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Peculiarities of atomic lines in sonoluminescence spectra

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Abstract. Alkali-metal lines in SL spectra are broadened, asymmetrically shifted toward the red spectral region, unshifted narrow parent peaks are observed. The shape is influenced a number of parameters. The effects have no explanation. We model a line shape, assuming that line broadening arises from a density and line asymmetry results from superposition of spectra generated at different densities of a perturbing medium. Simulation shows that broad-band emission occurs within the density range of 10-400 Amg for KCl, LiCl, NaCl aqueous solutions under Ar at the ultrasound frequency of 20 kHz. The lower limit of the range shifts to higher density in order of K<Li<Na following the increase of exited state energy. The effect of surfactant on the shape of Na D-line is also observed, which probably indicates the essential influence of nano-size layers on the dynamics of emitting process.

1. Introduction
Sonoluminescence (SL) was discovered about 80 years ago by Frenzel and Shultes as light emission from bubbles in liquids undergoing ultrasound irradiation [1]. Later it was called as multibubble SL (MBSL). It is considered that emission originates from bubbles violently collapsed by acoustic pressure - “hot-spot” hypothesis [2]. As result a bubble can focus sound energy by 12 orders of magnitude. About 20 years ago a great experimental result was gotten by Gaitan. He found regime for stable single bubble SL (SBSL) [3]. SBSL spectra are referred to blackbody, bremsstrahlung, eximer’s emission. The shape of MBSL spectra differs from SBSL shape and usually consists of a continuum and separate lines. The lines are emitted by atoms and molecules of irradiated solution, and their fragments.

Peak conditions inside the bubbles are really extreme (the values for pressure of 500 atm and temperature of 15000 K are experimentally defined). A lot of intrabubble estimations were received using SL spectra. MBSL temperature was estimated from the intensity of metal lines [4], SBSL temperature and the plasma density are estimated using the asymmetry of argon line [5]. Ionization degree for such electron density is about 3. Broadening and shift of metal lines are used for estimation of pressure and density of emission medium, for example, using high-volatile metal carbonyls dissolved in organic liquid with low vapor pressure [6]. In this work the pressure is evaluated as 300 bars and relative density as 20 Amg.

Alkali-metal atomic emission is one of unresolved problems of SL. Firstly the mechanism of non-volatile salt hitting into the bubble is unclear. Now most of experimental results support the injected-
The droplet model [2]. The structure of the lines of emission from metal atoms is distorted. The lines exhibit broadening, asymmetry and a long-wavelength shift as compared to the flame fluorescence spectra. Narrow peaks of the parent emission doublet are observed on the background of these broadened lines. The first estimations of bubble-collapse parameters from Na line broadening and shift were made in classic work and were appeared as: density about 40 Amg, pressure about 300 bars and temperature about 3000 K [7].

The shape of atomic lines is influenced different parameters, but most of the effects haven’t any explanation. The shape of K line is different in water and octanol [8]. However in [8] the shape is independent from dissolved gas, which fact is surprising. It is known that helium shifts the line toward violet side in contrast to argon. Recently it was shown that helium really shifts line toward violet side, and the line shape changes for different gases [9]. Also the noticeable ultrasound frequency effect is obtained for K line [10]. Line width grows when sound frequency falls. Authors do not explain the effect. It is interesting that frequency effect for Na is opposite than for K [11]. In [11] is also obtained that in case of water the wide component of spectrum is more pronounced as compared with the case of acid. Authors propose that something is superimposed on the Na line in water case. Results [11] show the shape of Na line is influenced by alcohol likewise for K line. Its width grows with increasing of ethanol content in water. Also the shape changes with ultrasound intensity. In spectra from [11], as like as in spectra presented in [9], one more peculiarity of SL line shape is obvious - the presence of unshifted narrow peaks of metal atoms in SL spectra. If one assumes the emission comes from very dense medium, it is strange. They should be spread over the spectrum under conditions near bubble collapse.

