Spatial Separation of Cavitating Bubble Populations: The Nanodroplet Injection Model

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Multibubble sonoluminescence (MBSL), the light emitted during the implosive collapse of clouds of bubbles in liquids irradiated with high-intensity ultrasound, is a consequence of acoustic cavitation and has been known for more than 70 years,[1] but only recently have we begun to quantify the conditions created in the gas phase of the collapsing bubble.[2] Our previous investigation on single-bubble sonoluminescence (SBSL) and MBSL in sulfuric acid revealed that an optically opaque plasma core was generated in submicron collapsing bubbles in both SBSL[3] and MBSL,[4] with effective emission temperatures inside the collapsing bubbles approaching 20 000 K.

The origin of the unexpected emission from nonvolatile species during MBSL, however, remains a central question in the mechanism of acoustic cavitation; two general models for the sonochemistry and sonoluminescence of nonvolatiles have been proposed, as shown in Figure 1, but no previous work has been able to differentiate between them.[5] We report here the direct observation of spatial separation of two types of sonoluminescing bubbles during MBSL: those that show emission from Na* D line emission in Na_2SO_4 solutions in sulfuric acid and others that do not. As discussed below, this result is consistent only with nanodroplet injection during cavitation (Figure 1).
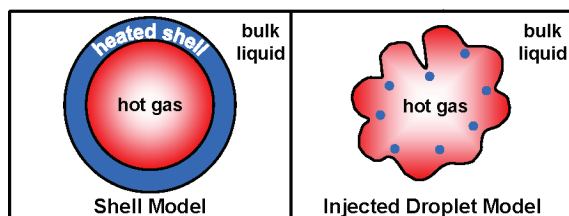

Figure 1. Two possible two-site models proposed to explain the sonoluminescence from and sonochemistry of nonvolatile solutes. The spatial separation in cavitating bubble clouds of emission from nonvolatiles is consistent only with the injected droplet model.

When nonvolatile metal ions are present in an aqueous solution irradiated with ultrasound, excited-state metal atom emission can be observed in both MBSL[6] and (in sulfuric acid) SBSL.[7] Similarly, it has long been recognized that nonvolatiles can undergo sonochemical reactions.[5,8] There are two models proposed to explain how nonvolatile species get heated in a collapsing bubble: the shell model and the injected droplet model, as illustrated in Figure 1. In the shell model, the metal ions in the initially liquid interfacial region are reduced and excited by radicals formed in the gas phase. In the injected droplet model, interfacial instabilities (capillary surface waves and microjet formation[5,9,10]) during bubble collapse are proposed to nebulize nanodroplets of liquid into the hot core of the collapsing bubble, with subsequent thermolysis and reduction of nonvolatile metal ions and excited metal atom emission. Direct experimental evidence in favor of one or the other model, however, has been difficult to obtain. Hydrodynamic calculations[5c] suggest

that the interfacial region between the bulk liquid and the gas phase inside the bubble remains relatively cool, but issues of vapor supersaturation and microjetting during collapse are complex.[9]

As shown in Figure 2A, we observe two spatially separate types of MBSL from 0.1 M Na_2SO_4 in 95% sulfuric acid: (1) blue-white emission near the horn and (2) orange emission (from electronically excited Na* atom D lines) further away (cf. Supporting Information (SI) for experimental details). We have previously observed[4] three different light emitting regimes upon varying the acoustic intensity: filamentous (<16 W/cm^2), bulbous ($16−24$ W/cm^2), and cone shaped (>24 W/cm^2). In all three regimes, we can clearly see that the orange emission is spatially separated from the blue-white emission. At lower acoustic intensities with filamentous emission (Figure 2A, left), we can clearly see that orange emission is outside but surrounds the blue-white bubble cloud; at higher intensities, the blue-white emission is well separated spatially from the orange emission.
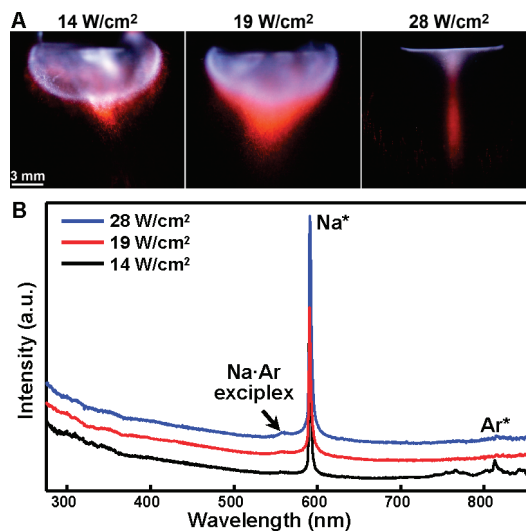

Figure 2. (A) Photographs (3 s exposures) of MBSL from a 0.1 M Na_2SO_4 solution in 95 wt % H_2SO_4 saturated with Ar at 298 K at different acoustic intensities. Addition of Na_2SO_4 did not alter the shape of bubble cloud. The Na* emission is orange rather than yellow due to pressure broadening (SI Figure 1). (B) MBSL spectra from a 0.1 M Na_2SO_4 solution in 95 wt % H_2SO_4 saturated with Ar at 298 K at different acoustic intensities. Spectra were normalized at 700 nm and offset for clarity.

