THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 9315−9318
Published on Web 06/30/2006

Plasma Quenching by Air during Single-Bubble Sonoluminescence

David J. Flannigan and Kenneth S. Suslick*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received: May 17, 2006; In Final Form: June 9, 2006

We report the observation of sudden and dramatic changes in single-bubble sonoluminescence (SBSL) intensity (i.e., radiant power, Φ_{SL}) and spectral profiles at a critical acoustic pressure (P_c) for solutions of sulfuric acid (H_2SO_4) containing mixtures of air and noble gas. Nitric oxide (NO), nitrogen (N_2), and atomic oxygen emission lines are visible just below P_c. At P_c, very bright (factor of 7000 increase in Φ_{SL}) and featureless SBSL is observed when Ar is present. In addition, Ar lines are observed from a dimmed bubble that has been driven above P_c. These observations suggest that bright SBSL from H_2SO_4 is due to a plasma, and that molecular components of air suppress the onset of bright light emission through quenching mechanisms and endothermic processes. Determination of temperatures from simulations of the emission lines shows that air limits the heating during single-bubble cavitation. When He is present, Φ_{SL} increases by only a factor of 4 at P_c, and the SBSL spectrum is not featureless as for Ar, but instead arises from sulfur oxide (SO) and sulfur dioxide (SO_2) bands. These differences are attributed to the high thermal conductivity and ionization potential of He compared to Ar.

Introduction

Under certain conditions,[1] a single bubble acoustically levitated in a liquid can undergo nonlinear oscillations in sync with the applied sound field and emit subnanosecond flashes of light at the point of maximum implosion: single-bubble sonoluminescence, SBSL.[2,3] The vast majority of SBSL studies have been conducted in partially degassed water, and some of this previous work has shown how chemistry affects the light emission.[4,5] Results suggest that polyatomic molecules that are able to enter the bubble cause a reduction in the overall sonoluminescence (SL) intensity.[6−8] This is thought to be due to endothermic processes and the build-up of molecular species inside the bubble.[9,10] As one increases the acoustic pressure (P_a) to some critical threshold (P_c), the maximum bubble radius initially decreases and then increases with the increasing P_a accompanied by the onset of light emission.[11] In addition to this, the SBSL displays hysteretic behavior; SBSL is not quenched until significant reduction below the P_a at which light was first observed.[12,13] These observations have been attributed to quasiadiabatic heating during the rapid bubble collapse which leads to dissociation of N_2, O_2, and H_2O and formation of soluble and reactive species. For an air bubble in water, this is thought to result in a mostly Ar bubble.[14,15] It is evident from these observations that polyatomic species inside the bubble are detrimental to the efficacy of cavitation for generating extreme intracavity temperatures due to the thermodynamics (i.e., lowering of γ, the polytropic ratio) associated with rapid compression of a molecular vapor/gas.[16]

Because of this, we have continued to explore SL in low-vapor-pressure liquids with hopes of gaining a better understanding of the mechanisms responsible for SL, and also to gain insight into the extent to which chemistry limits the peak energies generated during cavitation.[9,17−19] Recently, we observed that SBSL from H_2SO_4 was over 10^3 times brighter than SBSL from water; the spectra allowed for quantification of the intra-cavity conditions and provided experimental evidence of plasma formation.[20,21] The large increase in Φ_{SL} from H_2SO_4 compared to water is likely due to the large reduction in water vapor inside the bubble resulting in higher intracavity temperatures.

Here, we report the observation of abrupt and dramatic changes in Φ_{SL} and spectral profiles of SBSL from H_2SO_4 containing mixtures of air and Ar or He. The observed emitters and the sudden increase in Φ_{SL} indicate that small molecules suppress plasma formation during bubble collapse in the presence of Ar. When He is present, the SBSL arises from molecular emission as opposed to a plasma, likely due to the high thermal conductivity and ionization potential of He compared to Ar. Temperatures determined from emission lines observed pre and post-P_c show that molecular components of air significantly limit the peak temperatures reached during SBSL, as previously suggested by calculation for SBSL from water.[5,13]

Experimental Section

The SBSL resonator and technique for measuring P_a have been described elsewhere.[9,22] Solutions were prepared by diluting 95 wt % H_2SO_4 to the desired concentration with purified water (18 MΩ cm, 0.2 μm filters). Solutions were degassed to the desired air concentration with a direct-drive vacuum pump at 23 °C with vigorous stirring for 24 h. After degassing, the desired amount of He or Ar (≥ 99.995%) was

* To whom correspondence should be addressed. E-mail: ksuslick@uiuc.edu.

