Mechanoluminescence and Sonoluminescence from Acoustic Cavitation

Nathan Eddingsaas Final Seminar June 27, 2008

The chemical effects of ultrasound do not arise from the direct interaction of an acoustic field with chemical species on a molecular level; instead they arise from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid irradiated with high-intensity ultrasound.[1, 2] The growth of the bubble is relatively slow, allowing for the accumulation of gas and vapor within the bubble, while the collapse in its final stage becomes very rapid, reaching velocities of up to 1,500 $m \cdot s^{-1}$.[3] This high speed collapse effectively concentrates the diffuse energy of sound by compressing the contents of the bubble. One consequence of the compressional heating of the bubble contents is the creation of a short lived flash of light referred to as sonoluminescence (SL). The SL spectrum consists of a broad continuum extending from the near IR into the deep UV and an often contains atomic and molecular emission bands. The atomic and molecular emission bands provide data on the reactive species present within the bubble. The emission bands in SL spectra have also been used as a diagnostic tool of the conditions generated within the bubble during cavitation indicating that temperatures of up to 15,000 K, pressures of hundreds to thousands of bars, and cooling rates of up to 10^{13} $K \cdot s^{-1}$ are generated.[1, 4-8]

Acoustic cavitation also has effects on solids within a liquid exposed to ultrasonic irradiation. When the supersonic collapse causes the bubble to reach its minimum radius the bubble rebounds, launching a shock wave outward into the liquid at speeds of up to 5,000 $m \cdot s^{-1}$.[9, 10] In a liquid-powder slurry, the shock waves produced cause the small particles to be accelerated to half the speed of sound, resulting in high velocity interparticle collisions. These interparticle collisions generate temperatures of up to 3,000 K at the point of impact.[11, 12] The interparticle collisions can cause dramatic changes in surface size, surface morphology, composition, and reactivity.

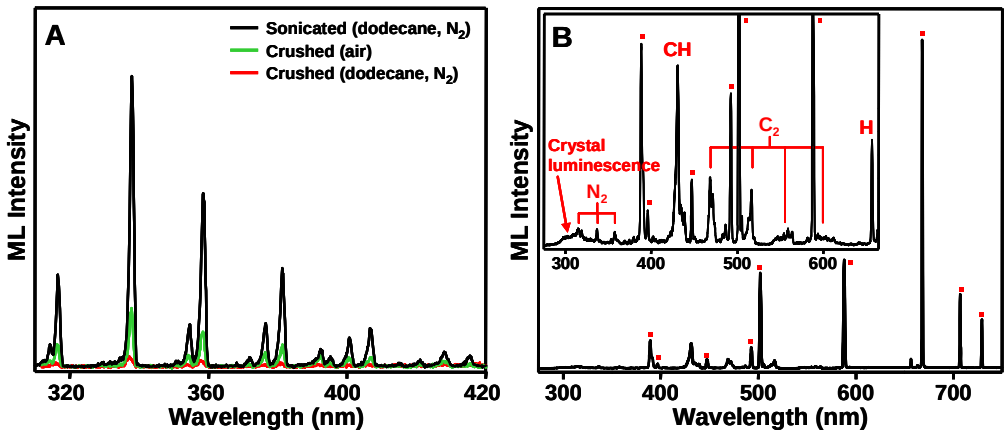

Figure 1. (A) ML from sucrose crushed in air, crushed in dodecane, and sonicated in dodecane. The ML as a result of sonication is an order of magnitude more intense. Emission lines are from N_2 $\left(C^3\Pi_u - B^3\Pi_g\right)$ and N_2^+ $\left(C^2\Sigma_u^+ - X^2\Sigma_g^+\right)$. (B) ML from resorcinol in hexadecane sparged with He. Emission lines observed are from He (red squares), C_2, CH, H, and He^+ (~ 77 eV above the ground state of He).