2. Results and discussion

In general, until recently, the width of a line was being considered, but asymmetry and presence of unshifted peaks were not been explained. Nevertheless, the line shape can keep the information about the conditions during the time when the emission occurs. Recently it was shown that metal emission occupies a rather long period of time during collapse phase [12]. So we assume that complex profile of metal line forms due to superposition of the spectra generated at different densities of a perturbing medium. The simple model based on the hypothesis of integral character of metal-line shape in SL successfully reproduces all features of experimental spectra (involving shift, broadening, asymmetry, and parent emission peaks) [13]. Simulation of the experimental spectra allows one to make a conclusion about the character of density variations during the emission, and to determine the interval of densities in which the emission from alkali-metal atoms occurs.

Figure 1 shows the high-resolution (0.26 nm) spectra in the vicinity of atom emission peaks (thick solid lines) and the results of simulation, heeding shift and the broadening by density during the emission (dotted lines). The spectra were measured from Ar-saturated 3M KCl, NaCl, LiCl aqueous solutions. Ultrasound frequency was 20 kHz. The procedure was described elsewhere [13]. The fluorescence spectra of a flame with salts additives, measured at the same resolution as that used for the SL spectra, are shown for the comparison (thin solid lines). The spectra are normalized at the first doublet component in respective flame spectrum.

The unshifted peaks are not prominent in Na spectrum in Fig. 1 whereas they are observed in some experimental spectra [9, 11]. From the viewpoint of our model the only origin of parent peaks is "low-density" emission with the value of about 1 Amg [13]. Recently [12], it was experimentally demonstrated that Na emission can occur in "low-density" phase far from the point of full collapse.
Using the model the lower and the upper values of density, when alkali-metal broad-band emission occurs, were estimated (Table 1). The model calculations show the increase of the lower density limit in order of K<Li<Na, which is probably caused by the growth of excited energy of atomic states in the same order. It is not unlikely that K, whose excited state energy is smaller than that for Na and Li, begins to emit at earlier stage of collapse and, hence, at lower density of perturbing medium. Thereupon Li starts to emit. Na emission begins at higher density.

| Metal | Wavelength, nm | Excited Energy, eV | Minimum Density, Amg | Maximum Density, Amg |
|-------|----------------|-------------------|----------------------|----------------------|
| Na    | 590            | 2.11              | 41                   | 415                  |
| Li    | 671            | 1.85              | 16                   | 279                  |
| K     | 768            | 1.62              | 10                   | 203                  |

The upper limit of density range also shifts toward the higher values with the increase of the energy of alkali-metal excited states. The reason why the alkali-metals cease to emit at high density, when the emission of continuum occurs, is unclear. Possibly, the emitting layers inside the collapsing bubble become optically opaque or, which is more likely, the duration of "high-density" emission is too short for noticeable contribution to SL spectrum.

Figure 2 shows a new result demonstrating the influence of surfactant on the shape of Na line in SL spectra. Earlier it was reported that small amount of surfactant leads to the growth of intensity of Na
line, as well as in a case of large concentration of salt [14]. It was also calculated that the thickness of a salt-solution layer of about 16 nm near bubble boundary is enough for explanation of Na line intensity [15]. In the case of surfactant addition a thinner layer is required. We propose that vaporization of the thin layer begins at less density. Possibly it is the reason why we obtain more narrow line for the case of addition of surfactant. The density range evaluated from the shape is shown in Table 2.

![Image](image.png)

**Figure 2.** Na D-line shape in MBSL high-resolution (0.26 nm) spectra from 3M NaCl Ar-saturated aqueous solution and with addition of 0.01M of surfactant. Ultrasound frequency is 20 kHz.

| Minimum Density, Amg | Maximum Density, Amg |
|----------------------|----------------------|
| 3M NaCl              | 38                   |
| 0.01M SDS            | 28                   |

We resume that the question about the peculiarities of atomic lines in SL spectra remains open and needs further investigations.

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