Multibubble Sonoluminescence Spectra of Water which Resemble Single-Bubble Sonoluminescence

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Multibubble sonoluminescence (MBSL) spectra of water from cavitation clouds were collected in the presence of different noble gases and at different acoustic intensities. Results show that at high acoustic intensity and with xenon as a dissolved gas the emission of the OH^* radical becomes indiscernible from the continuum. These spectra resemble single-bubble sonoluminescence (SBSL) spectra. It is concluded that the source of emission in MBSL and SBSL can be the same, the difference in spectra is due to the higher temperature inside the bubble during SBSL.

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Acoustic cavitation creates a number of physical and chemical effects, including erosion, disruption of cells, chemical reactions, light emission (sonoluminescence), and others. Sonoluminescence (SL) can be seen from clouds of bubbles [multibubble sonoluminescence (MBSL)] or from a single bubble levitated in a partially degassed liquid (SBSL) [1]. The similarity between SBSL and MBSL is that the source of emission in both cases is a highly nonlinearly pulsating bubble. The distinction: the spectra of water SBSL do not contain any particular lines or bands [2]. Several hypotheses were put forth to explain the shape of continuum in the spectra of single-bubble sonoluminescence, including black-body radiation with temperature ranging from 25 000 to 50 000 K [2], emission from a dense plasma [3], bremsstrahlung and electron-ion recombination from weakly ionized gas [4], and others. On the contrary, optical spectra of SL from a cavitation cloud have well-defined lines and bands superimposed upon the continuum [5]. In particular, MBSL spectra of water contain prominent emission of the excited OH radical at 310 nm [6]. Thus, MBSL has been considered luminescent in nature [6,7].

In this Letter, we present experimental conditions (dissolved xenon, high acoustic intensity) in which spectra of multibubble sonoluminescence appear similar to those of SBSL, i.e., without prominent emission of the excited hydroxyl radical at 310 nm. Apparently, the high temperature inside the bubble (SBSL or MBSL at high acoustic intensities and dissolved xenon) makes the OH emission indiscernible from the continuum. The trends in the spectra changes imply that the source of both single-bubble and multibubble sonoluminescence is molecular emission. Some previously unexplained SBSL results can be explained with this hypothesis.

High intensity ultrasound horns produce a strong cavitation field. The density of cavitation bubbles in the vicinity of the tip of the horn is significantly higher than in the field farther from the transducer. In this work, the spectra were collected [8] from the cavitation field located between the horn tip and the quartz window, 10 mm away, in the "near field" of the sonicator. For comparison, we collected the spectra of argon saturated water from the "far field" of the sonicator (8 cm from the tip of the horn) at the same total ultrasound power input.

We use the terms "far" field and "near" field of the transducer to distinguish between the strong and the dense cavitation field close to the emitting surface and the low-density cavitation field farther from the tip of the horn. This description is arbitrary because the shape and the size of the cavitation field near the transducer can change depending on the conditions. In any case, one would expect more violent collapse of cavitation bubbles in the near relative to the far field of the transducer.

The spectra of multibubble water sonoluminescence consist of both emission from the OH^* radical at 280, 310, and 340 nm and a continuum [6]. The intensity of OH^* emission at 310 nm in the near field is significantly decreased when compared to that of the far field [Fig. 1(a)]. Total intensity of SL from the near field was also much higher.

In our previous work in the far field [9], no changes in the SL spectra with the growth of ultrasound intensity at 22 kHz were observed. It was noted, however, that total intensity of SL increased. One of the possible explanations of this effect is that the increase of ultrasound intensity in the far field is accompanied by the growth of the number of cavitation bubbles rather than with the intensity of an individual bubble collapse.

In near field, the intensity of OH^* emission decreases in respect to continuum (OH^*/continuum ratio), and the total intensity of SL goes through maximum with increasing acoustic power [Fig. 1(b)]. The data regarding total intensity of SL are similar to previously published results [10].

