Molecular Emission and Temperature Measurements from Single-Bubble Sonoluminescence

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Single-bubble sonoluminescence (SBSL) spectra in H_2O show featureless continuum emission. From an acoustically driven, moving bubble in phosphoric acid (H_3PO_4), we observe very strong molecular emission from excited OH radicals ($\sim$310 nm), which can be used as a spectroscopic thermometer by fitting the experimental SBSL spectra to the OH $A\,^2\Sigma^+$–$X\,^2\Pi$ rovibronic transitions. The observed emission temperature (T_{em}) ranges from 6200 to 9500 K as the acoustic pressure (P_a) varies from 1.9 to 3.1 bar and from 6000 to >10 000 K as the dissolved monatomic gas varies over the series from He to Xe.

Single-bubble sonoluminescence (SBSL), light emission from an isolated bubble during ultrasonic irradiation, is a phenomenon that arises from acoustic cavitation: the formation, growth, and implosive collapse of a gas bubble in a sound field [1–4]. Light emission from SBSL usually reveals little about the physical conditions and chemical processes during bubble collapse because the typical SBSL spectrum is featureless. In fact, SBSL from pure water, the liquid used most often for SBSL experiments, displays a continuum whose intensity increases smoothly from the near-IR into the near-UV devoid of any lines or bands [5–7]. In only one instance has very weak emission from excited neutral OH radicals been reported from an extremely dim bubble in water [8]. In contrast, the emission of light from clouds of cavitating bubbles at higher acoustic pressures (i.e., multibubble sonoluminescence, MBSL) is dominated by molecular and atomic emissions [9–13]. Lack of spectral features during SBSL presents a problem when attempting to derive the effective temperatures and pressures or to describe the mechanisms ultimately responsible for the light emission. The featureless continuum spectra has been interpreted as arising from a variety of possible processes, including blackbody radiation [7,14,15], radiative plasma processes (e.g., bremsstrahlung and ion-electron recombination) [16–19], and severe line broadening in extreme high temperature and pressure environments [20–22].

We recently discovered that concentrated sulfuric acid (H_2SO_4) provides a dramatic increase in SBSL intensity and provides atomic, ionic, and molecular emission lines [23–25]. This suggests the study of similar liquids, and we now report SBSL from phosphoric acid (H_3PO_4) and measurement of emission temperatures from strong OH emission lines. Phosphoric acid is a strongly hydrogen-bonded liquid with a relatively high viscosity and low vapor pressure (2.4 torr for 85% H_3PO_4 vs 23 torr for H_2O at 300 K). Surprisingly, the vapor of H_3PO_4 consists only of water molecules; due to strong hydrogen bonding, the acid molecules themselves have no significant presence in the vapor phase even at high temperatures [26,27]. In addition, pyrolysis of H_3PO_4 only leads to dehydration forming poly-

phosphoric acids, so the exclusive volatile decomposition product of H_3PO_4 is H_2O. These unique properties of H_3PO_4 (together with a brief report of SL in dilute aqueous solutions of H_3PO_4 [28]) has prompted us to examine spectroscopically the SBSL in more concentrated H_3PO_4.

Because H_3PO_4 has a much lower vapor pressure than water, single-bubble collapse is much more efficient: less energy is consumed by endothermic bond dissociations [29]. As a result, the sonoluminescing bubble in SBSL in H_3PO_4 is exceptionally bright. Indeed, we are able to easily observe SBSL spectra from 65% H_3PO_4 dominated by strong molecular emission from excited OH radicals. This is unusual: only very weak emission from OH has been reported from MBSL in water [10] and from SBSL in weakly driven, dimly sonoluminescing bubbles in water or dilute H_2SO_4 [8,30]. Importantly, the high intensity of the emission in H_3PO_4 permits us to obtain the fine structure of OH $A\,^2\Sigma^+$–$X\,^2\Pi$ rovibronic transitions [31] using a high resolution grating (as previously described [25]), and the experimental spectra obtained can be fit well with synthetic spectra as a function of temperature. Solutions were prepared by diluting 85% H_3PO_4 as purchased with purified water (18 MΩ cm) to 65% and completely degassed via 3 cycles of freeze-pump-thaw. Solutions were then regassed in a closed system with 50 torr of monatomic gases (He, Ne, Ar, Kr, and Xe from Matheson Tri-Gas, research purity) with vigorous stirring at 25 °C for 1 h. All spectra have been corrected for absorption by the solution and the quartz round bottom flask as well as the optical response of the system against NIST traceable standard lamps.