10.1021/jp063023u CCC: $33.50

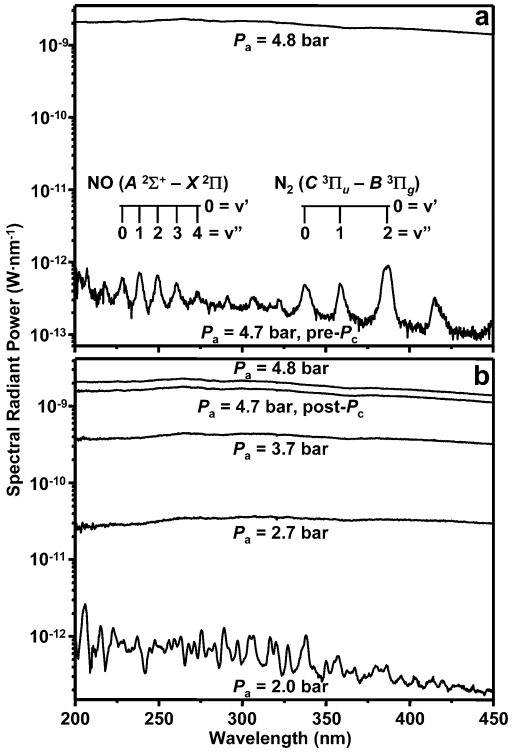

Figure 1. SBSL spectra from degassed 85 wt % H_2SO_4 regassed with 50 Torr of 40% Ar in air. There is a dramatic hysteresis in the emission spectra as the acoustic pressures (P_a, shown below each spectrum) are increased and then decreased. (a) The Φ_{SL} increases suddenly as the measured P_a is increased from 4.7 to 4.8 bar. Features within the spectra are labeled with the corresponding emitters. (b) As the P_a is gradually decreased from P_c (i.e., 4.8 bar) to 2.0 bar, the spectra gradually decrease in intensity but remain featureless until very low P_a. All spectra were acquired from the same sonoluminescing bubble.

added to the reaction flask. The flask was sealed and the solution was vigorously stirred at 23 °C for 1 h. At the gas concentrations employed here (6% of saturation), a single moving sonoluminescing bubble could be trapped at the center of the resonator.

SBSL 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 × 256 pixel LN_2-cooled CCD camera.[9] A 100 μm slit width was used for all experiments resulting in a resolution of 0.8 nm. The acoustic resonator was mounted to a micron-positioning stage allowing for precise alignment of the bubble with the slit. All spectra were corrected for absorption by the solution and the resonator, and absolute calibrations of spectral radiance (Φ_λ) were performed with NIST-traceable standards of spectral irradiance.[10,20]

Results and Discussion

Figure 1 shows the SBSL emission as a function of P_a from H_2SO_4 containing a mixture of air and Ar. Let us first focus on the behavior of Φ_{SL} with changing P_a; the changing spectral profiles will be discussed below. Initially, a nonluminescing bubble is trapped at the pressure antinode at low P_a (~1 bar). As the P_a is slowly increased, very dim SBSL is first detected at 4.0 bar. Upon further increase to 4.7 bar, emission bands become discernible (discussed below) while Φ_{SL} remains low (Figure 1a). If the P_a is now increased from 4.7 to 4.8 bar, Φ_{SL} suddenly increases by a factor of 7000. Note that the spectra are time-averaged so it is difficult to determine the number of acoustic cycles it takes to observe the increase in Φ_{SL}.[8,23] We have observed in some cases that the transition from dim to bright SBSL is very gradual and occurs over several seconds.

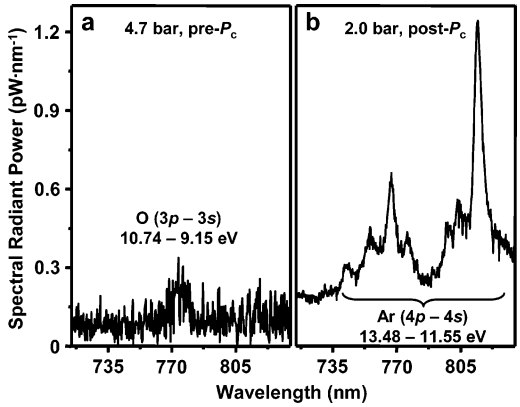

Figure 2. Spectra of very dim SBSL. (a) The spectrum acquired at 4.7 bar was obtained just below P_c, before bright SBSL was initiated. The low signal-to-noise reflects how dimly the bubble was luminescing in this region of the spectrum. The only observed emission is a very weak atomic O line. (b) After the bubble was driven above P_c and the P_a gradually lowered to 2.0 bar (to produce comparable low intensity SBSL), the spectrum shows strong lines from excited Ar atoms. The solution is the same as was used in Figure 1.

