Plasma Line Emission during Single-Bubble Cavitation

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Emission lines from transitions between high-energy states of noble-gas atoms (Ne, Ar, Kr, and Xe) and ions (Ar^+, Kr^+, and Xe^+) formed and excited during single-bubble cavitation in sulfuric acid are reported. The excited states responsible for these emission lines range 8.3 eV (for Xe) to 37.1 eV (for Ar^+) above the respective ground states. Observation of emission lines allows for identification of intracavity species responsible for light emission; the populated energy levels indicate the plasma generated during cavitation is comprised of highly energetic particles.

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Single-bubble sonoluminescence (SBSL) arises from the rapid heating of gas and vapor within a violently imploding bubble in a liquid. This phenomenon has attracted the attention of researchers and nonresearchers alike, and has been vigorously studied since the first well-known reports [1,2]. Current theories for the mechanism of light emission include blackbody radiation [3] from a relatively cold, optically transparent shell surrounding a hotter, optically opaque core [4] and thermal bremsstrahlung radiation from a partially ionized plasma [4–6]. Shell temperatures of 6000–20 000 K with much hotter core temperatures ($>10^6$ K) have been predicted by calculation [7,8] and by fits to featureless SBSL spectra in water [9,10]. The conditions generated during acoustic cavitation are even hypothesized to be extreme enough to facilitate deuterium-deuterium fusion, with recent controversial reports of such observations [11,12].

In spectra from water, the most thoroughly studied fluid for SBSL, there are typically no observable emission lines. While it is primarily the observation of such featureless SBSL spectra that has led to predictions of extreme conditions [4,13], there is limited definitive information to be gained from such emission. A better understanding of the origin of the continuum and the conditions generated during SBSL would be gained if the identities of the particular species involved in the radiative processes were known. Prior speculative predictions of extreme intracavity conditions are indirectly based on experimental evidence and are dependent on the presupposed mechanism of emission: the featureless spectra may originate from bremsstrahlung emission, from blackbody radiation, or even from highly line broadened emission of excited states of water and its sonolysis products (as discernable in multibubble sonoluminescence [14,15]). The wide ranging theories for SBSL illustrate the inherent ambiguity in interpreting the continuous emission spectra.

In continuing with our studies of single-bubble cavitation in low-volatility liquids [16], we recently discovered extremely intense SBSL from concentrated sulfuric acid (H_2SO_4) solutions [17]. In addition to being extraordinarily bright, the emission spectra contain numerous features, including extensive molecular (SO, SO_2), ionic (${O_2}^+$), and atomic (Ar, Xe) bands and lines [17,18]. Observation of these emitters have allowed for the first definitive spectral temperature measurements for emitting species during SBSL and provided the first conclusive experimental evidence of plasma generation during single-bubble cavitation. Indeed, detailed studies in concentrated inorganic acid solutions, including our SBSL work in H_2SO_4 and Walton and co-workers' report on liquid-hammer induced cavitation in phosphoric acid [19], are resulting in a wealth of information leading to a much better understanding of the events that occur in the final stages of bubble collapse.

We now find that SBSL spectra from a single weakly driven (i.e., low applied acoustic pressure, P_a), dimly luminescing bubble in concentrated H_2SO_4 consist not only of strong noble-gas atom emission (including Ne and Kr emission, reported here for the first time), molecular emission, and molecular ion emission, but also of *noble-gas ion emission* (Ar^+, Kr^+, and Xe^+). The states responsible for the observed atomic and ionic noble-gas emissions are very high in energy [20–22]; by comparison, the energy levels of emitters in previously reported sonoluminescence spectra are only a few eV [16,23]. All SBSL spectra were acquired from 85 wt% H_2SO_4 containing 50 torr of Ne, Ar, Kr, or Xe. The SBSL resonator, spectral acquisition system, and method for preparing the solution have been described elsewhere [16,18]. All spectra have been corrected for absorption by the solution and resonator wall as well as the optical response of the system against NIST traceable standard lamps. Each spectrum was acquired from a single-bubble that was rapidly moving within a small volume (~ 60 mm^3) at the center of the resonator. This type of bubble motion is similar to that observed in polar aprotic organic liquids [16]. A more detailed description of the bubble dynamics is given elsewhere [18].

