Line Emission in Single-Bubble Sonoluminescence

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We report that single-bubble sonoluminescence (SBSL) at low light intensities produces emission bands similar to multibubble sonoluminescence (MBSL) for pure noble gas bubbles. A smooth crossover between SBSL and MBSL behavior can be induced by varying the acoustic pressure amplitude and thereby the intensity of the light emitted. The relative intensity of the band emission depends both on the molecular weight of the noble gas and the water temperature. Our results provide a connection between the mechanisms SBSL and MBSL and show that molecular emission plays a role in SBSL.

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Sonoluminescence (SL)—the conversion of sound energy into light—occurs from the violent collapse of gas bubbles within ultrasonically driven liquids [1–3]. Though SL was first observed in acoustic cavitation fields in aqueous systems more than 60 years ago [4], the light emission mechanism is still a matter of debate; it is generally thought to involve the creation of extremely high temperatures and pressures at the center of the bubble during the collapse [5–9]. The light emitted from a cavitation bubble field, termed multibubble sonoluminescence (MBSL), often contains emission bands from neutral hydroxyl radicals as well as other molecules or atoms present in the liquid [10–13]. Under certain conditions, a single bubble can be trapped in an acoustic cavity and made to produce light [14]. This single-bubble sonoluminescence (SBSL) has been shown to have a spectrum with no discernible peaks or vibrational emissions [11,15–17]. Based on measurements of the relative intensities of emission lines from different bands in metal complexes, bubble interior temperatures of 2000–5000 K have been obtained for MBSL [18]. In contrast, interpretation of the SBSL spectrum in terms of radiation from a thermal blackbody or bremsstrahlung yields a bubble interior temperature of ~10 000–50 000 K [8,16,19].

Within the framework of the hydrodynamical theory of SL, the light emission in MBSL and SBSL is believed to be due to compressional heating of the gas inside the bubble, possibly with the aid of a converging shock wave [5,7,8]. The high temperatures produced in this way result in a plasma which radiates primarily via bremsstrahlung emission. In the case of MBSL, differences in the bubble dynamics, principally asymmetric collapse accompanied by jet formation and a lack of shock wave production, have been proposed to explain the lower bubble interior temperatures as well as the dominance of the liquid characteristics over those of the gas on the shape of the spectrum [6,20]. However, confirmation of such models through comparison with experiment is complicated by the fact that the optical absorption of water limits the measurable spectral range to between 200–800 nm. In addition, the experimental parameters needed to generate optimum SBSL differ markedly from that of MBSL. Consequently, the connection between the two types of SL has never been clarified and the two phenomena are often treated independent of each other.

In order to better understand the relationship between MBSL and SBSL, we have performed a systematic study of the spectra of SBSL as the overall intensity of the emitted light was varied. Because of the low intensities involved, previous studies of SBSL spectra have focused on the relatively bright emission of bubbles driven at pressure amplitudes close to their maximum stable limit [11,15–17]. To measure the spectra of very dim SL bubbles, a spectrometer capable of integrating over long time periods with extremely low background noise is required. For the present work, an Acton Research SP-300i imaging spectrometer with a Princeton Instruments liquid nitrogen cooled charge-coupled-device (CCD) detector was used. Special software was developed to periodically remove the charge accumulation in the CCD due to cosmic rays during long exposures. Additionally, the acoustic drive frequency was phase locked to the cavity resonance (~31 kHz) and the drive amplitude was automatically adjusted by a computer to provide stable light output at the desired brightness. This feedback loop was of low gain and long integration time; its digital nature eliminated the possibility that feedback transients might introduce cavitation which could affect the results. Continuous monitoring of the sound amplitude, drive transducer excitation, drive frequency, water temperature, and average SL brightness yielded no evidence of cavitation. The acoustic cavity and all of its components formed a closed, leak-tight system so as to ensure that the dissolved gas concentration did not vary appreciably with time.

The SL was produced using mixtures of deionized water and individual noble gases (He, Ar, Xe). The gas/water mixtures were all prepared with the same pressure head of ~150 torr at 25 °C. Pure noble gas SBSL bubbles at these high gas concentrations are "unstable"; i.e., their ambient radius grows with time until surface instabilities occasionally cause microbubbles to be ejected [2]. Though this behavior can be avoided by using much lower concentrations (~3 torr head), it is then impossible to achieve dim SBSL. This is because, for noble gases at low concentrations, the sound intensity threshold at which a bubble becomes stable against dissolution is higher than the threshold for producing light, so the bubbles dissolve while still emitting relatively bright light.

