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Sonochemiluminescence from a Single Cavitation Bubble in Water

Adam Brothie,^{*,[a]} Julia Schneider,^[a, b] Rachel Pflieger,^[b] Dmitry Shchukin,^[a] and Helmuth Möhwald^[a]

The dramatic effects of microbubble collapse in ultrasonic fields, that is, acoustic cavitation, are known and exploited throughout numerous industrial and research areas, such as the material sciences, environmental remediation, and medicine.^[1] The extremely rapid collapse process leads to localized heating of the bubble interior, which breaks molecular bonds of the gas and vapor within the bubble generating active radical species. The chemical effects of acoustic cavitation are referred to as sonochemistry. A further consequence of bubble collapse is the emission of light, sonoluminescence (SL). The exact mechanism of SL is complex and to a large extent depends on the intrabubble conditions. It is generally thought that under relatively mild conditions, radiative recombination of excited molecular species dominates, whereas under more extreme conditions, radiation emanates from a plasma in the form of bremsstrahlung (i.e., breaking radiation).^[2]

Ultrasonic systems typically give rise to clusters of many bubbles, often forming elaborate structures, which are categorized as “multibubble” systems. Although useful from an application perspective, multibubble systems are inherently difficult to study on a fundamental level due to the chaotic and ephemeral nature of the bubble field. With the advent of so-called “single-bubble” cavitation, such difficulties are circumvented, in that one can isolate spatially and study a single, acoustically driven bubble under specific and well-defined experimental conditions.^[3] In recent years, researchers have developed this into a tremendously powerful tool, providing rich insight into the enigmatic nature of cavitation.^[4]

However, the sonoluminescing single bubble is thought not to be representative of cavitation in a multibubble field due to the high symmetry of collapse that results from the absence of neighboring bubbles or surfaces. Initially, the re-

petitive collapse of a single bubble was shown to produce a broad SL spectrum devoid of emission lines in water.^[4a,5] In contrast, discrete molecular emission lines from excited solvent molecules, their degradation products, and alkali salts are routinely observed to punctuate the multibubble SL spectrum.^[4a,6] This fundamental difference was attributed to the nature of the collapse event itself: the symmetrical collapse of the single bubble facilitates more efficient concentration of energy and higher core temperatures, leading to the formation during single-bubble sonoluminescence (SBSL) of highly ionized plasma, in which the emission from the excited molecular states is quenched.^[4e] However, it should also be noted that under certain conditions, plasma formation has also been demonstrated in an aqueous MBSL system.^[7]

Interesting studies have been conducted bridging the gap between the two forms of cavitation (single and multibubble), in which a spatially stable single bubble was forced to “dance”,^[8] that is, erratic spatial translation on a microscopic scale was induced. The spectrum from the dancing bubble was found to contain sodium emission lines identical to the multibubble spectrum. The same behavior has also been reported for CN* emission in various organic solvents.^[9] In a similar vein, sonochemical reactions, such as the emission from luminol (which fluoresces upon oxidation by sonochemically produced primary OH[•] and oxidizing secondary radicals) and I₃[−] oxidation, have been reported not to occur from a stable SL emitting single bubble, but were observed when a spatial instability was introduced through an increase in dissolved gas content.^[10]

Lepoint et al. have reported visual evidence of sonochemical reactions (Weissler reaction) from a single bubble, noting that the conditions under which the bubble was spatially unstable favored sonochemistry and that sonochemistry was suppressed during intense sonoluminescence.^[3d] In contrast to the aforementioned studies, Didenko and Suslick have detected sonochemical reaction products under SBSL conditions (albeit at a relatively high frequency of 52 kHz and with higher gas content), which form with reaction efficiencies comparable to the multibubble system.^[11] Thus, the literature in the field of single-bubble sonochemistry is seemingly contradictory, and a systematic study is required to determine the specific conditions at which a single bubble is chemically active.

The apparent dichotomy of single and multibubble cavitation and the inconsistent reports of single-bubble sonochem-

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istry are probably attributable to the fact that most SBSL studies have been conducted at very high acoustic pressures, near the upper threshold of SL and with very low amounts of dissolved gas. Young et al. reported line emission in water for weakly driven noble gas bubbles, which was superimposed on a very dim broadband continuum.^[12] This study indicated qualitatively that at low acoustic pressures and with a sufficient amount of gas, the interior bubble conditions are comparable to those under multibubble cavitation. When the acoustic pressure was increased, the line emission was overwhelmed by the growing SL continuum. More recent studies have corroborated this, showing that the emission intensities from OH* and Na* from a stable single bubble follow an opposing trend compared with the continuum.^[13] The distinct parameter space, in which SL and sonochemical processes take place, is not restricted to single-bubble systems. Recent work from multibubble systems has shown that a spatial separation of SL emitting and sonochemistry producing bubbles exists, the former of which possess a larger size.^[14]

We have investigated the emission from luminol at different acoustic pressures of a single bubble in degassed water, with and without pre-equilibration with 70 mbar of argon, to further understand the conditions at which SL and sonochemistry occur and bridge the gap between single and multibubble cavitation. The specific objective was to observe whether the formation of active radical species in the single bubble, which can give rise to line emissions, translates to bulk sonochemistry and to identify the necessary conditions for these processes to occur.

