

## Sonoluminescence of aqueous solutions of lanthanide salts

G. L. Sharipov,\* R. Kh. Gainetdinov, and A. M. Abdrakhmanov

*Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences  
and Ufa Research Center of the Russian Academy of Sciences,  
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.  
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru*

The influence of salts ( $\text{TbCl}_3$ ,  $\text{Tb}(\text{NO}_3)_3$ ,  $\text{PrCl}_3$ ,  $\text{EuCl}_3$ ,  $\text{CeCl}_3$ , and  $\text{DyCl}_3$ ) on the spectrum and intensity of multi-bubble sonoluminescence (SL) of water was observed at a frequency of 20 kHz. Luminescence bands of the lanthanide ions were detected in the SL spectra of concentrated solutions of the  $\text{Ce}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$ , and  $\text{Dy}^{\text{III}}$  chlorides ( $0.1\text{--}1\text{ mol L}^{-1}$ ). No luminescence was observed for solutions of the other salts, and the shape of the spectra is due to the absorption of the water SL by the lanthanide ions. Possible mechanisms of the appearance of SL of lanthanides were considered. The first mechanism is the excitation of the lanthanide aqua ions in the solution bulk due to the absorption of the short-wave portion of glow of the excited water molecules and OH radicals emitted from the cavitation gas-vapor bubbles. The second mechanism involves the transfer of the lanthanide ions to the gas phase from the liquid layer adjacent to the cavitation bubble and their excitation in the bubble volume upon collisions with other "hot" or electron-excited particles.

**Key words:** sonoluminescence, lanthanides, photoluminescence.

The formation of vapor-gas bubbles during ultrasonication of liquids is accompanied by a weak glow, *viz.*, sonoluminescence.<sup>1</sup> Sonoluminescence (SL) manifests itself as short flashes appeared in the phase of maximum compression and warming of cavitation bubbles that form by acoustic oscillations. The SL spectra detected in the majority of works<sup>1–4</sup> are caused by light emission from bubbles, whose temperature is at most  $10^4\text{ K}$ . Under these conditions, chemical bonds are cleaved, atomic and radical products (possibly, ions) are formed, and molecules and products of their sonolysis are excited.

In particular, according to the published data,<sup>3,5</sup> three characteristic regions can be distinguished in the SL spectra of water: (1) short-wave region with a maximum at 270–290 nm related to the emission of the excited water molecules or their adducts with the molecules or atoms of dissolved gases, in particular, noble gases (excited state of  $\text{H}_2\text{O}$  involved in this process was not found); (2) peak at 310 nm (emission of the electron-excited  $\text{OH}^{\bullet}$  radical formed by  $\text{H}_2\text{O}^{\bullet}$  dissociation ( $^1\tilde{A}_1$ )); (3) continuum at 380–600 nm (glow appeared upon transitions between the states  $\tilde{C} \rightarrow \tilde{A}$  of  $\text{H}_2\text{O}$  molecules).

Along with the excitation of water molecules, the SL of aqueous solutions can result in the excitation of different solution components occurring in the bubbles. In addition, SL can be related to chemiluminescence reactions of the sonolysis products of the water molecules and water-dissolved substances in the solution bulk. For example,

alkaline metals contribute to the SL spectra of concentrated solutions of their salts, because the metal ions that occur in the cavitation bubbles,<sup>6</sup> and the glow during sonolysis of luminol solutions is caused by sonochemiluminescence (SCL).<sup>7</sup> The authors of Ref. 8 explain the SL of the 2,6-bis[*N,N*-bis(carboxymethyl)aminomethyl]-4-methylphenolterbium(III) chelate complex by the inner-sphere energy transfer from the organic ligand to the terbium ion. The influence of different substances on SL can also be associated with the absorption of glow from the bubbles or its re-emission.

Lanthanide compounds with characteristic absorption and emission spectra, which are used as luminescent probes, are of interest for the detailed study of mechanisms of SL of aqueous solutions. This work is aimed at the elucidation of the mechanism of the SL of concentrated aqueous solutions of inorganic lanthanide salts.

