Spectroscopic Studies of Sonoluminescence

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Sonoluminescence is the weak light emitted from liquids during ultrasonic irradiation. This phenomenon was first observed over 50 years ago from both aqueous solutions [1] and organic liquids [2], and has been reviewed recently [3,4]. An extensive study of sonoluminescence from aqueous systems was published by Sehgal and Verrall [5] in the early 1980's. The work presented here is the first systematic investigation of sonoluminescence from non-aqueous liquids.

Sonoluminescence is caused by acoustic cavitation: the formation, growth, and collapse of bubbles in an acoustic field. The rapid collapse of these bubbles causes near-adiabatic heating of the gaseous contents of the bubbles. Temperatures of 5200 ± 600 K have been determined for cavitational collapse by chemical rate thermometry [6]. The factors that influence the cavitational temperature include, among others, the solvent, vapor pressure, the thermal conductivity of the gas, the ratio of the heat capacities of the gas ($\gamma = C_p/C_v$), and the hydrostatic pressure.

Two detection systems were used in this work. A monochromator/PMT system with pulse-counting electronics was used for preliminary studies. A spectrograph equipped with an image-intensified diode array detector interfaced to a microcomputer was used for most of this work. The spectral response characteristics of the second system were determined by calibration with a standard lamp.

Sonoluminescence from non-aqueous liquids is characterized by emission from small molecules and free radicals [7,8]. Ultrasonic irradiation of alkanes, arenes, and silicone oil under Ar leads to sharp, banded emission from the diatomic molecules C_2 and CH, and a continuum emission assigned to

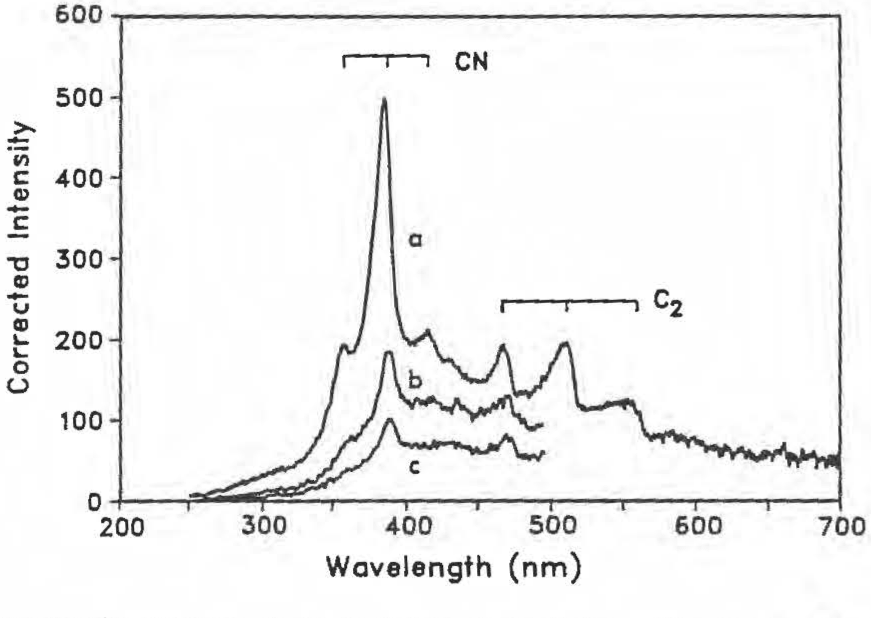

Figure 1: Sonoluminescence from systems containing nitrogen. **a**: Dodecane under 15% N_2/85% Ar. **b**: Ethylenediamine in dodecane under Ar. **c**: NH_3 in dodecane under Ar.

the triatomic C_2H. When a nitrogen source such as N_2, NH_3, or ethylenediamine is added, the distinctive emission bands of CN are produced, as shown in Figure 1. When oxygen is present, however, a continuum assigned to CO_2 emission is observed. Ultrasonic irradiation of halocarbons in the presence of Ar gives rise to emission assigned to Cl_2. The mechanism proposed for the formation of all of these species involves the gas-phase fragmentation of the solvent molecules by the high temperatures of the cavitation event. Subsequent reactions of these high-energy free radical, atomic, and molecular fragments produce the emitting species.