Similar to the single bubbles generated in polar aprotic organic liquids [32] and H_2SO_4 [23,33], the single cavitating bubble in H_3PO_4 is also moving within a small volume at the center of the quartz resonator. Because of the bright light generated during SBSL in H_3PO_4, we were able to capture the bubble motion with a general purpose digital camera (Nikon D90). As can be seen in Fig. 1, the bubble is moving around in a confined space ($\sim$20 mm^3) with no predictable route. The translational movement of the bubble varies with the applied acoustic pressures: as the acoustic pressure is increased, the bubble motion becomes
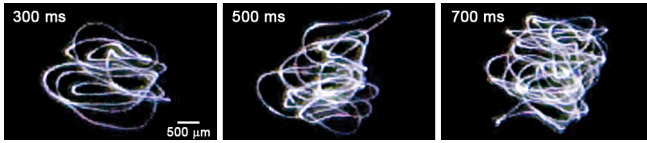
FIG. 1 (color online). Photographs (with different exposure times) of a moving sonoluminescing bubble in 65% H_3PO_4 regassed with 50 torr Ar at an acoustic pressure of 3.1 bar as determined from hydrophone measurements.

more rapid primarily near the center of the resonator cell while maintaining its bright sonoluminescence.

Figure 2 shows SBSL spectra obtained from H_3PO_4 as a function of acoustic pressure. The spectra contain strong molecular emission from OH excited states (~ 310 nm) and an underlying continuum, the radiant power of which increases from the near-IR to mid-UV. Chemical processes must be considered in the discussion of the light-emitting mechanism during single-bubble cavitation in order to explain the observation of OH emission. Excited OH radicals are formed either from the recombination of H and O atoms created during water vapor sonolysis or from the initial dissociation of water itself. As the acoustic driving pressure is increased, the intensity of OH emission decreases relative to the continuum emission, perhaps due to increasing dissociation of the OH radicals at higher bubble temperatures.

The quantification of intracavity conditions during single-bubble cavitation is of great interest both theoretically and experimentally. While the effective temperatures of multibubble cavitation have been previously determined (e.g., by comparative rate thermometry or MBSL from excited molecules or metal atoms [34–40]), temperature measurements from SBSL have proved much more difficult, given that SBSL spectra are usually featureless continua. Experimental estimates of temperatures from single-bubble cavitation therefore generally assume that the continuum is due to blackbody emission [7,14,15], an assumption that remains controversial [16,17,19]. Although there have been a few experimental observation of molecular emission during single-bubble cavitation, these spectra were too weak for quantitative analysis [8,32]. The OH emission that we now observe in phosphoric acid, however, is extremely bright and permits us to obtain high resolution OH $A^2\Sigma^+$–$X^2\Pi$ rovibronic spectra. We are thus able for the first time to determine SBSL temperatures from molecular emission by fitting the observed OH emission to synthetic spectra generated from known parameters. To this end, we have used LIFBASE, a database and spectral simulation program for diatomic molecules, which has been extensively applied to temperature determinations of excited molecular emission from flames and laser induced fluorescence, etc. [41].

In the OH spectrum taken at an acoustic pressure of 2.4 bar [Fig. 2(b)], for example, the OH emission spectrum can be very accurately simulated by a fully thermalized ($T_{rot} = T_{vib}$) emission at 8300 ± 200 K. OH emission tem-
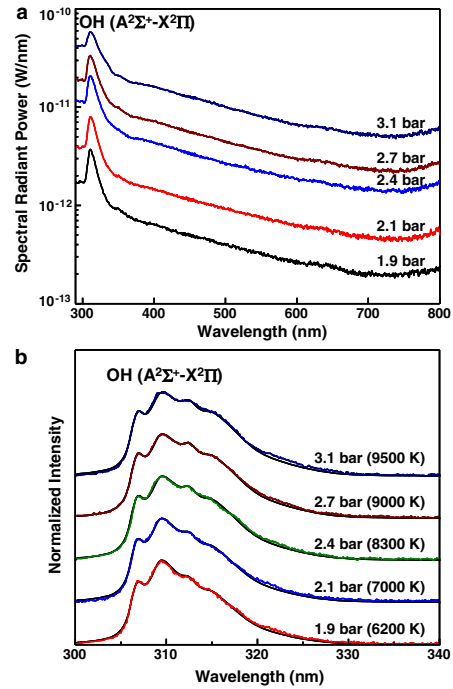