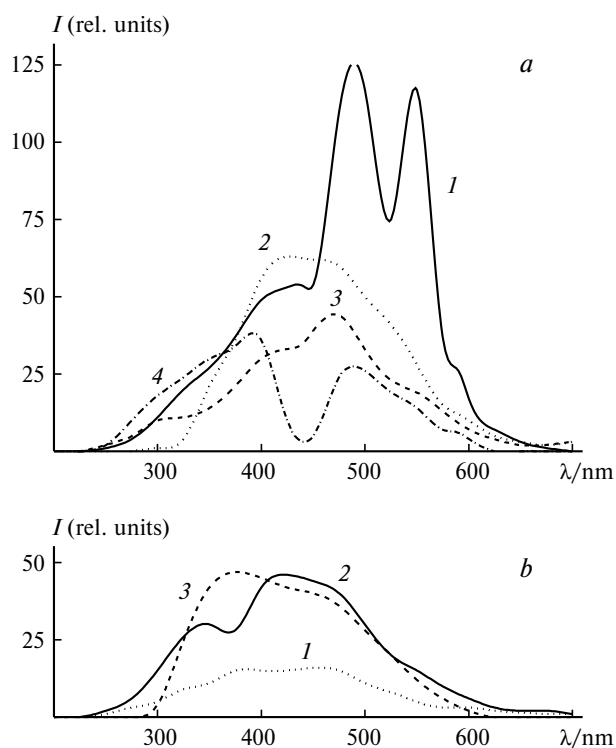
### Experimental

The SL and photoluminescence (PhL) spectra were recorded on an Aminco-Bowman spectrofluorimetric setup with a Hamamatsu 1P28 photomultiplier. Absorption spectra were obtained on a Specord UV-VIS spectrophotometer. Acoustic oscillations were generated by an Ace Glass ultrasonic generator with a titanium waveguide 130 mm in length, 6 mm in diameter, and a working frequency of 20 kHz equipped with a sensor of the emitted acoustic power. Experiments on the SL of lanthanide

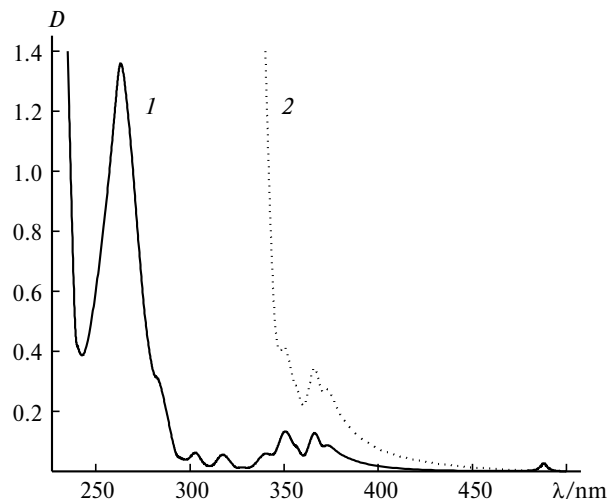
salts (reagent grade) were carried out at a radiation power of  $\sim 30$  W. Sonication was carried out in a 20-mL steel thermostatted reactor with a quartz lateral window. The distance from the waveguide axis to the window was 6 mm. The center of the generated cluster of cavitation bubbles was at this distance. However, the bubbles arranged in the cluster part nearest to the window contribute mainly to the detected SL intensity. Since the average optical path length passed by the radiation emitted from the bubbles is uncertain, we did not perform exact calculations of the efficiency of SL self-absorption by solutions in different spectral regions. The SL spectra were detected with the spectral resolution  $\Delta\lambda = 20$  nm. All solutions were saturated with air before spectra recording, and the temperature was maintained at  $4 \pm 2$  °C. The duration of recording of one spectrum was  $\sim 1$  min.

## Results and Discussion

The SL spectra of bidistilled water and aqueous solutions of Tb<sup>III</sup>, Eu<sup>III</sup>, Ce<sup>III</sup>, Dy<sup>III</sup>, and Pr<sup>III</sup> chlorides, and an aqueous solution of Tb<sup>III</sup> nitrate are presented in Fig. 1, *a*, *b*. The SL spectrum of air-saturated water (see Fig. 1, *b*) is a continuum at 250–650 nm with a broad maximum at 440 nm and corresponds to the published data.<sup>3,5</sup> All SL spectra of solutions contain the continuum of water emission.