Strong MBSL emission from sodium ($\sim$590 nm) was observed from the ultrasonic irradiation of 0.1 M Na_2SO_4 95% sulfuric acid solutions (Figure 2B). At low acoustic power ($\sim$14 W/cm^2), Ar emission is also observed which indicates a plasma core formed during bubble collapse.[4] The observed Na* emission arises from the well-known D lines ($3p$ to $3s$). In addition to the Na* emission, a relatively weak satellite band to the blue of the Na D lines is also observed and is attributed to emission from the Na·Ar exciplex.

Exciplex emission was first observed when Na vapor is rapidly compressed in an Ar atmosphere[11] and has also been previously observed during MBSL from aqueous alkali halide solutions[6] and recently during SBSL from Na_2SO_4 sulfuric acid solution.[7] Observation of the exciplex suggests that the emitting Na* atoms are in a gas phase state, regardless of their origin.

The simultaneous observation of Na* and Ar* emission at low acoustic power is, at first glance, paradoxical, because there is a substantial difference in the excitation energies of the populated states of these atoms: the energies of the emitting states of Ar are over 13 eV above the ground state ($^1S_0$), while the energies of the excited states of Na are only 2.1 eV above the ground state ($^2S_{1/2}$). This suggests that the two emitting species may be formed at different times during collapse, at different spatial locations within the collapsing bubble, or from different bubbles altogether.

Given the substantial spatial separation seen in Figure 2A of two very distinct sonoluminescing bubble populations, we can measure the MBSL spectrum as a function of position within the bubble cloud (cf. SI for experimental details). Figure 3 shows that at the top of the bubble cloud in the middle acoustic intensity regime (where there is only blue-white emission in the photographs), no Na* emission can be detected and the emission is strictly a broad continuum. While at the bottom of the bubble cloud, strong Na* emission is observed and the continuum is diminished 10-fold in intensity. This spatial separation of sonoluminescing species is not limited to sulfuric acid, and we observe exactly the same phenomenon from 0.1 M Na_3PO_4 in 85 wt % phosphoric acid (Figures S2, S3, S4, and S5 in the SI).
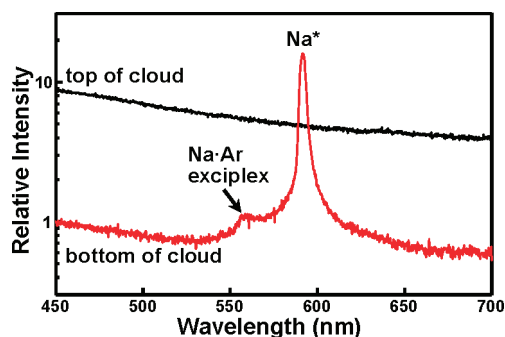
Figure 3. MBSL spectra taken at the top and bottom of the cavitating bubble cloud from a 0.1 M Na_2SO_4 solution in 95 wt % sulfuric acid saturated with Ar at room temperature, irradiated with 19 W/cm^2 ultrasound at 20 kHz.

The distinct sonoluminescing bubble populations from the intense orange and blue-white emissions provide the first experimental evidence for the injected droplet model over the heated-shell model for cavitation. Because the Na* emission is derived from an initially liquid region (Na$^+$ is obviously nonvolatile), *if the heated-shell model were correct, then a spatial separation of different sonoluminescence emitters ought not to occur.* For the heated-shell model, sonoluminescence from nonvolatiles should always be present whenever conditions are sufficient to give rise to sonoluminescence inside the bubble: even if interior conditions were so extreme as to lead to complete line broadening of sonoluminescence at the core of the bubble, somewhere in the interfacial region there would be a temperature gradient appropriate for Na* emission. The observed spatial separation supports our earlier speculation[2d] that the excited metal atom emission in MBSL is due to the injection of liquid nanodroplets into the interior of bubbles via capillary wave action, microjetting, or bubble coalescence only from significantly deformed bubble collapse. Once the nanodroplets enter the hot interior

of the bubble, they evaporate and complex redox processes analogous to those in flames generate the Na atom excited states responsible for the MBSL.

A coherent explanation for the sonochemistry and sonoluminescence involving nonvolatile species is now beginning to emerge. In SBSL, only moving single bubbles will undergo sufficient deformation to provide for nanodroplet injection and only moving single bubbles give emission from nonvolatile precursors.[7] In our bubble clouds, we estimate from the streak length of individual bubble emission from photographs with a known shutter speed that bubbles near the horn move only ∼4 mm/s, whereas the Na* emitting bubble far from the horn move at ∼17 mm/s (SI Figure S6). In cavitating bubble clouds, there are two distinct populations of cavitation events: (1) bubbles near the vibrating horn that are relatively stationary (probably due to interbubble Bjerknes forces), whose collapse is highly symmetric which produces a hotter core and only continuum emission, and (2) rapidly moving bubbles in a streaming liquid flow outside of the dense clouds, whose collapse is much less symmetric and from which emission from nonvolatiles becomes possible through the mechanism of nanodroplet injection (Figure 1). The spatial separation of these two very distinct sonoluminescing bubble populations provides the first experimental observation to favor the injected droplet model over the heated-shell model.

Supporting Information Available: Description of experimental details and similar data on MBSL from phosphoric acid doped with Na_3PO_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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