The SL light was coupled to the spectrometer using a fused silica optical fiber that was placed in the water 2–3 mm from the bubble. After months of continuous SL exposure, no cavitation-induced damage was detected on the fiber. Although the fiber and spectrometer were calibrated together using deuterium and quartz tungsten-halogen irradiance standards, a considerable uncertainty in the UV remained due to a dependence of the fiber absorptivity on the entrance angle. Also, no attempt was made to compensate for the absorption of the water. Because of these systematic effects, the spectral intensities in this paper should not be considered absolute.

At very low light levels, we found molecular band emission in the SBSL spectrum that had previously only been seen in MBSL spectra. Figure 1 shows the SBSL spectra of ~150 torr argon bubbles for different integrated intensities, with exposures ranging from 100 minutes for the brightest bubble to 5 days for the dimmest. For the dimmest bubbles studied in our experiment, the intensity of the light was reduced by ~3 orders of magnitude compared to the bright bubbles. As the average intensity was reduced, peaks in the spectrum became more distinct at 310 and 337 nm. The broad peak at 310 nm has been identified as emission from the $0 \rightarrow 0\ {}^2\Sigma^+ \rightarrow {}^2\Pi$ vibrational/rotational bands of neutral OH^* radicals [10,11,21]. The spectral peak at 337 nm is significantly weaker but was found to be reproducible in SL emissions from bubbles doped with other noble gases; its source is not clear, though it might be the $0 \rightarrow 1$ OH^* band [3]. While the data shown in Fig. 1 indicate that the relative magnitude of the OH^* emission decreased with increased integrated intensity, subtraction of the continuum shows that its absolute intensity actually increased over the range for which it was measurable. This suggests that in a bright SL bubble, the OH^* and other lines are largely "overwhelmed" by the continuum emission which grows faster than the OH^* emission.

Figure 2 shows spectral peaks from extremely dim SBSL bubbles doped with Xe, Ar, and He at 25 °C. All three gases clearly show spectral peaks at 310 and 337 nm. Apart from small differences in the spectral weight of the continuum emission, the main difference between the various gases is that the intensity of the 310 nm peak appears to increase with the molecular weight of the gas. The inset of Fig. 2 shows an intriguing dependence of the 310 nm peak intensity on the square root of the reduced mass of the noble gas and OH^* radical, for the same integrated light intensity. It is interesting that the 337 nm line does not appear to share this behavior. Helium seems to have a relatively large 337 nm peak compared to the other gases, as well as wings surrounding the peak that make it appear much broader.

Figure 3 illustrates the effect of water temperature on SL emission lines. At 5 °C the spectral peak at 310 nm is enhanced by ~2 times compared to the data at 25 °C. The 337 nm peak is not even visible in the 25 °C data but is quite prominent at 5 °C. In addition to the spectral peaks at

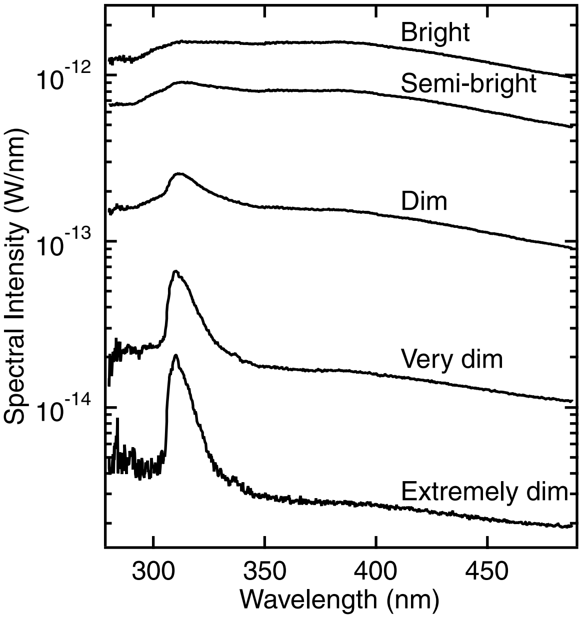

FIG. 1. Average intensity dependence of argon single-bubble sonoluminescence spectral peaks. Spectra are shown for five different levels of overall brightness. The sonoluminescence was produced using mixtures of deionized water and argon gas with a partial pressure of ~150 torr at 25 °C.

