On the emitters of sulfuric acid sonoluminescence

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A comparative study of the sonoluminescence spectra of water and argon-saturated aqueous H_2SO_4 solutions was carried out. At an H_2SO_4 concentration of 18 mol L^{-1}, the sulfuric acid sonoluminescence is fifty times more intense than water sonoluminescence. The sulfuric acid luminescence spectrum differs from the water sonoluminescence spectrum caused by the emission of excited water molecules and OH radicals from the gas phase of cavitation bubbles. The sulfuric acid sonoluminescence spectrum exhibits maxima at 330, 420, 500, and 630 nm. Emitters of sonoluminescence of sulfuric acid are the singlet (330—340 nm) and triplet (~420 nm) excited SO_2 molecules formed by sonolysis of H_2SO_4 molecules. Another product of sonolysis of H_2SO_4, atomic oxygen, is assumed to be responsible for the luminescence at $\lambda = 630$ nm.

Key words: sonoluminescence, aqueous solution, sulfuric acid, sulfur dioxide.

The mechanism of ultrasonic cavitation in liquids has been studied for about a century. Meanwhile, the essence of high-energy processes occurring in cavitation bubbles (CBs), which are responsible for sonoluminescence and sonochemical reactions, are still to be clarified.[1] Studies of sonoluminescence of aqueous solutions of various compounds including inorganic acids in comparison with the corresponding data for water are expected to clarify the mechanism of sonoluminescence, to find ways of enhancement of sonoluminescence intensity, and to disclose fields of application of this phenomenon.

The effect of ultrasonic cavitation on aqueous solutions of inorganic acids has been studied.[2—6] In argon-saturated H_2SO_4 solutions (at acid concentrations exceeding 9 mol L^{-1}) the H_2SO_4 molecules decompose into sulfur, SO_2, and H_2S.[2] It was assumed[3] that breakdown of H_2SO_4 molecules is due to energy transfer from the excited species produced in CBs to the H_2SO_4 molecules and HSO_4^- ions on the CB walls. In concentrated solutions, the H_2SO_4 molecules present within CBs can also evaporate and interact with electrons produced[2] in the gas phase on elecrical breakdown of CBs. No sonoluminescence of sulfuric acid has been studied by the authors of Ref. 2. Sonolysis of hydrochloric and phosphoric acids was also investigated[3,4] without studying sonoluminescence.

A sonoluminescence study[5] of argon-saturated aqueous nitric acid solutions revealed a selective quenching of the 310 nm band of $^{\bullet}OH$ radicals in the sonoluminescence spectrum on an increase in the HNO_3 concentration in the range 0—0.9 mol L^{-1} and an increase in the intensity of an H_2O^* luminescence band near $\lambda = 275$ nm. Further increase in the HNO_3 concentration leads to a decrease in the intensity of sonoluminescence throughout the entire spectrum.

Thus, only a few studies on sonoluminescence of aqueous solutions of inorganic acids are available. At the same time, information on sonoluminescence of aqueous solutions of strong electrolytes could clarify a "dispute" between the thermal and electric theories of sonoluminescence. According to the former theory, quasi-adiabatic compression of a CB leads to heating of its content. In this case sonoluminescence is due to either equilibrium thermal emission or deactivation of excited molecules that are produced in the CB by inelastic collisions of high-energy species.[7] The electric theory explains sonoluminescence by electric breakdown in a CB on compression or splitting.[1]

Earlier,[6] we observed sonoluminescence of air-saturated aqueous sulfuric acid solutions. We assumed[6] that the experimentally observed luminescence spectrum in the region $\lambda = 350—550$ nm with a broad maximum at $\lambda = 450$ nm is due to emission of several types of emitters including sulfur dioxide formed as a result of sonolysis of H_2SO_4 molecules inside CBs. We also reported[6] a nearly tenfold enhancement of sonoluminescence intensity after saturation of concentrated H_2SO_4 with argon. In this work, in order to obtain more detailed information on the emit-

ters of H_2SO_4 luminescence, we studied the sonolumi-nescence spectra of argon-saturated aqueous H_2SO_4 solu-tions, recorded with a higher resolution than in our earlier study.[6]
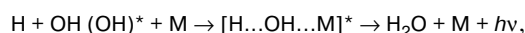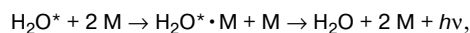
Experimental

