# Comparison of Multibubble and Single-Bubble Sonoluminescence Spectra

Thomas J. Matula, Ronald A. Roy, and Pierre D. Mourad
*Applied Physics Laboratory, University of Washington, 1013 NE 40th Street, Seattle, Washington 98105*

William B. McNamara III and Kenneth S. Suslick
*School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*
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Comparisons of the spectral characteristics of sonoluminescence from cavitation in bubble fields (MBSL) versus cavitation of single bubbles (SBSL) have been made for aqueous solutions under similar experimental conditions. In particular, alkali metal chloride solutions exhibit sonoluminescence emission from excited state Na or K atoms in MBSL, while SBSL exhibits no such emission. Since the metal ions are not volatile, participation of the initially liquid phase must occur in MBSL. Surface wave and microjet formation in cavitating bubble fields versus the high spherical symmetry of collapse of an isolated bubble may account for the observed differences.

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It has long been known that under certain conditions acoustic irradiation of a liquid can result in light emission, a phenomenon called sonoluminescence (SL) [1,2]. The process typically involves the application of high intensity ultrasound to a liquid by an immersed acoustic horn driven with a piezoelectric transducer. The resulting cavitation-bubble field is made up of a complex distribution of gas and vapor-filled bubbles of various equilibrium sizes that pulsate at various phases relative to the driving acoustic pressure field. The bubble dynamics is further complicated by interactions with neighboring bubbles [3] as well as with the vessel walls. Depending on the location within the pressure field and these other influences, some of the bubbles may grow dramatically during the negative portion of the sound field, followed by a quasiadiabatic collapse that results in the heating of the bubble interior and the subsequent emission of light [4].

In spite of the complexity of cavitating bubble fields, many studies have been made of multibubble sonoluminescence (MBSL) and the influences of fluid and gas properties. The optical spectra of MBSL typically contains distinct, pressure broadened molecular or atomic emission bands. Of particular significance here is the identification of individual transitions from excited states of diatomic carbon ($C_2$) that contribute to the optical spectrum of MBSL in nonaqueous liquids. The fitting of the measured spectrum of $C_2$ permitted the measurement of an effective rotational and vibrational temperature of the excited states of $C_2$ of 5100 K [5].

Recent experimental advances [6] have also made it possible to examine both the temporal and spectral nature of sonoluminescence from a single bubble (SBSL). Here a single bubble is acoustically levitated in an aqueous solution that has been partially degassed. The bubble can be made to undergo large-amplitude, nonlinear, presumably radial pulsations during which light emission can occur. Some properties of SBSL include [7] the synchronous emission of light with each and every acoustic cycle, temporal flash widths of less than 50 ps, and a continuous spectral energy density that increases from the visible into the UV, with eventual fall off due to UV absorption by the surrounding water. In addition, unlike in MBSL, there are little or no electronic or molecular bands associated with SBSL spectra. The shape of the spectrum of SBSL has led some researchers to suggest that SBSL is much "hotter" than MBSL, reaching temperatures as high as 50 000 K [8], and possibly much higher [9,10].

In order to probe the differences between MBSL and SBSL, we have explored emission from identical aqueous solutions containing potentially emissive, but nonvolatile, solutes using the same spectrometer for both systems. Nonvolatile solutes provide a test of the involvement of the initially liquid phase surrounding the cavitating bubble in the sonoluminescent event [11,12]. An observation of an SL emission peak from a nonvolatile solute requires either that a fluid shell surrounding the bubble be heated sufficiently [13], or that liquid droplets containing the nonvolatile species become entrained and heated within the bubble [4,14].

It was not possible to generate both MBSL and SBSL in a single apparatus, owing to the differences in techniques used to generate cavitation-bubble fields and isolated single bubbles. MBSL is generated using an ultrasonic horn, which produces large peak pressures within the liquid (around 10 bars), with high levels of gas saturation; while SBSL occurs with applied acoustic pressure amplitudes near 1 bar, and gas concentration levels that are a fraction of saturation. Nonetheless, comparison of the optical spectra can be made by using identical fluid preparation schemes under identical gases with a single calibrated spectrometer.