The intense shock wave launched from collapsing bubbles during the sonication of slurries allows for the study of chemical and physical events that occur when a solid is stressed or fractured. One such event is mechanoluminescence (ML): light produced by any mechanical action on a solid.[13-15] ML has been studied for over 400 years, but much is still not known about it because the emission is inherently weak.[16] Sonicating slurries of mechanoluminescent crystals (such as sucrose and resorcinol) in long chain alkanes has produced very bright ML, up to 1,000 fold more intense than from manual grinding (Fig. 1). The large increase in intensity has revealed a number of new emitting species including C_2, CH, CO, CO^+, CO_2^+, H, and He^+, many of which have not been reported before.[17, 18] In addition, the emission products show that gas phase reactions are occurring within the plasma generated from the ML discharge. In addition, the intense ML allowed the plasma to be characterized in terms of heavy atom temperature of ~ 400 K, electron density of ~ 10^{14} cm^{-1}, and electron energy of ~3.5 eV. These conditions are very similar to other highly reactive microdischarges.[19]

The discovery of very bright single-bubble sonoluminescence (SBSL) in concentrated sulfuric acid has expanded the parameter space of sonoluminescence.[5, 20, 21] SBSL from sulfuric acid has shown the existence of a plasma during single-bubble cavitation, how non-volatile species enter the bubble and emit photons, and how the composition of the liquid and gas affects the sonoluminescence and the species available for reaction.

To further extend the knowledge of the conditions generated with in a cloud of cavitating bubbles, multi-bubble sonoluminescence (MBSL) of sulfuric acid has been studied.[22] The MBSL spectrum from 95 wt % H_2SO_4 consists of a broad continuum extending into the UV with SO and Ar emission lines also observed (Fig. 2). The Ar lines were used to determine an effective emission temperature of ~ 8,000 K, which is substantially greater than in other low vapor pressure systems (e.g., silicone oil, where MBSL emission temperature[4] is only ~ 5,000 K). The observation of Ar lines at this temperature also indicates that a hot plasma core is probably generated during multi-bubble cavitation in sulfuric acid. In addition, SBSL from low concentrations of organics dissolved in sulfuric acid has been investigated.[23] The results of these studies have shown that the species in the interfacial layer of the bubble are important in determining the conditions reached and reactive species present within the bubble.

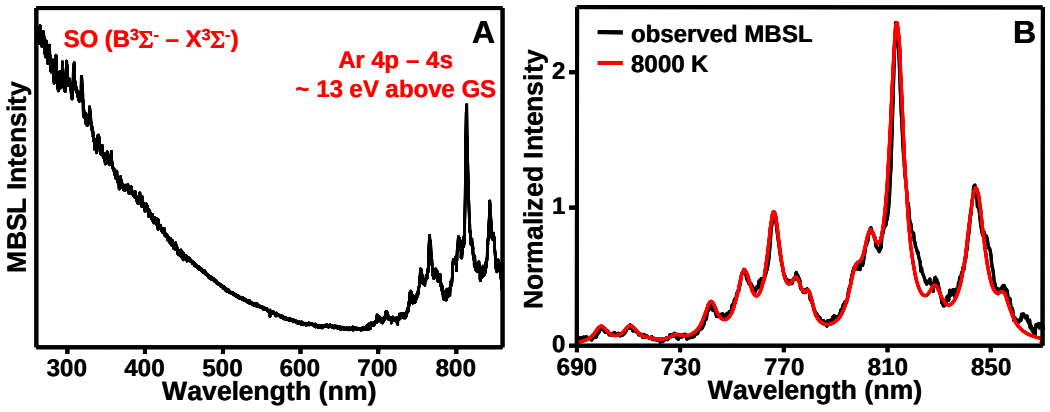

Figure 2. (A) MBSL from 95 wt % H_2SO_4 saturated with Ar. Emission lines are as marked. (B) Ar emission from MBSL along with best fit synthetic spectrum at 8000 K and line width of 6.4 nm.

