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**DRAMATIC EFFECT OF TEMPERATURE AND HYDROSTATIC PRESSURE**  
**ON SONOLUMINESCENCE OF Na ATOMS IN NaCl SOLUTIONS**

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*Multi-bubble sonoluminescence spectra from argon-saturated aqueous NaCl solutions were measured in the ambient temperature range of 1-29 °C at the normal and increased hydrostatic pressure. The spectra were collected in the concentration range of 0.5-4.5 M at the frequency of 22 kHz. The results show that line emission from excited state Na atoms grows rapidly with the increase in hydrostatic pressure and at low solution temperature. In all cases the increase of the intensity of underlying continuum and OH-radical emission was much lower than that of atomic emission at the same experimental conditions. We suppose the reduction of Na<sup>+</sup> and excitation of Na atoms occur in a heated interface region around the collapsing bubble. The volume of the region is increased due to more high "temperature of cavitation" in case of increased static pressure or decreased vapor pressure.*

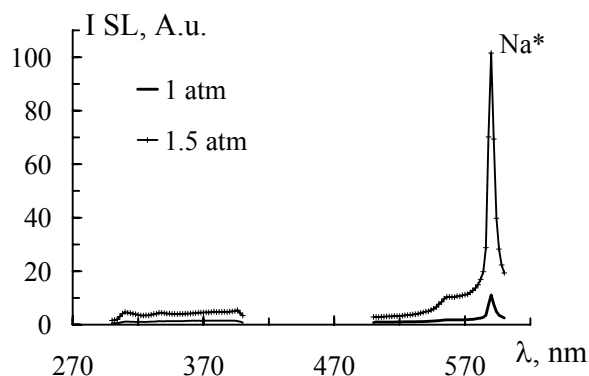
Sonoluminescence (SL), the weak light emission associated with acoustic cavitation - the formation of vapor-gas bubbles during ultrasonication of liquids [1]. SL is the consequence of the effective concentration of the acoustical energy, up to 12 orders of magnitude, that results in the creation of a wide assortment of excited state species inside a cavitation bubble [2]. The details of the processes leading to SL and sonochemical reactions, despite of wide use of ultrasound, in particular, in medicine and synthesis of nanoparticles, remain to be fully characterized. The shape of SL spectra is determined by the physicochemical state of cavitation bubble content in the moment when light is emitted (a final phase of compression): a vapor-gas mixture, temperature and pressure. Experimental estimations of temperature, reached in a cavitation bubble during the compression, «the temperature of cavitation», are 3000-5000 K for multi-bubble SL in the organic solutions [3] and 15000 K for single-bubble SL in the concentrated acids [4]. It was shown [5] that the magnitude of the temperature of cavitation significantly affects the shape of the SL spectra. The temperature within the bubble should increase with growth of hydrostatic pressure and decrease of ambient temperature. Studying of influence of these parameters on SL spectra can be useful to examination of the processes leading to SL.

The observation of emission from electronically excited alkali/alkaline-earth metal atoms [6] is difficult to understand: how do the nonvolatile metal ions get heated in a cavitation bubble? There are two general models but no one of them has strong experimental evidence. According the heated shell model, the metal ions are reduced and excited in the interfacial region of the bubble. In the injected droplet model, they enter the bubble interior with droplets through the development of surface capillary instability during the expansion [4]. The excited neutral atoms are created in hot gas phase during the violent compression of bubble.

The spectra aqueous alkali/alkaline-earth metal salt solutions saturated with noble gas (argon) consists of the broad continuum which is due to the overlap of several bands [2], emission from OH\* (~310 nm) and emission arising from the metal atoms excited states. It is known that the total SL intensity increases and reaches a maximum before it decreases with increasing hydrostatic pressure [7]. This is mainly due to the intensification of bubble collapse and, simultaneously, the diminution of the number of cavitation bubbles because of the increasing cavitation threshold [1]. The intensity of atomic emission changes in a similar manner with increasing static pressure [8]. However, as shown in our study [8], *atomic emission increases faster than the continuum* and OH-radical emission. The MBSL spectra measured [9] at hydrostatic pressure of 1 and 1.5 atm from 1.5 M solution of NaCl are shown in Fig. 1. The temperature of the solution is 5 °C. The increase of static pressure from 1 up to 1.5 atm leads to the growth of Na atomic emission by a factor of 10 whereas the intensity of continuum and OH-radical emission increases slightly.

