

HOT SPOT CONDITIONS DURING MULTI-BUBBLE CAVITATION

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1. Introduction

Together with the chemical effects of ultrasound, light is often emitted [1-5]. Such sonoluminescence provides an extremely useful spectroscopic probe of the conditions created during cavitation bubble collapse. Acoustic cavitation is the origin of both sonochemistry and sonoluminescence. The collapse of bubbles caused by cavitation produces intense local heating and high pressures, with very short lifetimes. As we will demonstrate in this chapter, in clouds of cavitating bubbles, these hot spots have equivalent temperatures of roughly 5000 K, pressures of about 1000 atmospheres, and heating and cooling rates above 10^{10} K/s. In single bubble cavitation, conditions may be even more extreme [6-7]. Thus, cavitation can create extraordinary physical and chemical conditions in otherwise cold liquids.

Fundamentally, chemistry is the interaction of energy and matter. Chemical reactions require energy in one form or another to proceed: chemistry stops as the temperature approaches absolute zero. Chemists have only limited control, however, over the nature of this interaction. In large part, the properties of a specific energy source determine the course of a chemical reaction. Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecule. The immense local temperatures and pressures together with the extraordinary heating and cooling rates generated by cavitation bubble collapse mean that ultrasound provides an unusual mechanism for generating high energy chemistry. Like photochemistry, very large amounts of energy are introduced in a short period of time, but it is thermal, not electronic, excitation. As in flash pyrolysis, high thermal temperatures are reached, but the duration is very much shorter (by $>10^4$) and the temperatures are even higher (by five- to ten-fold). Similar to shock-tube chemistry or multiphoton infrared laser photolysis, cavitation heating is very short lived, but it occurs within condensed phases. Furthermore, sonochemistry has a high-pressure component, which suggests that one might be able to produce on a microscopic scale the same macroscopic conditions of high temperature-pressure "bomb" reactions or explosive shockwave synthesis in solids. Figure 1 presents an interesting comparison of the parameters that control chemical reactivity (time,

pressure, and energy) for various forms of chemistry.

Figure 1. Chemistry: the interaction of energy and matter.

1.1 ACOUSTIC CAVITATION

Ultrasound spans the frequencies of roughly 15 kHz to 1 GHz. With sound velocities in liquids typically about 1500 m/s, acoustic wavelengths range from roughly 10 to 10^{-4} cm. These are not molecular dimensions. Consequently, no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry or sonoluminescence.

Instead, sonochemistry and sonoluminescence derive principally from acoustic cavitation [4], which serves as an effective means of concentrating the diffuse energy of sound. Compression of a gas generates heat. When the compression of bubbles occurs during cavitation, heating is more rapid than thermal transport, creating a short-lived, localized hot spot. There is a nearly universal consensus that this hot spot is the source of homogeneous sonochemistry. Rayleigh's early descriptions of a mathematical model for the collapse of cavities in incompressible liquids predicted enormous local temperatures and pressures [8]. Ten years later, Richards and Loomis

reported the first chemical effects of ultrasound [9], and these effects have been ascribed, nearly universally, to localized hot spots created during bubble collapse [10]. Alternative mechanisms involving electrical microdischarge have been occasionally proposed [e.g., 11-12], but remain an extreme minority viewpoint with many failings [13-14].

If the acoustic pressure amplitude of a propagating acoustic wave is relatively large (greater than ≈ 0.1 MPa), local inhomogeneities in the liquid can serve as nucleation sites for rapid inertial growth into a cavity of macroscopic dimensions, primarily filled with vapor and dissolved gases. Such a bubble is inherently unstable, and its subsequent collapse can result in an enormous concentration of energy. This violent cavitation event has been termed "transient cavitation" [10]. A normal consequence of this unstable growth and subsequent collapse is that the cavitation bubble itself is destroyed. Gas-filled remnants from the collapse, however, may serve as nuclei for continuation of the process.

