

REPORTS

Effect of Noble Gas Doping in Single-Bubble Sonoluminescence

Robert Hiller, Keith Weninger, Seth J. Putterman, Bradley P. Barber

The trillionfold concentration of sound energy by a trapped gas bubble, so as to emit picosecond flashes of ultraviolet light, is found to be extremely sensitive to doping with a noble gas. Increasing the noble gas content of a nitrogen bubble to about 1% dramatically stabilizes the bubble motion and increases the light emission by over an order of magnitude to a value that exceeds the sonoluminescence of either gas alone. The spectrum also strongly depends on the nature of the gas inside the bubble: Xenon yields a spectral peak at about 300 nanometers, whereas the helium spectrum is so strongly ultraviolet that its peak is obscured by the cutoff of water.

As the intensity of a standing sound wave in water is increased, the pulsations of a single trapped bubble of air display an abrupt transition (1) to a state where sound energy is concentrated by over 11 orders of magnitude and the bubble emits picosecond flashes (2) of ultraviolet (UV) light (3). Furthermore, the resonator can be tuned so that each cycle of sound creates one flash of light (4) with a clocklike regularity (2, 5). In addition to its potential use as a spherical UV light source, sonoluminescence is a laboratory paradigm for energy-focusing processes such as inertial confinement fusion. The bubble also creates conditions where matter is exposed to extreme temperatures and pressures, as well as huge quenching rates.

The origin of this phenomenon is very sensitive to the composition of the gas mixture in the pulsating bubble, especially the extent to which the bubble is doped with a noble gas (Fig. 1). For instance, the emission of light from a N₂ bubble is increased by about a factor of 30 as the Ar doping is increased to just 1%. This percentage (which is its natural concentration in air) maximizes the sonoluminescence (SL). The intensity of SL is also a strong function of the pressure at which the gas mixture is dissolved into the water (Fig. 2). As saturation is approached, SL from the doped bubble goes to zero and drops well below the SL signal generated by a pure Ar bubble.

The noble gas content of the bubble also has a dramatic effect on the spectral density of the emitted light. A bubble composed of 98% N₂ and 2% Xe has a broad spectral maximum at 280 nm (Fig. 3), whereas the spectrum of a bubble containing 99% N₂ and 1% Ar increases right up to the cutoff imposed by water at around 200 nm (6 eV). Use of He shifts the spectrum even more

strongly into the UV. In the limit where the bubble is pure He, the spectrum increases as $1/\lambda^{2.5}$ (where λ is the wavelength of light).

These experiments were conceived to exploit and explore the extreme sensitivity of SL to changes in control parameters. For instance, a lowering of the water temperature from 35° to 1°C increases the emission by a factor of over 100 (1). To further probe the energy-concentrating mechanism responsible for SL, we sought to change parameters such as the host liquid and the bubble gas. In nonaqueous fluids, we have been able to trap (non-light emitting) air bubbles with sound, but at high drive levels, these systems have resisted our attempts to observe the transition to SL. We propose that this difficulty is related to the unusually low solubility of gases in water (6), or

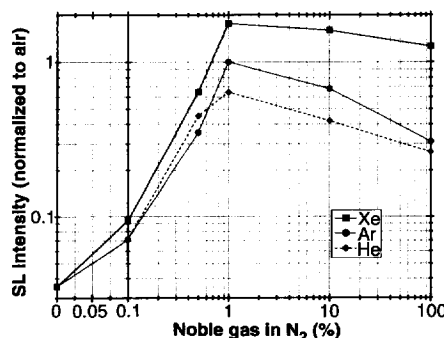


Fig. 1. Intensity of light emission from a sonoluminescing bubble in water as a function of the percentage (mole fraction) of noble gas mixed with N₂. The gas mixture was dissolved into the water at a pressure head of 150 mmHg. The data are normalized to the light emission of an air bubble in 24°C purified water with a resistance greater than 5 megohm-cm dissolved under a pressure head of 150 mmHg in a sound field running at 25 kHz. Such a bubble emits about 2×10^5 photons per flash, which we refer to as a standard unit of SL. Ambient pressure is 1 atm. The data for Figs. 1 and 2 were acquired in a resonator with acrylic walls, which passes light wavelengths longer than 380 nm.

equivalently to the fact that air is far more soluble in nonaqueous fluids such as alcohol and silicon oil. From this perspective, the observation of SL in liquids other than water would require the use of gases (such as H₂ and He) that are much less soluble than air. Thus, an extension of the phenomenon of single-bubble SL to new materials, either fluid or gas, necessitates the use of gases other than air. This report describes results on SL from various gas bubbles in water.