FIG. 2 (color online). (a) SBSL spectra from 65% H_3PO_4 regassed with 50 torr Ar at different acoustic pressures. All spectra were collected from the same rapidly moving bubble driven at different P_a, as labeled above the corresponding spectra. The peak around 310 nm arises from OH ($A^2\Sigma^+$–$X^2\Pi$) emission. The spectra were acquired with a 300 grooves/mm grating blazed at 250 nm. (b) Higher resolution spectra of OH ($A^2\Sigma^+$–$X^2\Pi$) emission from the SBSL of 65% H_3PO_4 at different acoustic powers regassed with 50 torr Ar compared to the best-fit synthetic spectra (underlying black lines). The underlying continuum has been subtracted; spectra are normalized to the highest intensity at ~ 309 nm. The calculated temperatures were obtained by fitting experimental SBSL spectra with synthetic spectra using the LIFBASE software package [41] and assumed thermal equilibrium and a Lorentzian profile. 1200 grooves/mm grating blazed at 330 nm.

peratures generated during SBSL from 65% H_3PO_4 were observed to increase with increasing acoustic pressure: 6200 K at 1.9 bar, 7000 K at 2.1 bar, 8300 K at 2.4 bar, 9000 K at 2.7 bar, and 9500 K at 3.1 bar. As the applied acoustic pressure increases, the bubble undergoes a more violent collapse, which increases the effective temperature inside the collapsing bubble. We note that these experimentally determined temperatures are consistent with theoretically predicted SBSL temperatures in water using a model that accounts for the endothermic decomposition of the water vapor trapped during bubble expansion [42–44].

With some hesitation, we have also fit the slope of the continuum to an effective blackbody temperature [7,15], which we find to be $\sim 11\,000$ K for each acoustic pressure. The meaning and accurateness of such a parameter, however, is open to question. First, it is not clear that the continuum is true blackbody emission [16,17,19], and
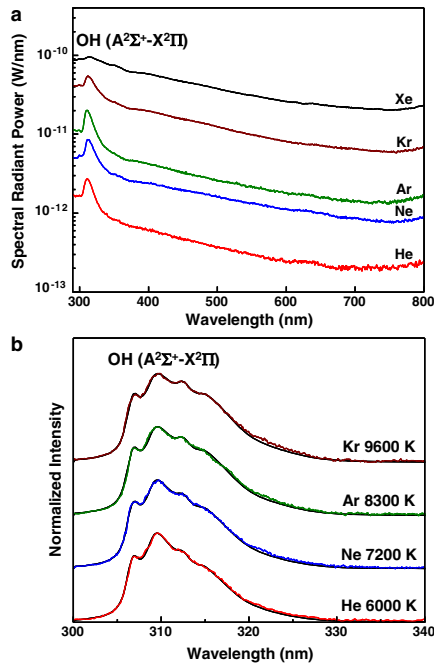
FIG. 3 (color online). The effects of dissolved noble gases on SBSL spectra. (a) SBSL spectra from 65% H_3PO_4 with 50 torr of various noble gases at an applied acoustic pressure of 2.4 bar. (b) High resolution spectra and calculated effective emission temperatures from SBSL with different noble gases at the acoustic pressure of 2.4 bar compared to the best-fit synthetic spectra (underlying black lines). The calculated temperatures were obtained by fitting experimental SBSL spectra with synthetic spectra using the LIFBASE software package [41]. The thermal conductivity of He is 156.7 mW/m K, Ne 49.8 mW/m K, Ar 17.9 mW/m K, and Kr 9.5 mW/m K [53].

second, the fit of the continuum region is limited to only a 200 nm range (due to strong OH emission in the near-UV and noble gas atom emission in the red) and therefore the fit is of limited accuracy.

It is generally accepted that the bubble content is a key parameter in controlling the intracavity conditions generated during bubble collapse [29], and so we have examined the SBSL spectra as a function of dissolved noble gas. Figure 3 shows SBSL spectra from 65% H_3PO_4 regassed with 50 torr of different noble gases at the acoustic pressure of 2.4 bar. The intensity of the SBSL depends dramatically on the dissolved gas [Fig. 3(a)] and increases roughly 100-fold from He to Ne to Ar to Kr to Xe. In all cases, an emission peak around 310 nm corresponding to molecular emission of neutral OH radicals is observed and broadens substantially as we progress from He to Xe. These results are consistent with prior MBSL experiments on effects of noble gases on cavitation temperatures [45].