Since the maximum bubble size and temperature within the bubble should increase with the growth of ultrasound intensity, we suggested that the OH^*/continuum ratio decreases as a result of high temperature inside the bubble. The increase of temperature inside the cavitation bubble
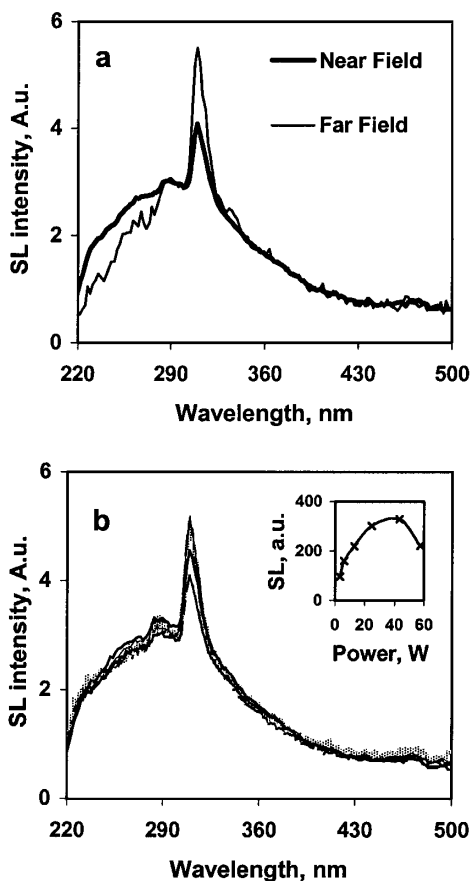
FIG. 1. MBSL spectra of argon/saturated water (a) in near and far fields of the transducer and (b) at different acoustic powers in the near field. Total absorbed acoustic powers are 57.7, 43.6, 12.9, and 3.5 W from the bottom to the top of the figure. Inset in (b) shows the SL intensity versus total acoustic power. In this and other figures, spectra are normalized at 400 nm.
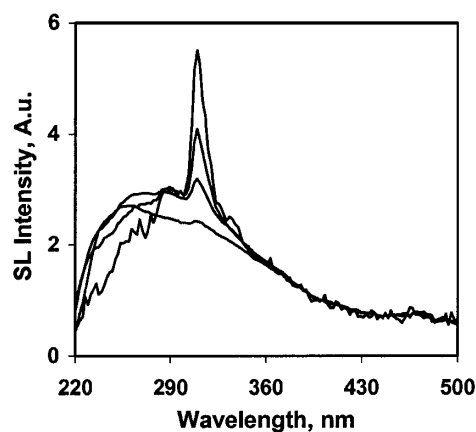

FIG. 2. MBSL spectra of water saturated with different noble gases: xenon, krypton, and argon, from the near field and with argon from the far field. From the bottom to the top of the figure.

in the order of noble gases from helium to xenon has recently been observed experimentally [11]. Thus, significant changes in the SL spectra would be expected if krypton or xenon replaced argon as a dissolved gas. Figure 2 shows that the intensity of OH^* emission decreases in respect to continuum in the order from Ar to Xe, and in the Xe case it becomes indistinguishable from the continuum. This MBSL spectrum of water in the presence of xenon resembles the SBSL spectra [12]. Thus, our results indicate that the increase in the temperature within the bubble is accompanied with a decrease in the OH^* emission with respect to the continuum.

A similar effect has been observed in MBSL spectra of chromium hexacarbonyl in octanol solutions saturated with noble gases [11]. The metal/continuum ratio decreased in the order of noble gases from He to Xe. It has been suggested that the increase of temperature inside the bubble (from He to Xe) is accompanied with the increase of the rate of disruption of solvent molecules inside the bubble. This produces multiple molecular species contributing to the continuum, limits the observed temperature, and decreases the metal/continuum ratio. That is, the continuum

grows faster with the increase in temperature inside the bubble than the metal emission does [11].

If one considers molecular emission as a mechanism of SL, the variance of the OH^*/continuum ratio reported herein can be explained. Adiabatic collapse of a cavitation bubble is accompanied with an increase in the energy of individual species inside the bubble. Water molecules excited into different rotational, vibrational, and electronic states via these inelastic collisions can dissociate into hydrogen atoms and hydroxyl radicals in different ground or excited states. The transition from the ground to the first excited state of water is fast and the lifetime of the H_2O $(\tilde{A})$ state is shorter than a period of vibration [13]. This is particularly relevant to SL as the time of the sonoluminescence flash is very short, less than 1 ns [14].