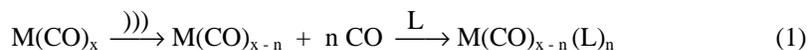
The generally accepted explanation for the origin of sonochemistry and sonoluminescence is the hot spot theory, which holds that the potential energy given the bubble as it expands to maximum size is concentrated into a heated gas core as the bubble implodes. The oscillations of a gas bubble driven by an acoustic field are generally described by the "Rayleigh-Plesset" equation or minor modifications thereof, such as the Gilmore equation [4]. The validity of these equations for computing the behavior of a single, isolated cavitating bubble has been experimentally confirmed. Various researchers have used light scattering off the bubble to measure the radius-time curve for single collapsing bubbles, simultaneously observing the optical emission from sonoluminescence (see below). The single-bubble sonoluminescent emission is seen as the sharp spike appearing at the final stages of bubble collapse. Note that the emission occurs at the point of minimum bubble size, and that the general shape of the theoretical curve is reproduced [15-17].

Single bubbles, while creating extreme conditions, simply do not contain sufficient material to be useful for driving chemical reactions in any practical amount. In multi-bubble systems ("cavitation clouds"), on the other hand, the interactions between bubbles as they collapse will lead to both substantial asymmetry and the formation of jets during collapse [4], which one may well expect to limit the collapse efficiency. Thus, the conditions created during multi-bubble cavitation, which is used of necessity for all sonochemical reactions, will be somewhat less extreme than those created during single bubble sonoluminescence.

1.2 TWO-SITE MODEL OF SONOCHEMICAL REACTIVITY

Probing the conditions present in the cavitation hot spot has proved to be a difficult problem. The transient nature of cavitation, especially in bubble clouds, precludes conventional measurement of the conditions generated during bubble collapse. Chemical reactions themselves, however, can be used to probe reaction conditions. The effective temperature realized by the collapse of clouds of cavitating bubbles can be determined by the use of competing unimolecular reactions whose rate

dependencies on temperature have already been measured. This technique of "comparative-rate chemical thermometry" was used by Suslick, Hammerton, and Cline to make the first experimental determination of the effective temperature reached during cavity collapse [18]. The sonochemical ligand substitutions of volatile metal carbonyls were used as the comparative rate probes (Eqn. 1).

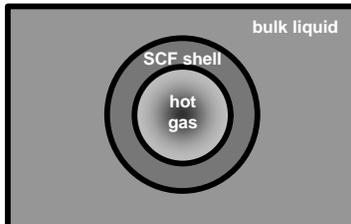


where M = Fe, Cr, Mo, W; L represents a substituting ligand;

and the symbol $\xrightarrow{\text{)))}}$ represents ultrasonic irradiation of a solution.

These kinetic studies revealed that there are in fact *two* sonochemical reaction sites: the first (and dominant site) is the bubble's interior gas-phase while the second is an *initially* liquid phase. The latter corresponds either to the heating of a shell of liquid around the collapsing bubble or to the injection of liquid droplets into the hot spot by surface wave distortions of the collapsing bubble, as shown schematically in Figure 2.

Thermal Diffusion Shell Model



Surface Wave Droplet & Jet Model

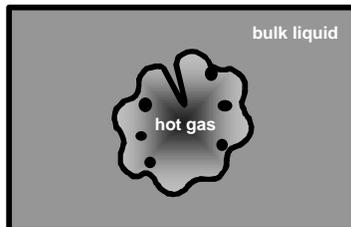


Figure 2. Two-site models of sonochemical reactions.

The effective local temperatures in both sites were determined by combining the relative sonochemical reaction rates for Eqn. 1 with the known temperature behavior of these reactions. The effective temperatures of these hot spots were measured at ≈ 5200 K in the gas-phase reaction zone and ≈ 1900 K in the initially liquid zone [18]. Of course, the comparative rate data represent only a composite temperature: during the collapse, the temperature within the bubble has a rapidly changing temporal and spatial profile. This two-site model has been confirmed with other reactions [19]. The study of sonoluminescence, which will now be discussed, has both confirmed and extended these temperature measurements of the cavitation hot spot.

2. Sonoluminescence as a Probe of Cavitation

2.1. TYPES OF SONOLUMINESCENCE

Sonoluminescence was first observed from water in 1934 by Frenzel and Schultes [20]. As with sonochemistry, sonoluminescence derives from acoustic cavitation. There are two classes of sonoluminescence: multiple-bubble sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) [6, 15, 21]. Cavitation is a nucleated process, and liquids generally contain large numbers of particulates that serve as nuclei. As a consequence, the "cavitation field" generated by a propagating or standing acoustic wave typically consists of very large numbers of interacting bubbles, distributed over an extended region of the liquid. If this cavitation is sufficiently intense to produce sonoluminescence, then we call this phenomenon "multiple-bubble sonoluminescence" (MBSL).