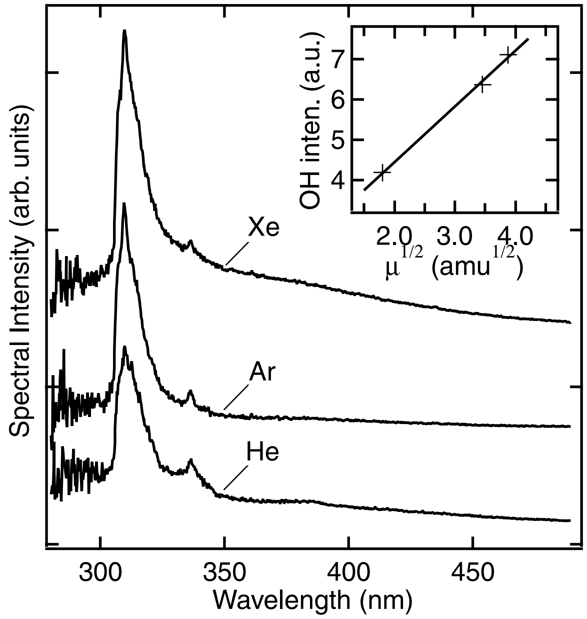

FIG. 2. Composition dependence of single-bubble sonoluminescence spectral peaks. Spectra for Xe, Ar, and He bubbles have been offset for clarity. The bubbles were all similar in brightness to the dimmest bubble in Fig. 1. Inset: Peak intensities of the OH^* emission at 310 nm vs $\sqrt{\mu}$, the square root of the reduced mass of the noble gas and OH^* radical, for the same integrated light intensity.

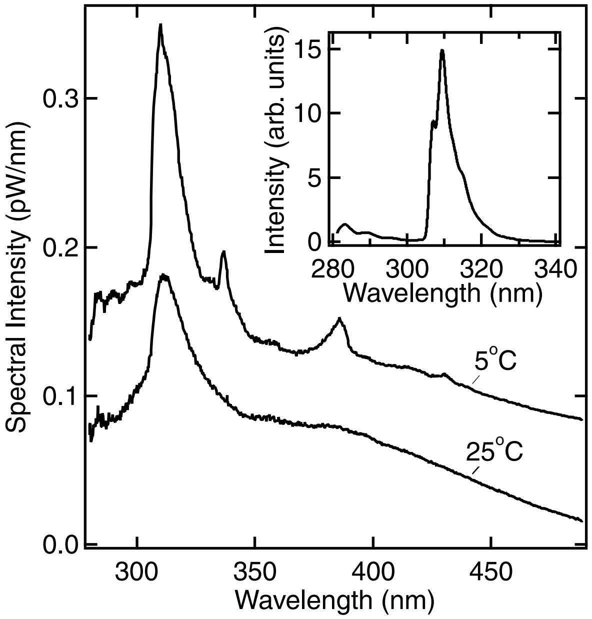

FIG. 3. Temperature dependence of argon single-bubble sonoluminescence spectral peaks. Spectra shown for 5 and 25 °C have been offset for clarity. The bubbles were similar in brightness to the median one of Fig. 1. Inset: The ultraviolet bands of OH* as taken from Ref. [21]. The individual lines were convoluted with the spectrometer's response function to give a smooth curve.

310 and 337 nm, features in the spectra at 386 and 431 nm become visible at the lower water temperature. The source of these peaks is currently unknown. The inset of Fig. 3 shows the ultraviolet bands of OH* for 3000 K [21] convoluted with the measured response function of the spectrometer. The similarity to the experimentally observed peaks leaves little doubt that the observed peak at 310 nm is due to band emission from neutral OH*.

The main discovery of our experiment is the presence of molecular emission lines in SBSL at low light levels. This complements work by others showing that MBSL molecular emission is suppressed when very high acoustic drive amplitudes are used [3,22,23]. These results taken together with the posited difference in bubble interior temperatures between bright SBSL and MBSL suggest that the spectrum of SBSL can evolve into that of MBSL and vice versa by changing the bubble interior temperature. At higher temperatures, the OH* emission might be suppressed or simply overwhelmed by the continuum emission.

This possible suppression of OH* emission in bright SBSL bubbles may be consistent with the recent proposal of quenching of molecular emissions in SBSL [19]. Quenching of line emission occurs when the population of excited states is reduced due to nonradiative transitions induced by the high rate of collisions at high pressures and temperatures sustained during SBSL. Since the quenching rate is expected to follow Arrhenius's law, the intensity of the quenched species should be roughly proportional to the square root of the reduced mass of the quenching and emitting species, $\sqrt{\mu}$. This may explain the observed compositional dependence of the 310 nm band as seen in Fig. 2.

