The Nature of the Continuum in Multibubble Sonoluminescence

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Irradiation of liquids with high-intensity ultrasound creates clouds of cavitating bubbles. In such a cavitation field, the bubbles form and expand during the rarefaction phase of the sound wave, and then implosively collapse during the compression phase.[1] During collapse, compressional heating of the contents of the bubble produces transient extreme conditions (e.g., 5000 K and 400 atm in silicone oil saturated with argon).[2,3] These conditions are responsible for both sonochemistry and the emission of light: multibubble sonoluminescence (MBSL).[4] The spectrum of MBSL depends on the contents of the bubble; typically it will consist of diatomic and atomic emission features as well as an underlying continuum.[5] The discrete molecular bands and atomic lines are well understood, but the nature of the continuum in MBSL is uncertain. The SL continuum has been variously ascribed to emission from confined electrons,[6] blackbody radiation,[7] electrical discharge,[8] and emission from small molecules formed during the cavitation event.[5] Understanding the source of this continuum is critical to understanding both the final conditions within the bubble and the processes that lead to (and perhaps limit) these conditions. We report here the relative intensity of the atomic features versus the continuum emission as the conditions within the bubble are varied. The observed behavior is consistent with a molecular continuum and cannot be explained as a plasma emission. Furthermore, our results indicate that chemical reactions within the bubbles play a major role in determining the effective temperature during cavitation.

The intensity of continuum emission relative to the intensity of atomic emission (I_{cont}/I_{atom}) in plasma emission is well understood. The differences between ionization energies and electronic excitation energies are large, thus I_{cont}/I_{atom} in a plasma increases dramatically with temperature. This is shown in eq 1,

$$\frac{I_{cont}}{I_{atom}} = \frac{1}{(8.5\times10^{-34})\nu}\,\frac{U_1(T_e)}{A_{ul}g_{ul}}\,\frac{kT_e e^6}{h^4c^3}\,\frac{\xi(\nu,T_e)+G(\nu,T_e)\exp(-h\nu/kT_e)}{\exp\left(\dfrac{X_i-\mathbf{X}_u-\Delta X_i}{kT_e}\right)} \quad (1)$$

where ν is the frequency of the emitted line from the neutral atom, A_{ul} is the Einstein transition probability for that transition, g_{ul} is the statistical weight of the excited state of the neutral atom, $U_1(T_e)$ is the statistical weight of the ground state of the ion, h is the Planck constant, c is the speed of light, k is the Boltzmann constant, T_e is the electronic temperature, and e is the electron charge.[9] X_i and X_u are the ionization energy and excitation energy of the atomic line emitter (e.g., for Cr atoms, 6.7 and 2.9 eV (427 nm) respectively), and ΔX_i is the lowering of the ionization energy of the atom by the plasma. $G(\nu,T_e)$[10] and $\xi(\nu,T_e)$[11] both describe the absorption of radiation by the plasma.

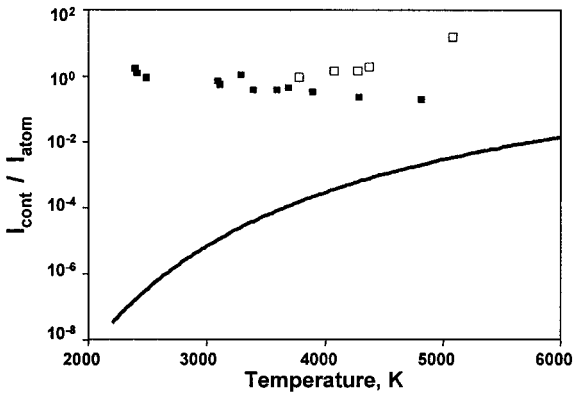

Figure 1. Relative intensities of the continuum vs atomic line emission (I_{cont}/I_{atom}) in multibubble sonoluminescence (MBSL) from silicone oil saturated with gaseous hydrocarbons (CH_4, C_2H_4, C_3H_8) in Ar (solid squares) and from octanol saturated with various noble gases (He, Ne, Ar, Kr, Xe) (hollow squares), compared to that expected from plasma emission (eq 1, solid line).