The absolute duration depends on the molar ratio of air to noble gas (X_{air}/X_{ng}) as well as the specific noble gas used; longer transition times are observed for larger X_{air}/X_{ng} and for noble gases with high thermal conductivities.

If the P_a is decreased from 4.8 back to 4.7 bar, only a slight decrease in Φ_{SL} occurs; further reductions in P_a result in further decreases in Φ_{SL} down to 2.0 bar (Figure 1b). If SBSL is now extinguished by reducing the P_a below 2.0 bar and allowing several seconds to pass, the P_a must again be increased to just below P_c before dim light emission is observed. If, however, the P_a is quickly increased after the SBSL is quenched, the Φ_{SL} gradually increases with increasing P_a from 2.0 bar. This behavior, though far less pronounced, has also been observed from partially degassed water and is attributed to the time scale for N_2 and O_2 diffusion into the bubble.[23]

Let us now turn our attention to the behavior of the SBSL spectral profiles with changing P_a. As shown in Figure 1, there are substantial differences in the spectral profiles before and after the bubble is driven above P_c. Before the bubble is driven above P_c, nitric oxide (NO, $A\ ^2\Sigma^+ - X\ ^2\Pi$) and nitrogen (N_2, $C\ ^3\Pi_u - B\ ^3\Pi_g$) emission bands are clearly visible in the spectrum (Figure 1a). With a very slight increase in P_a to P_c ($\Delta P_a = 0.1$ bar), the spectrum becomes featureless; the molecular emission bands observed before the bubble was driven above P_c are no longer present. As the P_a is gradually decreased after the bubble has been driven above P_c, the spectral profiles remain featureless until very low P_a (Figure 1b). Here, the spectrum again consists of emission lines, though assignment is complicated by the presence of several overlapping bands; the observed emission likely arises from sonolysis products of the solution such as SO, S_2, and others.[22] Comparison of this spectrum to the pre-P_c spectrum (Figure 1a) shows that the intracavity chemical and physical environment has been significantly altered. At this point, molecular emission is again observed in the SBSL spectrum because there is a decrease in the intracavity temperatures[20] due to the lower P_a. Changes in the spectral profiles of an SBSL bubble before and after being driven above P_c are also observed in the near-IR. The SBSL spectrum obtained from a bubble that has not been driven above P_c shows, in addition to NO and N_2 emission in the near-UV and visible, weak oxygen atom emission at 777 nm (Figure 2a). Once the bubble has been driven above P_c and is subsequently dimmed by reducing P_a, however, strong Ar atom emission is observed in the near-IR

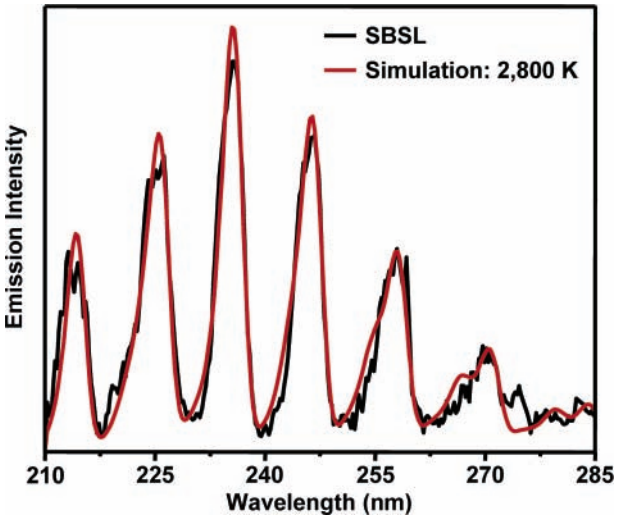

Figure 3. NO emission observed during pre-P_c SBSL of the same solution as in Figure 1 compared to the calculated thermalized NO emission at 2800 K. The peak correlation of the simulation is 0.98.