Previous experiments with air were greatly simplified by the presence of a free surface through which water was poured and a seed bubble could be introduced. Because air will dissolve into water through a free surface and then find its way to the bubble, measurements of SL with nonair gas mixtures require the seeding of a bubble into an airtight acoustic resonator. Elimination of the free surface also prevents the concentration of gas in the water from changing with time. Sealed cylindrical cells with quartz (or acrylic) side walls and brass end caps provided the best combination of acoustic properties, optical properties, and ease of fabrication. The quartz cell was used for the spectral measurements because of its transparency to UV light. Because the wavelength of sound is much larger than the radius of the bubble, the stress exerted on the bubble is spherically uniform over its surface regardless of the shape of the resonator. Thus, the use of a cylindrical rather than spherical resonator (1-3) still produces a spherical bubble collapse. Furthermore, the sound field positions the bubble at the

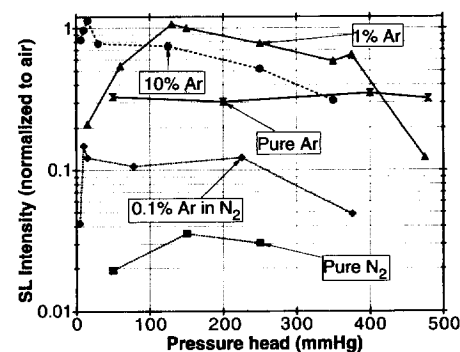


Fig. 2. Intensity of SL from a N₂ bubble doped with Ar as a function of the degree of saturation of the gas mixture in water. Ambient pressure is 1 atm, ambient temperature is 24°C, and the sound frequency is 24 kHz. The peaks near 10 mmHg are reproducible, and at this pressure for the 0.1% solution, the intensity of light goes down as the sound field is increased. In all cases, the light emission corresponds to the highest stable (duration >60 s) value that we could resolve. As saturation is approached, SL from a doped bubble decreases significantly. Thus, the observation of light emission from a single bubble requires the use of degassed water (4), in contrast with light emission from clouds of transient bubbles, which can appear in a cavitating saturated solution (18).

Physics Department, University of California, Los Angeles, CA 90024, USA.

location that maximizes the imposed spherical stress (the velocity node).

Water and gas preparation were done outside the resonator in a mixing chamber. First we removed the air from the water by degassing it under a vacuum while stirring (7). Next the desired gas was dissolved into the water while the partial pressure above the liquid was monitored, correcting for the vapor pressure of water. The mixture was transferred without contamination to the cell through a filling tube. A second filling tube was then used to pressure-release the sealed resonator to a static pressure of 1 atm. Quoted pressures and percentages in Figs. 1 and 2 refer to the properties of the gas mixture that was stirred into the water. We have been unable to assay the contents of the SL bubble, but a comparison of the low-amplitude (non-light emitting) bubble dynamics to the equation of mass diffusion indicated that the partial pressure of the dissolved gas matched the partial pressure above the liquid in the mixing chamber (8).

Seeding a bubble into the sealed cell can be achieved by passing a current pulse through toaster wire (NiCr) mounted inside

