Multibubble sonoluminescence (MBSL) spectra were collected from solutions containing volatile metal-containing compounds in silicone oil saturated with helium or argon. Ultrasonic irradiation of these solutions at 20 kHz and 90 W/cm² led to emission from excited states of the free metal atoms. The widths and peak positions of these lines varied as a function of the gas used to saturate the solution, indicating that the emission was from the gas phase of the bubble. High-resolution MBSL spectra showed that the pressure within the bubble at the point of emission was on the order of 300 bar in argon-saturated silicone oil, which is consistent with simple adiabatic compression during cavitation.

Results and Discussion

These studies rely on the change in MBSL metal-atom emission line profiles as a function of gas density within the bubble (i.e., the fwhm and the peak position). The broadening and shifting of spectral lines have been extensively discussed in the literature and result from the perturbation of the atomic...
The MBSL spectra of 2.5 mM Cr(CO)\textsubscript{6} in silicone oil saturated with helium and argon. Both spectra were collected with a slit width of 20 μm.

Figure 1. MBSL spectra of 2.5 mM Mo(CO)\textsubscript{6} in silicone oil saturated with helium and argon. Background continuum has been subtracted from MBSL spectra for clarity. Both spectra were collected with a slit width of 20 μm.

Figure 2. MBSL spectra of 2.5 mM Mo(CO)\textsubscript{6} in silicone oil saturated with helium and argon. Background continuum has been subtracted from MBSL spectra for clarity. Both spectra were collected with a slit width of 20 μm.

electronic energy levels by the surrounding gas. Lines are typically red-shifted and broadened by polarizable atoms such as Ar, as well as being blue-shifted and more substantially broadened by hard, less-polarizable atoms such as He. For quantitative evaluations, we will make particular comparisons later to data collected from ballistic compressors, in which atomic emission occurs under high-temperature and pressure conditions that approximate those within a cavitation bubble.

The MBSL spectra of Cr(CO)\textsubscript{6} in silicone oil saturated with helium and argon are shown in Figure 1. Both spectra were collected using a slit width of 20 μm. Each line under a helium atmosphere is broader (fwhm = 1.0 nm) and located at a higher energy than its counterpart under an argon atmosphere (fwhm = 0.5 nm). For comparison, the Cr hollow cathode lamp spectrum was characterized by a fwhm value of 0.1 nm. As discussed later, the lineshifts of Cr emission are consistent with literature reports on ballistic compressor studies. There are, however, no data in the literature describing the linewidth of Cr emission under conditions approximating those within a cavitation bubble. The emission under a helium atmosphere is clearly different than that observed under an argon atmosphere, which is also consistent with the behavior observed for other metals in ballistic compressors. The MBSL spectra of Mo(CO)\textsubscript{6} in silicone oil saturated with helium and argon are shown in Figure 2. Again, each line under a helium atmosphere is both broadened and blue-shifted, relative to its line profile under an argon atmosphere.

Similar results were observed in the MBSL spectra arising from the ultrasonic irradiation of Mn(C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3})(CO)\textsubscript{3} and Fe(CO)\textsubscript{5} under argon and helium atmospheres: all metal-atom MBSL lines were substantially broader than those emitted by the corresponding hollow cathode lamp. Furthermore, the lines under a helium atmosphere were blue-shifted and further broadened, relative to their behavior under an argon atmosphere. This has been documented for both metals in ballistic compressor studies. MBSL spectra were also obtained from the sonication of TiCl\textsubscript{4} and W(CO)\textsubscript{6} in argon-saturated silicon oil (the emission was too weak to obtain high-resolution spectra under a helium atmosphere). These spectra contained atomic emission lines from Ti and W, respectively, and, in both cases, the lines were broadened, relative to the corresponding lines from a hollow cathode lamp. All data are consistent with emission from a high-pressure noble gas environment: MBSL originates from the gas phase of the bubble.

These data refute the recent interpretation of MBSL as a “manifestation of the cooperative dynamical phase transition effect.” Kuhn et al. attributed the asymmetry of the Na lines in the MBSL spectra arising from the ultrasonic irradiation of argon-saturated aqueous NaCl solutions to the Rayleigh wing effect in nonequilibrium light emission, and they viewed the surrounding liquid as a gain medium. The asymmetry they observed was, in fact, well documented in emission from high-pressure gas environments almost fifty years ago and reflects the density of that environment rather than any special cooperativity or nonequilibrium emission.

The bubble contains not only noble gas, but also solvent vapor, the metal-atom precursor, and the sonolysis products of both of these components. The MBSL spectrum from neat silicon oil, for example, contains molecular features attributable to C\textsubscript{2}, CH, and atomic emission from silicon. The production of these species from silicone oil will lead to an increase in pressure within the bubble, as will the generation of CO from the destruction of the metal carbonyls. Each of these species could hypothetically perturb the profiles of the metal-atom lines.

Further experiments were conducted over a range of metal carbonyl concentrations to determine if resonance broadening by other metal atoms were operative or if collisions broadening from species other than helium or argon were important. The resulting line profiles were invariant of the metal carbonyl (and, hence, the metal atom) concentration, indicating that this was not the case. It is furthermore unlikely that the emission is greatly perturbed by the products of silicone oil sonolysis, or by CO that dissociates from the metal carbonyls during the bubble collapse. The sonolysis products should be the same under helium and argon atmospheres, although there may be some differences in their concentrations. If the sonolysis products or the volatile precursors were the dominant collisional partners for the excited-state metal atoms, the resulting linewidths and lineshifts would be similar under helium and argon atmospheres, which is clearly not the case. We are of the opinion, therefore, that the major factor influencing the line profile of the metal-atom emission is the high-density noble gas atmosphere within the bubble.