The resulting hydroxyl radicals and hydrogen atoms can initiate chemical reactions both inside the bubble and in the surrounding liquid following the bubble collapse. The hydroxyl radical in the ground state formed from water dissociation can then be excited via interparticle collisions to give an emission with maximum at 310 nm. Another possibility is a direct formation of the excited hydroxyl radical from excited $\tilde{B}$ or $\tilde{C}$ states of water [6].

One possible source of continuum is the recombination of H and OH radicals, which gives water molecules excited into the different vibrational and rotational levels [6]. The potential energy curve for a water molecule formed by this recombination can be repulsive, and the transition to the ground state will form a continuum. The UV cutoff for this continuum would be the energy of water dissociation (~ 7.5 eV), corresponding to $\lambda \sim 165$ nm. The shape of the continuum depends on the energy of colliding species: the higher the energy of colliding partners, the shorter the wavelength of the emission.

Recombination of OH and H radicals may not be the only source of the emission of continuum. The increase in the temperature inside the bubble would also lead to a greater *number and a variety* of molecular and atomic

species in the bubble. This results in a wide assortment of excited state species, many of which may contribute to the continuum. Thus, the continuum would grow faster than the OH* emission (Fig. 2) with the growth of temperature inside the bubble. A more detailed examination of this proposed mechanism could be performed by considering the mechanism of chemical reactions inside the bubble, along with the dynamics of cavitation bubble [15,16] and data on the parameters of OH excitation [17].

Another important parameter for sonoluminescence is the time of bubble collapse. If the time of collapse is short (e.g., at high acoustic frequencies for MBSL or high speed of bubble compression, SBSL), then this time would not be long enough for equilibration of all species inside the bubble. The sonoluminescence spectrum would thus appear as a nonequilibrium emission.

Studies of the MBSL spectra of water have shown that the part of MBSL spectrum below 300 nm is stronger compared to the rest of the spectrum for higher frequency (Fig. 3) [18]. The intensity of collapse and, consequently, the temperature inside the bubble should be higher for 22 kHz because (i) bubble size should be bigger for lower frequency for the same acoustic pressure [19], and (ii) the ultrasound intensity is higher for 22 kHz. Thus, if the OH emission is at equilibrium, then the UV part of the spectra should be stronger for 22 kHz. This is because the energies of the excited states of the OH radical (1 −0, 2 −0 at 280 and 260 nm, respectively, and other transitions below 300 nm wavelengths) are higher than the energy of 0-0 transition (emission of the OH radical at 310 nm) [17] and these high energy states will be preferentially populated at higher temperatures. It is seen from Fig. 3, however, that, even though the acoustic intensity is lower for 863 kHz, the OH* emission is less prominent at this frequency and the UV component is stronger. One possible explanation is that, at higher ultrasound frequency and, consequently, shorter time of bubble collapse, the OH* emission is not fully equilibrated. It does not have well-defined vibrational bands, and the emission is smeared out between different vibrational and rotational transitions in the region from
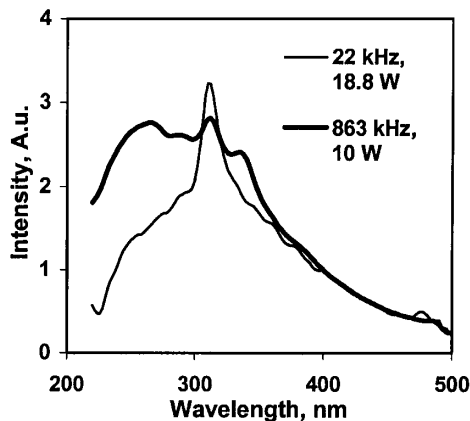

FIG. 3. MBSL spectra of Ar saturated water at 22 and 863 kHz from the far field. Adapted from [18].

~240 to 340 nm. This observation is relevant for SBSL where the speed of bubble compression is very high. Thus, another possible source of SBSL would be nonequilibrium molecular emission. We should mention here, however, that atomic and molecular emission from MBSL at 20 kHz appears to be at equilibrium [20].