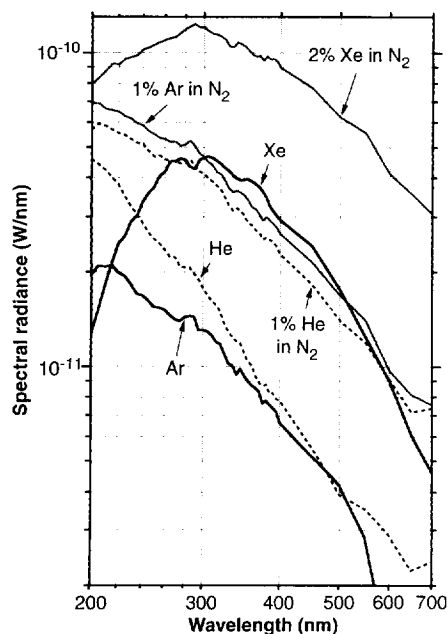


Fig. 3. Spectrum of SL from a single bubble for various gas mixtures dissolved into the water at a pressure head of 150 mmHg in a 33-kHz sound field at 24°C. Although the He bubble is over 10 times dimmer than the 2% Xe bubble, the He bubble has a much larger UV spectral density. Note (i) the similarity between the spectrum of Ar and that of N₂ doped with Ar and (ii) the difference between the spectrum of He and that of N₂ doped with He. The data have been corrected for the absorption of water and quartz and for the voltage dependence of the quantum efficiency of the photodetector. Inclusion of these corrections leads to small quantitative improvements over our previously published results (3).

the resonator. The vaporous cavities that form as a result of boiling near the wire quickly fill with whatever gas mixture has been dissolved into the liquid. The radiation pressure of the sound field then moves the gas bubbles to the nearest velocity node where they coalesce, and SL from a single bubble can be observed. The SL can be stabilized by phase-locking the microphone signal to a voltage-controlled oscillator used as the drive (9). Alternatively, the acoustic mode can be used as the oscillator: The microphone signal is amplified and sent to the driver with the appropriate phase to maintain the oscillation (10). The acoustic driver and microphone (piezoelectric ceramic transducers), the NiCr wire, a thermocouple for measuring liquid temperature, and the two filling tubes were all fed through the brass end caps of the resonator with little detriment to the sound field.

Because air is 80% N₂, the first experiment done with this technique studied the properties of a bubble composed solely of N₂ (99.7% pure). The light intensity from such a bubble as well as an O₂ bubble or a bubble containing a 4:1 mixture of N₂ and O₂ was down by over a factor of 20 compared to that from an air bubble. Subsequent experiments revealed the important effects of noble gas doping (Figs. 1 through 3).

An essential aspect of prospective theories of SL is that they provide a unifying explanation of why this phenomenon is universally sensitive to changes in controllable parameters. The key could be the electronic degrees of freedom that account for the radiation. The Penning effect (11, 12) provides an example of an electrical property (in this case, the breakdown voltage) that is sensitive to minute noble gas impurities. One can also speculate that the origin of the sensitivity could be the result of some process whereby energy is transferred to

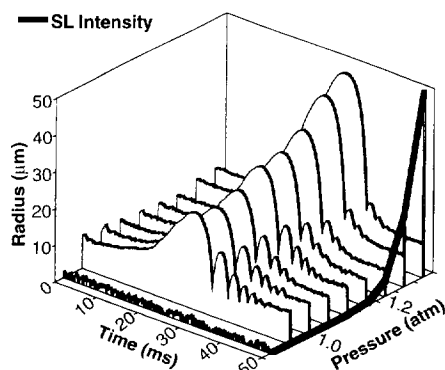


Fig. 4. Radius versus time curves for a pure Ar bubble in water (with Ar dissolved at 150 mmHg) as a function of increasing drive level for one cycle of the sound field. The ramp (labeled SL intensity) indicates the relative level of light emission. For a pure noble gas bubble, there is a smooth transition to the SL state.

electronic degrees of freedom from the hydrodynamic motion. The sensitivity may also stem from processes fully contained in the hydrodynamics of bubble motion. An imploding shock wave provides an example of a hydrodynamic state with prodigious ability to concentrate the initial energy.

According to the strong shock wave theory of SL (13–15), the supersonic collapse (16) of a bubble launches an imploding spherical shock wave whose strength increases to infinity as it focuses down to zero radius (17). In this model, the amount of focused energy that is available for transduction into light is strongly dependent on bubble parameters such as the ambient radius R_0 and the maximum radius R_m (1). This raises the possibility that the sensitivity of SL to doping with a noble gas could be due to the small changes that an impurity induces in bubble size.