Under the appropriate conditions, the acoustic force on a bubble can balance against its buoyancy, holding the bubble stable in the liquid by acoustic levitation. This permits examination of the dynamic characteristics of the bubble in considerable detail, from both a theoretical and an experimental perspective. Such a bubble is typically quite small compared to an acoustic wavelength (e.g., at 20 kHz, the resonance size is approximately 150 μm). It was recently discovered, for rather specialized but easily obtainable conditions, that a single, stable, oscillating gas bubble can be forced into such large amplitude pulsations that it produces sonoluminescence emissions on each (and every) acoustic cycle [22, 23]. This phenomenon is called single-bubble sonoluminescence (SBSL).

2.2. MULTIPLE-BUBBLE SONOLUMINESCENCE SPECTRA

Over the last three decades, the sonoluminescence of aqueous solutions has been studied at length, most recently and carefully by Didenko and co-workers [24, 25]. The spectrum of MBSL in water consists of a peak at 310 nm and a broad continuum throughout the visible region. The emission at 310 nm is from excited-state

OH^{\bullet} , but the continuum is difficult to interpret. MBSL from aqueous and alcohol solutions of many metal salts has been reported and are characterized by emission from metal atom excited states [26].

More recently sonoluminescence from non-aqueous liquids has been examined. Flint and Suslick reported the first MBSL spectra of organic liquids [27]. With various hydrocarbons, the observed emission is from excited states of C_2 ($d^3\Pi_g - a^3\Pi_u$, the Swan lines), the same emission that is seen in flames. Furthermore, the ultrasonic irradiation of hydrocarbons in the presence of N_2 (or NH_3 or amines) gives emission from CN excited states, but not from N_2 excited states. Emission from N_2 excited states would have been expected if the MBSL originated from microdischarge, whereas CN emission is typically observed from thermal sources. When oxygen is present, emission from excited states of CO_2 , CH^{\bullet} , and OH^{\bullet} is observed, again similar to flame emission.

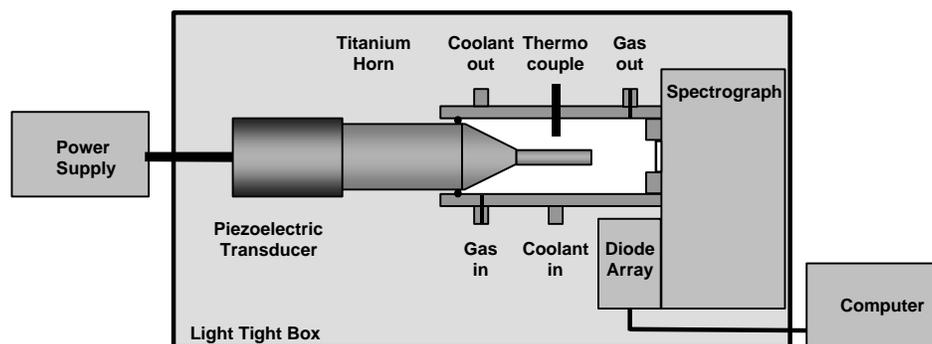


Figure 3. Block diagram of sonoluminescence spectrometer.

Most recently, we have extended our spectral analysis approach to MBSL from excited metal atom spectra. Volatile organometallics (such as $\text{Fe}(\text{CO})_5$ or $\text{Cr}(\text{CO})_6$), when irradiated with ultrasound in a low volatility organic liquid, emit an intense sonoluminescence that corresponds to the known atomic emission lines of the metals [28], again analogous to flame emission. Figure 3 shows a block diagram of our sonoluminescence spectrograph, which is carefully calibrated for both wavelength and radiance using standard lamps. Figure 4 shows a typical MBSL spectrum from a metal carbonyl solution. Note the intense line emission from the metal atom excited states as well as bands from excited states of the diatomics, C_2 and CH .