It should be noted here that the blackbody hypothesis cannot explain the observed effect of ultrasound frequency on the shape of continuum in MBSL. Actually, if the temperature inside the bubble is higher for 22 kHz, then the UV component of the spectrum should be greater for this frequency of ultrasound than for 863 kHz.

The most accepted theory regarding the shape of continuum in SBSL spectra purports that sonoluminescence is a plasma emission [3]. At the end of the bubble collapse, the formation of converging spherical shock waves inside the bubble has been predicted. This can ionize the bubble contents, resulting in a continuum emission, which extends from vacuum UV to IR.

The SBSL emission has recently been ascribed to both bremsstrahlung and electron-ion recombination radiation from weakly ionized gas [4]. These hypotheses [3,4] explained some details of the SBSL spectra at different conditions. Both of them presumed the existence of high temperatures inside the bubble ($\sim 15\,000 - 30\,000$ K). However, there are experimental results in the SBSL studies that are difficult to interpret from the point of view that SL is a plasma emission, but can be explained if one assumes that it is molecular emission.

One example of this stems from the fact that the addition of small amounts of 1-butanol significantly suppresses the intensity of SBSL. On the other hand, carbon disulfide added to water does not change the intensity of sonoluminescence [21]. These drastically different effects of n-butanol and carbon disulfide on SBSL cannot be explained if one assumes the existence of high temperatures inside the bubble. At high temperatures inside the bubble, both CS_2 and n-butanol will be completely dissociated. Thus, there should be no difference in their effect on SBSL of water, and these additives would have similar effects upon the SBSL if the high temperature hypotheses were correct.

These effects, however, can be explained in the molecular emission hypothesis of sonoluminescence. Similar effects of alcohols [22,23] and carbon disulfide [24] on sonoluminescence from cavitation clouds of water have been observed. The decrease of the intensity of water MBSL upon addition of alcohols and other organic liquids to water was explained as a result of the quenching of the emission [23] or as a consequence of chemical reactions within the bubble [22,24]. This explanation can be true for SBSL as well. 1-Butanol vaporizes with water into the bubble when it expands. During adiabatic compression, the temperature inside the bubble increases and at a given stage of the bubble compression water dissociates giving H atoms and OH radicals. Sonoluminescence occurs due to recombination and/or direct excitation of the

OH radical. If the vapors inside the bubble contain some amounts of n-butanol, it will chemically react with H atoms and OH radicals thus decreasing the intensity of SL. SL intensity would decrease further with the increase of 1-butanol concentration in the solution, and at high enough concentration it will be completely quenched. This simplified scheme allows one to understand the mechanism of n-butanol quenching and supports the molecular emission hypothesis.

Small amounts of carbon disulfide, on the other hand, increase the intensity of MBSL. This effect has been explained as the emission of CS_2 itself, or from the products of its reactions inside the bubble [24]. In SBSL, the intensity almost does not change upon addition of small amounts of CS_2 to water [21]. This can be explained as a competition of the two processes. First, SBSL should increase as suggested above. On the other hand, the increase of CS_2 concentration in water will increase the absorption of solution in the UV region and affect bubble dynamics. Thus, observed total intensity of SBSL almost does not change with the growth of carbon disulfide concentration in solution.

MBSL spectra of water in the near field and far field from the transducer were collected in the presence of different noble gases. Results show that under severe experimental conditions (high acoustic intensity, xenon as a dissolved gas) the emission of the OH* radical almost disappears. Under these conditions, MBSL spectra of water resemble SBSL spectra. We suggest that continuum in both SBSL and MBSL spectra can be a result of molecular emission. This hypothesis can explain the diverse effect of n-butanol and carbon disulfide on SBSL emission.