(Figure 2b); the Ar lines are not observed before the bubble has been driven above P_c when NO, N_2, and oxygen atom lines are observed. The dependence of the presence of Ar emission lines in the spectra on whether the bubble has been driven above P_c has strong implications for the role of Ar in bright SBSL and the effects of air on the population of Ar excited states, especially the important Ar metastable states (Ar^m, $^3P_{0,2}$). Because of the long lifetimes of Ar^m,[24] these states are very useful as energy carriers in plasmas.

Despite the complex behavior of SBSL emission in H_2SO_4, we can explain the changes in Φ_{SL} and the observed spectral profiles. In bubbles that have not yet been driven above P_c, oxygen atom, NO, and N_2 emission indicates that the intracavity temperatures during collapse are sufficient to result in dissociation of O_2 and N_2 and likely reach a few thousand degrees.[13,25,26] This can be verified by simulating the NO band emission. As shown in Figure 3, NO emission is well-simulated[27] by fully thermalized ($T_{rot} = T_{vib}$) emission at 2800 ± 100 K (also see Supporting Information, Figure 1).[28] Due to possible temporal variations in the intracavity conditions, this should be taken simply as an "effective" SBSL temperature.[21] The emission from NO, N_2 and O atoms strongly indicates that the components of air are indeed reacting (and subsequently dissolving into the liquid surrounding the bubble), as has been suggested for water SBSL.[4,13,14] It is important to note that the oxidation of N_2 to NO_x in strongly heated air is known to occur via a chain mechanism with the rate-determining step being the oxidation of N_2 by atomic oxygen to give NO and atomic nitrogen ($\Delta H^\circ = 313$ kJ mol^{-1}).[25] The P_c represents the point at which essentially all the N_2 and O_2 originally inside the bubble have been burned off, which should also produce a rapid change in the ambient bubble size.[13] This substantially changes the gas content of the bubble and removes a major endothermic process (i.e., N_2 and O_2 dissociation) during the bubble collapse. Post-P_c, the bubble collapse generates a much hotter bubble, as clearly demonstrated by the dramatic increase in Φ_{SL}, the general featurelessness of most of the emission, and the appearance of Ar atom emission. While the effects of changing P_a on the bubble dynamics in water are reasonably well understood,[13] for SBSL from H_2SO_4, the role of bubble dynamics is less clear.[30]

In addition to the chemical reactions that occur, energy-transfer reactions likely play a critical role in suppressing plasma formation and the consequent bright SBSL. It is well known

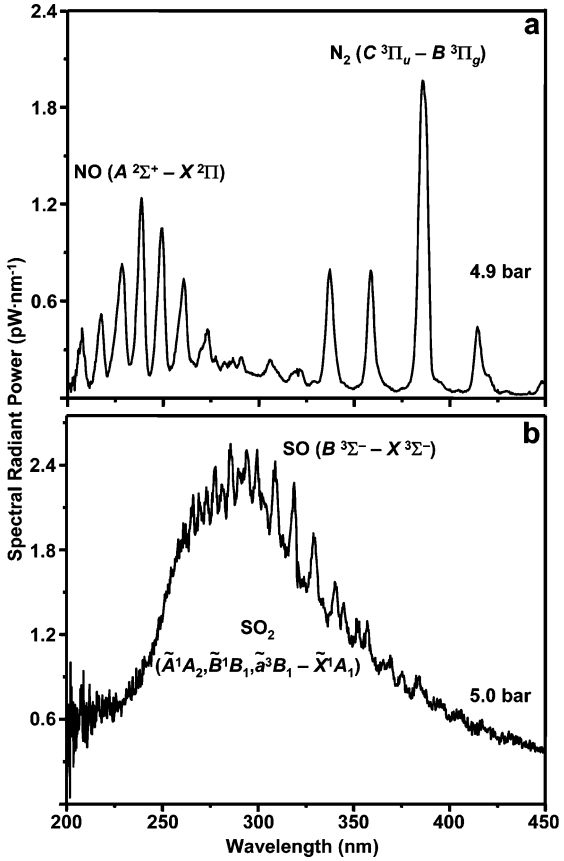

Figure 4. SBSL spectra of 85 wt % H_2SO_4 regassed with 50 Torr of 10% air in He. The applied acoustic pressure (P_a) is shown next to each spectrum. Features within the spectra are labeled with the corresponding emitters and transitions. The spectrum in (a) was acquired just below P_c while the spectrum in (b) was acquired just above P_c. The spectra were acquired from the same sonoluminescing bubble.