Sulfuric acid ("extra pure" grade) was distilled until UV ab-sorption in a cell ($l = 1$ cm, $\lambda > 200$ nm) was absent. Solutions were prepared using bidistilled water and the concentration of H_2SO_4 was determined by titration. The solutions were soni-cated in a cylindrical reactor (inner diameter 36 mm, height 100 mm) equipped with a thermostatting water jacket. Sono-luminescence was monitored through a quartz window in a lat-eral wall of the reactor. In all experiments, the volume of the sonicated liquid was 35 mL. Sonication was performed with an ACE GLASS (USA) ultrasonic apparatus (operating frequency of 20 kHz, maximum electric power of 100 W, titanium horn 6 mm in diameter), equipped with a sensor of acoustic power. In all experiments the solutions were sonicated at an acoustic power of 30 W. The temperature inside the reactor was maintained at 4 ± 2 °C. Prior to recording the sonoluminescence spectra all solutions were saturated with argon for 30 min, which was pre-dried and pre-purified from oxygen by successive passage through columns with alumina and activated copper.

Sonoluminescence spectra were recorded using an MDR-23 monochromator (inverse linear dispersion was 1.3 nm mm^{-1}) and a FEU-100 photomultiplier. Signal from FEU-100 was transmitted to a high-resistance K-201 X-Y-recorder. The total sonoluminescence intensity in the region $\lambda = 200-700$ nm was measured using a chemiluminometer equipped with a FEU-39 photomultiplier operating in the current regime as a photode-tector. The chemiluminometer was calibrated against a refer-ence radioluminescent light source ($2\cdot10^7$ photon s^{-1}, liquid scintillator containing ^{14}C-labelled acetic acid).

Results and Discussion

The sonoluminescence spectra of argon-saturated wa-ter and aqueous H_2SO_4 solutions, recorded with a resolu-tion $\Delta\lambda = 3$ nm, are shown in Fig. 1.

The sonoluminescence spectrum of water (see Fig. 1, *a*) is consistent with the results of water sonication studies (sonolysis at 22 and 337 kHz [7] and at 459 kHz [8]). The band with maximum in the region $\lambda = 270-290$ nm is due to luminescence of $H_2O\cdot Ar$ exciplex and (or) elec-tronic-excited complex [H...OH...M]*, which are pro-duced as a result of triple collisions in CBs[7]:

$$H_2O^* + 2\,M \rightarrow H_2O^*\cdot M + M \rightarrow H_2O + 2\,M + h\nu,$$

$$H + OH\,(OH)^* + M \rightarrow [H...OH...M]^* \rightarrow H_2O + M + h\nu,$$

where M denotes the water molecule or the inert gas (argon) atom.

Besides, a vibrationally excited complex [H...OH...M]$^{\#}$ can also be formed inside CBs. Emission
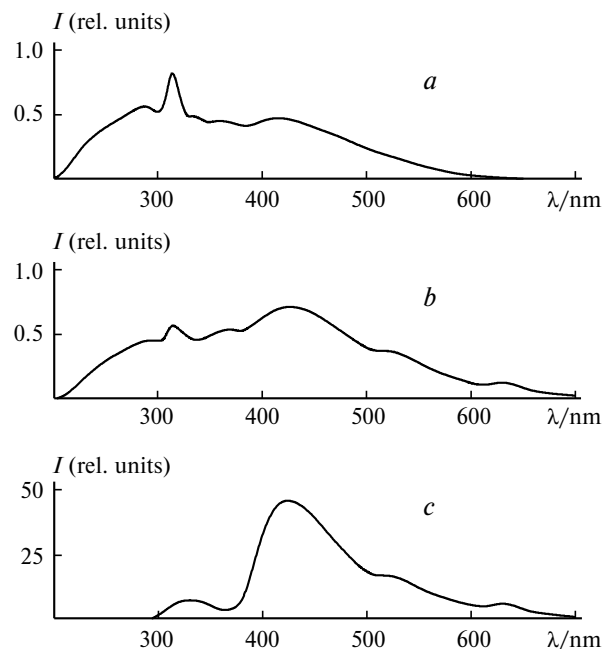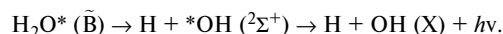

