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Effects of rare-gases on MBSL spectrum of K atom emission

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ABSTRACT

Sonoluminescence from alkali-metal salt solutions has been studied because emission mechanism from non-volatile alkali-metal ions has been interested. We measured multi-bubble sonoluminescence spectra from KCl solutions saturated with Ar, Xe and He gases at temperatures in the range of 15 - 40 °C at the frequency of 148 kHz. For Ar-saturated solutions, the spectral line width of K atom emission, which broadened asymmetrically to the red side, was independent of temperature whereas the K line intensity decreased with increasing temperature. These results showed that an amount of water vapor does not affect on the K-line width but on the line intensity. The results for Xe-saturated solution indicated that the spectrum of K atom emission is composed of two peaks, unshifted narrow line and shifted broad line. We also observed in some ultrasound-irradiation condition that each K line was clearly separated into two peaks. In contrast to the cases of Ar and Xe saturation, the spectrum in He-saturated solution showed symmetrically-broadened doublet of K line which are shifted to blue side by 0.21 nm. These results strongly suggest that the excited K atoms are perturbed by rare gase inside bubbles. The rare-gas effect observed is in good agreement with results by gas-phase spectroscopy. We conclude that K atom emission occurs in gas phase inside bubbles.

INTRODUCTION

Sonoluminescence (SL) can be used as a spectroscopic probe of species produced at bubble collapse. Studies of multibubble sonoluminescence (MBSL) from alkali-metal salt solutions have revealed emission from the excited alkali-metal atoms [1-9]. However, there are several unsolved problems for the alkali-metal atom emission. The subject of the problem is where alkali-metal emission occurs, in gas phase or liquid phase [10]. Sehgal et al. [2] measured MBSL spectra from NaCl and KCl solution and estimated the final temperature and pressure at the bubble collapse from the broadening or shift of the spectral line, assuming that the emission arises from the highly compressed gas-phase condition within bubbles. The proposition that atomic emission originates from the gas phase is also supported by Lepoint Mullie et al [3]. They demonstrated that the blue satellite that accompanies the broadened rubidium line is due to the B-X transition of alkali-metal/rare-gas van der Waals molecules within the bubbles. On the other hand, Flint and Suslick [4] reported the effects of solvent vapor pressure and an inert gas on the potassium line and observed no change in the line width or peak shift. They concluded that alkali-metal emission originates from the liquid phase. In surfactant solutions such as sodium pentylsulfonate, the intensity of sodium emission was enhanced [5]. This is caused by the higher local concentration of Na^+ at the surfactant-coated bubble surface compared with that in bulk solution. On the basis of this observation, Ashokkumar et al. [6] suggested that the reduction of Na^+ occurs at the bubble/liquid interface.

It is still under debate where alkali-metal emission occurs, how alkali-metal ions are reduced, and how alkali-metal atoms are excited. Choi et al. [7] investigated the concentration and acoustic power dependences of MBSL spectra from NaCl solution doped with ethanol. The close investigation of line width and intensity indicated that the sodium emission occurs in the gas phase. The purpose of the present paper is to investigate effects of temperature and saturation gas on line width and shift of alkali-metal emission. Potassium atom emission is favorable for evaluating the line-broadening, peak shift and symmetry since the two lines of K doublet are more widely separated than those of sodium doublet. We measured MBSL spectra from KCl aqueous solutions saturated with Ar, Xe and He gases at temperatures in the range of 15 - 40 °C at frequency of 148 kHz. The results indicate that the potassium emission occurs in gas phase within bubbles.