The initial stage of bubble collapse is slow and isothermal, during which the energy deposited in the bubble interior is readily transferred to the surrounding liquid via thermal conduction. As the speed of collapse increases the interior of bubble undergoes compressional heating and becomes increasingly adiabatic due to the rapidity of the

bubble collapse. The extent of adiabaticity will depend on the thermal conductivity of the gas-vapor mixture within the bubble. Compressional heating of the bubble should therefore be affected by the thermal conductivity of the gas within the bubble due to increased thermal transport from the heated gas to the cold surrounding liquid. Indeed, theoretical calculations using combined hydrodynamic and chemical kinetic modeling indicate that the higher thermal conductivity of the lighter noble gases leads to cooler SBSL temperatures [46–48]. By varying the composition of Ar and Ne mixtures, Flannigan and Suslick were able to determine the effect of thermal conductivity during single-bubble cavitation based on the Ar emission temperature [23]; this method, however, neglects the possibility that different noble gas molecules in the bubble might segregate spatially during bubble collapse [49,50]. Because we are able to observe strong OH emission from SBSL in phosphoric acid, we were able to experimentally determine the effect of noble gases directly on sonoluminescence temperatures during single-bubble cavitation. As shown in Fig. 3(b), the emission temperature of SBSL increases as the thermal conductivity of the gas within the bubble decreases. The observed emission temperatures range from 6000 K for He up to 9600 K for Kr, consistent with the published simulations [42]. Fitting the very limited continuum region (400 to 600 nm) gives an effective blackbody temperature of ~12 000 K for each noble gas, with the same substantial caveats discussed earlier.

SBSL in liquids other than water (including both low-volatility organic liquids [32] and concentrated sulfuric acid [23–25]) has lead to valuable insights on the conditions created in the gas phase of the collapsing bubble. Comparing these studies in phosphoric acid with our recent work in sulfuric acid, we find that the emission temperature in 85% H_2SO_4 (based on excited atomic Ar emission) is much hotter and can approach 20 000 K. In addition, the existence of a hot, optically opaque plasma core was also experimentally confirmed for SBSL in H_2SO_4 [23]. In contrast, we do *not* observe atomic emission from noble gases in the SBSL from H_3PO_4. We suggest that this difference is due (at least in part) to the relatively high vapor pressure of water in 65% H_3PO_4 (8.7 torr) compared to that of 85% H_2SO_4 (40 mtorr): more of energy of cavitation is consumed by endothermic bond dissociations of the water vapor (leading to the formation of hydrogen and oxygen atoms, and OH, etc.). Thus, the water vapor trapped inside a cavitating bubble is a major temperature-limiting factor and collapsing bubbles are considerably cooler in phosphoric than in sulfuric acid.

We can also compare MBSL to SBSL spectra from phosphoric acid: in both systems, strong molecular emission is observed from OH with comparable effective temperatures, but PO emission is only observed in MBSL [51]. In both the SBSL and MBSL of phosphoric acid, OH excited states are produced during collapse from the water vapor inside the bubble. The collapse of single bubbles is expected to be highly symmetric, whereas bubble collapse

in a cloud gives rise to more asymmetric collapse; this greater asymmetry in MBSL explains the observation of PO emission, which must arise from the liquid phase by the introduction of nanodroplets into the hot core of the collapsing bubble [51,52].

In conclusion, we observe strong molecular emission in the SBSL spectra from phosphoric acid. Observation of intense OH emission from a bright, rapidly moving bubble enables us for the first time to acquire high resolution spectra and to use the rovibronic emission of excited-state OH radicals as a direct spectroscopic probe of the emission temperature inside the collapsing bubble. The effective OH emission temperatures measured from phosphoric acid increase with increased applied acoustic pressure and also increase with decreasing thermal conductivity of the noble gases inside the bubble. The observed temperatures (6000 to $\sim$10 000 K) from SBSL in phosphoric acid are limited by the vapor pressure of water inside the collapsing bubble and are comparable to the emission temperatures observed from MBSL.

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