Spectra acquired from solutions containing Ar, Kr, or Xe all show strong noble-gas atom emission in the near-IR and noble-gas ion emission in the visible wavelengths (Figs. 1–

3). The states involved in the observed electronic transitions, especially of the noble-gas ions, are very high in energy relative to the ground states of the neutral atoms. This is especially true for the $4p$ states involved in the Ar^+ line emission [Fig. 1(b)] which lie over 37 eV above the Ar $3p^6$ ground state [20]. The $5p$ states of Kr^+ and the $6p$ states of Xe^+ are also high in energy being 33 and 27 eV above the Kr $4p^6$ and Xe $5p^6$ ground states, respectively, [Figs. 2(b) and 3(b)] [21,22]. From previous work we found that the temperature during single-bubble cavitation in concentrated H_2SO_4 is 15 000 K [16]. A simple Boltzmann calculation shows that gas kinetic temperatures of this magnitude are not sufficient to significantly populate the states of the noble-gas ions involved in the observed line emissions. The excitation mechanism is likely impact by particles (e.g., electrons) originating from a hot plasma core. Note that local thermodynamic equilibrium (LTE) is established in Ar plasmas with temperatures $\geq 11\,000$ K and pressures ≥ 1 atm [24], and the establishment of LTE during sonoluminescence has been previously verified [17,23,25].

SBSL spectra acquired from solutions containing 50 torr Ne show extensive molecular SO emission, strong SO_2 quasicontinuum emission, and strong Ne atom emission (Fig. 4). While SBSL from H_2SO_4 with Xe, Kr, and Ar appears blue/white to the eye, SBSL from H_2SO_4 with Ne looks *pink* due to the strong Ne atom emission in the red region of the spectrum. Gas kinetic temperatures necessary

