Evidence for a Plasma Core during Multibubble Sonoluminescence in Sulfuric Acid

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Multibubble sonoluminescence (MBSL) is the light generated during the implosive collapse of many bubbles in liquids irradiated with ultrasound.[1] Recently, we have investigated the single-bubble sonoluminescence (SBSL) of sulfuric acid, which is >1000 times brighter than prior SBSL, and discovered new emission lines (i.e., noble gas neutrals and ions, O_2^+, SO); from these lines, temperatures greater than 15 000 K and pressures in excess of 1500 bar have been experimentally determined.[2] In addition, the observation of molecular and atomic ions is the first experimental demonstration of an inner ionized plasma core during single-bubble cavitation.

We have now examined MBSL in sulfuric acid. The spectrum under Ar, at relatively low acoustic power, consists of a broad continuum extending into the UV with SO and Ar emission lines on top of this continuum. The observation of the Ar lines strongly suggests that an optically opaque plasma is generated inside the bubble during cavitation. Interestingly, we find three distinct light emitting morphologies for multibubble sonoluminescence from an ultrasonic horn; as the acoustic intensity is increased, the bubble cloud emission changes from filamentous, to bulbous, to cone shaped, and it is only from the filamentous emission that strong atomic and molecular emissions are observed.

Historically, MBSL had been studied mainly in water, which gives a spectrum consisting of a broad continuum extending into the UV and an often broadened peak around 310 nm from the excited-state of $OH^•$.[3] Low vapor pressure liquids such as long chain alkanes and silicone oils with volatile organometallic solutes have provided more information about the conditions generated during MBSL.[4] MBSL of these liquids produced new well-resolved emission lines from excited states of C_2, CH, CN, and metals such as Fe, Cr, and Mo. Using these emission lines as probes of the conditions within the bubbles, temperatures around 5000 K and pressures of hundreds of bar have been measured.[4] The production of low molecular weight sonolysis products (e.g., H_2, CH_4, and C_2H_2)[5] can prove to be problematic. These volatile products can have limited solubility in the liquid and therefore accumulate in the bubbles; subsequent cavitation events will thereafter dissipate much of their energy in the increased heat capacity (i.e., polyatomic vibrations and rotations) and especially bond dissociations.[6]

Liquids that have *both* a low vapor pressure *and* highly soluble sonolysis products are therefore preferred for the generation of higher temperatures during cavitation. Sulfuric acid is one such liquid because it has a very low vapor pressure (e.g., <1.5 mTorr for 95 wt % H_2SO_4 at 25 °C), and its sonolysis products (e.g., SO_x, trace amounts of H_2S, and elemental sulfur)[7] are either highly soluble or solids. Prior MBSL studies in sulfuric acid have shown that the light intensity is much greater than in water, and recently, low-resolution spectra have revealed two broad peaks, assigned to SO and SO_2.[8]

The sonoluminescence spectrum from concentrated (95 wt %) sulfuric acid saturated with Ar is shown in Figure 1.[9] The spectrum includes emission from a broad continuum extending into the UV
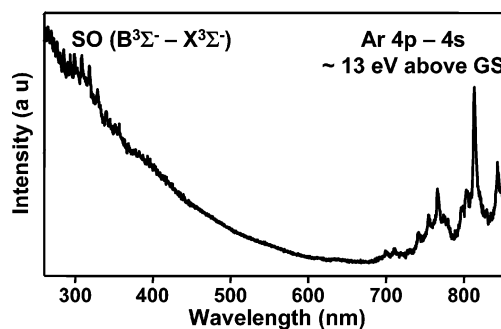

Figure 1. MBSL spectrum from concentrated sulfuric acid under Ar. Sonication at 20 kHz (14 W/cm²) with a Ti horn directly immersed in 95 wt % sulfuric acid, ~298 K.
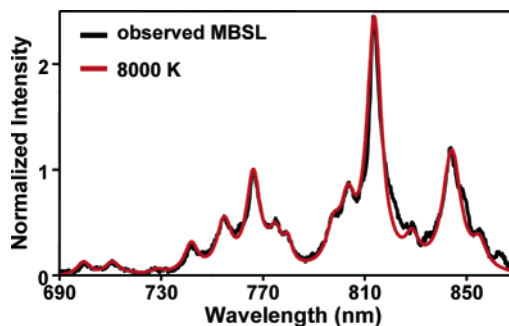

Figure 2. Spectrum of Ar (4p−4s manifold) emission from the MBSL compared to the best fit synthetic spectrum, which gives an effective emission temperature of 8000 K. The synthetic spectra assumed thermal equilibration and a Lorentzian profile (FWHM = 6.4 nm).

(due to blackbody or bremsstrahlung) together with SO ($B^3\Sigma^- - X^3\Sigma^-$), Ar (4p−4s manifold), and oxygen atom (at 777 nm) emission.

Effective emission temperatures can be determined by comparing the observed Ar lines to synthetic thermalized spectra.[4,10] By such analysis, we find an effective temperature of ~8000 K (Figure 2). Interestingly, at this temperature, there would *not* be any appreciable number of Ar atoms thermally excited into the 4p state (which is ~13 eV above the ground state). This apparent paradox indicates that, as with SBSL,[2] an optically opaque plasma[11] is probably formed at the core of the collapsing bubble in sulfuric acid, and that the Ar emission results from collision excitation with higher-energy ions (e.g., electrons[12]). The presence of a plasma during MBSL has been postulated numerous times,[13] but until now, there has been no experimental evidence.

