mathrm{Ln^{III}}$ ion is independent of the action of another oscillator. Therefore, the rate constant of the radiationless transition can be written as follows:

$$k_{\mathrm{nr}} = mk_{\mathrm{H_2O}} + nk_{\mathrm{D_2O}},$$

where *m* and *n* are the numbers of water or heavy water molecules, respectively, directly contacted (localized in the first coordination sphere) with the $\mathrm{Tb^{III}}$ ion; $k_{\mathrm{H_2O}}$ and $k_{\mathrm{D_2O}}$ are the rate constants of radiationless quenching with one H_2O or D_2O molecule, respectively.

Table 1. Number of H_2O (*m*) and D_2O (*n*) molecules in the first coordination sphere of $\mathrm{Tb^{III}}$ and the corresponding percentage content of D_2O in H_2O

m	*n*	D_2O (%)
8	0	0
7	1	13.7
6	2	27.1
5	3	40.0
4	4	52.6
3	5	64.9
2	6	76.9
1	7	88.6
0	8	100

The *m* and *n* values can be estimated from the known coordination number characteristic of trivalent lanthanide compounds. Let us assume that the nearest environment of the terbium ion in an aqueous solution consists of 8 solvent molecules,[17] then the *m* and *n* values vary from 0 to 8 depending on the composition of the mixture (Table 1).

Using these concepts, the rate constants k_{e}, $k_{\mathrm{H_2O}}$, and $k_{\mathrm{D_2O}}$ can be estimated from the experimental data for τ and the quantum yield of PL of $\mathrm{Tb^{III}}$ in H_2O—D_2O mixtures.

The values of τ and quantum yield of PL of terbium aqua ions given above and the estimates of the corresponding rate constants have a fairly large scatter. Based on published data and our measurements of τ and the quantum yield of PL of $\mathrm{Tb^{III}}$, we accepted the following values used in subsequent calculations: ${\tau_{\mathrm{liq}}}^{\mathrm{H}} = 400\ \mu\mathrm{s}$, ${\tau_{\mathrm{liq}}}^{\mathrm{H,D}} = 4.0\ \mathrm{ms}$, quantum PL yield in water 0.08, radiative lifetime $\tau_{\mathrm{e}} = 1/k_{\mathrm{e}}$ 5 ms, $k_{\mathrm{e}} = 200\ \mathrm{s^{-1}}$, $k_{\mathrm{H_2O}} = 287.5\ \mathrm{s^{-1}}$, and $k_{\mathrm{D_2O}} = 6.25\ \mathrm{s^{-1}}$.

The theoretical curves obtained using these values by the formula

$$\left(\frac{I_{\mathrm{H,D}}}{I_{\mathrm{H}}}\right)_{\mathrm{PL}} = \frac{\tau_{\mathrm{liq}}^{\mathrm{H,D}}}{\tau_{\mathrm{liq}}^{\mathrm{H}}} = \frac{k_{\mathrm{e}} + 8k_{\mathrm{H_2O}}}{k_{\mathrm{e}} + mk_{\mathrm{H_2O}} + nk_{\mathrm{D_2O}}}, \qquad (2)$$

agree satisfactorily with the experimental data for the ratios of the intensity and τ of PL of terbium in an H_2O—D_2O mixture to the intensity and τ of PL in water (see Figs 3 and 4).

In addition, estimates of the t_{b}, χ, and τ parameters of terbium in the gaseous phase of bubbles are necessary for the adequate description of a similar dependence of the ratio of SL intensities by formula (1). These parameters were fitted if the $(I_{\mathrm{D}}/I_{\mathrm{H}})_{\mathrm{SL}}$ ratio calculated by formula (1) was equal to the experimental value equal to 4. To calculate τ in the gaseous phase, we used formulas similar to the equations for calculations of τ in liquid solvents

$$\tau^H{}_g = (k_e + lk_{H_2O})^{-1}, \tau^D{}_g = (k_e + lk_{D_2O})^{-1},$$

where the number of quenching molecules of the solvent $l = m + n$ was chosen under conditions of decreasing the solvent density from 1 g cm^{-3} in the liquid phase ($l = 8$) to 10^{-1}—10^{-3} g cm^{-3} in the gaseous phase ($l = 0.8$—0.008). For a density of 10^{-3} g cm^{-3} approximately corresponding to the gas density (vapor of the solvent) under normal conditions (pressure of 1 atm and room temperature), one can neglect the quenching of terbium with solvent molecules, *i.e.*, $\tau_g{}^H \approx \tau_g{}^D \approx \tau_e$ with a sufficient accuracy. In this case, since the SL quenching kinetics of terbium inside bubbles is virtually the same for H_2O—D_2O solutions of any composition, a decrease in the isotope effect for SL compared with this effect for PL is determined only by the t_b and χ parameters, *i.e.*, by the contribution of the "gaseous part," which is the same for solutions in H_2O and D_2O, to the total SL intensity.

However, conditions inside the bubbles are far from normal: the temperature, pressure, and density of the gas (vapor) in them can take extreme values. The density, in particular, can take the values approaching the density of the liquid phase,[12] and the quenching of solvent molecules in the bubbles, at least for solutions in H_2O, already cannot be neglected. Nevertheless, the predominant role of the t_g and χ parameters in the deuteration effect for SL is evident in this case as well.

The calculations using the $\tau_g{}^H$, $\tau_g{}^{H,D}$, and $\tau_g{}^D$ values obtained for the average value from the density interval for the gas phase (10^{-2} g cm^{-3}), the earlier presented value t_g = 300 μs, and parameter $\chi = 0.38$ obtained by fitting gave satisfactory agreement between the experimental and theoretical curves for the dependence of the $(I_{H,D}/I_H)_{SL}$ ratio on the composition of an H_2O—D_2O mixture (see Fig. 2).

Thus, the results obtained in the framework of the proposed model of nonexponential SL decay with the transfer of some excited ions to the liquid phase of the solvent confirm the hypothesis about the inner-bubble excitation of Tb^{III} ions during sonolysis of aqueous solutions. This mechanism explains the experimentally observed considerable decrease in the influence of solvent deuteration on the SL intensity compared to its influence on the PL intensity. It can be expected that the isotope effect would increase with an increase in the frequency of ultrasonic oscillations acting on the solution (compared to a frequency of 20 kHz) and, on the contrary, would decrease with the frequency decrease due to the decrease or increase in the average duration of existence of cavitation bubbles, which is synchronous with the ultrasonic frequency.

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