Figure 1 contains the emission spectra as a function of acoustic pressure for degassed water (24 mbar) and a degassed alkaline solution of luminol (0.1 mM, pH 11). The behavior of water is as expected based on numerous previous investigations, in which the onset of strong broadband SL occurs at about 1.05 bar, thereafter increasing sharply in intensity. The luminol solution, in contrast, exhibits the typical luminol sonochemical luminescence (SCL) band centered at $\lambda = 425$ nm at significantly lower acoustic pressures (0.90–1.05 bar), in which the SL broadband is either not present

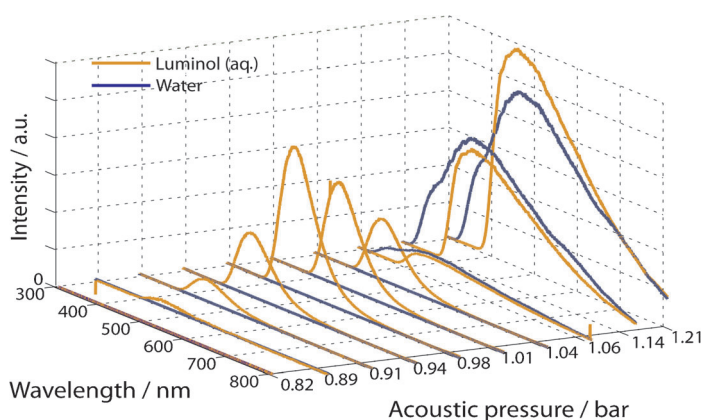


Figure 1. Single-bubble emission spectra from degassed water (24 mbar) and a luminol solutions (0.1 mM) as a function of acoustic pressure.

or below the detection limit of our system. This form of luminescence, as mentioned, is chemical in nature (i.e., distinct from SL) and occurs in the solution surrounding the bubble through an oxidative radical process.^[15] The intensity of this band increases, achieving a maximum just below approximately 1.0 bar before decreasing. At the lower threshold for SL emission, there is only a very faint SCL emission observed. At higher pressures (1.05–1.21 bar), the SL from the luminol solution appears similar to that from water (the sharp cut off at about $\lambda = 400$ nm is simply due to absorbance of luminol in solution), and there is no indication of any SCL superimposed on the SL spectrum.

It is clear that two acoustic pressure domains exist, with SCL and SL at low and high pressure, respectively, occurring almost exclusively of each other. This is also apparent in Figure 2, in which the normalized emission intensities are

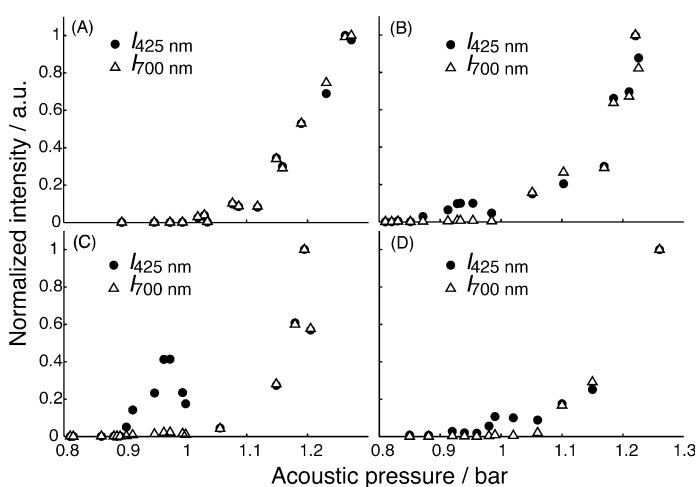


Figure 2. Normalized emission intensities at $\lambda = 425$ and 700 nm for degassed water (A) and luminol solutions (0.01 and 0.10 mM; B, and C, respectively), and for a luminol solution (1.0 mM) pre-equilibrated with 70 mbar argon (D).

shown as a function of acoustic pressure. By taking the normalized intensities of the luminol peak emission wavelength of $\lambda = 425$ nm and the intensity at an arbitrary higher wavelength of $\lambda = 700$ nm, which is unaffected by luminol, the evolution of the two forms of luminescence and the discrete pressure domains can be clearly seen. The presented data are for pure water, 0.01, and 0.10 mM luminol solutions in degassed water (Figure 2A, B, and C, respectively) and also for a 1.0 mM luminol solution, pre-equilibrated with argon at 70 mbar (Figure 2D). The intensity of the luminol emission increases with concentration, and is significantly reduced, although still present, in the pure argon bubble. This is presumably due to the larger number and range of oxidizing species that can form through reaction with oxygen and nitrogen in the air bubble. It is important to emphasize that above the lower SL threshold, argon rectification takes place, because the diatomic gases are burnt and expelled

from the bubble.^[16] This does not take place at lower pressures at which luminol emission is observed.