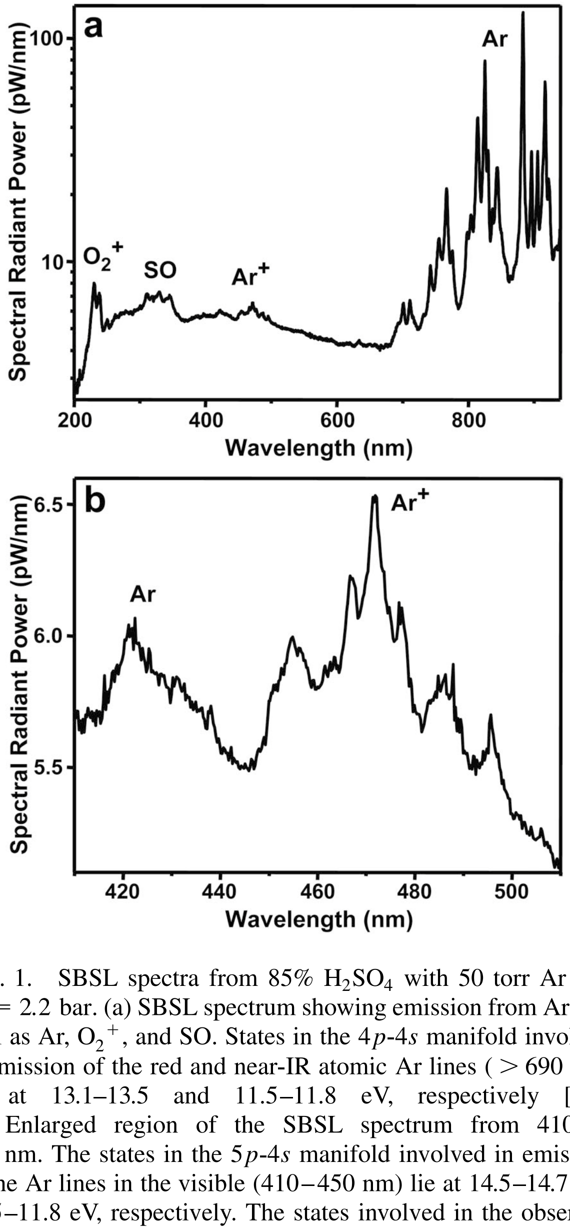

FIG. 1. SBSL spectra from 85% H_2SO_4 with 50 torr Ar and $P_a = 2.2$ bar. (a) SBSL spectrum showing emission from Ar^+ as well as Ar, O_2^+, and SO. States in the $4p$-$4s$ manifold involved in emission of the red and near-IR atomic Ar lines ($>$ 690 nm) lie at 13.1–13.5 and 11.5–11.8 eV, respectively [20]. (b) Enlarged region of the SBSL spectrum from 410 to 510 nm. The states in the $5p$-$4s$ manifold involved in emission of the Ar lines in the visible (410–450 nm) lie at 14.5–14.7 and 11.5–11.8 eV, respectively. The states involved in the observed Ar^+ emission (450–500 nm) are in the $4p$-$4s$ manifold; the Ar^+ $4p$ and $4s$ states lie at 35.0–37.1 and 32.4–34.2 eV above the Ar ground state ($3p^6$), respectively [20].

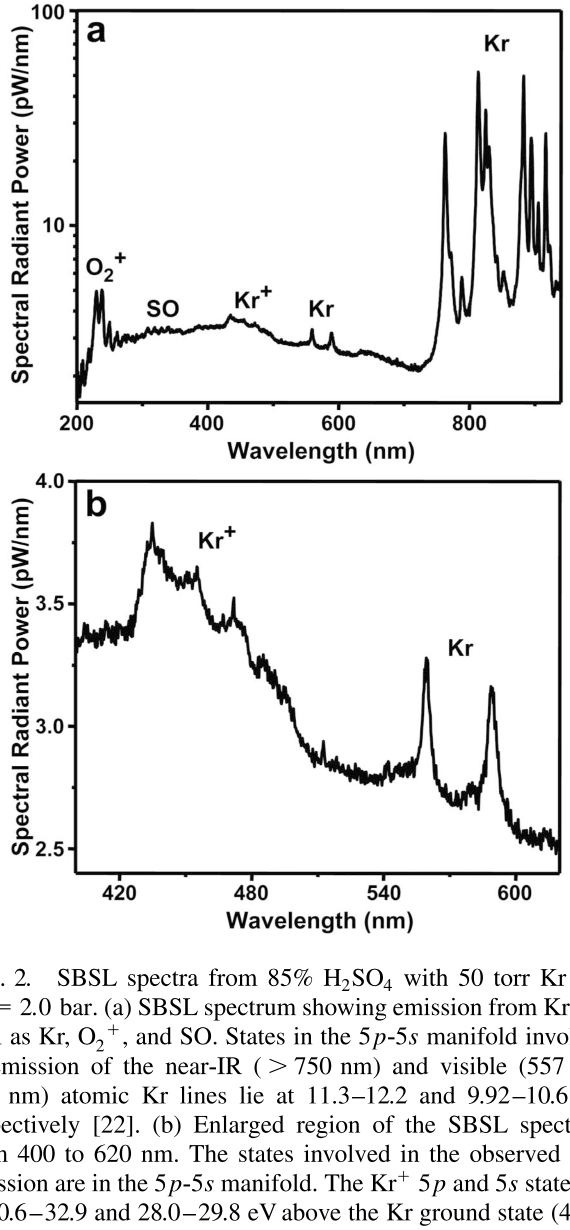

FIG. 2. SBSL spectra from 85% H_2SO_4 with 50 torr Kr and $P_a = 2.0$ bar. (a) SBSL spectrum showing emission from Kr^+ as well as Kr, O_2^+, and SO. States in the $5p$-$5s$ manifold involved in emission of the near-IR ($>$ 750 nm) and visible (557 and 587 nm) atomic Kr lines lie at 11.3–12.2 and 9.92–10.6 eV, respectively [22]. (b) Enlarged region of the SBSL spectrum from 400 to 620 nm. The states involved in the observed Kr^+ emission are in the $5p$-$5s$ manifold. The Kr^+ $5p$ and $5s$ states lie at 30.6–32.9 and 28.0–29.8 eV above the Kr ground state ($4p^6$), respectively [22].

