Molecular and atomic emission during single-bubble cavitation in concentrated sulfuric acid

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Abstract: Concentrated acid solutions have been reported to produce bright light emission during cavitation. Single-bubble sonoluminescence (SBSL) from sulfuric acid (H_2SO_4) is much brighter than SBSL from water by over three orders of magnitude when both are regassed with Ar. In contrast to water, SBSL spectra of concentrated H_2SO_4 contain extensive atomic, molecular, and ionic emission revealing details about intracavity physical conditions and chemical processes. Observation of specific emitters coupled with detailed studies of the temporal emission of the emitters relative to one another and to the overall bubble oscillation will lead to a much more detailed understanding of SBSL.

1. Introduction

A single gas bubble in a liquid can be acoustically levitated and driven into highly nonlinear oscillations. Under the proper conditions, the nonlinear oscillations can result in subnanosecond flashes of light at the point of maximum implosion synchronous with the applied sound field.[1,2] This light emission from single acoustically driven bubbles, dubbed single-bubble sonoluminescence (SBSL), typically reveals little about the physical conditions and complex chemical processes occurring during bubble collapse. In fact, spectra obtained from water, the fluid used most often for SBSL experiments, consist of featureless broadband emission extending from the near-UV to the near-IR.[3] These continuous spectra have led to predictions of extreme conditions within a single sonoluminescing bubble. Fitting of the featureless spectra to theoretical continuous emission mechanisms such as blackbody and bremsstrahlung emission have led to predictions of visible temperatures being upwards of 10^4 K with core temperatures being much higher.[4–6] It is difficult, however, to determine the exact nature of the continuum in SBSL from pure water since no observable emitters are typically present. The continuum could be due to a combination of continuous emission mechanisms including blackbody, bremsstrahlung, and overlapping contributions from multiple atomic and small molecule emitters arising from sonolysis of water. Though the currently accepted theories of SBSL predict at least a weakly ionized plasma, these theories, until very recently, lacked definitive experimental support.[7]

Due to the lack of features in the SBSL spectra of water, SBSL in other liquids could lead to valuable insights into the physical and chemical processes occurring during single-bubble cavitation. In fact, SBSL spectra from organic liquids[8,9] have been previously reported. Most recently, we have found concentrated sulfuric acid (H_2SO_4) to be an extremely interesting and effective liquid for the study of SBSL.[7] It was observed that SBSL from 85 wt% H_2SO_4 was much brighter than SBSL from pure water under similar conditions. In fact, the SBSL from the concentrated acid solution was found to be over three orders of magnitude brighter than that of pure water. Also, H_2SO_4 SBSL spectra contain valuable information in terms of the emitters present with emission being observed from atoms, molecules, and molecular ions. Here, we report on how SBSL spectra of concentrated H_2SO_4 change with different noble gases dissolved into solution and also report on several atomic and molecular emitters observed in the spectra.
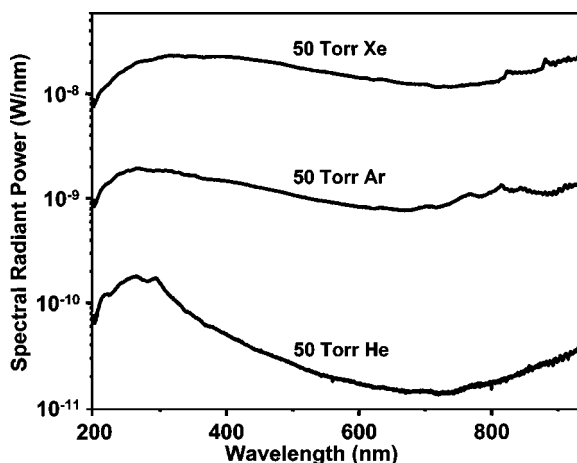
Fig. 1. SBSL spectra of 50 Torr of He, Ar, and Xe in 85% H_2SO_4. All spectra were obtained at the maximum acoustic intensity possible before the bubble was violently forced from the center of the resonator. The Xe spectrum was obtained at 5.65 bar, the Ar spectrum at 6.36 bar, and the He spectrum at 8.20 bar measured acoustic intensity. Spectra have been corrected for the absorptivity of one cell wall, 3 cm of solution, and the optical response of the spectral acquisition system against NIST traceable standard lamps.