One puzzling feature of Fig. 1 is the lack of shift in the spectral weight of the continuum emission for increasing overall brightness. If the continuum were due entirely to "hot spot" emission such as bremsstrahlung, one would expect the spectral weight to shift towards the UV due to higher bubble interior temperatures. The fact that this is not the case lends support to the notion that SBSL at low acoustic drives may involve light production mechanisms other than bremsstrahlung. Based on the data collected over the years, there is strong evidence that emissions from the recombination of molecular radicals and the relaxation of excited molecules play a major role in MBSL [3]. The recombination of radicals such as H and OH has been shown to yield a continuous spectrum which resembles the MBSL continuum [3,10,23]. Furthermore, the introduction of certain chemical scavengers into the water dramatically alters the shape of the MBSL spectrum [3,24]. These scavengers decrease the concentration of selected radicals and so alter the radiative contributions from different species. It is possible that similar types of molecular emissions may contribute significantly to the continuous spectrum of SBSL. It remains to be seen whether the SBSL spectrum exhibits sensitivity to chemical scavengers.

As shown in Fig. 3, the molecular band features are significantly enhanced relative to the continuum at lower water temperatures. An increase in continuum intensity with reduced temperature has long been observed in both MBSL [25] and SBSL [26]. In the case of SBSL, it has been proposed that lower water temperatures enhance bubble stability, allowing higher bubble interior temperatures, and hence, more light [27]. However, the bubble interior temperatures for both water temperatures in Fig. 3 should be roughly the same since the overall light intensity was held the same for both. Consequently, the relevance of this model in explaining the enhancement in OH* emission at lower temperatures remains unclear.

One possible explanation for the water temperature dependence on the band emission is that the increase in gas solubility of the water at lower temperatures decreases the density of the quenching species in the bubble. The observed dependence of the OH* emission intensity on the reduced mass of OH and the dissolved noble gas suggests that the latter may be playing the role of a quenching agent. However, the vapor pressure of water also decreases with lower temperatures. Thus a decrease in temperature should also cause a decrease in the OH density inside the bubble unless there exists a nondiffusive mechanism for introducing water vapor into the bubble. Jet formation is one such possibility [28]. Also, the mass shedding process that is characteristic of unstable bubbles might also increase the amount of water vapor inside the bubble.

An unanswered question is whether the dim SBSL bubbles studied here might appear MBSL like due to their unstable nature rather than their dimness. In particular, what effects might the mass shedding transients of unstable bubbles have on SL emission? One possibility is that SBSL emission occurs most of the time and MBSL-like molecular emission occurs only during the mass ejection. Since the average time between these transients is several orders of magnitude longer than the bubble's oscillatory period, the spectral intensity of the molecular emission relative to the continuum would have to be correspondingly larger than what was observed in order to produce the measured spectra. Considering that published MBSL spectra show relative OH^* to continuum intensities on a par with our results, this scenario is unlikely. Another possibility is that our bubbles produce molecular emission during the transient but are below the SL threshold for most of the time and only intermittently produce SBSL flashes. Because of our low photon yields, this possibility cannot be completely ruled out. However, we did find that the cycle to cycle photon distributions from even our dimmest bubbles closely matched Poisson statistics and are consistent with a flash for every acoustic cycle. From comparisons with Monte Carlo simulations we established a conservative lower bound that flashes occurred more than 10% of the time. Because of the large discrepancy between this result and the bubble transient time scale, we feel that this intermittent flash possibility is also unlikely.

In conclusion, we have uncovered molecular emission bands and other unidentified features in the SBSL spectrum. The appearance of neutral OH^* emission at reduced light intensities suggests that the internal conditions of SBSL bubbles become like MBSL at low levels of acoustic drive. These results along with the apparent lack of shift in the spectral weight of the SBSL continuum with acoustic drive level suggest that nonthermal mechanisms may contribute substantially to the continuum of SBSL. Based on the MBSL data collected over the years, recombination of molecular radicals is a possible candidate for this mechanism [3,10,23]. In the brightest bubbles, hot spot emissions may dominate the molecular contribution to the continuum while the band emissions are overwhelmed, if not completely quenched, making them undetectable.

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