Fig. 1. Sonoluminescence spectra of argon-saturated water (*a*) and aqueous H_2SO_4 solutions with concentrations of 5 (*b*) and 18 mol L^{-1} (*c*).

of this complex can provide an explanation for lumines-cence in the longer-wavelength region $\lambda = 370$ nm.[8]

The band at $\lambda = 270-290$ nm is overlapped with the short-wavelength region of the luminescence spectrum of $^\bullet OH$ radical (280 nm). The maximum at $\lambda = 310$ nm and glow in the region $\lambda = 340$ nm are also explained by radiative transitions of excited $^\bullet OH$ radical produced in the dissociation of excited water molecules:

$$H_2O^*\,(\tilde{B}) \rightarrow H + {}^*OH\,(^2\Sigma^+) \rightarrow H + OH\,(X) + h\nu.$$

Continuum glow in the sonoluminescence spectrum of water in the range $\lambda = 380-600$ nm with a broad maxi-mum near 420 nm is due to the $\tilde{C} \rightarrow \tilde{A}$ transitions of excited water molecules.[7,8]

The sonoluminescence spectrum of argon-saturated H_2SO_4 solution with an acid concentration, *c*, of 5 mol L^{-1} (see Fig. 1, *b*) also exhibits maxima at $\lambda = 270-290$, 310, and 370 nm and a broad continuum glow in the region $\lambda > 380$ nm. Apparently, both excited water molecules and hydroxyl radicals are emitters of sonoluminescence in these regions. The experimentally observed spectral changes, namely, narrowing of the band with maximum at $\lambda = 420$ nm, an increase in the intensity of this band compared to that of the $^\bullet OH$ band at $\lambda = 310$ nm, and the appearance of new maxima in the region $\lambda > 500$ nm can be associated with production of new emitters of sono-luminescence (in particular, SO_2) in the solution.

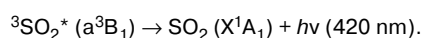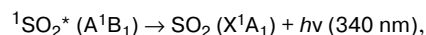Considerable amounts of sulfur dioxide are formed not only during sonolysis[2] but also in the course

of radiolysis[9] of concentrated H$_2$SO$_4$ solutions (c > 9—10 mol L^{-1}). It was assumed[9] that production of SO$_2$ during radiolysis is a result of the action of radiation on undissociated H$_2$SO$_4$ molecules whose concentration in aqueous solutions increases nonlinearly with an increase in the acid concentration[10] and becomes significant (more than 0.1 mol L^{-1}) only at c > 12 mol L^{-1}. The formation of SO$_2$ in concentrated H$_2$SO$_4$ solutions by a radiolysis-type mechanism seems to become the main channel of sulfuric acid sonolysis. At c = 18 mol L^{-1}, the concentration of the undissociated H$_2$SO$_4$ molecules in the acid is 15 mol L^{-1} [10] and SO$_2$ is efficiently produced in such solutions.[2,9] However, small amounts of undissociated H$_2$SO$_4$ molecules probably arrive inside CBs at c = 5 mol L^{-1}, which affects the sonoluminescence spectra and intensity.

Therefore, it was reasonable to expect not only an increase in the intensity of luminescence (see above) but also more pronounced changes in luminescence spectrum on an increase in the H$_2$SO$_4$ concentration. Indeed, the sonoluminescence spectrum of a more concentrated H$_2$SO$_4$ solution (c = 18 mol L^{-1}) is strongly different from the sonoluminescence spectra of water and less concentrated (5 mol L^{-1}) acid solution. Namely, the bands resulting from the emission of excited water molecules and hydroxyl radicals (at λ = 270—290, 310, and 370 nm) disappeared but two intense allowed bands in the regions λ = 330 and 420 nm were observed, as well as local maxima at λ = 500—520 and 630 nm (see Fig. 1, *c*). The sonoluminescence spectrum of H$_2$SO$_4$ solution obtained in this work is similar to the photoluminescence spectra of H$_2$SO$_4$ aerosols[11] formed in argon atmosphere by the reaction

$$H_2O + SO_3 \rightarrow H_2SO_4,$$
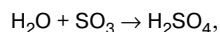
and to the photoluminescence spectrum of gaseous sulfur dioxide.[11,12] These spectra exhibit bands with maxima in the ranges λ = 330—340, 420, and 500—520 nm, which are probably due to emission of the excited states of SO$_2$.[11] In the case of H$_2$SO$_4$ aerosols the glow is emitted by the SO$_2$ molecules adsorbed on the surface of the aerosol droplets.