Another important parameter for SL is the temperature of bulk solution [10]. The decrease of ambient temperature leads to decrease of water vapor pressure inside a cavitation bubble and so to the

growth of final temperature. We assumed that the intensity of atomic emission would be greater at low temperature.

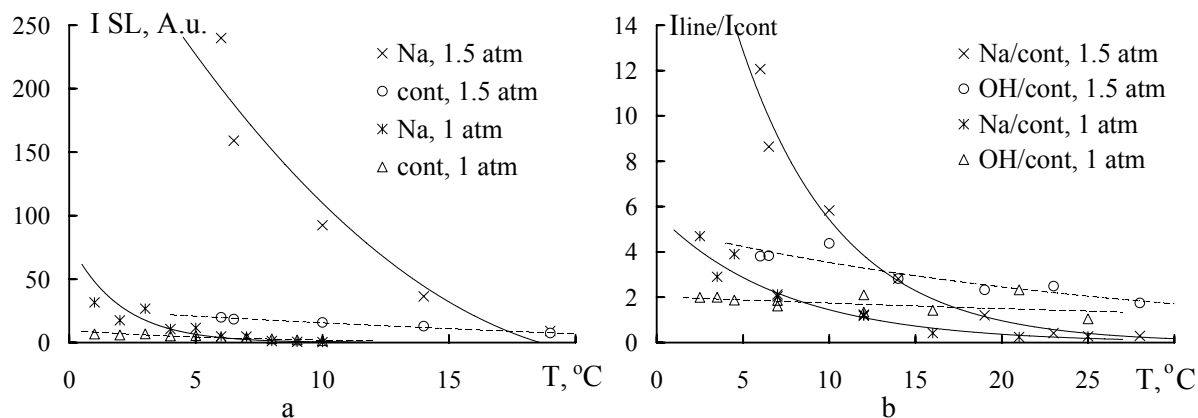


**Fig. 1.** Shortwave part of continuum and Na\* emission in MBSL spectra from 1.5 M NaCl solution at normal and increased hydrostatic pressure. Solution temperature is 5 °C

We have investigated the ambient temperature dependency of the MBSL spectra in argon-saturated NaCl aqueous solutions for concentrations of 0.5, 1.5 and 4.5 M in the temperature range of 1-29 °C (Fig. 2). The spectra were measured at various hydrostatic pressures. The results are shown in Fig. 2 only for the cases of 1.5 M and 1 and 1.5 atm for clarity. The solid and dashed lines in Fig. 2 denote the trends of temperature dependencies of separate components of spectra.

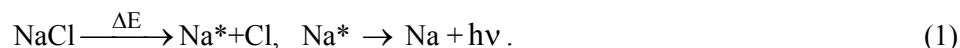
In all cases the dominant growth of Na atom emission is observed at low temperature. The increase of the intensity of underlying continuum and OH-radical emission was much lower than the increase of atomic emission at the same experimental conditions. The tendency is more evident when the pressure is increased. Figure 2b shows a summary of the ambient temperature dependence of the intensity of Na ( $I_{\text{Na}}$ ) and OH-radical ( $I_{\text{OH}}$ ) emission relative to the continuum ( $I_{\text{cont}}$ ). The  $I_{\text{Na}}/I_{\text{OH}}$  ratio increases exponentially with the decrease of ambient temperature. The degree of the growth of the  $I_{\text{Na}}/I_{\text{cont}}$  ratio is much greater for the case of 1.5 atm in comparison with the case of normal pressure. The  $I_{\text{OH}}/I_{\text{cont}}$  ratio grows insignificantly and almost linearly up to low temperature.

Thus, our results indicate that the decrease of ambient temperature as well as increase of hydrostatic pressure is accompanied by an increase of atomic emission in respect to the other components of SL spectra. This effect is much higher if both of the factors are involved. The ambient temperature and pressure influence the temperature of cavitation through different mechanisms. We suppose that the growth of temperature of cavitation is the reason of the observed effect.