The SBSL apparatus consisted of a quartz cylindrical levitation cell (8 cm tall by 4.5 cm diameter), as shown in Fig. 1(a). The cell was closed on top with a glass plate. A hollow cylindrical PZT transducer, cemented to the glass, was used to drive the levitator in tandem with a power

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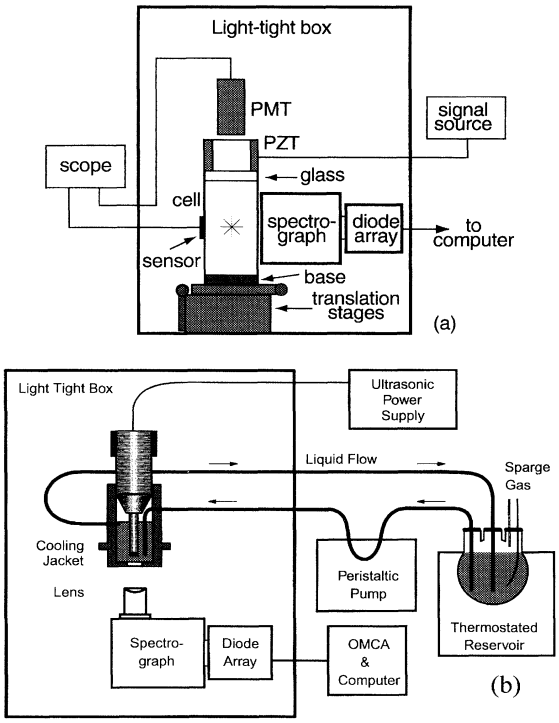


FIG. 1. Illustration of the experimental apparatus used. (a) The SBSL cell was mounted on micropositioning translation stages to facilitate alignment with the monochromator. An oscilloscope was used to monitor the acoustic resonance of the cell as well as the PMT output from the SBSL bubble. (b) The monochromator was repositioned within the light-tight enclosure to view MBSL. A quartz lens was used to focus the light onto the input slit of the monochromator.

amplifier (Khronhite 7500) and function generator (SRS DS335), which are not shown. A brass plate (with valved fluid ports to facilitate closed fluid processing, not shown) was cemented to the bottom of the levitator. The cell was filled with microfiltered, deionized water, and degassed to 0.17 bar [15] by evacuating the levitator and drawing the water into the cell through the valved fluid ports. The cell was then brought back to atmospheric pressure by opening the inlet port, being careful not to introduce air bubbles. The gas concentration level was maintained by keeping the valved ports closed during the experiment.

Creation of a cavitation bubble was accomplished by heating a small protruding nichrome wire sufficiently to cause boiling [16]. The bubble was levitated by a standing wave generated in the cell (at a pressure amplitude of approximately 1.2 bars) driven at 32 kHz. A photomultiplier tube (PMT) that looked down into the cell through the glass plate was used for diagnostic purposes so that data runs resulting in large fluctuations in intensity could be, and were, discarded. These fluctuations correspond to a detuning of the acoustical apparatus [17].

For the SBSL experiments the entrance slit to the spectrograph (described below) was placed close to the side of the levitation cell, so that the bubble-to-entrance slit distance was approximately 2.25 cm. Micrometer positioners were used to manipulate the cell and thus align the bubble position to the entrance slit of the monochromator. No collection lens was used, although low light throughput required signal averaging lasting approximately 2 h. All data involving SBSL were taken at or near room temperature.

The MBSL apparatus consisted of a temperature jacketed metal cylinder (10 cm tall by 4 cm diameter) attached by O ring to a 1 cm diameter titanium ultrasonic horn (Heat Systems model 375) at the top with a quartz window on the bottom [Fig. 1(b)]. The cavitation field was concentrated between the tip of the horn and the quartz window. A quartz lens was used to focus the light onto the entrance slit of the monochromator. The thermostated jacket of the cell, combined with continual circulation of the interior liquid through a cooled reservoir, kept the cell temperature constant at 5.0 °C. In addition, gas ports in the cell were used to maintain 100% air saturation in solution. Details of the cell can be found elsewhere [18].

A 0.18 m Thermo Jarrell-Ash monochromator (Spec 18) with a wavelength resolution of 2 nm was used for the low resolution studies for both MBSL and SBSL in a range extending from approximately 290 to 700 nm. An image intensified 512 diode array (Princeton Instruments IRY-512N) was used to collect data over 250 nm ranges; overlapping data sets were taken in order to cover the entire spectral range. The spectrometer was radiance calibrated over the entire range against NIST-traceable standard lamps.

