

Sonoluminescence as a Probe of Acoustic Cavitation

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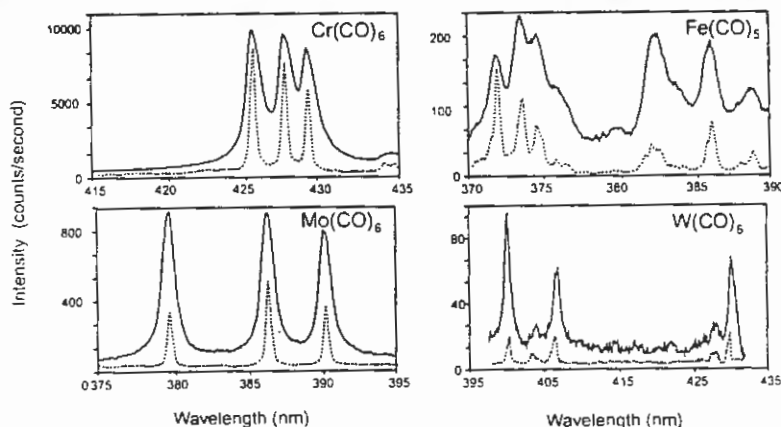
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Sonoluminescence, the light emitted when a liquid is irradiated with ultrasound, was first observed from aqueous systems in 1934 [1] and from non-aqueous systems in 1936 [2]. Sonoluminescence and sonochemistry result from a process known as acoustic cavitation: the formation, growth and implosive collapse of bubbles in an acoustic field. Because of the transient nature of cavitation, it has been difficult to experimentally determine conditions created within the collapsing bubble. In 1991, Flint and Suslick [3] reported the first direct determination of the temperature of the cavitation event. The temperature of excited-state C_2 emission was determined from sonoluminescence spectra of silicone oil to be approximately 5000 K. The work presented here represents the use of sonoluminescence from metal carbonyls to determine the pressure of the cavitation event.

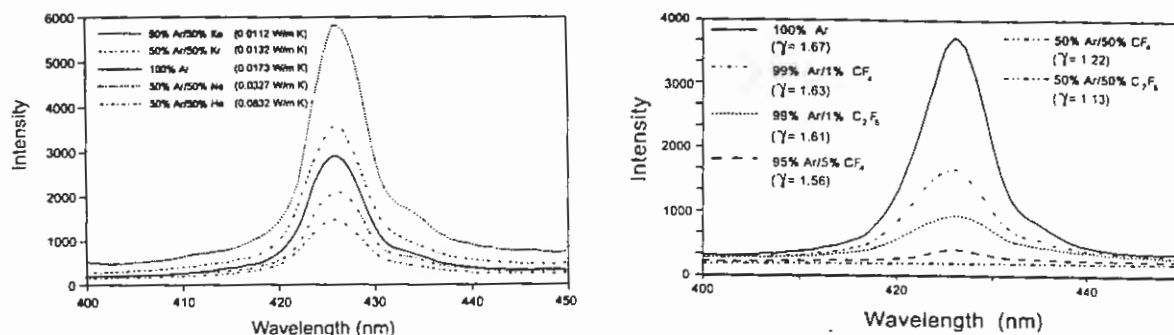
The sonochemical reactions associated with the ultrasonic irradiation of metal carbonyl solutions are quite diverse and include ligand loss to form amorphous metals [4,5], metal-metal bond formation [6,7], and ligand substitution [8,9]. Since the metal carbonyls are volatile compounds and exhibit substantial sonochemical activity, sonoluminescence from metal carbonyls was studied to determine the feasibility of the carbonyls as probes of the cavitation event.

Sonoluminescence is observed during ultrasonic irradiation of chromium, iron, molybdenum, and tungsten carbonyl solutions as shown in Figure 1 [10]. The observed spectral lines correspond to atomic emission from the bare metal center [11], and it is possible to distinguish the individual metal atomic emission lines. For comparison, atomic emission spectra from the corresponding metal hollow cathode lamps are shown as dotted lines in Figure 1.