2. Experimental

The SBSL apparatus, spectral acquisition system, and technique for measuring acoustic intensity have been previously described.[9] The spectra in Figs. 1 and 4 were acquired with a 300 g/mm grating blazed at 250 nm. The spectra in Figs. 2 and 3 were acquired with a 300 g/mm grating blazed at 500 nm. All spectra were acquired with a 100 μm slit width. Note that because these are moving single bubbles, the acoustic intensity measured with a hydrophone is an upper bound; some of the applied acoustic power goes into translational motion of the bubble. The actual acoustic intensity going into the radial motion of the bubble is therefore lower than the
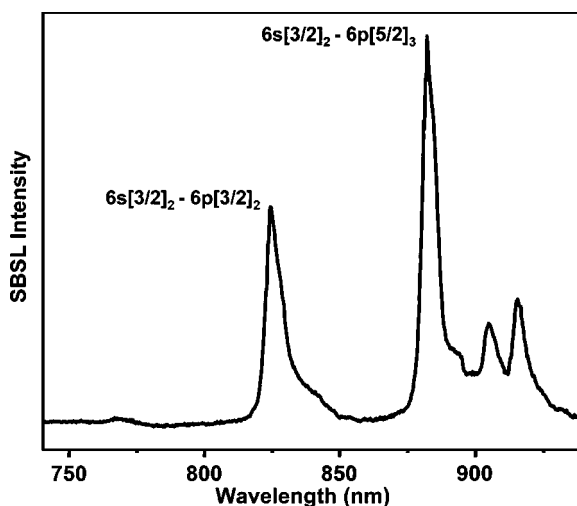

Fig. 2. Atomic Xe emission in the SBSL spectrum of 85% H_2SO_4 regassed with 50 Torr Xe. The two most prominent Xe lines are labeled with their corresponding transitions. The spectrum was obtained at 1.78 bar acoustic intensity.
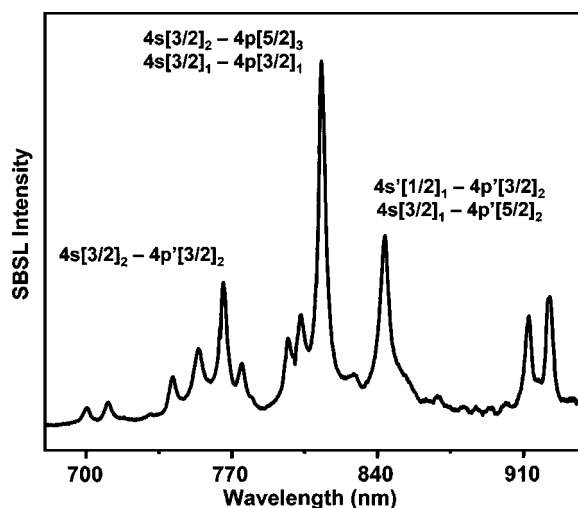
Fig. 3. Atomic Ar emission in the SBSL spectrum of 85% H_2SO_4 regassed with 50 Torr Ar. Some of the most prominent Ar lines are labeled with their corresponding transitions. The lines at 810 and 840 nm consist of two relatively strong unresolved lines and are thus labeled with each transition. The spectrum was obtained at 3.00 bar acoustic intensity.

measured value.[8] Solutions were prepared by diluting 95–98 wt% H_2SO_4 [Mallinckrodt, AR Select® (ACS)] with purified water (18 MΩ·cm) to 85 wt% and were degassed under vacuum (<0.1 Torr) with vigorous stirring at 30 °C for 24 h. Solutions were regassed in a closed system with either 50 Torr He (Matheson, 99.995%), 50 Torr Ar (Matheson, 99.999%), or 50 Torr Xe (Matheson, 99.995%) with vigorous stirring at 25 °C for 1 h. Special attention must be paid to thorough degassing for such viscous liquids; shorter degassing times (e.g., a few hours) are *not* sufficient. Controls run at longer degassing and regassing times did not result in observable differences in the SBSL spectra. After regassing, the solution was transferred to the SBSL resonator which has a 7 mm diameter opening to allow the solution to remain under ambient pressure. During the course of the experiment, SBSL spectra did not change.

3. Results and discussion

SBSL spectra from 85% H_2SO_4 regassed with 50 Torr of He, Ar, and Xe are shown in Fig. 1. As can be seen, the overall SBSL intensities vary greatly with noble gas. The Xe SBSL spectrum is roughly an order of magnitude brighter than the Ar SBSL spectrum and is roughly two orders of magnitude brighter than the He SBSL spectrum. Broadened atomic Xe and Ar emission can be seen in the near-IR region of the SBSL spectra of Xe and Ar, respectively. Note that we are able to drive the bubble with much higher acoustic intensities than is the case for single bubble cavitation in water. We believe that the higher viscosity of H_2SO_4 solutions suppresses bubble shape instabilities, allowing for higher applied acoustic intensities. Consistent with this, we do not observe "shattering" or rapid disappearance of a bubble in 85% H_2SO_4.

    When the acoustic intensity is decreased, atomic Xe and Ar emission become more prominent (Figs. 2 and 3). The Xe lines arise from transitions between the $6p$ (10 eV) and $6s$ (8 eV) energy levels while the Ar lines arise from transitions between the $4p$ (13 eV) and $4s$ (11 eV) energy levels. Note that atomic Xe emission has been previously reported from bubble compression in phosphoric acid (H_3PO_4) by a tube-arrest ("water hammer") method.[10]