EXPERIMENTAL SECTION

We measured MBSL spectra in the 270 - 800 nm range from KCl aqueous solutions with concentration of 1 M. The ultrasonic frequency and power used are 148 kHz and 2.3 W, respectively, unless otherwise specified. An experimental apparatus used for the measurement of the MBSL spectrum is described elsewhere [11]. A cylindrical cell was made of stainless steel. The size of the sample container was 46 mm in diameter and 150 mm in length. The top and bottom faces of the cell were equipped with a quartz glass window and a sandwich-type transducer, respectively. The temperature of the sample was controlled from 15 to 40 °C by circulating water. The solution was carefully degassed, and then re-gassed with rare gas for at least 2 hours. Since the sample container was closed without air, no air was introduced

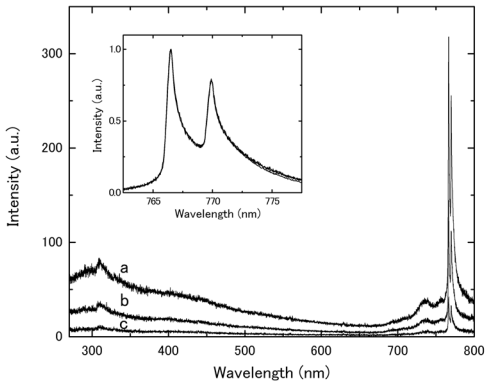

Figure 1. MBSL spectra from Ar-saturated KCl solutions at the temperature of 15 (a), 25 (b) and 30 °C (c). The inset shows the normalized K lines obtained at three different temperatures.

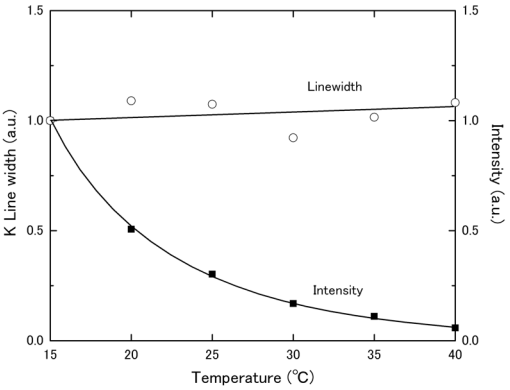

Figure 2. Dependences of the line width and intensity of K atom emission on solution temperature. The circles denote the line width and the squares indicate the line intensity.

during the experiments. The signal from a function generator (Agilent, 33250A) was amplified using a power amplifier (NF Circuit, HSA4014) and was matched for impedance to the transducer using a transformer. Emitted light was analyzed using a system of a monochromator (Acton Research, SpectraPro-300i) and a cooled-CCD detector (Princeton, Pixis). Broad-band spectra were collected using a grating of 600 grooves/mm blazed at 300 nm. The narrow-band spectra around the K emission line were collected using a grating of 1200 grooves/mm blazed at 500 nm. The instrumental bandwidth was estimated to be 0.315 nm from the measurement of the He-Ne laser line. The spectral response was calibrated for detection efficiency against a standard halogen lamp and Xe lamp. The total power of the irradiated ultrasound was determined by calorimetry using a type-K thermocouple.

RESULTS AND DISCUSSION

Temperature dependence of MBSL spectrum from potassium atom

Broad-band spectra of MBSL from Ar-saturated KCl solutions were measured at temperatures in the range of 15－40 °C. The results are represented in Fig. 1 only for the case of 15, 25 and 30 °C for clarity. The spectra appear to consist of a continuum and several peaks. The peak at about 310 nm has been identified as the emission from electronically excited OH radicals [12,13]. The double peaks around 770 nm are attributed to emission from electronically excited K atoms. A blue satellite peak at about 735 nm accompanied the potassium line. This satellite peak has been reported in several works [2,4], and may resulted from electronically excited K-Ar* molecule [3]. The intensities of the K lines and the continuum decreased with increasing temperature. The K lines at different temperatures are normalized and shown in the inset of Fig.1, which indicates no effect of temperature on the line width.