**Fig. 1.** Sonoluminescence spectra of aqueous solutions: *a*, TbCl<sub>3</sub> (1), Tb(NO<sub>3</sub>)<sub>3</sub> (2), DyCl<sub>3</sub> (3), and PrCl<sub>3</sub> (4); *b*, bidistilled water (1), EuCl<sub>3</sub> (2), and CeCl<sub>3</sub> (3).  $C = 1$  mol L<sup>-1</sup> (for PrCl<sub>3</sub>  $C = 0.5$  mol L<sup>-1</sup>).



**Fig. 2.** Absorption spectra of aqueous solutions of TbCl<sub>3</sub> (1) and Tb(NO<sub>3</sub>)<sub>3</sub> (2) ( $C = 1$  mol L<sup>-1</sup>,  $l = 1$  cm).

The PhL spectrum of the terbium aqua ion is known<sup>9</sup> to be caused by transitions from the <sup>5</sup>D<sub>4</sub> level to the sub-levels of the ground multiplet <sup>7</sup>F<sub>*j*</sub>. The SL spectrum of a solution of TbCl<sub>3</sub> (see Fig. 1, *a*) exhibits transitions with maxima at 488 (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>6</sub>) and 545 nm (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub>), indicating that the Tb<sup>3+</sup> ions are excited by sonolysis. The SL intensity in these transitions is proportional to the TbCl<sub>3</sub> concentration in an interval of 0.05–1 mol L<sup>-1</sup>. These bands are absent from the SL spectrum of terbium nitrate. This spectrum represents only the continuum of water emission with the boundary shifted to 320 nm due to the absorption of the short-wave portion of the continuum by a solution of Tb(NO<sub>3</sub>)<sub>3</sub> (Fig. 2).

The PhL spectrum of the Ce<sup>3+</sup> aqua ion consists of a broad band at 313–407 nm with a maximum at  $\sim 355$  nm.<sup>9</sup> The data in Fig. 1, *b* show that the presence of the Ce<sup>3+</sup> ion increases the intensity in the SL spectrum of water in this interval. This influence is observed from the concentration  $[\text{CeCl}_3] = 1 \cdot 10^{-3}$  mol L<sup>-1</sup> with a sharp increase in the 0.05–1 mol L<sup>-1</sup> region. In concentrated solutions of cerium chloride, the short-wave boundary of the SL spectrum is shifted to 300 nm due to the absorption of water luminescence by the Ce<sup>3+</sup> aqua ions in a region of 250–300 nm.

The dysprosium(III) aqua ion is characterized by a weak yellow PhL. The visible region of the spectrum contains a band with a maximum at 477 nm and a weaker band at 570 nm, which corresponds to the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> transitions.<sup>9</sup> These regions in the SL spectrum also contain the maximum and inflection in the curves of the luminescence intensity. The light absorption by a concentrated solution of dysprosium chloride exerts a noticeable effect on the intensity distribution in this spectrum. According to the published data,<sup>9</sup> the absorption spectrum of DyCl<sub>3</sub> contains a set of lines (328, 352,

and 365 nm) with the molar absorption coefficients  $1.9\text{--}2.6\text{ L mol}^{-1}\text{ cm}^{-1}$ . At high concentrations, this results in a noticeable absorption of the light emitted in this region by water from the cavitation bubbles. As a result, a minimum at 350 nm and false inflections at 300 and 400 nm appear in the SL spectrum (see Fig. 1, *a*).

The europium aqua ion exhibits a bright orange PhL. In the visible spectral region, the brightest band has a maximum at  $\sim 612\text{ nm}$  corresponding to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition.<sup>9</sup> In the SL spectrum of europium(III) chloride, this transition was not observed in our experiments (see Fig. 1, *b*). The formation of a separate maximum at 340 nm in the continuum glow attributed to the emission of water molecules is caused by the peak at 394 nm ( $\epsilon = 2.9\text{ L mol}^{-1}\text{ cm}^{-1}$ )<sup>9</sup> in the absorption spectrum of  $\text{EuCl}_3$ , and this peak produces a minimum in the SL spectrum.

