Effect of Noble Gases on Sonoluminescence Temperatures during Multibubble Cavitation

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Sonoluminescence spectra were collected from Cr(CO)$_6$ solutions in octanol and dodecane saturated with various noble gases. The emission from excited-state metal atoms serves as an internal thermometer of cavitation. The intensity and temperature of sonoluminescence increases from He to Xe. The intensity of the underlying continuum, however, grows faster with increasing temperature than the line emission. Dissociation of solvent molecules within the bubble consumes a significant fraction of the energy generated by the collapsing bubble, which can limit the final temperature inside the bubble.

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Large oscillations of gas and vapor filled bubbles in liquids occur during acoustic cavitation [1,2]. This highly nonlinear bubble motion is accompanied by the emission of light—sonoluminescence (SL). Spectral analysis of SL from clouds of cavitating bubbles (multibubble sonoluminescence, MBSL) has shown that the implosive col-lapse of bubbles in argon saturated silicone oil creates local hot spots with extreme transient conditions: 5000 K and 500 atm [3,4]. The effective temperature decreases as the polytropic ratio of the bubble content decreases, consistent with compressional heating during cavitation [4]. We have now been able to measure directly for the first time the effect of the thermal conductivity of the bubble contents on the observed emission temperature of cavitation. We reach two conclusions: first, bubble collapse is not completely adiabatic, and second, the final temperature is significantly affected by chemical reactions occurring within the bubble.

MBSL intensity and sonochemical reaction rates are well known to be affected by the thermal conductivity of the dissolved gas in the liquid [5–9]. This has generally been attributed to a decrease in the effective maximum temperature reached in the collapsing bubbles due to increased thermal transport from the heated gas to the cold surrounding liquid [7,10]. It has been widely accepted that cavitation bubbles filled with helium should be cooler than those filled with xenon, but to date there has been no direct experimental evidence for this.

We have collected MBSL spectra from solutions of volatile metal carbonyls in different solvents saturated with various noble gases in order to definitively probe the effect of thermal conductivity on the temperature reached within a cavitating bubble. The observed emission is from excited state metal atoms and serves as an accurate spectroscopic thermometer for the cavitation event [4].

We have found that both the intensity and temperature of MBSL increase as the atomic weight of the noble gas increases, from He through Xe. This is consistent with the thermal conductivity of the bubble contents during collapse, which decreases roughly thirtyfold from He to Xe.

MBSL spectra were collected [11] from dodecane and octanol solutions of chromium hexacarbonyl, Cr(CO)$_6$. The use of long-chain hydrocarbons or alcohols gives high MBSL intensity due to their low volatility; in addition, these solvents have well-measured physical properties (e.g., vapor pressure, gas solubilities, etc.), which are often not available for the previously used silicone oils [3,12]. The experimental apparatus is shown in Fig. 1. Details of synthetic spectra calculations and the determination of metal emission temperatures are described elsewhere [4]. Briefly, synthetic spectra are generated using the well-understood theory of atomic emission [13]. This technique has been well established for flame and plasma diagnostics [14,15], and it is proving to be a versatile method of determining the effective temperature of cavitation bubble collapse under a variety of experimental conditions.

The normalized Cr spectra from octanol solutions at 285 K are shown in Fig. 2. Analogous spectra from dodecane solutions at 298 K are shown in Fig. 3. Two observations are immediately apparent. First, the ratio of the intensities of the two triplets at 360 nm and 430 nm, and thus the temperature of Cr emission [4], decreases monotonically as the thermal conductivity of the dissolved gas increases. The observed temperatures of Cr emission ($T_{em}$) range...
from 5100 K for Xe to 3800 K for He in octanol solutions (Fig. 2) and from 3800 K for Xe to 2600 K for He in dodecane (Fig. 3). Second, this range is significantly less than that predicted by previous theoretical models. For example, Young calculated that the ratio of hot spot temperatures for He vs Xe to be 2.4 [7], whereas we observe a ratio of only 1.3.

As the bubble collapses, the potential energy of the liquid surrounding the bubble is transformed both into the kinetic energy of the moving liquid and into the internal energy of the bubble contents. The initial stage of the bubble compression is relatively slow and isothermal, and the energy deposited in the bubble interior is readily transferred to the surrounding liquid via thermal conduction. As the speed of collapse increases, however, the rate at which energy is deposited in the bubble exceeds the rate at which it can be transferred to the surrounding liquid. The interior of the bubble undergoes compressional heating and, if the compression is rapid enough, the bubble collapse becomes increasingly adiabatic. The extent of adiabaticity will depend on the thermal conductivity of the gas/vapor mixture within the bubble. Bubbles containing gases with low thermal conductivities (e.g., Xe) will be more adiabatic than those with gases that have high thermal conductivities (e.g., He). The amount of the bubble’s potential energy that can be converted into internal energy, and, consequently, the temperature inside the bubble, should be largest for Xe and smallest for He, as observed.