that there are many channels by which Ar^m states are depopulated.[31] One relevant and well-known example is the energy-transfer reaction between Ar^m and N_2 ($X\ ^1\Sigma_g^+$) to form N_2 ($C\ ^3\Pi_u$).[32] The $C\ ^3\Pi_u$ state of N_2 lies 11.1 eV above the ground state and matches well with the Ar^m states that lie slightly higher in energy (11.5 and 11.7 eV). The importance of these metastable states in generating bright SBSL likely cannot be overemphasized; collisional excitation/dissociation reactions of Ar^m with many molecular species are well known.[33] If the excitation and ionization of Ar atoms is necessary to observe large Φ_{SL}, then depopulation of the Ar excited states via collisional quenching will suppress bright SBSL. The presence of significant amounts of O_2 and N_2 molecules inside the bubble will hinder plasma formation through collisional quenching of Ar as well as their endothermic dissociation, and, hence, suppress bright SBSL below P_c. Consistent with this, no Ar emission is observed when O, NO, and N_2 emission is observed below P_c.

The presence of He inside the bubble leads to interesting similarities and differences compared to Ar. When a 50 Torr mixture of 10% air in He is dissolved in 85 wt % H_2SO_4, NO and N_2 emission are observed at 4.9 bar (Figure 4a), just as for Ar bubbles. When the P_a is increased to 5.0 bar, the spectral profile abruptly changes and emission is now observed from SO and SO_2 together with a relatively modest increase in Φ_{SL} (factor of 4, Figure 4b). This is much different than the air/Ar spectra observed post-P_c, which consists of featureless continua (i.e., no SO or SO_2 emission) and a much larger increase in Φ_{SL}.

These differences can be rationalized by comparing the properties of He and Ar. The thermal conductivity of He at 25 °C is larger than that of Ar ($\kappa_{He}/\kappa_{Ar} = 8.6$). This results in lower peak temperatures for the He bubble, as has previously been observed for MBSL.[34] The ionization potential of He is also much higher than that of Ar (24.6 vs 15.8 eV). This, coupled with the lower peak temperatures, will result in a lower degree of excitation and ionization relative to the Ar bubble. These differences are reflected in the SBSL spectra. Since the metastable states of He (He^m: $2\ ^1S$, $2\ ^3S$) are much higher in energy (20 eV) than Ar^m, the number density of He^m atoms will be much lower than that of Ar^m atoms for a given temperature. A much lower concentration of O_2 and N_2 is therefore expected to be sufficient to collisionally quench and depopulate He^m, provided they are populated in the first place; He emission lines have yet to be observed during SL.

The quenching of highly emissive species and of plasma by small molecules during SBSL is observed from concentrated H_2SO_4 solutions containing mixtures of air and noble gas. As the acoustic pressure is increased above P_c, there are dramatic changes in Φ_{SL} and in the spectral profile. Below P_c, the emission spectra consist of bands from species produced by chemical reactions of N_2 and O_2, whereas above P_c the emission spectra changes to either a featureless continua (for a very bright Ar bubble) or bands from sonolysis products of the liquid (for a He bubble). These observations, together with measured SBSL temperatures below and above P_c, show that the molecular components of air significantly limit the peak conditions generated inside the bubble due to reduction in the polytropic ratio, endothermic reactions, and energy-transfer reactions.

Acknowledgment. This work was supported by the NSF (CHE0315494) and DARPA.

Supporting Information Available: The supporting material contains simulations of the spectral profiles of nitric oxide emission bands as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hilgenfeldt, S.; Lohse, D.; Brenner, M. P. *Phys. Fluids* **1996**, *8*, 2808.

(2) Brenner, M. P.; Hilgenfeldt, S.; Lohse, D. *Rev. Mod. Phys.* **2002**, *74*, 425.

(3) Putterman, S. J.; Weninger, K. R. *Annu. Rev. Fluid Mech.* **2000**, *32*, 445.

(4) Lohse, D.; Brenner, M. P.; Dupont, T. F.; Hilgenfeldt, S.; Johnston, B. *Phys. Rev. Lett.* **1997**, *78*, 1359.

(5) Storey, B. D.; Szeri, A. J. *Proc. R. Soc. London, Ser. A* **2000**, *456*, 1685.