The PhL spectrum of the praseodymium(III) aqua ion contains intense bands with maxima at 243, 260, and 271 nm and much weaker bands at 395 and 480 nm.<sup>10</sup> These maxima were not detected in the SL spectrum of  $\text{PrCl}_3$  (see Fig. 1, *a*). According to our estimates, the minimum at 440 nm in the continuum of the SL spectrum, forming false maxima at 390 and 490 nm, and an insignificant minimum at 585 nm are caused by light absorption by the  $\text{Pr}^{3+}$  ions ( $\epsilon = 10.1\text{--}1.95\text{ L mol}^{-1}\text{ cm}^{-1}$ ).<sup>9</sup>

In addition, the data in Fig. 1 show that high concentrations of all lanthanide ions noticeably (up to fourfold near 440 nm) increase the total intensity of the water continuum glow. This effect, which does not exceed 20–30%, cannot be ascribed to an increase in the amount of absorbed acoustic energy due to an increase in the solution density.

The data obtained on sonolysis of aqueous solutions of the trivalent lanthanide ions can be explained in the framework of two mechanisms: (1) traditional photo-excitation mechanism exhibits the standard PhL of ions in the solution bulk related to the absorption of the UV radiation emitted from the cavitation bubbles; (2) emission in the SL spectra is caused by the transfer of the lanthanide ions from the liquid layer adjacent to a pulsating or collapsing bubble to the gas phase accompanied by the excitation of these ions in the bubble volume upon direct collisions with other vibration- or electron-excited species.

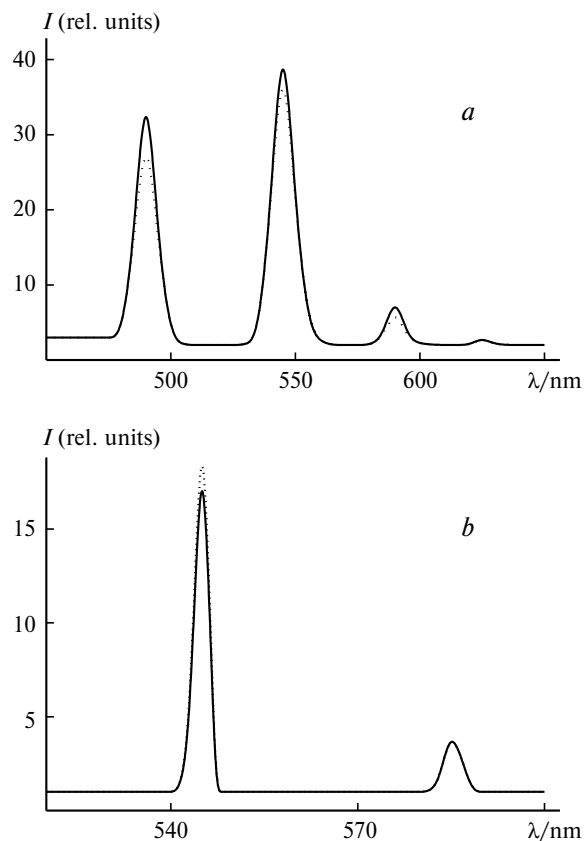
The mechanism of SCL<sup>8</sup> does not take place because the solution contain no organic compounds that could be oxidized by the  $\text{OH}^\bullet$  radicals followed by the excitation of the lanthanide ions, *e.g.*,  $\text{Tb}^{3+}$ . Note that SCL was observed at the concentration of the terbium ions equal to  $1 \cdot 10^{-5}\text{--}1 \cdot 10^{-3}\text{ mol L}^{-1}$ , whereas specific SL of the majority of lanthanide ions was observed in our experiments only in concentrated solutions.

