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LETTERS

Sonoluminescence from Single Bubbles in Nonaqueous Liquids: New Parameter Space for Sonochemistry

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The emission of light by a single pulsating bubble of xenon trapped in nonaqueous fluids has been observed. The intensity of sonoluminescence displays a remarkable structure as a function of the temperature and partial pressure of solution. At the light-emitting moment the bubble is so focused and stressed that Swan lines are absent from the spectrum of single bubble sonoluminescence in organic liquids.

We have observed the emission of a steady stream of repetitive flashes of light from a single bubble driven by sound in nonaqueous fluids. As shown in Figures 1 and 2, the intensity of sonoluminescence (SL) from a single bubble is a strong function of the fluid, the partial pressure at which gas is dissolved into the fluid, and the temperature.

Remarkably, the spectral density of the emitted light is independent of the chemical nature of the fluid and shows no evidence of lines due to molecular transitions. This observation is apparent from Figure 3, which shows the spectrum of SL from a single bubble of xenon trapped in *n*-dodecane and ethanol. Not only are these spectra similar, and in strong contrast with measurements of SL from homogeneous cavitation in organic liquids,[1] but also we find that the Swan lines due to transitions among excited states of C_2 are absent. This appears to imply that the densities and temperatures reached in single bubble experiments are much higher than the 5000 K sources generated with cell disrupters.[2]

The search for synchronous SL in nonaqueous fluids was sparked by the extraordinary properties it displays in water. These include flash widths less than 50 ps,[3] strongly ultraviolet spectra, sensitivity to temperature,[4] and noble gas doping.[5] Isolation of a single pulsating bubble[6] is essential to these investigations. By studying SL in new fluids, we hoped to learn about the means whereby diffuse acoustic energy is concentrated by at least 12 orders of magnitude and transduced into light.

Our first efforts with nonaqueous fluids were carried out with air bubbles which at best gave a very weak signal that could barely be seen above the noise. Since we hypothesized that gas solubility was a key experimental parameter, we tried to

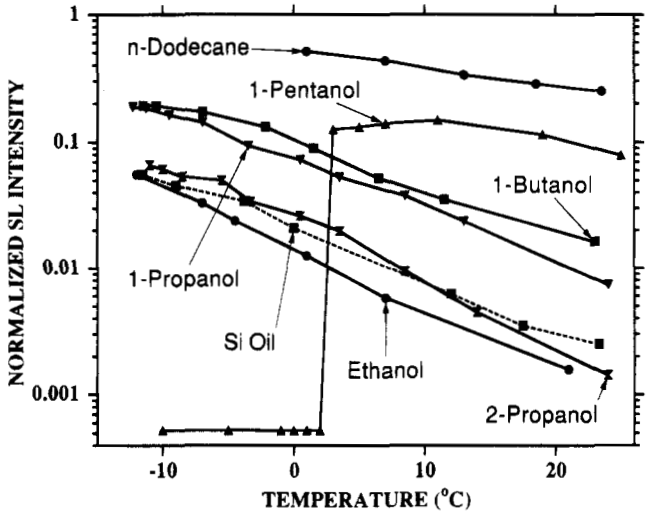

Figure 1. Intensity of sonoluminescence from a single xenon bubble trapped in various fluids as a function of temperature (normalized to 150 mmHg air in water at room temperature). The xenon is dissolved into the degassed liquid at a partial pressure of 150 mmHg at room temperature, and then the system is sealed. These are the largest signals that can be attained for 30 s or longer. The noise level recorded on the lock-in amplifier with sound on but in the absence of a light-emitting bubble is 10 μV (0.0005 when normalized as is data in the figure). For 1-pentanol below 1 °C, non-light-emitting bubbles can be sustained. By sweeping the drive level, a signal of 1−2 mV (0.05−0.1 normalized) can be attained for about 50 ms from this system. The signal for an air bubble in water at room temperature is 20 mV. Si oil is Dow Corning 200 fluid (1 cSt viscosity).