(6) Tögel, R.; Hilgenfeldt, S.; Lohse, D. *Phys. Rev. Lett.* **2000**, *84*, 2509.

(7) Ashokkumar, M.; Crum, L. A.; Frensley, C. A.; Grieser, F.; Matula, T. J.; McNamara, W. B., III.; Suslick, K. S. *J. Phys. Chem. A* **2000**, *104*, 8462.

(8) Guan, J. F.; Matula, T. J. *J. Phys. Chem. B* **2003**, *107*, 8917.

(9) Didenko, Y. T.; McNamara, W. B., III.; Suslick, K. S. *Nature* **2000**, *407*, 877.

(10) Didenko, Y. T.; Suslick, K. S. *Nature* **2002**, *418*, 394.

(11) Hiller, R.; Weninger, K.; Putterman, S. J.; Barber, B. P. *Science* **1994**, *266*, 248.

(12) Asai, T.; Watanabe, Y. *Jpn. J. Appl. Phys., Part 1* **2000**, *39*, 2969.

(13) Toegel, R.; Lohse, D. *J. Chem. Phys.* **2003**, *118*, 1863.

(14) Lohse, D.; Hilgenfeldt, S. *J. Chem. Phys.* **1997**, *107*, 6986.

(15) Ketterling, J. A.; Apfel, R. E. *Phys. Rev. Lett.* **1998**, *81*, 4991.

(16) Colussi, A. J.; Hoffmann, M. R. *J. Phys. Chem. A* **1999**, *103*, 11336.

(17) Flint, E. B.; Suslick, K. S. *J. Am. Chem. Soc.* **1989**, *111*, 6987.

(18) Oxley, J. D.; Prozorov, T.; Suslick, K. S. *J. Am. Chem. Soc.* **2003**, *125*, 11138.

(19) Flannigan, D. J.; Hopkins, S. D.; Suslick, K. S. *J. Organomet. Chem.* **2005**, *690*, 3513.

(20) Flannigan, D. J.; Suslick, K. S. *Nature* **2005**, *434*, 52.

(21) Flannigan, D. J.; Suslick, K. S. *Phys. Rev. Lett.* **2005**, *95*, 044301.

(22) Flannigan, D. J.; Suslick, K. S. *Acoust. Res. Lett. Onl.* **2005**, *6*, 157.

(23) Matula, T. J.; Crum, L. A. *Phys. Rev. Lett.* **1998**, *80*, 865.

(24) Katori, H.; Shimizu, F. *Phys. Rev. Lett.* **1993**, *70*, 3545.

(25) Zel′dovich, Y. B.; Raizer, Y. P. *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*; Dover Publications: Mineola, 2002.

(26) Laux, C. O.; Spence, T. G.; Kruger, C. H.; Zare, R. N. *Plasma Sources Sci. Technol.* **2003**, *12*, 125.

(27) Luque, J.; Crosley, D. R. *LIFBASE, Database and Spectral Simulation for Diatomic Molecules* (v. 2.0.55); Report MP-99-009; SRI International, 1999.

(28) This observed temperature in H_2SO_4 is roughly 2-fold lower than the predicted temperature for a collapsing air bubble in water before the onset of SBSL (5500 K).[13] This may be at least partly due to the translational motion of a bubble in H_2SO_4, which leads to a less spherical collapse and less heating (just as the conditions generated during multibubble sonoluminescence (MBSL) are thought to be less extreme than SBSL conditions due to aspherical bubble collapse[29]).

(29) McNamara, W. B., III.; Didenko, Y. T.; Suslick, K. S. *Nature* **1999**, *401*, 772.

(30) Hopkins, S. D.; Putterman, S. J.; Kappus, B. A.; Suslick, K. S.; Camara, C. G. *Phys. Rev. Lett.* **2005**, *95*, 254301.

(31) Golde, M. F. Reactions of Electronically Excited Noble Gas Atoms. In *Gas Kinetics and Energy Transfer*; The Chemical Society: London, 1977; p 123.

(32) Fishburne, E. S. *J. Chem. Phys.* **1967**, *47*, 58.

(33) Bourène, M.; Le Calvé, J. *J. Chem. Phys.* **1973**, *58*, 1452.

(34) Didenko, Y. T.; McNamara, W. B., III.; Suslick, K. S. *Phys. Rev. Lett.* **2000**, *84*, 777.