Sonoluminescence of terbium chloride in an H₂O—D₂O 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 Tb³⁺ ion on the composition of an H₂O—D₂O mixture is similar to an analogous dependence of its photoluminescence (PL) but with a much smaller isotope effect. In pure D₂O, 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 Tb³⁺ 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, H₂O—D₂O 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.”

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 and radicals •H and •OH and in the excitation of bubbles of dissolved particles, in particular, metal ions, and gases 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 Tb³⁺ ion as the luminescent probe for studying these processes. This choice is caused by several factors. First, it has been found 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 Tb³⁺ are well known. Third, the luminescent state of this ion ⁵D₄ 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 Tb³⁺ ion is excited upon sonolysis mainly via the mechanism of collisions with “hot” particles inside the bubbles (“inner-bubble mechanism”). 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 H₂O and D₂O (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 TbCl₃ (0.1 mol L⁻¹) provided the practical absence of the UV sonoluminescence absorption of the solvent by the Tb³⁺ ions in the solution bulk and induced noticeable sonophotoluminescence (re-emission of the absorbed light) for solutions in neither...
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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 $4 \pm 2$ °C. The time of recording of one spectrum was $\sim 1$ min.

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

**Results and Discussion**

Figure 1 presents the SL spectra of solutions of terbium chloride in H$_2$O and D$_2$O. The spectra consist of a broad (250—700 nm) continuum glow of water (excited molecules H$_2$O*, D$_2$O* 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$_2$O is replaced by D$_2$O. This indicates that the excitation conditions in the bubbles in H$_2$O and D$_2$O 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 non-radiative deactivation of the electron-excited state.

It is found that in D$_2$O 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 $\lambda = 545$ nm in a H$_2$O—D$_2$O mixture, and $I_H$ is the luminescence intensity in H$_2$O) vs. content of D$_2$O 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$_2$O 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

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**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$_2$O content in H$_2$O for SL of Tb$^{III}$: (1) experimental data and (2) calculation.

**Fig. 3.** Plot of the $I_{H,D}/I_H$ ratio vs. D$_2$O content in H$_2$O for PL of Tb$^{III}$ ($\lambda_{exc} = 365$ nm): (1) experimental data and (2) calculation.

**Fig. 4.** Plot of the $\tau_{H,D}/\tau_H$ ratio vs. D$_2$O content in H$_2$O for PL of Tb$^{III}$: (1) experimental data and (2) calculation.