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Sonoluminescence of aqueous solution of gadolinium chloride

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A line of the Gd^{III} ion was detected at 311 nm in the multibubble sonoluminescence spectrum of a concentrated (1 mol L^{-1}) solution of gadolinium chloride. A comparison with the earlier studied sonoluminescence of the Ce^{III} and Tb^{III} ions shows that the Gd^{III} ion is excited in the volume and/or on the surface of cavitation bubbles upon collisions with "hot" particles. The efficiency of excitation of the lanthanide ions *via* this mechanism depends on the type of electron transition. For the same energy of the excited state, the efficiency of Gd^{III} excitation (f—f transition) exceeds by at least 50 times that of Ce^{III} excitation (f—d transition).

Key words: sonoluminescence, lanthanides, photoluminescence, gadolinium chloride.

Sonolysis and sonoluminescence (SL) are being studied for a long time. However, mechanisms of many processes accompanying the appearance of cavitation gas-vapor bubbles in the liquid upon ultrasonication remain unclear.[1] The characteristic emission lines of dissolved metal compounds have previously[2—8] been found in the SL spectra, indicating their excitation upon sonolysis of the aqueous solutions. However, this phenomenon is described in general features only.

It is believed[2] that at low concentrations (10^{-4}—10^{-3} mol L^{-1}) additives are excited due to chemiluminescence reactions involving sonolysis products in bubbles of water molecules that get into the solution volume. At high concentrations (>0.1 mol L^{-1}), the additives get into gas bubbles and are excited similarly to water molecules, *i.e.*, due to inelastic collisions with other particles in the gaseous phase heated to high temperature ($(3—5) \cdot 10^3$ K).[8]

Neither the role of a traditional optical mechanism, *viz.*, re-emission by additives after absorption (mainly in the UV region) of the luminescence of water molecules, nor the role of factors affecting the efficiency of inner-bubble excitation and luminescence of the additives are considered in the above-mentioned works.[2—8] Although states with any quantum numbers can be excited upon collisions of electrons, ions, atoms, and molecules,[9] unlike optical transitions, the efficiency (cross section) of excitation depends on both the energy (including the energy of the formed excited state) and quantum states of these particles. Both the intrinsic (determined by intramolecular processes) quantum yield of luminescence and different reactions of quenching by the sonolysis products should affect the SL intensity of the additives.

Lanthanide compounds with characteristic wide-range absorption and emission spectra, from the UV to IR region, are best suited to solve these problems.[10]

We have earlier[11] studied the SL of concentrated aqueous solutions of lanthanide chlorides (C = 1 mol L^{-1}). The SL spectra consist of a broad (λ = 250—650 nm) continuum glow of excited water molecules and OH$^{\bullet}$ radicals, and the characteristic luminescence bands of Ln^{III}, *e.g.*, Tb^{III}, Dy^{III}, or Ce^{III}, are superimposed on this glow. For the ions with a high photoluminescence quantum yield in solution ($\varphi \approx 1$), the efficiency of characteristic SL is found to be low: no SL of the Pr^{III} ion, which does not absorb in the region of UV emission of the sonolysis products of water, was found. The low-intensity SL of the Ce^{III} ion is mainly caused by the absorption of the light emitted from bubbles by the sonolysis products of water, *viz.*, cerium ions, in the liquid bulk (optical mechanism) (Fig. 1, insert). The sonoluminescence of the Tb^{III} and Dy^{III} ions with lower quantum yields ($\varphi \le 0.1$) is much more intense than the SL of the cerium ion and is not related to the optical mechanism. As in Ref. 8, the SL of these ions was attributed to their electron excitation in the cavity and/or on the surface of bubbles. This process is assumed to be much more efficient than the inner-bubble electron excitation of the Pr^{III} and Ce^{III} ions, which do not differ substantially from the Tb^{III} and Dy^{III} ions by the ability of incorporation into the bubbles.

The different efficiencies of SL generation in cavitation bubbles can be a consequence, first, of differences in the energy of the excited state of Ln^{III} ions (in the case of praseodymium and cerium, it is ~47 000 and ~32 200 cm^{-1}, respectively; for terbium and dysprosium, it is much lower: ~20 000 cm^{-1}). Second, the electron states are different: excitation in praseodymium and cerium is caused by the f—d transitions, while the f—f transitions produce the electron states in terbium and dysprosium.[10] Since the excitation cross sections of lanthanide ions for collisions of particles were not calculated, experimental data on the