The dependence of SL intensity on solution temperature is discussed in terms of water vapor in bubble. The total SL intensity decreases with increasing the solution temperature. This result can be explained as follows. A bubble temperature at collapse is known to depend on the liquid temperature. Water vapor from liquid enters bubble during its expansion, and prevents from increasing a final temperature at bubble collapse. Accordingly, SL intensity at higher temperature is smaller due to higher vapor pressure. In fact, our results are in good agreement with those of single-bubble SL studies. Vazquez and Putterman [14] reported that the SL intensity from single bubble at 20 °C increased by a factor of 5 compared to that at 34 °C even though the bubble dynamics hardly changed. They suggested that water vapor trapped inside a collapsing bubble is a key parameter. On the basis of their observation, Yasui [15] computed the final temperature and amount of molecules produced inside an Ar bubble at bubble collapse at the liquid temperature of 20 and 34 °C. He estimated the final temperature of 24000 K at 20 °C and 15000 K at 34 °C for the Ar bubble. He explained that the bubble temperature at collapse is lower in a hotter liquid due to the endothermal heat of water vapor dissociation and its large molar heat. It is noted that the final bubble temperature obtained in our MBSL system may be much lower than Yasui's estimation.

Figure 2 shows temperature dependences of the intensity and width of K line obtained from the results in Fig. 1. The intensity of the K line exhibits a rapid decrease similar to the total SL intensity. We consider, however, that the origin of potassium emission differs from that of continuum emission. Abe and Choi [8] showed that alkali-atom emission originated from lower temperature bubble compared to the bubbles that produce a continuum emission, and its intensity directly corresponded to amount of OH radicals produced by dissociation of water molecules [7]. Therefore, the decrease in the K line intensity with temperature is probably caused by the reduction of the production of OH radicals due to lower temperature bubble in higher temperature solution. The line width of K line, on the other hand, was not affected by the solution temperature, accordingly by the amount of water vapor. In general, a line broadening effect reflects an environmental condition of emitting species, such as kind of foreign gases and gaseous concentration. The present result suggests that increase in internal pressure at bubble collapse due to evaporation of water can be neglected, assuming potassium emission originates from gas phase within bubbles. On the contrary, Choi et al. [7] found that the sodium line width increased due to addition of small amount of ethanol having volatile nature. This difference can be explained by supposition that the line broadening of alkali-metal atom is not effected by water vapor or its derivatives but other gas components within bubbles because ethanol molecules decomposes into CO or hydrocarbons [16]. In above discussion, it is important that the shape of potassium line does not depend on the final temperature at bubble collapse but on gas components.

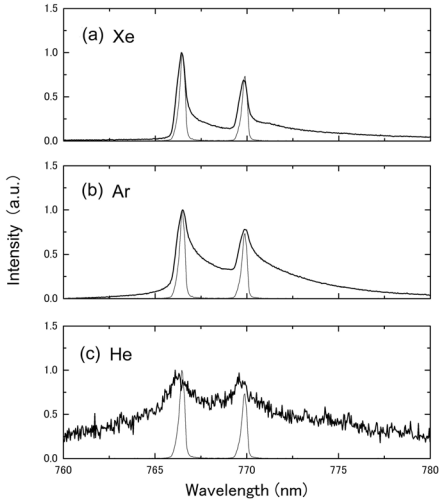

Figure 3. Spectra of K atom emission from KCl solution saturated with Xe (a), Ar (b) and He (C) at the temperature of 15 °C. A thin line in the figure indicates a flame spectrum obtained from KCl.