Figure 2 shows the results of the spectral analysis of SL from air bubbles in the 0.1$M$ sodium chloride solution. Note the two prominent peaks in the MBSL data, one near 310 nm and the other near 589 nm. The peak near 310 nm is attributed to excited hydroxyl emission. In contrast to the MBSL spectra, there appears to be no obvious peak near 310 nm seen in SBSL spectral studies, confirming previous results [16]. Interpretation of the apparent difference in the spectra near 310 nm is not straightforward. The nature of the spectrum in this region is complicated by the fact that water vapor exists both in solution and in the bubble. The apparent lack of a peak at 310 nm in SBSL may simply be due to extreme pressure broadening of the emission lines.

More strikingly, the prominent sodium $D$ emission line near 589 nm, which dominates the MBSL spectrum, is undetectable in the SBSL spectrum. Relative to the overall emission in the UV, the decrease in sodium emission in SBSL is at least fiftyfold [19]. Similar observations were made with 0.1$M$ potassium chloride solutions where the emission at 770 nm from excited state potassium atoms is present in MBSL but not SBSL. The sodium and potassium atom emission in MBSL requires that during cavitation in a bubble field either a fluid shell surrounding the bubble is being substantially heated or that liquid droplets containing the nonvolatile species become entrained and heated within the bubble. The lack

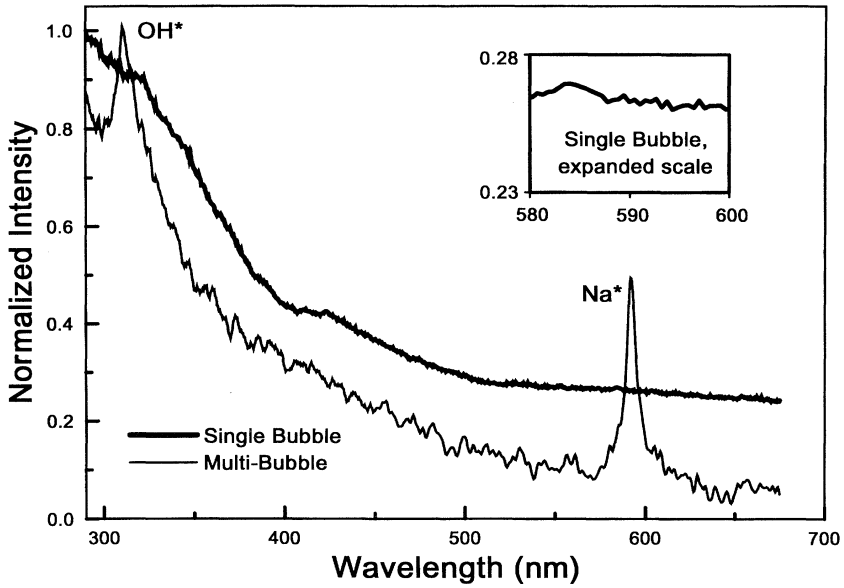


FIG. 2. Comparison of the background subtracted spectra of MBSL and SBSL in a 0.1$M$ sodium chloride solution. Each spectrum was normalized to its highest intensity. Absolute radiance comparisons cannot be made due to differences in light gathering techniques. Note the prominence (in MBSL) and absence (in SBSL) of the sodium emission line near 589 nm. The inset illustrates the absence of structure associated with SBSL around 589 nm. The signal level in this region is a factor of 3 above background.

of sodium and potassium emission lines in SBSL suggests that the sodium emission in MBSL is due to the injection of liquid droplets into the hot interior of bubbles in the cavitation field. Note that if a significant heating of a fluid shell surrounding the bubbles occurred, then one would expect sodium emission from both MBSL and SBSL. The calculations of Kamath, Prosperetti, and Egolfopoulos on adiabatic heating of cavitation bubbles are consistent with this conclusion, since they predict that the temperature at the bubble wall is nearly the same as the surrounding liquid [4].

