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Single-Bubble Sonochemiluminescence in Aqueous Luminol Solutions

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Ultrasonic irradiation of liquids provides a unique environment where high-energy chemical reactions occur.¹ The chemical effects originate from acoustic cavitation bubbles, which generate extremely high temperatures and pressures at collapse.² The extreme conditions in the interior of bubble also lead to the emission of light, called sonoluminescence (SL), which is manifested in two forms: multibubble (MB) SL and single-bubble (SB) SL.³ The light intensity in the MB case increases significantly upon adding a small amount of luminol to alkaline solutions. This emission is referred to as sonochemiluminescence (SCL) and is distinguished from SL,⁴ because the emission is identical to *chemiluminescence* in the bulk liquid region, which results from the chemical reaction of luminol molecules with OH radicals produced within bubbles.⁵ No counterpart has been reported for SCL in the SB case despite the well-known MB case.⁶

Recently, Ashokkumar and Grieser reported the third type of emission referred to as sonophotoluminescence (SPL), where SL is absorbed to excite dissolved fluorescent solutes, leading to the emission of fluorescence associated with *photoluminescence*.⁷ Their study of SPL covers both cases of MB and SB.⁸

The missing case, SCL for SB, is important in sonochemistry, because many sonochemical reactions involve radicals produced within bubbles, and we have successfully observed the SBSCL in aqueous luminol solutions through spectral measurement. The most important point is that no SCL is observed from a stable single bubble that emits high-intensity SL. Instead, SCL is observed from an unstable dancing single bubble, which grows and ejects tiny bubbles, making it "dance" by counteraction.

Experiments were performed using a rectangular quartz glass cell of $56 \times 56 \times 80$ mm³ internal dimensions.⁹ The bottom of the cell was attached to a bolted Langevin-type transducer (Honda Electronics) driven by a function generator (NF Electronic Instruments, 1946) through a power amplifier (ENI, 240L). Partially degassed distilled water of 220 mL at 20 °C and 2.0 mg/L in dissolved oxygen (saturation = 8.8 mg/L) was filled to 70-mm depth. A bubble was inserted with a syringe and trapped at a pressure antinode in a standing wave at 24.5 kHz. By adjusting pressure amplitude, SBSL was observed at 1.26 atm, as measured with a calibrated hydrophone (RESON, TC4038) at the position of the bubble. SL spectra were collected using a monochromator (Bunkoukeiki, M25-T) through a quartz optical fiber with an intensified charge-coupled device detector (ANDOR, ICCD 501-18F) with 0.1 s exposure for 300-cycle accumulation in the range of 250–710 nm. Aqueous sodium carbonate–luminol solutions were substituted for 1 mL of distilled water in the cell (pH = 11.3). Sequent measurement of spectra was performed within 1 min under the same conditions. The absorbance of luminol was measured with a spectrophotometer (HITACHI, U-2000).

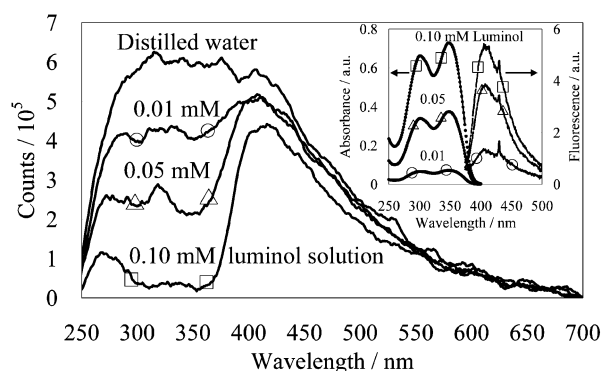


Figure 1. Single-bubble sonoluminescence spectra in distilled water and in 0.01, 0.05, and 0.10 mM aqueous luminol solutions. The insert shows the absorption and fluorescence ($\lambda_{\text{ex}} = 355$ nm) spectra of the luminol.

Figure 1 shows uncorrected spectra from a single bubble in distilled water and in 0.01, 0.05 and 0.10 mM luminol solutions. The insert shows the absorption and fluorescence spectra of the same luminol solutions. It is found that the spectrum of the distilled water is absorbed by the addition of luminol, and the absorption increases as the concentration of luminol increases. The spectral modification can be explained entirely by subtracting the luminol absorption spectrum from the water SBSL spectrum. On the other hand, the fluorescence of luminol photoexcitation is proportional to the luminol absorption, as shown in the insert. Since SPL results from direct photoexcitation,^{7,8} the SPL intensity of luminol would correspond to an increase in luminol emission intensity with luminol concentration. Therefore, the failure to observe the increasing intensity at 420 nm excludes the possibility that SPL contributions are significant.

To examine the ratio of SCL to SL in the spectrum for luminol solutions, we added ethanol to quench SBSL. The quenching effect of alcohol on SBSL in water was reported by Ashokkumar et al.¹⁰ Furthermore, Yasui¹¹ showed, on the basis of simulation, that a methanol additive quenches SBSL but hardly reduces the number of OH radicals produced within a bubble. This is also valid for ethanol. Thus, the ethanol additive should quench SL but hardly SCL. Figure 2 shows the effect of 2.0 mM ethanol additive (26 μ L) on the SB spectra in distilled water and 0.1 mM luminol solution. The SBSL spectrum in the ethanol solution is quenched preferentially at shorter wavelengths, which is consistent with ref 10. Note that the spectrum in the presence of luminol is also quenched similarly to that in the absence of luminol at 420 nm. If SCL contributions were significant, the intensity of luminol emission would become substantially independent of ethanol when the solution contains luminol. Therefore, SCL also cannot contribute significantly to the observed single stable bubble emission spectra, because adding ethanol produces the same fractional reduction in 420 nm emission intensity in both the presence and absence of luminol.