The trend in the relative SCL intensity with acoustic pressure shows some similarity to that of OH* and Na* emission in the SBSL spectra.^[13] However, there are several fundamental differences between the trends for the two types of emission. First, OH* and Na* line emission is only observed above the lower SL threshold (>1.05 bar, as was measured in our system), superimposed on a dim broadband signal, that is, this has been never observed in the absence of weak continuum emission. The lines effectively vanish upon the onset of intense SL at about 1.15–1.20 bar. In contrast, luminol emission is exclusively observed below the lower SL threshold pressure (0.90–1.05 bar). Thus, solution sonochemistry and intrabubble processes, such as those that lead to line emission from radicals, do not correlate in the case of a single bubble.

The parameter space for unstable and stable single-bubble cavitation is well characterized, and the cavitation leading to luminol emission at low pressure is within the dancing-bubble regime, in which the bubble undergoes relatively mild and asymmetric collapse due to the spatial instability. This can be expected to lead to enhanced transport of active species to the bulk solution. In the second domain, in which strong line emission and weak SL is observed, the bubble is spatially stable and undergoes a more intense collapse producing temperatures comparable to those of multi-bubble cavitation.^[4k,17] Driven at higher pressure, the bubble collapse becomes very intense, leading to extremely high temperatures and the formation of a plasma with a greater degree of ionization. Under these extreme conditions, emission from excited states is quenched.^[4k,18]

The different pressure domains of SB cavitation are well established. However, correlation between the lower pressure domain, in which line emission occurs, and bulk sonochemistry has not been investigated. Luminol emission reports only on the radicals that escape the bubble following collapse, whereas OH* emission reports on the radicals formed inside the bubble core, moreover, it reports on those in an excited state. The fact that at the onset of weak SL and atomic and molecular line emission luminol emission ceases has important implications. First and foremost, this shows that despite the much greater amount of OH* radicals that are expected to be formed inside the bubble, they do not (at least in a significant quantity) escape the bubble on collapse. The number of OH* radicals that enter the bulk phase and react with luminol can be expected to be relatively low based on the high symmetry of bubble collapse above the SL threshold.

The second important difference between the luminol emission and OH* emission is that OH* emission requires a pure noble gas bubble, whereas luminol emission is more intense for an air bubble. The implication is that despite significant radical production in air, the presence of the diatomic gases precludes emission from the excited states. There are several mechanisms, through which the dependence on the saturating gas type may occur. For example, the

OH radical concentration itself is depleted through reaction with hydrogen peroxide (enhanced in the presence of molecular oxygen) leading to the formation of superoxide radicals, which can also oxidize luminol.^[15] In addition, the excited A²Σ⁺ state is likely to be significantly deactivated through collisions with molecular oxygen and nitrogen.^[19]

In summary, this study has revealed the conditions required for a single bubble to be sonochemically active. Evidence of radical-induced processes surrounding the bubble was only observed below the SL threshold, where the bubble was not spatially stable, and did not correlate with emission from excited molecular states inside the bubble. Moreover, this work substantiates recent progress that has been made in bridging the gap between single and multibubble cavitation.

Experimental Section

All solutions were prepared in Milli-Q purified water. Luminol (3-amino-phthalhydrazide) and sodium hydroxide were provided by Sigma-Aldrich. Spectra were recorded in a cylindrical, hermetically sealed resonator cell with a piezoelectric transducer (PZT) glued to the base. Each solution (105 mL) was degassed under vacuum to <24 mbar. For partially saturated argon solutions, the degassed solution was allowed to equilibrate at 70 mbar argon for 30 min. Before the measurement, the argon pressure was increased to 1 bar, which was necessary to ensure bubble stability.

The signal to the PZT was supplied by a Krohn-Hite function generator (model 1200 A) and amplified with a Krohn-Hite wideband power amplifier (model 7500). Bubble generation was achieved by tapping or by dropping a few drops of water on the liquid surface with a syringe. The resonance frequency of the cell was 27 kHz and the acoustic pressure above the pressure antinode was measured with a needle hydrophone (Dapco Industries, model NP-10-1). Despite a large error (±0.2 bar) associated with the hydrophone, there was excellent internal precision for each experimental run, in which the hydrophone was kept at a fixed location. Spectra were acquired with an Acton Research SP-300i imaging spectrometer and a charge-coupled device detector (PIXIS 100B, Princeton Instruments). Wavelength calibration of the spectrometer was performed with a Hg(Ar) pen ray-light source, and the spectra were then corrected against those of a calibrated halogen lamp. A high-pass optical filter (λ = 320 nm) to avoid detection of second-order stray or scattered light and a triplet lens (Edmund Optics) to focus the light onto the detector were also used. All spectra were normalized with respect to the acquisition time, which was varied between 10–60 s, depending on the light intensity. The slit width was set at 3 mm.

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Keywords: cavitation • luminescence • luminol • ultrasound • radicals

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