We have collected MBSL from solutions of $Cr(CO)_6$ in silicone oil saturated with mixtures of hydrocarbons in argon and in octanol saturated with various noble gases. We have recently reported the use of metal atom emission in MBSL as a thermometer of cavitation, and showed that the temperature of MBSL decreased as the adiabatic index ($\gamma = C_p/C_v$, the ratio of heat capacities) of the gas within the bubble was decreased,[3] and as its thermal conductivity increased.[12]

We compare the observed intensities of the Cr atom emission with background continuum in the MBSL spectra as a function of the measured emission temperature in Figure 1 from ultrasonic irradiation of $Cr(CO)_6$ in either silicone oil or octanol.[13] The ionization energy for Cr is substantially lower than that of any other species in the bubble, so one may assume that any contribution to the continuum from a plasma arises primarily from the ionization of Cr. From eq 1, one concludes that the observed I_{cont}/I_{atom} is *orders of magnitude greater* than that expected from a plasma. Thus, the continuum is *not* due to hot plasma emission.

It is worth noting that I_{cont}/I_{atom} increases with temperature for octanol solutions containing noble gases, but decreases in the

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(13) MBSL spectra were obtained with a thermostated stainless steel cell with a quartz window mounted to a 0.5 m spectrograph (Acton Research 505F with a Princeton Instruments IRY 512N UV-enhanced, image intensified diode array detector). The response of the spectrographic apparatus was calibrated against NIST traceable lamps. 20 kHz ultrasound was generated (Heat Systems Mysonix 375 with a 0.5 in. Ti horn) at 90 W cm^{-2} for the silicone oil solutions (poly(dimethylsiloxane), Dow Fluid 200, 100 centistokes viscosity, 2.5 mM $Cr(CO)_6$) and 70 W cm^{-2} for the octanol solutions (>99% purity, 1.25 mM $Cr(CO)_6$) as determined calorimetrically. The solutions were sparged before and during sonication with the appropriate gas, the spectra were corrected for absorption by the solution, and each data point represents the average of at least 15 10-s spectra.

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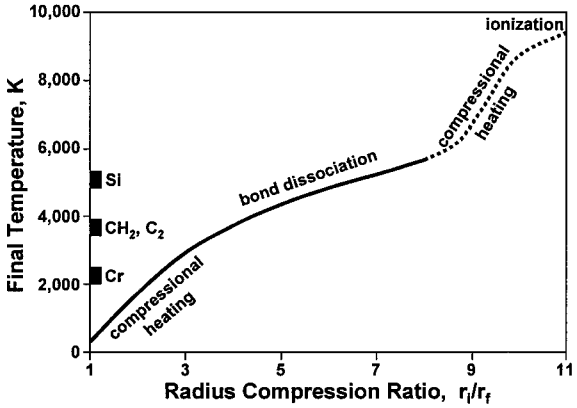

Figure 2. Schematic representation of processes occurring within a bubble during its collapse. The boxes on the final temperature axis represent roughly the expected onset temperatures for the appearance of emission from Cr atoms, CH_2 and C_2, and Si atoms, as shown. The dotted region represents further heating after complete atomization and is beyond that yet observed for MBSL, but may have relevance for single-bubble sonoluminescence.[4]

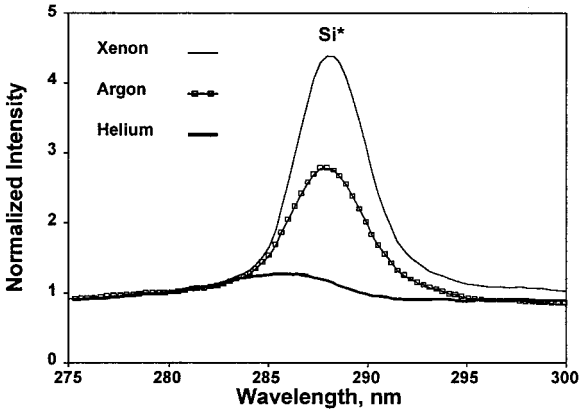

Figure 3. Intensity of MBSL from Si atoms relative to the continuum emission under Xe, Ar, and He.

silicone oil systems. This is due to the two different methods used to decrease the emission temperature during cavitation. For the silicone oil solutions, the cavitation temperature was lowered by doping Ar with gaseous hydrocarbons (i.e., changing C_p/C_v by adding, e.g., methane, propane). In contrast, for the octanol solutions, the cavitation temperature was decreased by changing the dissolved noble gas (and its thermal conductivity and hence the adiabaticity of collapse).