Sonoluminescence from Na^+ and K^+ in water was used by Sehgal and Verrall as a probe of the temperatures and pressures produced in the cavitation event [5a]. They measured the linewidth and wavelength shift of the emission lines and calculated the pressures and temperatures by comparison to other known systems. In an attempt to use this method to study the effects of various extrinsic parameters (vapor pressure, gas thermal conductivity) on cavitational temperature, a study of sonoluminescence spectra from alkali metal salts in primary alcohols was conducted [9]. The sonoluminescence intensity decreased in the expected fashion as the vapor pressure increased, which indicates that gas-phase sonochemical reactions are occurring. However, the linewidths and peak positions were independent of cavitational temperature. The two-phase model [6] of sonochemical reactivity was invoked to explain these results. Radicals and atoms that are formed in the high temperature cavitation event diffuse into a heated liquid shell surrounding the collapsed bubble. In this heated, initially liquid zone these high-energy species react with the alkali metal cations, reducing and exciting them.

The electronic spectra of diatomic molecules have been used to determine temperatures of flames and plasmas [10]. Since the resolution of our spectrograph was not sufficient to collect non-overlapped spectra, and the sonoluminescence intensity is too weak to use higher resolution instruments, synthetic spectra were calculated to model the experimental spectra. These synthetic spectra were calculated by determining the wavelength and intensity of all the relevant rotational lines for nine or ten vibrational transitions, and then calculating the effect of each of these lines on the spectrum as a whole [11]. The intensity of each rotational line was calculated with Equation 1, where I is the intensity, ν is the frequency of the transition, A is the Franck-Condon factor, S is the rotational transition probability, h is Planck's constant, c is the speed of light, k is Boltzmann's constant, G is the vibrational energy, F is the rotational energy, T_v is the vibrational temperature, and T_r is the rotational temperature. Spectra vary dramatically as a function of T_v and T_r.

$$I = \nu^4 \, A \, S \, \exp[(-hc/k)\{(G/T_v)+(F/T_r)\}] \qquad (1)$$

Sonoluminescence spectra from silicone oil under Ar were collected and corrected for spectrometer response, and the continuum was subtracted from the banded spectra. A comparison between experimental and synthetic spectra is given in Figure 2 for the $\Delta\nu = +1$ manifold of the Swan band ($d^3\pi_g$-$a^3\pi_u$) of C_2. The synthetic spectrum was calculated with $T_v = T_r = 4900$ K. The fit for the synthetic spectrum calculated for the $\Delta\nu = 0$ band with the same parameters is also quite good. The error in the calculated temperature is estimated to be ± 400 K.

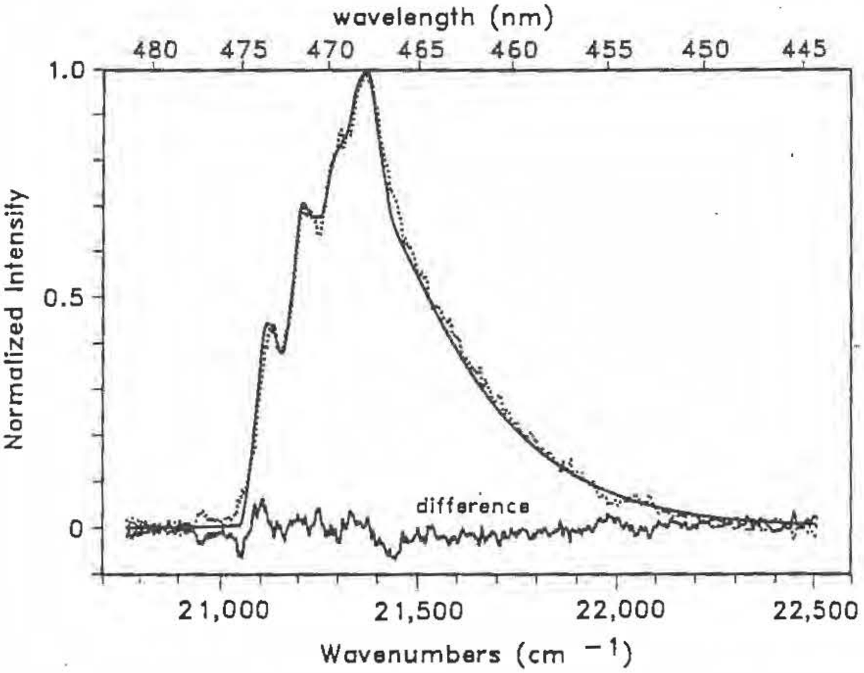

Figure 2: Comparison between sonoluminescence and synthetic spectra.

Sonoluminescence spectra from solutions of metal carbonyls were also collected. Atomic emission from Cr and Mo was seen during the ultrasonic irradiation of alkane solutions of $Cr(CO)_6$ and $Mo(CO)_6$, respectively. The compounds are decomposed and excited by the high temperature of the cavitation event. Low solvent vapor pressures favor this emission since they produce higher cavitational temperatures, and thus more complete ligand loss [12].

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