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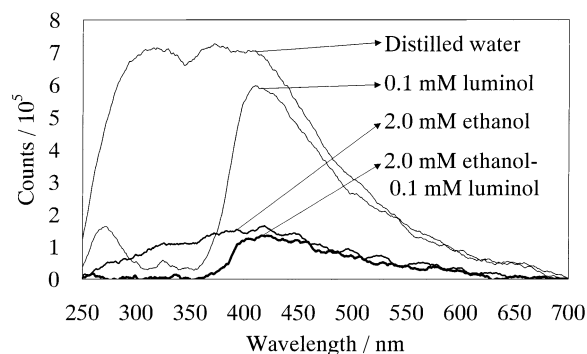


Figure 2. Effect of 2.0 mM ethanol additive on the spectra from a stable single bubble in distilled water and 0.1 mM aqueous luminol solution.

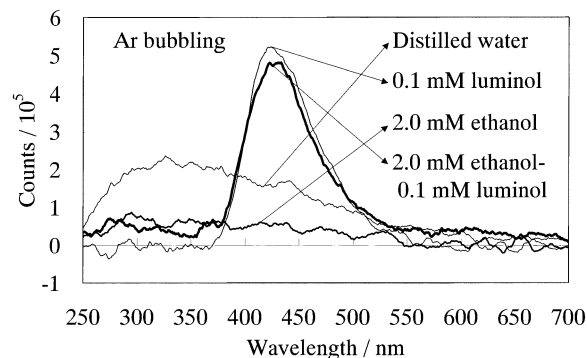


Figure 3. Effect of 2.0 mM ethanol additive on the spectra from dancing bubbles in distilled water and 0.1 mM aqueous luminol solution with Ar-bubbling pretreatment.

Although the intensity of SCL is 10–100 times higher than that of SL in MB cases,¹² we could not distinguish SCL in the stable SB case. Unstable bubble collapse seems to promote the emission of SCL. Thus, we performed further experiments under the condition of “a dancing bubble.” A dancing SB grows in size with every acoustic cycle and emits tiny bubbles, “daughter bubbles”, repeatedly, making it “dance” around the pressure antinode by counteraction.¹³ We obtained dancing bubbles by Ar-gas bubbling (100 mL/min \times 3 min) in the cell of the same water above. The dancing bubble condition is a shape-unstable one. Although daughter bubbles are, in a manner of speaking, multibubbles, the bubbles cannot be generated without an injection of bubble for the cavitation inception in contrast to MBSL cases. Figure 3 shows the spectra from dancing bubbles in distilled water and 0.1 mM luminol solutions in the absence and presence of 2.0 mM ethanol. Note that the spectral intensity in the luminol solution exceeds that in distilled water at 420 nm and is hardly affected by ethanol, despite the quenching in distilled water. These results confirm that the luminol SCL contributes significantly to the observed dancing SB emission spectra.

We conclude that unstable bubble collapse is a key factor in SCL, that is, sonochemistry. Lepoint et al.¹⁴ reported similar results in Weissler's reaction, where they observed I_3^- formation from a dancing SB but noted that this product was virtually eliminated if the bubble was stabilized. Didenko et al.¹⁵ also noted that the emission from an unstable “moving bubble” gave rise to CN emission in methylformamide but that this feature disappeared when the bubble was made stable. They argued that the stable SB produced such high core temperatures that molecular species were dissociated. In theory, Storey and Szeri¹⁶ showed that most OH radicals produced within a stable SB are confined to the bubble interior by the bubble wall. They discussed that the bubble that is unstable on collapse and breaks apart is much more productive in

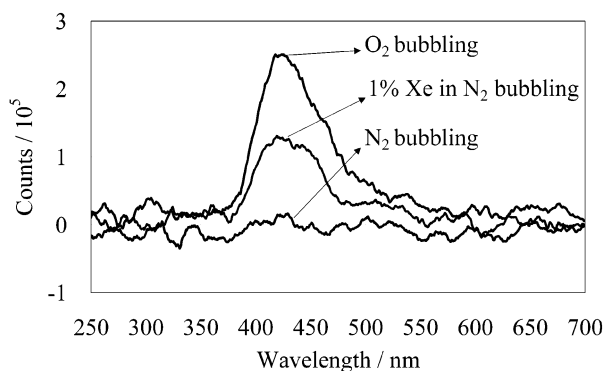


Figure 4. Influence of gas contents on sonochemiluminescence (SCL) spectra from nonsonoluminescing dancing bubbles in 0.1 mM aqueous luminol solutions.

sonochemistry. We consider that OH radicals may be produced much more in the dancing SB and may be transported into liquid together with daughter bubbles.

Figure 4 shows the spectra from dancing bubbles in 0.1 mM luminol solutions for the various gases, O₂, N₂, and 1% Xe in N₂. In these solutions, the air including Ar was partially dissolved. Under these conditions, SL was not detected in distilled water. Nevertheless, luminol SCL is seen in the cases of O₂ and 1% Xe in N₂. Non-SL bubbles are chemically active if the acoustic amplitude is above a threshold one, which is consistent with the MB case.¹² Again, similar result was shown in ref 14. Evidently the dancing SBSCL intensity is increased with O₂ or Xe because these gases promote OH radical and H₂O₂ formation¹⁷ and hence production of the superoxide radical anion required for luminol chemiluminescence.⁵

In summary, the SCL of luminol was observed not from stable single bubbles but from dancing bubbles. The SCL was observed from dancing bubbles even when SL was not observed, depending on gas content. One of the key parameters in SCL is the instability of bubble collapse, in addition to the chemical reactions within the collapsing bubble.

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