These data favor the first mechanism. In the absorption spectrum of  $\text{TbCl}_3$  (see Fig. 2), the most intense band with  $\lambda_{\text{max}} = 219\text{ nm}$  cannot provide the re-emission

effect, because the short-wave glow in the region  $<230\text{ nm}$  is absent from the SL spectrum of water. The absorption band of  $\text{Tb}^{3+}$  with  $\lambda_{\text{max}} = 265\text{ nm}$  provides the increasing light absorption in an interval of 250–300 nm in the concentration region from 0.05 to  $1\text{ mol L}^{-1}$ . The SL of terbium is observed just at these concentrations. The hypothesis that the characteristic luminescence of terbium is a result of re-emission of the water glow absorbed in the interval from 250 to 300 nm was checked by comparison of the data on SL and PhL of terbium(III) chloride and nitrate.

For excitation at 365 nm or in the resonance absorption band with  $\lambda_{\text{max}} = 488\text{ nm}$  (see Fig. 2), the PhL yields of solutions of terbium(III) nitrate and chloride are very close (Fig. 3). At the same time, unlike  $\text{TbCl}_3$ , whose quantum yield of PhL is independent of the excitation wavelength,<sup>9</sup> no PhL of a concentrated solution of  $\text{Tb}(\text{NO}_3)_3$  is observed upon excitation with the light  $<300\text{ nm}$ .

These facts indicate the traditional mechanism of SL excitation of the terbium ions, because the absence of SL in solutions of terbium nitrate and its PhL at the excitation wavelengths  $<300\text{ nm}$  are due to the absorption of exciting emission by the  $\text{NO}_3^-$  ions, which cannot trans-



**Fig. 3.** Photoluminescence spectra of aqueous solutions of  $\text{TbCl}_3$  (solid line) and  $\text{Tb}(\text{NO}_3)_3$  (dotted line):  $\lambda_{\text{exc}} = 365$  (*a*) and 488 nm (*b*) ( $\Delta\lambda = 5\text{ nm}$ ,  $C = 1\text{ mol L}^{-1}$ ).

fer the energy to the  $\text{Tb}^{3+}$  ions. Concentrated solutions of terbium(III) nitrate exhibit a strong absorption in this spectral region due to the nitrate ion. At the wavelengths  $>350$  nm, the absorption of the  $\text{Tb}^{3+}$  aqua ions is almost the same as that in solutions of  $\text{TbCl}_3$ , which allows PhL (see Fig. 2).

However, the quantum yield of PhL of terbium(III) chloride in water ( $\sim 0.08$ )<sup>11</sup> is insufficiently high to explain the emission intensity of  $\text{Tb}^{3+}$  observed in the SL spectrum by re-emission only. Estimation of the integral intensity of the water luminescence absorbed by terbium(III) based on the quantum yield of its PhL and the data in curve 1 (Fig. 1, *a*) gives the value sixfold higher than the measured integral intensity of the water continuum glow. Although this is a rough estimate, but the above conclusion remained unchanged after various corrections were introduced.

The  $\text{Ce}^{3+}$  ions absorb at 200–300 nm more efficiently than the  $\text{Tb}^{3+}$  ions, and the quantum yield of PhL of cerium(III) is equal to unity.<sup>12</sup> However, the contribution of  $\text{Ce}^{3+}$  to SL of water is low compared to the contribution of  $\text{Tb}^{3+}$ , whose quantum yield of PhL and, hence, the re-emission efficiency are lower by an order of magnitude. This is indicated by comparison of Figs. 1 and 4. The influence of the  $\text{NO}_3^-$  ions on the SL of terbium(III) cannot be reduced to the simple absorption of water emission. True quenching of the SL of the  $\text{Tb}^{3+}$  ions (excited *via* a mechanism different from the traditional one) by the nitrate ion occurs.

This mechanism is, most likely, due to occurring the lanthanide salts taken in high concentrations in the cavitation bubbles. This is indicated by an increase in the intensity of the water glow continuum.