    The Xe and Ar spectra also show very broad peaks in the near-UV region of the spectra with the peak in the Ar spectrum blueshifted relative to the peak in the Xe spectrum. This has also been reported for SBSL from pure water.[3] Interestingly, the He spectrum also shows a broad peak centered at 280 nm. This is very different from He SBSL spectra in pure water in which the
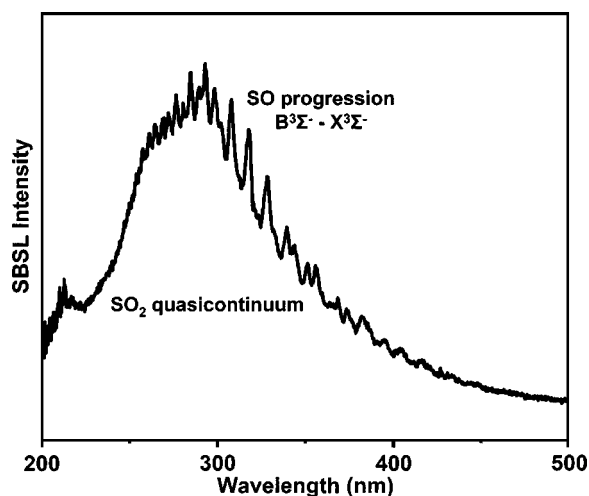
Fig. 4. Molecular SO emission and SO_2 quasicontinuum emission observed in the SBSL spectra of 85% H_2SO_4 regassed with 50 Torr He. The peak at ~220 nm likely arises from the $A\,^2\Pi_u - X\,^2\Pi_g$ second-negative-system of O_2^+. The spectrum was obtained at 3.50 bar acoustic intensity.

continuum shows no peak but instead continues to increase in intensity below 200 nm.[11] The broadened peak at 280 nm consists mainly of the well-known sulfur dioxide (SO_2) quasicontinuum emission, though there are likely contributions from other molecular species such as sulfur monoxide (SO). At lower acoustic intensities, well-resolved extensive SO vibronic progressions arising from the $B^3\Sigma^- - X^3\Sigma^-$ system as well as the quasicontinuum SO_2 emission centered at 300 nm are very apparent (Fig. 4). Note that these emissions are very similar to the emissions observed during electron impact on SO_2.[12] Weak O_2^+ emission is also observed in the spectrum at ~230 nm.[13]

Since the thermal conductivity of He is much higher than that of Ar and Xe, peak temperatures are expected to be lower; small molecules would therefore dissociate to a lesser degree and would contribute more strongly to the SBSL spectrum. Also, the ionization energy of He is much higher than that of Ar and Xe. If a significant portion of the SBSL emission arises from plasma emission, which recent observations indicate is the case,[7] it would be expected that the He SBSL spectrum would have a lower percentage of its overall emission contributed to by emission resulting from He atom ionization. This, too, would result in more molecular structure in the SBSL spectra, as is observed.

As the maximum acoustic intensity was approached for the Xe and Ar bubbles, the light emission no longer appeared continuous to the naked eye. That is, the SBSL was visibly intermittent, indicating the bubble was no longer emitting light during each and every collapse. SBSL from bubbles driven at lower acoustic intensities did not display observable "blinking." Also, SBSL from 85% H_2SO_4 containing smaller amounts of noble gas (e.g., under 20 Torr) showed no such behavior. Only at relatively high noble gas concentrations driven at high acoustic intensities was the "blinking" phenomenon observed.

The translational movement of the bubble varies with the applied acoustic intensity. At low acoustic intensities, the bubble moves slowly about the center of the resonator, moving in circles or ellipses ≤5 mm diameter, similar to a moving single bubble in aprotic organic liquids.[9] As the acoustic intensity is increased, the translational motion of the bubble becomes more rapid, though the side-to-side diameter does not noticeably increase. If the solution is too gassy, microbubbles are shed from the main bubble and can be seen moving slowly away from the resonator center and then rapidly moving back and coalescing; at lower dissolved gas

content, bubble-shedding is not observed, even at very high acoustic intensities. Detailed $R(t)$ studies obtained via light scattering (which will be published elsewhere) in collaboration with Professor Putterman show that there is in fact only a single bubble present within the parameter space reported here.

At acoustic intensities slightly above those at which the brightest SBSL was observed, the bubble was violently forced from the center of the resonator and a loud "ping" could be heard as the bubble collided with the resonator wall; note that immediately prior to the bubble being forced from the center of the resonator no loud "pings" were heard. If the acoustic intensity was increased further, many very loud "pings" could be heard as bubbles were nucleated at defect sites along the resonator wall as well as within the bulk liquid. Bubbles nucleated within the bulk liquid could be seen streaking to the resonator wall upon formation. At very high acoustic intensities ($\sim$10 bar at the center of the resonator), many very brightly luminescing bubbles could be seen adorning the resonator wall.

4. Conclusions

Concentrated H_2SO_4 solutions are proving to be extremely valuable for the study of fundamental SBSL mechanisms including the physical conditions and chemical processes occurring during bubble implosion. Dramatic increases in overall brightness are seen, and intense and extensive molecular, atomic, and ionic emission are also observed. The overall intensities and shapes of SBSL spectra from concentrated H_2SO_4 have been shown to be strongly dependent upon the type of gas dissolved in solution. In addition, single bubbles driven at lower acoustic intensities reveal a wealth of information in their spectra.

Acknowledgments

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