Some of the energy deposited in the bubble will also be consumed by chemical reactions within the bubble. The internal energy of the collapsing bubble consists of the thermal energy of molecules within the bubble. This includes translational, rotational, vibrational, and electronic energy, and each of these degrees of freedom absorbs energy during the bubble collapse. At the temperatures reported here, however, the internal energy must also include the energy of bond dissociation. Solvent and solute molecules undergo sonolysis to give atoms and radicals in the ground and excited states:

\[
\text{Cr(CO)}_6 \rightarrow \text{Cr(CO)}_{6-n} + n\text{CO} \rightarrow \text{Cr} + 6\text{CO} \rightarrow \text{Cr}^+, \quad (1)
\]

\[
\text{C}_n\text{H}_{2n+2} \rightarrow z\text{C}_x\text{H}_y + C_2^* + \ldots . \quad (2)
\]

The scheme of chemical reactions that occur under extreme conditions relevant to cavitation is quite complicated. Alkanes, for example, give rise to dozens of products during sonolysis, including \( \text{H}_2 \) and \( \text{C}_2\text{H}_2 \), as well as a variety of terminal alkenes [8]; the presence of \( \text{C}_2^* \) and \( \text{CH}^+ \) emission in these systems (not shown here; see, for example, [12,16,17]) is further proof that C—C and C—H bonds are being broken. The complexity of high
The mechanism of Cr/H₂O₈₄₉ vapor pressure of 0.13 torr (i.e., solution temperature 3600 K under Ar and 3000 K under He, while at solvent temperature 376 K [21]), the emission temperature under Ar is 4300 K in octanol, but only 3600 K in dodecane; under He, it is 3800 K in octanol, but only 3000 K in dodecane.

As the temperature within the bubble increases, the MBSL intensity should increase for all emitting species. The rates at which the intensity of each feature increases, however, will not be identical, due to the difference in energies required to form each emitting species. The Cr—CO bond is much weaker than C—C and C—H bonds: 1.6 eV compared to 3.1 and 4.3 eV, respectively. The rates of bond dissociation will approximately follow Arrhenius behavior, \( k_{um} \sim e^{-U/kT} \), where \( k_{um} \) is the unimolecular rate constant and \( U \) is roughly the bond dissociation energy. As the temperature is increased, therefore, the rate of solvent sonolysis and the formation of small molecules will increase relative to the rate at which free atomic Cr is formed. The intensity of the continuum would thus be expected to increase relative to that of atomic emission as the temperature increases.

This is in fact the case, as is shown in Fig. 4. The rate of solvent sonolysis, and the consequent production of the multiple molecular emitters that contribute to the continuum, increase substantially as the temperature inside the bubble increases. This will consume a greater amount of energy in the hotter bubbles than in the cooler bubbles, and will serve to mitigate the increase in temperature as the thermal conductivity of the bubble contents is decreased in going from He to Xe. We believe this is the reason for the temperature chemistry in determining the conditions within the bubble.

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It is generally observed that solvent vapor pressure has a substantial effect on both sonoluminescence and sonochromeity [20]. In this work, we also find vapor pressure to have influence on the measured emission temperature. For example, the temperature of Cr emission decreases as the bulk solution temperature (and vapor pressure) of dodecane increases. At a solvent vapor pressure of 0.02 torr (i.e., solution temperature 276 K [21]), \( T_{em} \) is 3600 K under Ar and 3000 K under He, while at solvent vapor pressure of 0.13 torr (i.e., solution temperature 298 K), \( T_{em} \) is 3200 K under Ar and 2600 K under He.

As the vapor pressure of the solvent increases, the increased polyatomic content of the bubble decreases the adiabatic index (\( y = C_p/C_v \), the ratio of heat capacities), lowering the temperature rise during compression. The additional vapor molecules may also consume larger amounts of the compressional energy by dissociation and other endothermic reactions, further reducing the final temperature. Furthermore, any temperature gradient between the bubble wall and its center will also create a chemical species gradient.

The effect of vapor pressure, however, is complex and solvent dependent. Surprisingly, the measured emission temperatures at identical vapor pressures are higher in octanol than in dodecane. At 0.02 torr (285 K for octanol, 276 K for dodecane), the emission temperature under Ar is 4300 K in octanol, but only 3600 K in dodecane; under He, it is 3800 K in octanol, but only 3000 K in dodecane.

There are two possible explanations for this observation. First, the endothermic chemical reactions that the solvent vapor undergo will not be the same for these two solvents and would not consume the same quantity of energy liberated during bubble collapse. Second, the effective vapor pressures of the two solvents may not, in fact, be identical during bubble collapse.

For identical vapor pressures inside the bubble, the amount of energy expended in their chemical reactions during cavitation may be smaller for octanol than for dodecane. We know that extensive bond breakage occurs during sonolysis [8]. Consider the limiting case of complete atomization of the solvent vapors within the bubble. Octanol has fewer bonds to break than dodecane (26 vs 37). Consequently, from the total of the bond dissociation
energies, complete atomization would require roughly 10.7 MJ/mol for octanol vs 15.3 MJ/mol for dodecane. In comparison, the amount of energy necessary to heat these molecules intact to 5000 K is almost an order of magnitude less. Thus, one may expect that a smaller amount of the energy generated by bubble compression...