The MBSL spectra reported here are compared to spectra from hollow cathode lamps that have been collected under identical spectrograph parameters, and the lineforms of these
metal-atoms emission spectra are taken to represent the natural linewidth and peak positions of the respective atomic lines. This is not rigorously true, because the spectra recorded by the diode array detector will also be dependent on the slit function of the spectrograph. The slit function, however, can be treated as a minor perturbation, relative to the linewidths observed in MBSL. Scattering from the bubble cloud more seriously broadens the emitted MBSL lines. To measure the effects of light scattering by the cavitation field, a different cell design was used. A glass tube with a distance of 2 cm between the end of the tube and the horn was placed at an orientation of 90° in front of the slit of the spectrograph, such that the slit was aligned 1 cm from the horn surface. The extent of broadening due to scattering was then estimated by placing a hollow cathode lamp opposite the spectrograph slit, so that its light passed through a cavitation cloud in neat silicone before entering the spectrograph.

Apparent broadening from the slit function and light scattering was not negligible, although it accounted for less than half of the observed MBSL linewidths. Such apparent broadening is sufficient, however, to make detailed analysis of the MBSL linewidths problematic. This is particularly true, given the fact that MBSL occurs from within a volume rather than from a surface, and each photon will experience a different degree of scattering. As will be discussed below, the MBSL linewidths do indeed reflect the high-pressure environment within the cavitation bubble; they cannot, however, be used to determine the pressure within the bubble with much accuracy.

It has been well documented that the positions of lines emitted by metal atoms in a noble gas atmosphere are sensitive to the density of the gas. This behavior is well understood for the alkali metals, and theory has advanced to the point of being reasonably rigorous for these systems at low pressures. Such is not the case for the transition metals, however, and the shift and width of a given line cannot yet be used to determine a priori the density of the surrounding noble gas. Rather, the pressure during emission is best determined by comparing MBSL spectra with spectra of the same metal collected under similar conditions:


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Chromium is the only metal that meets these criteria, and, as such, it was studied in further detail. The red shift of the lines constituting the Cr triplet at 27 800 cm\(^{-1}\) lines, as a function of the relative density of argon, is shown in Figure 3 (similar data for the triplet at 23 300 cm\(^{-1}\) are also available). These data represent ballistic pressure measurements conducted at 3300 K and serve as the reference data against which our MBSL spectra will be compared.

![Figure 3](image.png)

**Figure 3.** Frequency shift of Cr atom emission lines from ballistic compression data at 3300 K.\(^{15}\)

The spectra of chromium MBSL collected in the second order of the 1200 groove/mm grating, along with those from a hollow cathode lamp collected using the same experimental configuration, are shown in Figure 4. The MBSL resulted from the ultrasonic irradiation of a 2.5 mM solution of Cr(CO)\(_6\) in silicone oil saturated with argon (MBSL under a helium atmosphere was too weak to be observed in the second order of the grating; thus, no quantitative pressure estimates can be made under a helium atmosphere).

The lineshapes observed in Figure 4 were compared to the published ballistic compression data,\(^{15}\) which are reported in terms of argon density, relative to that at 298 K and 1 atm. The MBSL pressure was determined by scaling from ambient temperature using the ideal gas law to the known temperature of chromium MBSL in silicone oil saturated with argon (4700 K).\(^{7}\) Use of the ideal gas law could have been problematic if the cavitation pressures had proved to be extreme. As shown in Table 1, the experimentally observed MBSL lineshapes and the corresponding relative densities and pressures are not so high as to require a more sophisticated equation of state.

As shown in Figure 4, the frequency shifts are well defined for five of the six Cr emission lines. These yield a relative density of 19 (standard deviation of ±2) and a pressure of 300...
± 30 bar. (The Cr line at 23 499 cm\(^{-1}\) was less well defined; after fitting to a Lorentzian curve, the resulting peak position corresponded to a relative density of 20, which is consistent with the other data.) It should be noted, however, that the reference ballistic compressor data were collected at 3300 K, and the authors reported that the lineshift decreased as the temperature increased. The values reported here, therefore, should be taken as the minimum pressure of argon within the bubble, and the actual pressure is likely somewhat higher.

The experimentally measured pressure is comparable to that predicted from adiabatic compression. If the collapse of the bubble is purely adiabatic, a gas with a polytropic ratio \(\gamma (\gamma = C_p/C_v)\) that is compressed from an initial radius \(R_i\) to a final radius \(R_f\) will be heated from an initial temperature \(T_i\) to a final temperature \(T_f\) and pressure \(P_f\), according to eqs 1 and 2:

\[
T_f = T_i \left( \frac{R_i}{R_f} \right)^{(\gamma - 1)}
\]

\[
P_f = P_i \left( \frac{R_i}{R_f} \right)^\gamma
\]

The Cr atom emission temperature during MBSL is 4700 K under an argon atmosphere, which has a constant polytropic ratio of \(\gamma = 1.67\). If \(T_i\) and \(P_i\) are assumed to have values of 298 K and 1 atm, respectively, the corresponding compression ratio, \(R_f/R_i\), is 3.95. This, in turn, implies a final pressure, according to eq 2, of \(\sim 1000\) atm. As a bubble collapses, it is generally agreed that the transition from slow, isothermal compression to fast, adiabatic compression occurs relatively late in the cycle, at pressures below ambient (i.e., \(P_i < 1\) atm), which would decrease the calculated final pressure. Equations 1 and 2 are obviously oversimplifications of the very complex events that occur during cavitation. Nonetheless, the experimental results are in reasonable agreement, even with the very simple model of adiabatic compression during bubble collapse.

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**References and Notes**