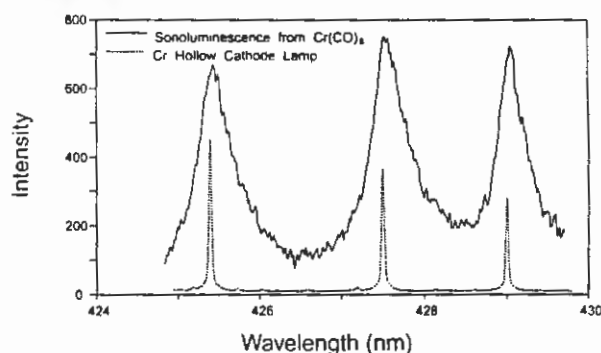


There are two gas properties which appear to have a strong effect on the cavitation temperature and intensity of sonoluminescence: Thermal conductivity and the polytropic constant, $\gamma (C_p/C_v)$. Since all the noble gases have a γ value of 1.67, the intensity of sonoluminescence from silicone oil solutions of $Cr(CO)_6$ under mixtures of noble gases was studied. As predicted by thermal mechanisms of sonoluminescence, the intensity of excited-state chromium emission decreases with increasing thermal conductivity of the noble gas as shown in Figure 2 [12]. This result is in good agreement with the results from previous sonoluminescence studies [13,14].

Polyatomic gases such as CF_4 and C_2F_6 have much lower γ values than the noble gases. As shown in Figure 3, the intensity of sonoluminescence from silicone oil solutions of $\text{Cr}(\text{CO})_6$ was found to decrease with decreasing γ value [12]. When a gas is compressed during bubble collapse, the heat produced is partitioned across all the degrees of freedom of the gas, and heating is lost through partitioning into vibrational and rotational modes. This loss of energy leads to lower cavitation temperatures and lower sonoluminescence intensity, as observed in this study.



Because sonoluminescence from $\text{Cr}(\text{CO})_6$ gives the highest intensity observed to date, $\text{Cr}(\text{CO})_6$ was chosen for high resolution studies. As seen in Figure 4, the sonoluminescence linewidth from $\text{Cr}(\text{CO})_6$ is much broader than the linewidth from a typical gas-phase hollow cathode lamp spectrum [15]. The large linewidth of the metal emission is caused by the short excited-state lifetimes that result from collisional deactivation (i.e. Heisenberg pressure broadening). By using the Heisenberg Uncertainty Principle and the full width at half-maximum for the three chromium lines, the effective lifetime of the emitting species (Cr^*) before collisional deactivation was calculated to be 0.20 ± 0.02 pico-seconds.



If deactivation of excited-state chromium atoms occurs by collision with argon atoms, then local fluid densities following cavitation collapse can be calculated using the equation

$$N^{-1} = 2\pi\sigma_{12}^2[2\pi RT(m_1+m_2)/(m_1m_2)]^{1/2}$$

where N is the density, π is the lifetime, and σ_{12}^2 is the cross-section of the colliding atoms [16]. The temperature of the emitting species was taken to be 5000 K, as determined by spectral analysis of C_2 emission [3]. The local fluid density during chromium atom emission was calculated to be $0.15 \pm 0.01 \text{ g/cm}^3$.

From the lifetime and density it is possible, by using the Virial Equation of State, to calculate the effective pressure in the region of the emitting chromium atoms.

$$P = RT\rho/m [1 + B_T\rho/m + C_T\rho^2/m^2 + \dots]$$

For the Virial Equation of State, B_T and C_T are the virial coefficients as a function of temperature and ρ is the density. Using this equation, the effective pressure during sonoluminescence in the region of the excited-state chromium atoms was calculated to be 1700 ± 110 atmospheres. This result represents the first experimental determination of the pressure of the cavitation event.

References

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