A single bubble in isolation undergoing SBSL collapses with a high degree of radial symmetry, probably generating radially converging shock fronts in the bubble interior. This in turn generates very high pressures and temperatures at the center of the bubble. Shape distortions are likely minimized due to the relatively low applied acoustic pressure and the associated symmetry of single bubbles in isolation [20]. The absence of nonvolatile emission from SBSL is consistent with a highly symmetric bubble collapse. Without significant deformation of the bubble during the collapse of an isolated bubble, there will be no mechanism for the injection of liquid containing the nonvolatile solute and therefore no emission from it.

Bubbles in cavitation fields, on the other hand, are subjected to high acoustic fields (around 10 atm in this study). This, as well as interactions with neighboring bubbles and with solid boundaries, results in large shape distortions that may prevent radial shock wave formation or at least their convergence to the same degree as may occur for single bubbles. Local heating can still occur by adiabatic compression or by incomplete shock wave convergence, but is likely to be less severe than in SBSL.

The lowered symmetry of bubble collapse can provide a mechanism for the involvement of an initially liquid-phase sonochemical reaction site by the injection of liquid droplets (via surface wave action or microjetting) into the interior of the bubbles. In addition, liquid entrainment in MBSL may help prevent any shock waves that form from focusing as the bubble collapses, and, in fact, may be a prelude to bubble fragmentation. Thus, we expect that the bubble interior should not reach as high a temperature in MBSL as in SBSL. However, it is expected that even in a cavitation field, there may be some bubbles undergoing transient SBSL-like behavior involving symmetric collapses. As a solution is degassed, a cavitation field will contain fewer bubbles. With a decrease in the number density of bubbles, interactions with neighboring bubbles will decrease, and hence a shift in spectral characteristics may be observed. Experiments are underway to attempt to measure spectra from this previously unexamined regime of "few-bubble sonoluminescence."

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[1] A. J. Walton and G. T. Reynolds, Adv. Phys. **33**, 595–660 (1984).

[2] K. S. Suslick, Science **247**, 1439–1445 (1990).

[3] L. A. Crum, J. Acoust. Soc. Am. **57**, 1363–1370 (1975).
[4] V. Kamath, A. Prosperetti, and F. N. Egolfopoulos, J. Acoust. Soc. Am. **94**, 248–260 (1993).
[5] E. B. Flint and K. S. Suslick, Science **253**, 1397–1399 (1991).
[6] D. Felipe Gaitan *et al.,* J. Acoust. Soc. Am. **91**, 3166–3183 (1992).
[7] B. P. Barber *et al.,* J. Acoust. Soc. Am. **91**, 3061–3063 (1992).
[8] R. Hiller, S. Putterman, and B. P. Barber, Phys. Rev. Lett. **69**, 1182–1184 (1992).
[9] W. C. Moss *et al.,* Phys. Fluids **6**, 2979–2985 (1994).
[10] C. C. Wu and P. H. Roberts, Proc. R. Soc. London A **445**, 323–349 (1994).
[11] K. S. Suslick and E. B. Flint, J. Phys. Chem. **95**, 1484–1488 (1991).
[12] L. Becker *et al.,* Marine Chem. **40**, 315–320 (1992).
[13] K. S. Suslick, D. A. Hammerton, and R. E. Kline, J. Am. Chem. Soc. **108**, 5641–5642 (1986).
[14] K. S. Suslick, in *Ultrasound: Applications to Materials Chemistry,* edited by R. W. Cahn, Encyclopedia of Materials Science and Engineering 3rd suppl. (Pergamon Press, Oxford, 1993).
[15] The Henry law solubility constant for air at 20 °C is $H = 6.55 \times 10^4$ bars per mole fraction of solute in solution, while at 5 °C, $H = 4.82 \times 10^4$; see, e.g., *International Critical Tables* (McGraw-Hill, New York, 1928), Vol. 3.
[16] R. Hiller *et al.,* Science **445**, 248–250 (1994).
[17] R. G. Holt *et al.,* Phys. Rev. Lett. **72**, 1376–1379 (1994).
[18] K. A. House, Ph.D. thesis, University of Illinois, 1994.
[19] Current efforts are underway to increase the signal/noise ratio in this region since the measured signal is highly sensitive to bubble alignment with the entrance slit of the spectrometer. Such a misalignment may account for the slight differences seen when compared with spectra from Ref. [16].
[20] M. P. Brenner, T. F. Dupont, and D. Lohse, Phys. Rev. Lett. **75**, 954–957 (1995).