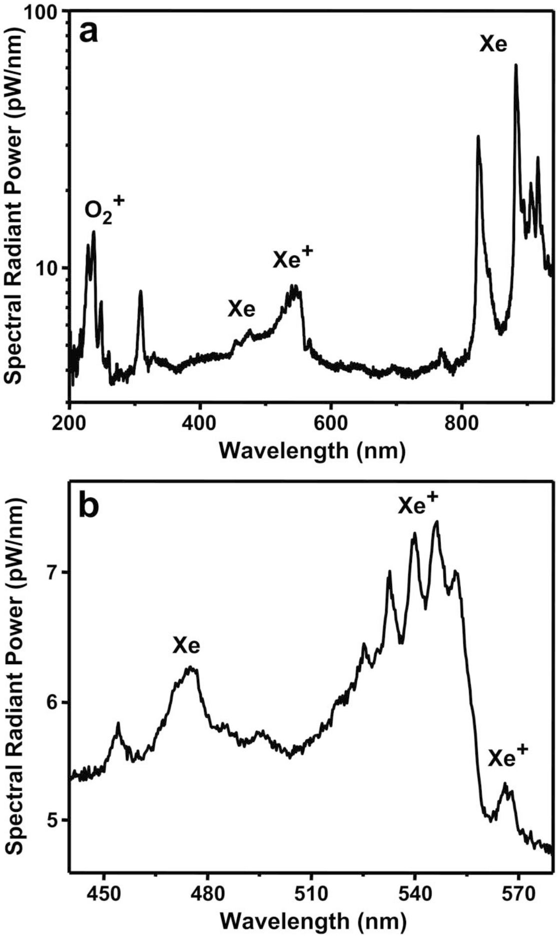

FIG. 3. SBSL spectra from 85% H_2SO_4 with 50 torr Xe and $P_a = 1.7$ bar. (a) SBSL spectrum showing emission from Xe^+ as well as Xe and $O_2{}^+$. States in the $6p$-$6s$ manifold involved in emission of the near-IR Xe atom lines (> 780 nm) lie at 9.58–9.93 and 8.31–8.44 eV, respectively [21]. (b) Enlarged region of the SBSL spectrum from 440 to 580 nm. The states in the $7p$-$6s$ manifold involved in emission of the Xe lines in the visible (450–500 nm) lie at 10.9–11.0 and 8.31–8.44 eV, respectively. The states involved in the observed Xe^+ emission are in the $6p$-$6s$ manifold. The Xe^+ $6p$ and $6s$ states lie at 26.0–27.2 and 23.7–24.9 above the Xe ground state ($5p^6$), respectively [21].

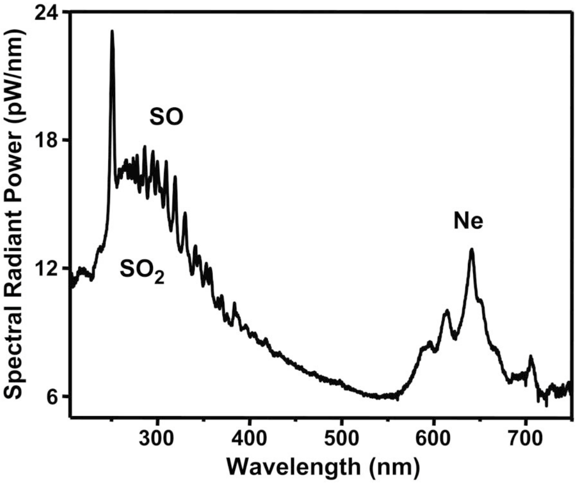

FIG. 4. SBSL spectrum from 85% H_2SO_4 with 50 torr Ne and $P_a = 5.7$ bar. States in the $3p$-$3s$ manifold involved in emission of the atomic Ne lines (550–750 nm) lie at 18.4–19.0 eV and 16.6–16.8 eV, respectively [20]. The SO_2 quasicontinuum emission centered at 300 nm results from transitions between three different excited states and the ground state. The SO emission bands (250–450 nm) are due to $B\,^3\Sigma^- \rightarrow X\,^3\Sigma^-$ transitions while the sharp feature at 250 nm is due to $A\,^3\Pi \rightarrow X\,^3\Sigma^-$ transitions [26].