In this vein, a previously developed light scattering technique (16) has been used to obtain radius-time curves for the various bubbles. In Fig. 4 is shown the time dependence of the radius of an Ar bubble as a function of increasing drive level. According to this figure (as well as

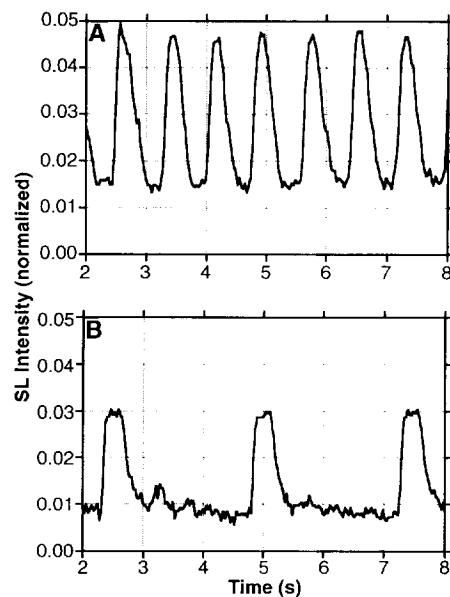


Fig. 5. Time dependence of SL from a pure N₂ bubble in water (with N₂ dissolved at 150 mmHg): (A) low drive, (B) high drive. The SL intensity has been normalized to the emission of an air bubble at the standard parameters delineated in Fig. 1. Uncertainty in the impurity concentration is about 0.05%. The long-term memory (over 100,000 cycles of sound) displayed in this data is indicative of an as yet unidentified physical process that is an essential aspect of the transition to SL. We were unable to observe steady SL from a single N₂ bubble. The average radius also drifts on the same time scales in these regimes. Because of this nonsteady motion and weak emission, we were unable to obtain a spectrum of a N₂ bubble.

our measurements of He and Xe), the transition to SL for a pure noble gas bubble is smooth: At low levels of drive, the bubble pulsates but no light is emitted, and as the drive is increased, the bubble smoothly distorts until its amplitude of pulsation is large enough to concentrate the energy to the level required for SL. This observation stands in contrast to the behavior of doped bubbles (air for example) where the transition is abrupt (1). For the case of a pure N₂ bubble, the dynamical properties are difficult to probe because of its nonsteady behavior (Fig. 5). The properties of this bubble can only be measured in real time without the benefits of long-time averaging. Such measurements find an expansion ratio (R_m/R_0) that varies in time between 6 and 10. At low sound field amplitudes (where the N₂ bubble does not glow), the pulsations are periodic and in agreement with the Rayleigh-Plesset equations.

The transduction of sound into light is surprisingly efficient: Light from the 2% Xe mixture is comparable to the bulk sound energy dissipated by viscosity in the absence of the bubble. In fact, as the water containing the 2% Xe bubble was cooled to 1°C, the overall intensity increased by a factor greater than 10 to an average power of 0.5 μW. If the flash widths of such a bubble are still bounded by the 100-ps (5) characteristic of air, then the peak powers will be greater than 0.15 W (because there are 33,000 flashes per second in this resonator).

From a practical perspective, the sensitivity of SL to gas content and ambient temperature suggests that further substantial improvements in the characteristics of the emitted radiation are possible. Theoretically, the picture of SL being generated by the implosion of a shock wave that is launched by the collapsing bubble is incomplete. Shock dynamics are not affected by small gas impurities. An unidentified physical process (that is sensitive to doping with noble gases) controls the long-time dynamics and the transition to SL. In this regard, the ambient radius remains a key theoretical unknown (for 1% Ar, $R_0 = 4 \mu\text{m}$; but for 2% Xe, $R_0 = 8 \mu\text{m}$; whereas for pure N₂, it is nonsteady). The light-emitting mechanism is also strongly dependent on the gas content of the bubble. The spectrum for He is steeper than can be accounted for by thermal Bremsstrahlung from hot gases. Perhaps the high density and small size of the plasma that forms in the imploded bubble need to be accounted for in a theory of the spectrum of SL. A unifying feature of our investigation is that although SL is a sensitive phenomenon, it is nevertheless robust throughout a rich parameter space.