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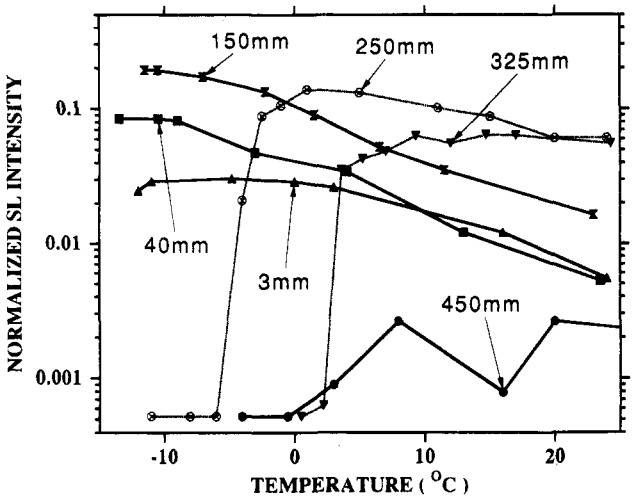

Figure 2. Intensity of SL (normalized as in Figure 1) for a single xenon bubble in 1-butanol as a function of partial pressure and temperature. For the 250 mm and 325 mmHg curves at cold temperatures, the same comments given for the 1-pentanol curve in Figure 1 apply.

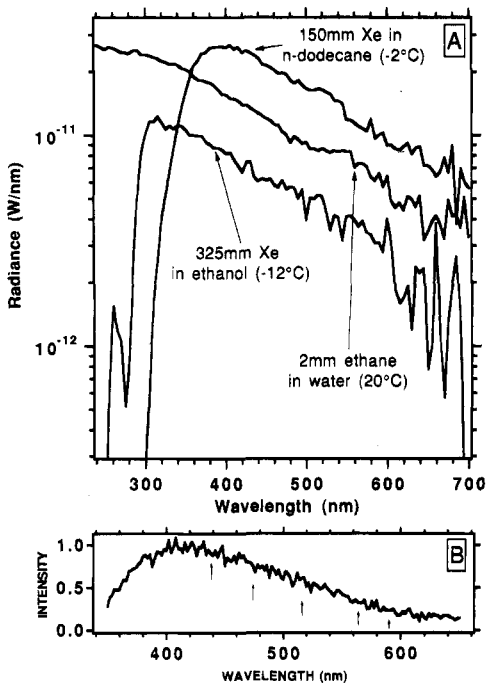

Figure 3. Spectra of light emitted by a single pulsating bubble of xenon in *n*-dodecane and ethanol. Data in (A) has resolution 10 nm fwhm. Shown in (B) is a higher resolution scan (3 nm fwhm) of 150 mmHg of xenon in *n*-dodecane at −2 °C. Arrows indicate the expected location of the Swan lines. To align the bubble with the axis of the spectrometer, this experiment was run at acoustic intensities *lower* than those used for acquiring Figure 1. The UV cutoffs are consistent with the various extinction coefficients. For comparison, the spectrum of ethane gas in water is shown in (A).[8,13]

achieve SL with mixtures of gas in nonaqueous fluids that had the same (low)[7] solubility as air in water. This meant using helium, which (like argon) displays no SL at room temperature for the liquids shown in Figure 1. Finally, we found that xenon in cold liquids appears to be the most propitious route to the effects reported. As compared to air in water though, these new systems are not entirely satisfactory. The bubbles tend to jitter spatially a few millimeters around the pressure antinode which traps them. Also, the phase of the light emission with respect to the sound field is typically spread over a few hundred

