

A Quest to Find the Mechanism for the Formation of Excited State Metal Atoms During Acoustic Cavitation

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Abstract

Line emission from excited state metal atoms (e.g., Na*) can be observed in sonoluminescence (SL) spectra when aqueous solutions containing metal salts, such as NaCl, are sonicated. With a view to understanding the metal ion reduction process, we have investigated the influence of various experimental parameters, such as, counter ions, dissolved gases, the presence of volatile solutes, ultrasound frequency, etc. on the intensity of emission from Na*. An identical emission intensity from Na* was observed from aqueous solutions containing 1 M sodium ions with chloride or bromide or iodide as counter ions. However, the emission intensity was affected by counter ions, such as, alkyl sulfonates, alkyl carboxylates. The presence of such surface active counter ions enhanced the Na* emission intensity significantly. We postulate that reduction of Na⁺ and excitation of Na atoms occur in a hot shell around the collapsing bubbles.

1. Introduction

Acoustic cavitation commonly refers to the ultrasound-driven formation, growth and collapse of microbubbles [1,2]. The collapse of these microbubbles leads to sonochemical reactions that have a number of applications such as, synthesis of metal, polymer and semiconductor nanoparticles and degradation of chemical pollutants in aqueous solutions [3].

The bubble collapse is also accompanied by the emission of a broad wavelength spectrum of light, sonoluminescence (SL). The presence of solution solutes affects both the quality and quantity of the SL spectrum. For example, volatile solutes, such as alcohols decrease the SL intensity observed from pure water. This SL quenching is also found to be wavelength selective, at least in single bubble sonoluminescence [4]. The presence of volatile metal complexes in organic solvents seems to introduce new emissions (line or band) that can be assigned to the emission from excited state metal atoms [5]. When aqueous solutions containing metal salts are sonicated, similar line emission from excited state metal atoms have been observed [6]. The observation of emission from excited state metal atoms in an organic solvent is

relatively easy to understand. Since the metal complexes used are volatile, they can evaporate inside the cavitation bubbles during bubble expansion. These complex molecules can be thermally decomposed on bubble collapse generating free metal atoms. These metal atoms then can be thermally excited to higher energy levels. However, the observation of emission from excited state metal atoms in aqueous solutions is difficult to understand. The key reaction steps involved for such emission to occur are the reduction of the metal ions followed by the excitation of the neutral atoms to higher energy levels. The extreme thermal conditions reached by the (acoustic) cavitation bubbles are more than sufficient for the second process to occur. However, an acceptable mechanism for the first process, namely, the formation of the neutral atoms from the metal ions is yet to be established. The aim of this work is to investigate several experimental parameters that influence the emission intensity of excited state metal atoms in order to identify the possible mechanism for the metal ion reduction process.

2. Experimental Details

All solutions were prepared with research grade chemicals and Milli-Q water. The ultrasound unit used was an Allied Signal RF generator and transducer with a plate diameter of 54.5 mm operated at 363 kHz in continuous wave mode. The volume of the solutions sonicated was 200 mL in all experiments. The effective power delivered to the solutions was 2.5 W/cm², as determined by calorimetry. SL spectra were recorded by placing the cell in the cell compartment of a spectrofluorimeter (Hitachi, F-4500). A full scan (200 nm to 800 nm) could be recorded in about 2 minutes. The solutions were purged with argon prior to the spectral measurements.

3. Results and Discussion

A typical sonoluminescence spectrum observed from an argon-saturated aqueous solution containing 1.0 M NaCl is shown in Figure 1. The broad emission observed in Figure 1 is due to the overlap of several emission bands [1,2]. The peak at ~ 590 nm is the emission from excited state sodium (Na*) atoms [7].