REFERENCES AND NOTES

1. B. P. Barber, C. C. Wu, R. Löfstedt, P. H. Roberts, S. J. Putterman, *Phys. Rev. Lett.* **72**, 1380 (1994).
2. B. P. Barber and S. J. Putterman, *Nature* **352**, 318 (1991).
3. R. Hiller, S. J. Putterman, B. P. Barber, *Phys. Rev. Lett.* **69**, 1182 (1992).
4. D. F. Gaitan, L. A. Crum, C. C. Church, R. A. Roy, *J. Acoust. Soc. Am.* **91**, 3166 (1992).
5. B. P. Barber, R. Hiller, K. Arisaka, H. Fetterman, S. J. Putterman, *ibid.*, p. 3061.
6. R. Battino, T. Flettich, T. Tomimaga, *J. Phys. Chem. Ref. Data* **13**, 563 (1984).
7. R. Battino, M. Banzhof, M. Bogan, E. Wilhelm, *Anal. Chem.* **54**, 806 (1972).
8. R. Löfstedt, B. P. Barber, S. J. Putterman, *Phys. Fluids A* **5**, 2911 (1993).
9. S. L. Garrett, *J. Acoust. Soc. Am.* **88**, 210 (1990).
10. A. B. Pippard, *The Physics of Vibration* (Cambridge Univ. Press, Cambridge, 1989).
11. F. M. Penning and C. C. J. Addink, *Physica* **1**, 1007 (1934).
12. J. M. Meek and J. D. Craggs, Eds., *Electrical Breakdown of Gases* (Wiley, New York, 1978).
13. H. P. Greenspan and A. Nadim, *Phys. Fluids A* **5**, 1065 (1993).
14. C. C. Wu and P. H. Roberts, *Phys. Rev. Lett.* **70**, 3424 (1993).
15. W. C. Moss, J. W. White, R. A. Day, D. B. Clarke, preprint UCRL-JC-110666 (Lawrence Livermore National Laboratory, Livermore, CA, 1993).
16. B. P. Barber and S. J. Putterman, *Phys. Rev. Lett.* **69**, 3839 (1992).
17. L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, ed. 2, 1987).
18. A. J. Walton and G. T. Reynolds, *Adv. Phys.* **33**, 595 (1984).
19. We are indebted to R. Löfstedt and K. Suslick for valuable discussions. Research supported by the U.S. Department of Energy Division of Advanced Energy Projects.

21 June 1994; accepted 23 August 1994

Electronic Coherence and Nonlinear Susceptibilities of Conjugated Polyenes

Shaul Mukamel, Akira Takahashi, Hong Xiang Wang, Guanhua Chen

A dynamic theory that connects electronic motions and the nonlinear optical response of conjugated polyenes is developed by introducing the concept of electronic normal modes. A useful picture for the mechanism of optical nonlinearities is obtained by identifying the few dominant modes. This quasi-particle electron-hole representation establishes a close analogy with small semiconductor particles (quantum dots) and is very different from the traditional approach based on electronic eigenstates. The effective conjugation length (coherence size), which controls the scaling and saturation of the static third-order susceptibility $\chi^{(3)}$ with the number of double bonds, is related to the coherence of the relative motion of electron-hole pairs created upon optical excitation.

The mechanism of optical nonlinearities of conjugated polyenes constitutes an open challenge that poses important fundamental as well as practical problems related to the synthesis of new optical materials with large susceptibilities (1–4). Questions such as structure-property relations (5) and comparison with other molecular, semiconductor, or metallic materials (6) have drawn considerable attention. Quantum chemists traditionally calculate susceptibilities by expanding them using the global (many-body) electronic eigenstates, and optical properties are then related to the eigenvalues and to matrix elements of the dipole operator. Physical insight is developed in terms of the nature of the relevant eigenstates, which serve as a convenient link between experiment and theory. Despite the tremendous progress in computational methods, the calculation of the global eigenstates remains a very demanding objective, which restricts such calculations to rela-

tively small systems (2, 7). Finite field methods, which are based on calculating the ground-state energy in the presence of an external field, are much more effective for off-resonant susceptibilities, which are most relevant for device applications (7). However, they do not provide the frequency dependence and shed very little light on the mechanism of the optical response.

It has long been recognized that, by virtue of their delocalized electronic states, conjugated polyenes may have very large polarizabilities (8). A scaling of the third-order susceptibility $\chi^{(3)} \sim N^b$, where N is the number of carbon atoms and $4 \leq b \leq 6$, was found for short chains. A crossover of the scaling exponent to $b = 1$ is expected, however, for larger sizes, because the existence of a proper thermodynamic limit (that is, the independence of macroscopic properties on system size) requires that $\chi^{(3)}/N$ should saturate and become independent of N . This saturation reflects some effective conjugation length. Its origin is puzzling if we approach the problem from the chemists' perspective. Off-resonant susceptibilities de-

Department of Chemistry, University of Rochester, Rochester, NY 14627, USA.