Indeed, it is known[12] that transitions from the singlet and triplet excited states to the ground state of the SO$_2$ molecule are accompanied by emission near λ ~340 and λ ~420 nm, respectively:

$$^1SO_2^* \ (A^1B_1) \rightarrow SO_2 \ (X^1A_1) + h\nu \ (340 \ nm),$$

$$^3SO_2^* \ (a^3B_1) \rightarrow SO_2 \ (X^1A_1) + h\nu \ (420 \ nm).$$

It should be noted that in the case of excitation to the corresponding absorption bands of the singlet and triplet states the quantum yields of fluorescence and phos-

phorescence of sulfur dioxide in the gas phase approach unity,[12,13] being appreciably higher than the quantum yields of photoluminescence of H$_2$O* and OH* (φ = 0.02—0.05).[14] This can be a reason for higher intensity of sonoluminescence of H$_2$SO$_4$ solutions compared to the intensity of water sonoluminescence. Probably, as a consequence, the contribution of the SO$_2$* glow to sonoluminescence becomes pronounced at a H$_2$SO$_4$ concentration of 5 mol L^{-1}.

No unambiguous assignment of the maximum at λ = 500—520 nm in the photoluminescence spectrum of SO$_2$[11] and in the sonoluminescence spectra of H$_2$SO$_4$ solutions obtained in this work has been reported so far.

At low pressure (100—130 Pa), SO$_2$ vapors usually exhibit a structurized phosphorescence spectrum in the region λ = 380—500 nm.[11,12] The emission band of triplet-excited SO$_2$ molecules shows no fine structure in the sonoluminescence spectra recorded in this work. This can probably be explained by the high pressure and temperature characteristic of the CBs generated in the course of sonolysis, which causes broadening of spectral lines.

A maximum near λ = 630 nm can be due to radiative transitions of excited O (^{1}D) atoms produced as a result of H$_2$SO$_4$ sonolysis:

$$O^* \ (^1D) \rightarrow O \ (^3P) + h\nu.$$
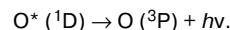
It should be noted that the absorption spectra of the solutions under study exhibited no additional bands at λ > 250 nm after sonolysis, which could distort the sonoluminescence spectra.

Using the estimates obtained in this work for the total sonoluminescence intensity of the solutions under study in the region λ = 200—700 nm at an acoustic power of 30 W (10^{10} photon s^{-1} for water and $1.3 \cdot 10^{10}$ and $5 \cdot 10^{11}$ photon s^{-1}, for the 5 and 18 *M* H$_2$SO$_4$ solutions, respectively), it is possible to calculate the energy yield of sonoluminescence.[15] Calculations with an average energy of emitted photons of $4.4 \cdot 10^{-19}$ J (λ_{av} = 450 nm) give $1.4 \cdot 10^{-10}$, $1.9 \cdot 10^{-10}$, and $7 \cdot 10^{-9}$, respectively. These results are in agreement with the known estimates.[15]

Based on the results obtained, one can assume that sonoluminescence of sulfuric acid and concentrated aqueous sulfuric acid solutions is due to the following processes.

The Frank—Hertz inelastic collisions of the first kind produce excited H$_2$SO$_4$ molecules in CBs heated on quasi-adiabatic compression:

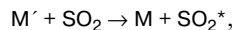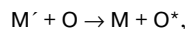$$M' + H_2SO_4 \rightarrow M + H_2SO_4^*,$$
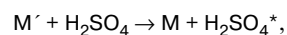
where a prime denotes an increased kinetic energy of the particle.

By analogy with the scheme of sulfuric acid radiolysis[9] the dissociation of $H_2SO_4^*$ molecules produces oxygen atoms and sulfur dioxide:
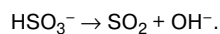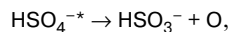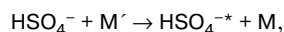
$$H_2SO_4^* \rightarrow H_2SO_3 + O,$$

$$H_2SO_3 \rightarrow H_2O + SO_2.$$
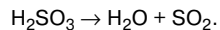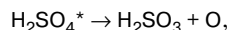
These species then also undergo excitation:

$$M' + O \rightarrow M + O^*,$$

$$M' + SO_2 \rightarrow M + SO_2^*,$$

where $M = H_2O$, OH, H_2SO_4, SO_2, O, Ar.