In flame spectroscopy, it is well accepted that continuum emission is dominated by emission from multiple hydrocarbon fragments.[14] Doping with gaseous hydrocarbons in silicone oil solution increases the number of hydrocarbon precursors that we believe are responsible for the molecular contributions to the continuum. There is, in fact, a good linear correlation between that I_{cont}/I_{atom} and the percentage of carbon in the gas.

The positive slope of I_{cont}/I_{atom} observed in the case of octanol saturated with various noble gases can be understood by viewing the temporal evolution of the conditions and contents of the bubble during bubble collapse. The bubble reaches a maximum radius during the rarefaction phase of the acoustic wave, at which point the liquid surrounding the bubble is capable of doing a given amount of work on the bubble contents during the ensuing compression. The initial stage of bubble collapse is relatively slow and isothermal, and the transition to "adiabatic" compressional heating depends on the thermal conductivity of the gas within the bubble. Collapsing bubbles containing Xe (low thermal conductivity) become more adiabatic earlier than do those containing Ar, etc. Thus, the liquid is capable of doing more work on a Xe bubble than on an Ar or He bubble. This energy initially is expended in heating and vibrationally exciting the contents of the bubble. As the temperature increases, however, an increasing fraction of this energy is consumed in sonolysis of the bubble contents, as shown schematically in Figure 2.

The weakest bonds in the bubble are the M−CO bonds (1.6 eV vs 3 to 4 eV for the bonds in octanol), and they are the first bonds broken, producing free metal atoms. The next process to occur is the thermal excitation of the free metal atoms (2.9 eV), coincident with the first steps of octanol dissociation. Thus, the first feature to appear during bubble collapse is metal atom emission. As compression continues and the temperature increases, the rate at which the octanol is decomposed increases relative to the rate at which the metal atoms are formed and excited to emission. As the production of the small hydrocarbon fragments (whose emission constitutes the bulk of the observed continuum in flames)[14] increases, so too does I_{cont}/I_{atom} in MBSL.

The hypothesis that the MBSL continuum is molecular in nature can be tested. For Cr atoms, the temperature required to produce emission is lower than that for hydrocarbon fragments. Let us consider the inverse situation, in which the production of atomic emission requires a temperature *greater* than that required for hydrocarbon sonolysis and subsequent formation of a molecularly based continuum. Silicone oil saturated with various noble gases provides such a system. These MBSL spectra contain both an intense underlying continuum and atomic emission from Si* at 288 nm that arises from an excited state at 5.1 eV. The bond energies in silicone oil are slightly less than those in aliphatic alcohols and hydrocarbons, and the ionization energy of silicon is 8 eV. If the continuum arises from plasma emission, then I_{cont}/I_{atom} would increase from He to Ar to Xe. In contrast, if the continuum is molecular in nature then I_{cont}/I_{atom} would decrease. The results are shown in Figure 3: I_{cont}/I_{atom} decreases from He to Ar to Xe, again consistent with a molecular continuum.

We conclude that chemical reactions within collapsing bubbles are a major factor in determining and limiting the conditions reached during cavitation. Support for this is seen in the remarkable insensitivity of the temperature of MBSL to the thermal conductivity of the dissolved gas. We have previously reported that cavitation temperatures as determined by metal atom MBSL from alcohol solutions of metal carbonyls range from 5100 K under Xe to 3800 K under He,[12] a much smaller range than is predicted by theory.[15] Recent experiments on silicone oil solutions reveal similar behavior. In both cases, while the observed emission temperature is not dramatically different under He than under Xe, the intensity of MBSL does increase almost 2 orders of magnitude.

These results are consistent with the expected effects of sonolysis: more of the energy of compression is consumed by bond dissociations under Xe than under He, thus giving greater MBSL intensity while diminishing the expected rise of temperature inside the bubble, as shown schematically in Figure 2. Such reactions convert larger molecules (e.g., octanol, poly(dimethylsiloxane)) into many small gas molecules (e.g., H_2, CH_4, C_2H_2, C_2H_4, CO_2, as previously shown for alkanes),[16] increasing the pressure within the bubble and hindering further compression and heating. We believe these effects combine to limit heating of the interior of the bubbles in MBSL, as shown in Figure 2: chemistry limits the final cavitation temperature in bubble fields.

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