References

1. Suslick, K. S.; Didenko, Y.; Fang, M. M.; Hyeon, T.; Kolbeck, K. J.; McNamara, W. B., III; Mdleleni, M. M.; Wong, M. Acoustic Cavitation and Its Chemical Consequences. *Philos. Trans. R. Soc. London, Ser. A* **1999,** *357*, 335.
2. Suslick, K. S. Sonochemistry. *Science* **1990,** *247*, 1439.
3. Barber, B. P.; Wu, C. C.; Lofstedt, R.; Roberts, P. H.; Putterman, S. J. Sensitivity of Sonoluminescence to Experimental Parameters. *Phys. Rev. Lett.* **1994,** *72*, 1380.
4. McNamara, W. B., III; Didenko, Y. T.; Suslick, K. S. Sonoluminescence Temperatures During Multi-Bubble Cavitation. *Nature* **1999,** *401*, 772.
5. Flannigan, D. J.; Suslick, K. S. Plasma Formation and Temperature Measurement During Single-Bubble Cavitation. *Nature* **2005,** *434*, 52.
6. McNamara, W. B., III; Didenko, Y. T.; Suslick, K. S. Pressure During Sonoluminescence. *J. Phys. Chem. B* **2003,** *107*, 7303.
7. Flannigan, D. J.; Hopkins, S. D.; Camara, C. G.; Putterman, S. J.; Suslick, K. S. Measurement of Pressure and Density inside a Single Sonoluminescing Bubble. *Phys. Rev. Lett.* **2006,** *96*, 204301.
8. Suslick, K. S.; Price, G. J. Applications of Ultrasound to Materials Chemistry. *Annu. Rev. Mater. Sci.* **1999,** *29*, 295.
9. Pecha, R.; Gompf, B. Microimplosions: Cavitation Collapse and Shock Wave Emission on a Nanosecond Time Scale. *Phys. Rev. Lett.* **2000,** *84*, 1328.
10. Holzfuss, J.; Ruggeberg, M.; Billo, A. Shock Wave Emissions of a Sonoluminescing Bubble. *Phys. Rev. Lett.* **1998,** *81*, 5434.
11. Doktycz, S. J.; Suslick, K. S. Interparticle Collisions Driven by Ultrasound. *Science* **1990,** *247*, 1067.
12. Prozorov, T.; Prozorov, R.; Suslick, K. S. High-Velocity Interparticle Collisions Driven by Ultrasound. *J. Am. Chem. Soc.* **2004,** *126*, 13890.
13. Chandra, B. P. Mechanoluminescence. In *Luminescence of Solids*; Vij, D. R., Ed.; Plenum Press: New York, 1998; pp 361-389.
14. Zink, J. I. Triboluminescence. *Acc. Chem. Res.* **1978,** *11*, 289.
15. Sweeting, L. M. Triboluminescence with and without Air. *Chem. Mater.* **2001,** *13*, 854.
16. Bacon, F. *Of the Advancement of Learning*. J. M. Dent and Sons: London, 1915.
17. Eddingsaas, N. C.; Suslick, K. S. Mechanoluminescence: Light from Sonication of Crystal Slurries. *Nature* **2006,** *444*, 163.
18. Eddingsaas, N. C.; Suslick, K. S. Intense Mechanoluminescence and Gas Phase Reactions from the Sonication of an Organic Slurry. *J. Am. Chem. Soc.* **2007,** *129*, 6718.
19. Eddingsaas, N. C.; Suslick, K. S. Plasma Characteristics of the Discharge Produced During Mechanoluminescence. *Phys. Rev. Lett.* **2007,** *99*, 234301.
20. Flannigan, D. J.; Suslick, K. S. Plasma Line Emission During Single-Bubble Cavitation. *Phys. Rev. Lett.* **2005,** *95*, 044301.
21. Flannigan, D. J.; Suslick, K. S. Emission from Electronically Excited Metal Atoms During Single-Bubble Sonoluminescence. *Phys. Rev. Lett.* **2007,** *99*, 134301.
22. Eddingsaas, N. C.; Suslick, K. S. Evidence for a Plasma Core During Multibubble Sonoluminescence in Sulfuric Acid. *J. Am. Chem. Soc.* **2007,** *129*, 3838.
23. Eddingsaas, N. C.; Suslick, K. S. Hot and Cold Molecular Emission from SBSL. (In preparation)