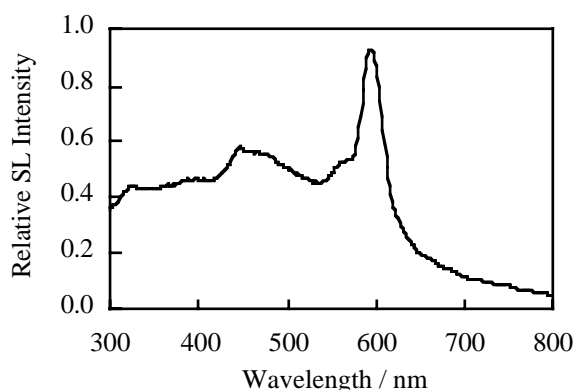


Figure 1: Sonoluminescence spectrum from an aqueous solution of 1.0 M NaCl.

SL spectra were recorded from a series of solutions containing 1 M Na⁺ with varying counter ions (Cl⁻, Br⁻ and I⁻) and the intensity of Na* emission was compared. As shown in Figure 2, the relative intensity of Na* was observed to be identical (within experimental errors) for solutions containing different counter ions. What this observation suggests is that the reduction of the metal ion to form a neutral atom does not depend upon the counter ions present in the solution.

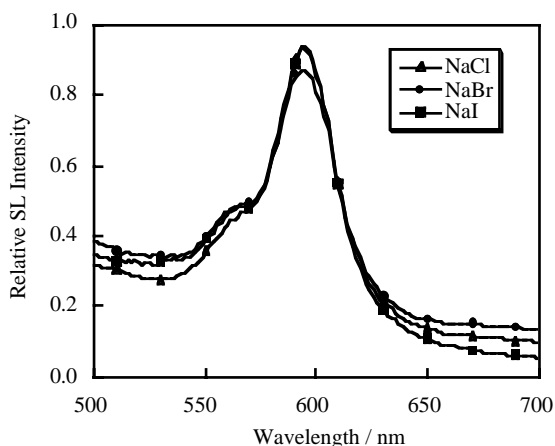


Figure 2: Sonoluminescence spectrum from aqueous solutions of 1.0 M NaCl, NaBr and NaI.

In the absence of any effect by these counter ions the investigation was extended to counter ions that are surface active. Figure 3 shows a SL spectrum observed from an argon-saturated aqueous solution containing 10 mM sodium pentylsulfonate (C₅H₁₁SO₃Na; SPS). The pentylsulfonate anion, owing to its surface activity, accumulates at bubble/solution interface. The surface concentration of this anion is much higher than its bulk concentration. Also, the adsorption of this surfactant at the bubble/solution interface leads to an enhanced Na⁺ concentration in the vicinity of the bubble/solution interface. By comparing the Na* emission intensity

from 1 M NaCl (Figure 1) and 10 mM SPS (Figure 3) it can be seen that the Na* emission intensity is significantly higher in 10 mM SPS solution. This suggests that the intensity of Na* emission strongly depends upon Na⁺ concentration at the bubble/solution interface.

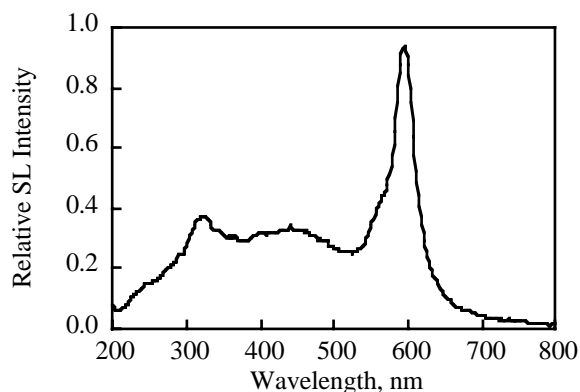


Figure 3: Sonoluminescence spectrum from an aqueous solution of 10 mM sodium pentylsulfonate.

The above discussion suggests that the reduction process occurs at the bubble solution interface. However, it cannot be completely ruled out that droplets from the interface may be injected into the collapsing bubble and then heated followed by the reduction of the metal ions in the core of the bubble.

4. Conclusions

A comparison of Na* emission intensity observed from aqueous solutions containing sodium ions with different counter ions suggests that the reduction of the metal ions to form metal atoms occurs either at the bubble/solution interface.

5. References

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