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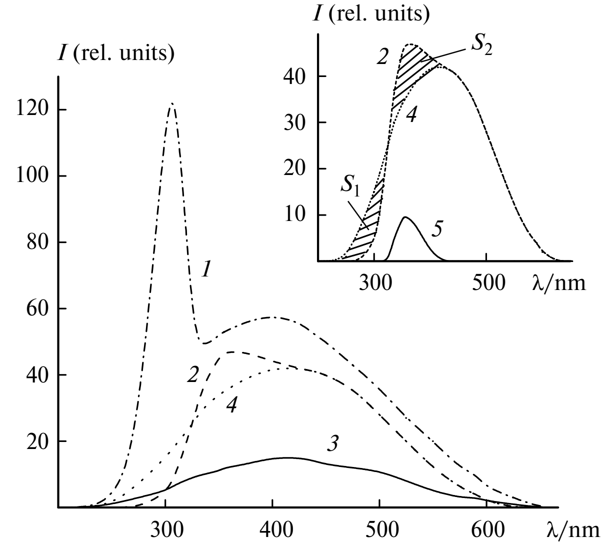

Fig. 1. Sonoluminescence spectra (T = 4±2 °C) of aqueous solutions of gadolinium chloride (*1*), cerium chloride (*2*)[11] (C = 1 mol L^{-1}), and bidistilled water (*3*) and the reduced spectrum of the continuum glow of water during sonolysis of a cerium solution (*4*). The spectrum (*5*) obtained by subtraction of curve *4* from curve *2* in a region of 320—450 nm and coinciding with the photoluminescence spectrum of Ce^{III} is shown in insert. The hatched regions S_1 and S_2 equal in surface area are the part of the bubble glow of water absorbed by cerium and the sonoluminescence emitted by cerium, respectively.

influence of these factors on the inner-bubble SL of lanthanides are required.

For this purpose, in this work we studied the earlier unknown SL of an aqueous solution of gadolinium chloride. The energy of the excited state of the Gd^{III} ion (~32 000 cm^{-1}) is higher than the resonance levels of the terbium and dysprosium ions and is close to the level of the excited state of the cerium ion. At the same time, the excitation of the gadolinium, terbium, and dysprosium ions is caused by a transition of the f—f type.

Experimental

Gadolinium chloride was prepared from metallic gadolinium of 99.9% purity and hydrochloric acid (special purity grade) using a known procedure.[12] The experimental setup is similar to that described earlier.[11] Sonoluminescence spectra were recorded on an AMINCO-BOWMAN spectrofluorimetric technique with a HAMAMATSU 1P28 photomultiplier tube (PMT). To obtain acoustic oscillations, an ACE GLASS ultrasonic generator with a titanium waveguide (length 130 mm, diameter 6 mm, and working frequency 20 kHz) equipped with a sensor of the emitted acoustic power was used. Experiments were carried out at a radiation power of ~30 W. Sonoirradiation was carried out in a steel thermostatted 20-mL reactor with a quartz window. Glow was detected from a bubble cluster with a volume of ~1 cm^3. Sonoluminescence spectra were recorded with the spectral resolution $\Delta\lambda$ = 20 nm. The temperature of all air-saturated (before spectra recording) solutions was maintained at a level of 4±2 °C. One spectrum was recorded within ~1 min.

The SL yield of the Gd^{III} ions was estimated by a comparison of integrated glows of the band at λ = 311 nm and a reference radioluminescent light source (λ_{max} = 520 nm) similarly to a known procedure.[13] The total number of photons emitted by gadolinium from the whole cavitation region was estimated with allowance for the spectral sensitivity of the PMT and geometry of measurement.

Results and Discussion

The SL spectra of bidistilled water and aqueous solutions of $GdCl_3$ and $CeCl_3$ are given in Fig. 1. It is seen that the spectrum of a solution of gadolinium chloride contains an intense band with a maximum at λ = 311 nm corresponding to the transition $^6P_{7/2} \rightarrow {}^8S_{7/2}$ in the Gd^{III} ion.[10] The line corresponding to the transition $^6P_{5/2} \rightarrow {}^8S_{7/2}$ (λ = 306 nm) is not resolved under the experimental conditions. The intensity of the characteristic band of the gadolinium ion, as in the case of the SL of the terbium ion,[11] increases linearly with an increase in the concentration from 0.05 mol L^{-1} (detection limit) to 1 mol L^{-1}. In addition, high concentrations of the gadolinium ion, as well as other lanthanide ions[11] or alkaline metal salts,[4—8] noticeably increase the intensity of the continuum glow of water (up to a factor of four near the maximum at λ = 420 nm). These regularities, as well as the high redox potential of the Gd^{IV}/Gd^{III} pair (E° = 7.9 V),[14] make it possible to exclude the earlier proposed[2] redox chemiluminescence mechanism for the SL of aqueous solutions of the organic terbium chelate (oxidation of the emitter or its precursor with the $OH^\bullet$ radical followed by excitation accompanying reduction with a hydrogen atom).