Yasui [16] has recently suggested that MBSL originates from excited molecules. These molecules are also formed in SBSL bubbles but their emission is strongly quenched by high pressure and temperatures inside the bubble, and the source of SBSL is a weakly ionized gas. At high acoustic intensities, some bubbles in a cavitation field will collapse SBSL-like [16], and thus emit only continuum. Conversely, the emission spectra of SBSL bubbles driven at low acoustic intensity may contain molecular bands. Thus, the spectra of both MBSL and SBSL can be a combination of molecular and higher energy components (bremsstrahlung, electron-ion recombination). The only difference is in temperature, which is higher in SBSL. Future experimental and theoretical works can elucidate the detailed mechanism of sonoluminescence.

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[1] D. F. Gaitan *et al.*, J. Acoust. Soc. Am. **91**, 3166 (1992).
[2] R. Hiller, S. J. Putterman, and B. P. Barber, Phys. Rev. Lett. **69**, 1182 (1992).
[3] W. C. Moss, D. B. Clarke, and D. A. Young, Science **276**, 1398 (1997).
[4] S. Hilgenfeldt, S. Grossmann, and D. Lohse, Nature (London) **398**, 402 (1999).
[5] K. S. Suslick *et al.*, Proc. R. Soc. London A **357**, 335 (1999).
[6] Y. T. Didenko and S. P. Pugach, J. Phys. Chem. **98**, 9742 (1994).
[7] K. S. Suslick, S. J. Doktycz, and E. B. Flint, Ultrasonics **28**, 280 (1990).
[8] The experimental setup used in this work is described elsewhere [9]. Distilled water sparged with appropriate gas 1 h before the irradiation and in the course of the work in 0.5 l glass reservoir placed in a thermostated water bath. Liquid was constantly rotated through a thermostated stainless steel irradiation cell (inner diameter 2 cm, volume 50 ml) with the help of a peristaltic pump. Temperature of the solution inside the cell during irradiation was constant at $6 \pm 1\,°C$. Sonication was conducted at ultrasound frequency of 22 kHz with variable intensity. Total absorbed acoustic power was measured calorimetrically. Emission spectra were collected from 200 to 500 nm using 0.6 m monochromator equipped with a 1200/mm grating with a resolution of 2.5 nm. A photomultiplier tube (FEU-100) sensitive in the 200–800 nm region was used as a detector. Each spectrum given in the figures is a concatenation of at least 15 individual spectra. The spectra were corrected against a calibrated 30 W deuterium lamp.
[9] Y. T. Didenko, T. V. Gordeychuk, and V. L. Koretz, J. Sound Vib. **147**, 409 (1991).
[10] G. Gimenez, J. Acoust. Soc. Am. **71**, 839 (1982).
[11] Y. T. Didenko, W. B. McNamara, and K. S. Suslick, Phys. Rev. Lett. **84**, 777 (2000).
[12] R. A. Hiller, S. J. Putterman, and K. R. Weninger, Phys. Rev. Lett. **80**, 1090 (1998).
[13] V. Engel *et al.*, J. Phys. Chem. **96**, 3201 (1992).
[14] T. J. Matula, R. A. Roy, and P. D. Mourad, J. Acoust. Soc. Am. **101**, 1994 (1997).
[15] V. Kamath, A. Prosperetti, and F. N. Egolfopoulos, J. Acoust. Soc. Am. **94**, 248 (1993).
[16] K. Yasui, Phys. Rev. Lett. **83**, 4297 (1999).
[17] G. H. Dieke and H. M. Crosswhite, J. Quant. Spectrosc. Radiat. Transfer **2**, 97 (1962).
[18] T. V. Gordeychuk, Y. T. Didenko, and S. P. Pugach, Acoust. Phys. **42**, 240 (1996).
[19] H. G. Flynn and C. C. Church, J. Acoust. Soc. Am. **84**, 985 (1988).
[20] W. B. McNamara, Y. T. Didenko, and K. S. Suslick, Nature (London) **401**, 772 (1999).
[21] K. Weninger *et al.*, J. Phys. Chem. **99**, 14 195 (1995).
[22] C. Sehgal *et al.*, J. Phys. Chem. **81**, 2618 (1977).
[23] M. A. Margulis and A. F. Dmitrieva, Russ. J. Phys. Chem. **66**, 751 (1992).
[24] Y. T. Didenko, W. B. McNamara, and K. S. Suslick, J. Phys. Chem. A **103**, 10 783 (1999).