to populate the $3p$ energy levels of atomic Ne (19 eV) are more than sufficient to extensively dissociate SO and SO_2 to their atomic components. The spectrum in Fig. 4, however, shows strong molecular SO, SO_2, and Ne atom emission. From previous work we know that temperatures calculated from SO emission in SBSL spectra are no more than 5000 K [17]. From the partial pressure of Ne equilibrated with the H_2SO_4 solution and the equilibrium bubble size, we estimate that there are $\sim 10^{10}$ Ne atoms present inside the bubble. For 10^{10} Ne atoms, not even one Ne atom would be thermally excited to the $3p$ states at 5000 K on the time frame of bubble collapse. Temperature calculations from Ne atom emission were not possible due to convolution of nearly 30 known lines having similar intensities in the $3p$-$3s$ manifold [20]. It is interesting to note that spectra produced by the impact of electrons, with energies ranging from 8 to 100 eV, on SO_2 gas are very similar to SBSL spectra of 85% H_2SO_4 containing Ne [26]. Based upon these observations, it appears that the excitation mechanism for molecular SO, SO_2, and especially atomic Ne could also be impact from energetic electrons formed in a plasma core. Given the temporal and possibly spatial temperature gradients generated during bubble collapse, it is also possible the SO and SO_2 excited states are populated thermally, but either earlier or later or at different locations (e.g., further out from the bubble center) than the excited state Ne atoms. Flash widths in the blue and red regions of the spectrum during SBSL in H_2SO_4 remain to be determined, but may shed further light on this issue.

The most intense line emission relative to continuum emission during SBSL in H_2SO_4 occurs from a weakly driven bubble. This appears to be independent of the solution studied; similar observations have been made during SBSL from water [27] and polar aprotic organic liquids [16]. With Ar, Kr, or Xe dissolved in H_2SO_4, as P_a is increased, the ion, molecular, and weaker neutral atom emission lines broaden and quickly become indistinguishable from the continuum emission. Strong neutral atomic emission lines in the near IR also noticeably broaden and become relatively less intense but are still observable even at high P_a [17,18]. Decrease in intensity of the lines relative to the continuum is likely due to a combination of increasing pressure broadening and increasing continuum emission (e.g., bremsstrahlung and recombination as more neutral atoms are ionized) [28].

Ne behaves slightly differently than the heavier noble gases dissolved in H_2SO_4: in order to observe Ne atom emission it is necessary to drive the bubble at a relatively high P_a. The high thermal conductivity of Ne ($49.8\ \mathrm{mW/m \cdot K}$) coupled with its high ionization energy (21.6 eV) likely causes the interior of the collapsing bubble to have lower temperatures and the contents to be less ionized. This means the bubble must be driven at higher P_a to deposit more energy into the bubble motion in order to observe strong Ne atom emission. If the H_2SO_4 SBSL continuum is due to emission resulting from a plasma, then spectra acquired at relatively low P_a will consist mainly of line emission while spectra acquired at higher P_a will consist mainly of continuum emission together with weaker and broadened line emission. The P_a at which this crossover occurs should depend upon the thermodynamic properties of the intracavity species. For gases with low ionization energies and low thermal conductivities (e.g., Xe) the crossover will occur at low P_a, while for gases with high ionization energies and high thermal conductivities (e.g., Ne) it will occur at higher P_a, as is observed [17,18].

Observation of emission lines from atoms and monatomic ions in high-energy configurations has provided conclusive experimental evidence for the generation of an energetic plasma during single-bubble cavitation in H_2SO_4 containing noble gases. Gas kinetic temperatures previously determined from neutral emitting species generated during SBSL in H_2SO_4 [17] are too low to thermally populate the observed excited states. Unlike molecular excitation and dissociation (for which there are numerous closely spaced vibronic states), the lack of intervening states makes stepwise excitation to the observed atom and ion excited states untenable. This provides further evidence for the formation and excitation of atoms and ions by electron impact from a hot plasma core. The similarities between SBSL spectra reported here and spectra acquired from noble-gas plasmas and electron impact on SO_2 [26] are remarkable. The numerous discrete emission features observed in the spectra should allow for more detailed SBSL diagnostics leading to a better understanding of the conditions generated during cavitation, including the density of the emitting region and spectroscopic temperature determinations of the emitting ions.

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