It is known[10] that the absorption spectrum of the Gd^{III} aqua ion contains bands at 272, 273, and 275 nm (*i.e.*, at the UV spectral edge of the SL continuum of water) with molar absorption coefficients of 3.16, 1.12, and 1.9 L mol^{-1} cm^{-1}, respectively. A small linewidth and low molar absorption coefficients impede the optical excitation of the gadolinium aqua ion during sonolysis. When assuming that the SL of the Gd^{III} ion appears *via* the optical mechanism, then, taking into account its photoluminescence quantum yield in solution ($\varphi \approx 0.2$),[15] it is difficult to explain a higher glow intensity at λ = 311 nm compared to the SL intensity of the Ce^{III} ion ($\varphi \approx 1$) (see Fig. 1). The contributions from the gadolinium and terbium glows ($\varphi \approx 0.1$)[11] to the SL of an aqueous solution are close. Therefore, the gadolinium glow in the solution bulk related to the absorption of radiation from water and $OH^\bullet$ radicals is not the main source of its SL. Sonoexcitation of gadolinium can be explained by the inner-bubble mechanism proposed previously[11] for the SL of terbium and dysprosium (see below).

According to the modern concepts,[8] "hot" particles are formed inside a pulsatory cavitation bubble due to its compression in a ultrasonic field. Collisions of the "hot" particles produce electron-excited water molecules and $OH^{\bullet}$ radicals. It is assumed[8] that both the contents of a bubble and an adjacent liquid layer with a thickness up to 10^{-5} cm can be heated at maximum compression. The parameters achieved at the liquid—gas interface are sufficient for the evaporation of nondissociated metal salts, in particular, lanthanides. Getting into the gas phase, the Ln^{III} ions can be excited upon inelastic collisions with "hot" particles and, perhaps, due to the electron-excitation energy transfer if the collisions occur with the already excited particles, for example, H_2O^* and OH^*.

The estimates presented below show that the ions at the liquid—gas interface, for instance, in a thin "monoaquaionic" layer, can also be excited upon collisions.

To check this hypothesis, we estimated the luminescence yield of the Gd^{III} ions. We found that for a solution with $C = 1$ mol L^{-1} at a radiation power of $\sim 6.4 \cdot 10^{-10}$ W the photoacoustic efficiency is $\sim 2.1 \cdot 10^{-11}$ and the number of excited ions generated per period of an ultrasonic field oscillation is $N_e^* \approx 10^5$.

Let us estimate the efficiency of Gd^{III*} ion generation upon collisions, ignoring a possibility of excitation in the bubble volume and assuming that the latter occurs only on the bubble surface. For this purpose, by analogy to Ref. 8, we estimate the minimum number of gadolinium ions on the cavitation bubble surface at the moment of its maximum compression, when a glow flash occurs. Since the minimum radius of a bubble is $\sim 10^{-4}$ cm[16,17] and the kinetic diameter of water molecules is $4 \cdot 10^{-8}$ cm, the total number of molecules on the bubble surface is $\geq 10^8$. Since the molar fraction of dissolved gadolinium is equal to 1 : 55 (55 is the number of water moles in solution), the number of the gadolinium ions on the bubble surface is $\sim 2 \cdot 10^6$. For the bubble concentration $n \approx 10^3$—10^4 cm^{-3},[18] the total number of gadolinium ions on the bubble surface is $N \approx 2 \cdot 10^9$—$2 \cdot 10^{10}$ and the fraction of the excited ions N_e^*/N is $\sim 10^{-5}$. Thus, only an insignificant portion of the Gd^{III} ions capable of excitation on the surface is excited, which is quite reasonable in the framework of the collision mechanism.

These data suggest that the Gd^{III} ions are excited upon collisions, most likely, due to the transformation of the kinetic energy of "hot" particles into the electron-excitation energy rather than the energy transfer from the excited particles H_2O^* and OH^*. Otherwise, the continuum glow of water in the short-wave region would be quenched.

We can conclude the following. Although the energy gap between the ground and first electron-excited states is considerable and close to that for the Ce^{III} ion (f—d type), the Gd^{III} ion (f—f type) is excited in bubbles with an efficiency close to that of the inner-bubble excitation of the Tb^{III} and Dy^{III} ions (f—f type). Thus, the influence of differences in energies of the excited state of the Ln^{III} ions on their inner-bubble SL is less significant than the effect of the electron transition type.