The SO and O lines observed in Figure 1 originate from the sonolysis of trace amounts of sulfuric acid that enter the cavitating bubble as either a vapor or injected as liquid microdroplet. The production of SO_2 is confirmed by the absorption profile of the H_2SO_4 after sonication with strong absorption below ~350 nm. SO_2 absorbs strongly in the UV. This absorption increases in
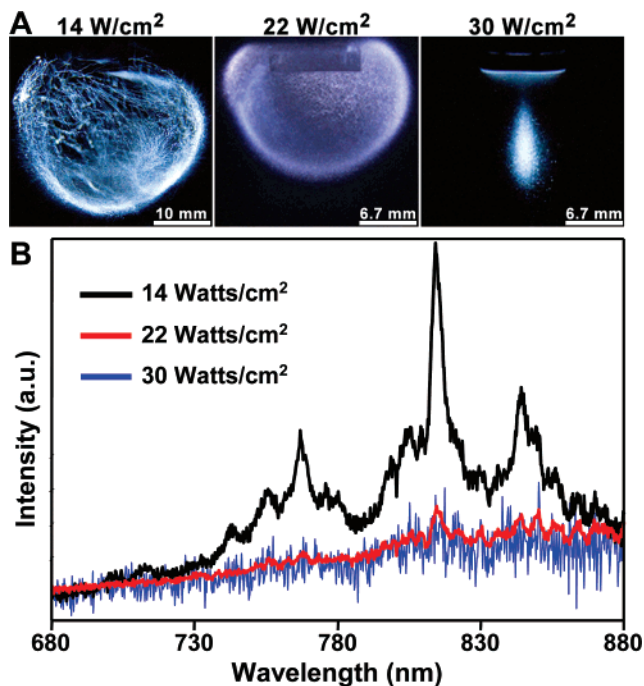
Figure 3. MBSL of concentrated H₂SO₄ at different acoustic powers. (a) Photographs (10 s exposures) of different light emitting regimes of MBSL of H₂SO₄, from left to right, with increasing acoustic intensity, filamentous, bulbous, and cone shaped emission; (b) MBSL spectra of concentrated H₂-SO₄ at the three acoustic intensities shown. As the acoustic power is increased, the Ar lines become weaker.

intensity upon additional sonication as SO₂ builds up in the liquid, and this adsorption must be taken into account. Even though SO₂ is generated during sonication, it is highly soluble in sulfuric acid, with most of it dissolving in the liquid rather than poisoning the bubble.

We also find an unusual effect of acoustic power on the MBSL spectra of sulfuric acid. Upon varying the acoustic power, large and abrupt changes in bubble-cloud dynamics, light intensity, and the emission profiles were observed, as illustrated in Figure 3.

There are three different light emitting regimes as a function of acoustic intensity; Figure 3 shows representative spectra of MBSL of 95 wt % H₂SO₄ for each of these. At very low intensities (<1 W/cm²), one is below the cavitation threshold, and no emission is observed. As the acoustic power is increased, a wispy, filamentous emission is observed, and strong Ar and SO lines are observed along with the continuum. Above a second threshold (~16 W/cm²), the cavitating bubbles suddenly form a bulb near the horn tip, creating a small globe of light consisting of very weak Ar lines along with the broad continuum. A third threshold (~24 W/cm²) gives rise to a sudden change to emission from a cone of light at the tip surface with only the broad continuum extending into the UV and no Ar or SO lines. Prior studies[8] have been at high acoustic intensities and thus did not observe the more complex spectra.

The diminishing and subsequent loss of atomic and molecular line emission with increasing acoustic intensity may be due to either (1) an increase in the continuum as the temperature and strength of the inner plasma increases with increasing acoustic intensity or (2) a decrease with increasing acoustic intensity of the maximum temperature upon collapse of individual bubbles that could be

due to a less spherical collapse (which itself could result from turbulence, higher bubble density, or the influence of the solid surface at the horn tip).[14] Adding to the difficulty of distinguishing among these, it is difficult to obtain an accurate number of total emitting bubbles in these complex clouds. We note with hope for a solution to the latter problem with the recent publication by Grieser and co-workers.[15]

In conclusion, we find a rich set of sonoluminescence behavior from clouds of cavitating bubbles in concentrated sulfuric acid saturated with Ar. At low acoustic powers, the spectrum consists of a broad continuum extending into the UV along with SO, O, and Ar emission lines. The presence of Ar emission strongly suggests the presence of an optically opaque plasma core. There are three light-emitting bubble-cloud formations during sonication of H₂SO₄: filamentous emission at low acoustic intensity, bulbous globe emission at medium intensity, and cone emission from the vibrating tip at high acoustic intensity. Counter to initial expectations, strong Ar lines and SO lines are present only at low acoustic intensities and are lost as acoustic intensity is increased.

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(9) Ultrasonic irradiation was performed using a Sonics and Materials VCX 600 Vibra Cell at 20 kHz with a 1 cm diameter Ti horn immersed in 95 wt % sulfuric acid in a 300 mL quartz round bottom flask after sparging with Ar for a minimum of 2 hours at ~298 K. The MBSL measurements were made with an 0.32 m monochromator equipped with a 300 gr mm⁻¹ grating blazed at 250 nm and fitted with a 1024 pixel × 256 pixel LN₂-cooled CCD camera. A 100 μm slit width was used for all experiments resulting in a resolution of 0.8 nm.
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