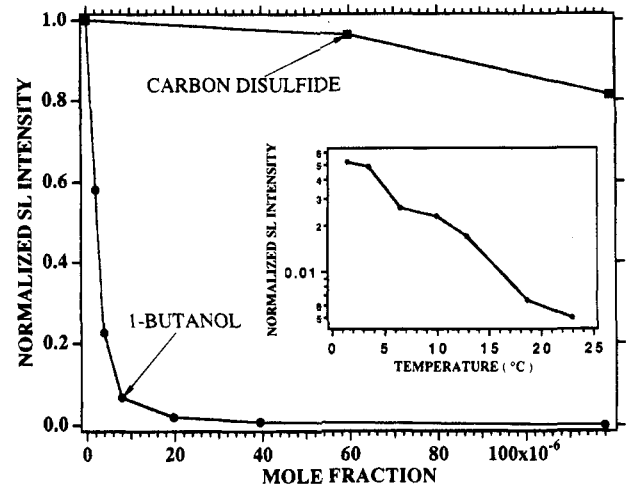

Figure 4. Normalized intensity of SL from an air bubble (150 mmHg) in water plus some impurity at room temperature. Any signal at 118 × 10^{-6} mole fraction of 1-butanol in water is less than the noise level of 10 μV. The signal for air in pure 1-butanol is 100 μV and for air in water is 20 mV. At 118 x 10^{-6} mole fraction of 1-butanol, by sweeping the drive SL can be seen for about 1 s at approximately 300 μV intensity. Adding water which was not degassed (at molar concentrations comparable to those in the figure) to water prepared with 150 mmHg air did not degrade the SL signal. The inset shows the temperature dependence of the 40 × 10^{-6} mole fraction 1-butanol in water system.

nanoseconds, in contrast with air in water which can display sound sync to SL flash synchronicity of a few nanoseconds and flash to flash synchronicity at the picosecond level.[3] Yet another difference with air bubbles in water is that the maximum drive at which bubbles in nonaqueous fluids emit light is not well defined. Increasing the drive causes these bubbles to change their location in the resonant sound field while maintaining about the same level of SL.[8] This tendency to walk away from the pressure antinode at increased drive is also observed in non-light-emitting helium bubbles in silicone oil, xenon bubbles in water at temperatures close to 0 °C, and air bubbles in water at static pressures less than 1 atm.

In view of the weak signal, the output of the photomultiplier tube was acquired with a lock-in amplifier referenced to the sound field frequency (24−28 kHz). Light emission becomes visible to the unaided (youthful) eye above 0.05 on the scale of Figures 1 and 2 (approximately 1.5 × 10^4 photons per flash). Experimental techniques for SL in a sealed system and spectra acquisition are described in refs 4, 5, and 9 with the additional comment that the acoustic resonators have a pressure release component which maintains the static pressure at 1 atm during the 35 deg temperature changes of these experiments while maintaining a sealed experimental environment.

These measurements develop a number of mysteries. Why does cooling the liquid generally increase the intensity of SL? Why does xenon give more intense SL than other gases? What physical process accounts for the precipitous change in signal such as occurs in 1-butanol with 250 mmHg of dissolved xenon at −5 °C? What accounts for the different SL signals emitted by "1" and "2" alcohols? Why does the addition of tiny amounts of alcohol (1-butanol) to water rapidly degrade the SL to a level that is lower by at least a factor of 10 from that which can be seen in the pure alcohol? These measurements of SL from water containing impurities (shown in Figure 4) were part of our initial effort to elucidate the difficulties attendant to attaining SL with air bubbles in nonaqueous fluids.

Sonochemistry and traditional sonoluminescence[10] have studied energy focusing mediated by transient clouds of

cavitating bubbles. Our measurements further suggest that SL from a single bubble may be a different physical phenomenon[11] involving greater degrees of stress possibly due to highly spherical bubble collapses.

Future experiments will study SL at temperatures near the freezing point of ethanol (−117 °C) [12] and attempt to stabilize the bubble through use of appropriate gas mixtures (e.g., 2% xenon + 98% nitrogen) so as to make possible dynamic measurements of bubble motion.

We have found that the pulsations of a trapped gas bubble provide an extremely stressed region for the study of fluids and chemical transport processes. Due to the fact that the solubility of air in water (0.127×10^{-4} mole fraction) and that of xenon in 1-butanol (101×10^{-4} mole fraction)[7] differ by a factor of 10^3, it now appears that gas solubility in liquids is not a key parameter of SL. In addition, the observation of SL in each of the pure liquids *n*-dodecane, water, and ethanol whose room temperature vapor pressures are 0.012, 20, and 55 mmHg, respectively, suggests SL is not sensitive to the vapor pressure of the liquid. In addition to the unknowns mentioned above, we would in conclusion raise the following question: why on the one hand is the integrated SL intensity so different for (say) *n*-dodecane and ethanol while on the other hand the spectra are so similar?

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