**Fig. 2.** Ambient temperature dependence of the intensity of Na atom and continuum emission (a) and the intensity of Na atom and OH-radical emission relative to the continuum (b) in MBSL spectra from NaCl solution. The data are shown for the case of 1.5 M at hydrostatic pressure of 1 and 1.5 atm

If one considers injected droplet model as a mechanism, salt which has penetrated into a bubble with droplets loses the water coat because of high temperature during the bubble compression and dissociation proceeds from molecules of neutral salt with the excited-state Na atom formation:



It is also proposed [11] that the excitation mechanism of metal atoms is through chemical reaction involving OH and H radicals that are produced from water molecules within high-temperature core of collapsing bubble:

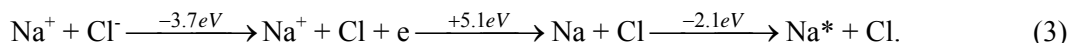


Experimentally observed strong correlation between the sodium line and OH radical production supports this reaction [12]. We should note, however, that in our experiments the rate of  $\text{H}_2\text{O}_2$  formation which is a measure of OH-radicals production grows more slowly for 1.5 M solution in comparison to that of 0.5 M solution with the decrease of temperature. Similar behavior of the intensity of OH-radical emission is observed. On the contrary, the intensity of Na emission increases more promptly with the decrease of ambient temperature in case of 1.5 M solution.

The rate of the salt dissociation and excitation is higher at higher temperatures. Nevertheless, dramatic growth of atomic emission is difficult to explain by only intensification of these processes. Besides, it was shown [5] the continuum would grow faster than line emission with the growth of temperature inside a bubble. We suppose that the reason, probably, is the increase of amount of ions which are trapped in the region of emission. We propose the heated shell model to explain the observed effect.

According to [13] (calculations are carried out for SBSL at ultrasound frequency of 26.5 kHz), “above 50 ns before the minimum radius is reached, the time scale of the bubble collapse become smaller than the time scale for the diffusion of water...the temperature has only risen to about 500 K...Only ~30 ns later, the accelerating bubble wall becomes fast enough that heat not longer escape the bubble...the temperature exceeds roughly 4000 K...”. However, the liquid layer adjacent to liquid/bubble interface “feels” the magnification of temperature and pressure. If the conditions close to a critical point (647 K and 218 atm) are reached at the bubble interface the opalescence occurs. Having not time to diffuse  $\text{Na}^+$  ions remain separated from  $\text{Cl}^-$  and oscillate near the positions where they are overtaken by “thermal wave”. Thus, the energy of 4.3 eV for dissociation of NaCl molecules is not necessary. The energy of excitation of neutral Na atom is 2.1 eV. Before the excitation  $\text{Na}^+$  should be reduced with the energy release of 5.1 eV. It is reduced, probably, through reaction with neighboring  $\text{Cl}^-$ .

Thus, we have



Consequently, only 0.7 eV is needed for excitation of Na atom.

The kinetic energy of particles at the liquid/bubble interface is increased and can be converted into the energy of electronic excitation of Na atoms by means of inelastic collisions with neighboring water molecules that have excess energy



(the energy of first excited state of water molecule is about 7.5 eV) and/or through reaction (2).

We assume that in extreme conditions and for time interval less than time scale for diffusion, a layer adjacent to liquid/bubble interface is formed in which liquid is in the state indistinguishable from gas phase. The volume of the layer and, hence, the amount of Na ions gotten in a trap is incremented with the increase of the temperature of cavitation, providing the observed intensive growth of atomic emission. The fact that the emission intensity of  $\text{Na}^*$  in NaCl solutions is enhanced by addition of surface active counter ions [14], supports our assumption. However we should note that the injected droplet model cannot be completely ruled out.

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9. The experimental setup used in this work is described elsewhere [5, 15]. All salt solutions were prepared with research grade chemicals and distilled water. Prepared salt solution sparged with argon 2 h before the irradiation and in the course of the work in 0.5 l glass reservoir placed in a thermostated bath. The solution was constantly rotated through a thermostated stainless steel irradiation cell (inner diameter 2 cm, volume 50 ml). As a source of ultrasound a 22 kHz magnetostrictor with 1.5 cm tip diameter horn was used. The ends of the cell were fitted with a 2 cm diameter quartz window and the horn respectively. A peristaltic pump was used for hydraulic pressurisation of the solution in the cell. Total absorbed acoustic power (41 W) was measured calorimetrically. Emission spectra were measured using a 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. The spectra were collected from the intense cavitation field located in the 1 cm space between the tip of the horn and the quartz window. The temperature of the solution inside the cell during irradiation was maintained within  $\pm 0.5$  °C by refrigerated and heating circulator (Julabo, F12-MB) and kept at 9 °C for the experimental study of hydrostatic pressure effect.
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