Dissolve-gas dependence of K lines

Figures 3 (a)- 3(c) shows the K atom emission from KCl solution at 15 °C saturated with Xe, Ar and He, respectively. A collecting time of the spectrometer was 1, 3 and 30 min for the solution with Xe, Ar and He, respectively. A flame spectrum of KCl was also measured and indicated as a thin line in Fig.3. The double peaks from the flame spectrum are at 766.5 nm ($^2P_{3/2}\rightarrow{}^2S_{1/2}$) and 769.9 nm ($^2P_{1/2}\rightarrow{}^2S_{1/2}$). For Xe and Ar-saturated KCl solutions, it is noticed that the spectral peaks are not shifted and broadened asymmetrically to the red side (longer wavelength) compared with the lines from the flame spectrum. The peaks of K line in the case of Xe in Fig. 3(a) are prominent in comparison with that in the case of Ar in Fig. 3(b), and can not be analyzed as single lines. This result suggests that the spectrum of K atom emission is composed of two types of peaks, unshifted narrow line and shifted broad line. We also observed K atom emission from He-saturated solutions. On the contrary to the cases of Xe and Ar, the K lines broadened symmetrically and shifted to blue side by 0.21 nm in the case of He, as shown in Fig. 3(c).

As shown in Fig. 3, the line shape of K atom emission considerably depends on the kind of gas saturated in the solution. The spectra from Xe and Ar saturated KCl solution suggest that the unshifted narrow line and shifted broadened line overlap each other. On the contrary, the unshifted narrow lines were observed in the case of He and only shifted broadened line was obtained. Those results make us to expect that spectra of K atom in the case of Ar or Xe may be separated under certain experimental conditions. We performed a further experiment in Ar-saturated KCl solutions under various conditions by changing ultrasonic frequency and power. Eventually, we obtained a spectrum indicating clear separation of unshifted narrow line and shifted broad line at the frequency of 47.9 kHz and high acoustic power of 23 W, as shown in Fig. 4. The broadened lines shift to red side by about 0.6 nm.

The line broadening and shift shown in Figs. 3 and 4 can be explained by the results of gas-phase spectroscopy [17]. Spectroscopic studies have shown that the effect of He perturbers on the collisional broadening of K atom emission

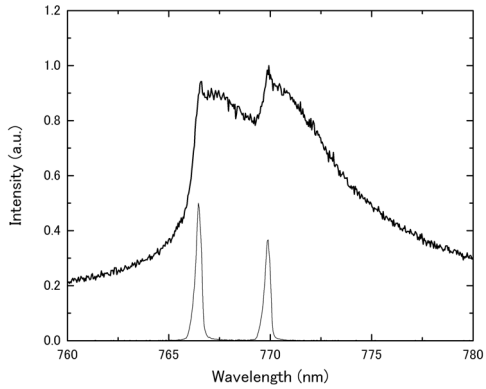

Figure 4. Spectrum of potassium atom emission from Ar-saturated KCl solution at the temperature of 15 °C. The ultrasonic frequency was 47.9 kHz and the power used was 23 W.

is markedly different from that of Xe and Ar perturbers. He perturbers cause slightly-asymmetric broadening toward the blue side, whereas Xe and Ar cause asymmetric broadening toward the red side. Similar results have been reported in the case of Na line [18]. We can estimate a relative gas density at bubble collapse from the peak shift and line width in the case of He by comparing with the spectroscopic data [17,19]. The comparison gives a relative density of 43.7 and 39.3 from the peak shift and line width, respectively. Our relative densities estimated are consistent with values reported by previous work [2]. Further analysis for the case of Ar and Xe are in progress.

CONCLUSION

Sonoluminescence from KCl aqueous solutions was observed at temperatures in the range of 15 - 40 °C at the frequency of 148 kHz for various rare-gases saturation. The line broadening of potassium atom emission was independent of amount of water vapor and final temperature at bubble collapse. MBSL spectra from Xe and Ar-saturated KCl solutions showed that the spectrum of potassium atom emission is composed of unshifted narrow line and shifted broad line. In He-saturated solutions, the K lines shifted to blue side, and broadened asymmetrically. The effects of dissolved gas are in good agreement with data by spectroscopy studies. Hence, we conclude that the site of alkali-metal emission is in gas phase inside bubbles. Excitation mechanism of the unshifted narrow line is unclear, and it should be investigated in future.

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