In dilute H_2SO_4 solutions, fragments (ions) of H_2SO_4 molecules which penetrate into the cavitation bubbles, can also be sonolyzed:

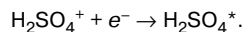$$HSO_4^- + M' \rightarrow HSO_4^{-*} + M,$$

$$HSO_4^{-*} \rightarrow HSO_3^- + O,$$

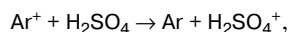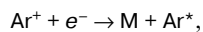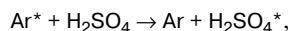$$HSO_3^- \rightarrow SO_2 + OH^-.$$
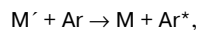
A possible reason for the excitation of emitters is also energy transfer from electronic-excited H_2O or H_2SO_4 molecules:

$$H_2O^* \ (OH^* \ or \ H_2SO_4^*) + SO_2 \ (O) \rightarrow H_2O$$

$$(OH \ or \ H_2SO_4) + SO_2^* \ (O^*).$$
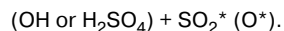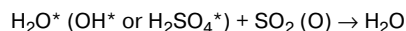
This is followed by emission of the SO_2 molecules and O atoms, while H_2SO_4 molecules undergo nonradiative deactivation (see the scheme given above). As a result the sonoluminescence spectrum of sulfuric acid, in contrast to the sonoluminescence spectrum of water, exhibits no continuum glow due to radiative deactivation of the H_2SO_4 molecules.

An increase in the water sonoluminescence intensity in the presence of argon is associated with energy transfer from excited Ar atoms, H_2O molecules, and with involvement of Ar^+ ions in the charge-discharge processes.[16] Probably, analogous processes can also occur in H_2SO_4 solutions:

$$M' + Ar \rightarrow M + Ar^*,$$

$$Ar^* + H_2SO_4 \rightarrow Ar + H_2SO_4^*,$$

$$M' + Ar \rightarrow M + Ar^+ + e^-,$$

$$Ar^+ + e^- \rightarrow M + Ar^*,$$

$$Ar^+ + H_2SO_4 \rightarrow Ar + H_2SO_4^+,$$

$$H_2SO_4^+ + e^- \rightarrow H_2SO_4^*.$$

Besides, saturation of the solutions with argon leads to removal of molecular oxygen (efficient quencher of triplet states) and, as a consequence, to additional increase in the intensity of $^3SO_2^*$ luminescence in the region $\lambda = 420$ nm.

Yet another plausible reason is the formation of $SO_2^* \cdot Ar$ exciplexes in the presence of argon in the H_2SO_4 solutions. Along with the effect of the high temperature and pressure inside CBs these species can e responsible for broadening and changes in the structure of the SO_2 photoluminescence bands.

An important role is played by the quenching of emitters of sonoluminescence with H_2O molecules and their fragments inside CBs.[17] Probably, similar processes also occur in dilute H_2SO_4 solutions. An increase in the H_2SO_4 concentration and, correspondingly, a decrease in the concentration of H_2O molecules and their fragments in CBs causes the efficiency of quenching of sonoluminescence emitters with water to decrease, which should lead to additional increase in the sonoluminescence intensity.

Thus, the high intensity and characteristic sonoluminescence spectrum of sulfuric acid can be explained by the production of sulfur dioxide (efficient emitter of luminescence) as a result of sulfuric acid sonolysis.

The electric theory of sonoluminescence can hardly be applied to the describe the results obtained. In H_2SO_4 solutions, electric charges appeared at the CB boundary can be compensated due to conduction. If the sonoluminescence is due to electric discharges inside CBs, the sonoluminescence intensity of H_2SO_4 solutions should also be lower than the sonoluminescence intensity of water, which contradicts experimental data. At the same time it should be noted that, in order to unambiguously refute the electric nature of sonoluminescence in the systems under study, one should compare the rates of the processes of charge accumulation on the CB walls and charge compensation due to conduction.

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