Note that the SL efficiencies of the Gd^{III} and Ce^{III} ions were compared ignoring the influence of possible quenching reactions of luminescent states of these ions by the sonolysis products. The question arises: which step of inner-bubble processes is more affected by the excited state nature, namely, the primary step of Ln^{III} ion excitation upon collisions or subsequent steps of radiation and radiationless deactivation of the excited ions?

At the first sight, the low SL intensity of the cerium ion and no SL of the praseodymium ion[11] can also be attributed to the inner-bubble quenching reactions. Ions with the f—d type of excitation are good electron donors[19,20] and can react, *e.g.*, with the $OH^{\bullet}$ radical.

$$Ce^{3+*} + OH^{\bullet} \longrightarrow Ce^{4+} + OH^-$$

$$Pr^{3+*} + OH^{\bullet} \longrightarrow Pr^{4+} + OH^-$$

However, the probability of this quenching is low under the experimental conditions, because the $OH^{\bullet}$ radicals are efficiently trapped by the known[21] acceptor, *viz.*, Cl^- ions. They are present in the solution and, hence, in the bubbles in a much higher concentration than that of the excited lanthanide ions having, in addition, a short lifetime (44 ns for cerium).[10]

Sonolysis is known[22] to have many common features with radiolysis. Therefore, note that the efficiencies of SL generation for lanthanides and the earlier[23] determined relative yields of their luminescence during radiolysis correlate. It should be emphasized that, similarly to inner-bubble collisions with "hot" particles, the main source of lanthanide ion excitation during radiolysis of aqueous solutions is the direct effect of radiation, *i.e.*, their collisions with ionizing particles. The study of the effect of radical acceptors on radioluminescence of lanthanide ions showed a certain influence of track quenching reactions on the luminescence yield. However, the latter is more significant for the Tb^{III} ion with the f—f type of excitation (quenching with a hydrated electron)[23,24] rather than for the cerium ion (quenching with the $OH^{\bullet}$ radical).*

$$Tb^{3+*} + e^-_{aq} \longrightarrow Tb^{2+} \text{ (or } Tb^{3+} + e^-_{aq}{}^*\text{)}$$

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* The excited state of the terbium ion has a much longer lifetime (400 μs for the aqua ion[10]) than the Ce^{3+*} ion and, probably, it is more vulnerable for quenching by the radiolysis products or water sonolysis. Note that the lifetime of the Tb^{3+*} ion is comparable with the oscillation period of a bubble, which can disappear after one or several oscillations due to collapse, yielding the excited and radical products to the solution. The transfer of the Tb^{3+*} ions from the gaseous to aqueous phase provides additional (compared to the cerium ion) opportunities for quenching during sonolysis. Nevertheless, the SL intensity of the terbium ion is higher than that of the cerium ion.

However, the above-presented quenching reaction have no decisive influence on the radioluminescence yield, which would strongly change the ratio between the luminescence yields of different ions.[23] Most likely, this conclusion is also true for inner-bubble SL, the more so, sonolysis is characterized by the formation of a weaker (compared to a hydrated electron) reducing agent (H atom) and a more diffuse distribution of the primary $OH^•$ and $H^•$ radicals.[22] For sonolysis and radiolysis of aqueous solutions, the terbium, dysprosium, and gadolinium ions luminesce and are excited, evidently, much more efficiently than the cerium and praseodymium ions.

Thus, the influence of the excitation state type on the efficiency of inner-bubble excitation of lanthanide ions rather than on the step of their quenching seems most probable for explanation of the results obtained.

This effect can quantitatively be estimated in the first approximation, *i.e.*, ignoring the spectral sensitivity of the PMT in the absorption and emission regions of cerium and gadolinium ions, losses for multiple reemission (in the case of cerium), and influence of possible reactions of inner-bubble quenching and changing φ of the gadolinium ions that transfer to the gaseous phase. A comparison of the integrated intensities of the radiation absorbed by cerium from bubbles (S_1 = 505±25 rel. units) and the glow emitted by cerium (S_2 = 507±25 rel. units) shows (see Fig. 1, insert) that the SL intensity of the cerium ion, which could be related to its inner-bubble excitation, *viz.*, $I = S_2 - S_1\varphi$, is lower than the detection threshold and does not exceed $0.1S_1$ = 50 rel. units, taking into account measurement errors S_1 and S_2 (5%). A comparison of this value with the integrated SL intensity of the gadolinium ion (surface area of the band at λ = 311 nm, which is equal to 2840±140 rel. units) suggests that at the same excitation state energy the efficiency of excitation of an ion of the f—f type in inner-bubble processes is more than 50-fold higher than that of excitation of an ion of the f—d type.

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