A similar effect of the solute observed previously<sup>6</sup> for the SL of solutions of the alkaline and alkali-earth metal chlorides and nitrates was explained by warming of both the content of the cavitation bubble and adjacent

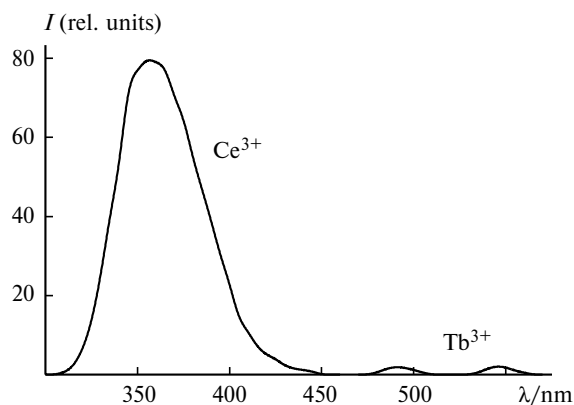
liquid layer  $\sim 1 \cdot 10^{-5}$  cm thick at the final stage of compression of the cavitation bubble. The parameters achieved at the bubble–liquid interface are sufficient even for evaporation of undissolved metal salts. In this case, the glow related to the excitation of water molecules is enhanced.

The multiply repeated compression and evaporation cycles should result in the accumulation of the lanthanide ions and other products of dissociation of their salts in the bubbles. Perhaps, the lanthanide ions are excited when they interact with the products of water sonolysis. The luminescence yields of  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$  during SL were found to be not proportional to the quantum yields of PhL of these ions, which contradicts the hypothesis of re-emission. This contradiction can be explained by the formation of the main portion of the excited terbium ions precisely in the gas phase. Cerium(III), taking into account its SL in dilute solutions, produces luminescence, probably, *via* the re-emission mechanism, while in the bubbles its excitation is much weaker than that of terbium(III) because of less favorable conditions of energy transfer from different excited states of water. For example,  $\text{Tb}^{3+}$  can accept the energy from almost all states of water and the  $\text{OH}^\bullet$  radical involved in the SL, while  $\text{Ce}^{3+}$  can accept the energy only from the high-lying levels. In addition, the luminescence of  $\text{Tb}^{3+}$ , unlike the d–f-luminescence of  $\text{Ce}^{3+}$ , is caused by f–f-transitions, affecting the efficiency of excitation of these ions in the bubbles. An additional source of differences in luminescence in the liquid and gas phases under ultrasonic cavitation conditions can be the fact that several lanthanide ions (for example,  $\text{Tb}^{3+}$ ) are characterized by the lifetime of the excited state longer than the period of bubble oscillation.

The quantum yield of PhL of the  $\text{Pr}^{3+}$  aqua ion is unity.<sup>10</sup> However, it absorbs in the UV region at  $\lambda_{\text{max}} = 215$  nm and, unlike  $\text{Ce}^{3+}$ , has a "window" in the absorption spectrum at 250–400 nm. This ion exhibits no SL, because the excited products of water sonolysis ( $\text{H}_2\text{O}^*$  and  $\text{OH}^*$ ) cannot excite  $\text{Pr}^{3+}$  either radiatively (in the solution bulk) due to the absence of glow from the bubbles at  $\lambda < 230$  nm, or nonradiatively (in the bubble volume).

An insignificant ( $\text{Dy}^{3+}$ ) or unobserved ( $\text{Eu}^{3+}$ ) contribution of these ions to SL is due<sup>9</sup> to a much lower (compared to that of  $\text{Tb}^{3+}$ ) quantum yield of PhL in both solution and the gas phase.

Thus, our data indicate that the SL of lanthanides is excited by both the re-emission mechanism (for example, in dilute solutions of  $\text{Ce}^{3+}$ ) and the mechanism of their transfer from the liquid layer adjacent to the cavitation bubble to the gas phase ( $\text{Tb}^{3+}$ ). The influence of the lanthanide ions on SL can also be the absorption of some SL spectral regions of water (solutions of  $\text{Pr}^{3+}$  and  $\text{Eu}^{3+}$ ).



**Fig. 4.** Photoluminescence spectra of aqueous solutions of  $\text{CeCl}_3$  and  $\text{TbCl}_3$  ( $\lambda_{\text{exc}} = 219$  nm,  $\Delta\lambda = 5$  nm,  $C = 1$  mol  $\text{L}^{-1}$ ). The spectra were recorded in the reflection mode with complete absorption of the excitation radiation in a thin layer of solutions.

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