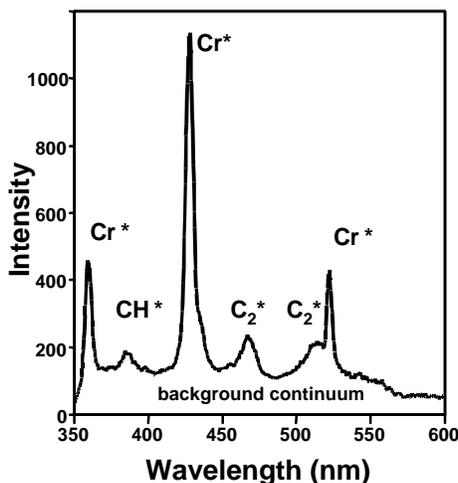


Figure 4. Typical MBSL spectrum from a metal carbonyl solution in silicone oil.

For both aqueous and non-aqueous liquids, MBSL is caused by chemical reactions of high-energy species formed during cavitation by bubble collapse. Its principal source is most probably not blackbody radiation or electrical discharge. MBSL is a form of chemiluminescence, not unlike flame emission.

2.4 SPECTROSCOPIC PROBES OF CAVITATION CONDITIONS

Determination of the conditions reached in a cavitating bubble has remained a difficult experimental problem. Spectral analysis of MBSL provides a solution. We have used two very different spectroscopic reporters to provide such information: (1) resolved molecular emission from diatomics (notably C_2) produced during cavitation and (2) atomic line emission derived from the sonolysis of volatile organometallic compounds.

Flint and Suslick first reported high-resolution MBSL spectra from silicone oil under Ar [29]. The observed emission comes from excited state C_2 and has been modeled with synthetic spectra as a function of rotational and vibrational temperatures, as shown in Figure 5. From comparison of synthetic to observed spectra for several different emission bands, the effective rotational and vibrational emission temperature is 5050 ± 150 K. The excellence of the match between the observed MBSL and the synthetic spectra provides definitive proof that the sonoluminescence event is a thermal, chemiluminescence process, although the issue of thermal equilibration in such systems is not without its complexities [30]. The agreement between this spectroscopic determination of the cavitation temperature and that made by comparative rate thermometry of sonochemical reactions [18] is surprisingly good.

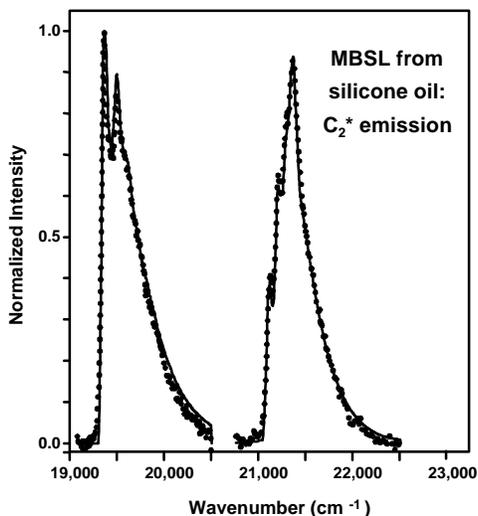


Figure 5. Excited state C₂ MBSL spectrum from silicone oil under Ar.

Emission from the $\Delta v = +1$ manifold of the $d^3\Pi_g - a^3\Pi_u$ transition (Swan band) of C₂.

- Observed MBSL spectrum from polydimethylsiloxane silicone oil under Ar at 0°C.
- Best fit synthetic spectrum for these two bands, with $T_v = T_r = 4900$ K.

We have now analyzed the relative intensities of atomic emission lines in the sonoluminescence spectra of excited state metal atoms produced by sonolysis of volatile Fe, Cr, and Mo carbonyls dissolved in silicone oil under argon. Sufficient spectral information about emissivities of many metal atom excited states are available to readily calculate emission spectra as a function of temperature. Because of this, the emission spectra of metal atoms are extensively used to monitor the surface temperature of stars. For example, the expected spectra for iron emission as a function of temperature is shown in Figure 6.

From comparison of such calculated spectra and the observed MBSL spectra from metal carbonyls, another measure of the cavitation temperature can be obtained. The effective emission temperature during cavitation under argon at 20 kHz is 4900 ± 250 K, with excellent agreement among the three systems tested (5150 ± 300 K for Fe, 4700 ± 400 K for Cr, and 4750 ± 400 K for Mo), as shown in Figures 7 through 9. Again, agreement with our prior comparative rate thermometry and the MBSL emission temperature of C₂* excited states is excellent.

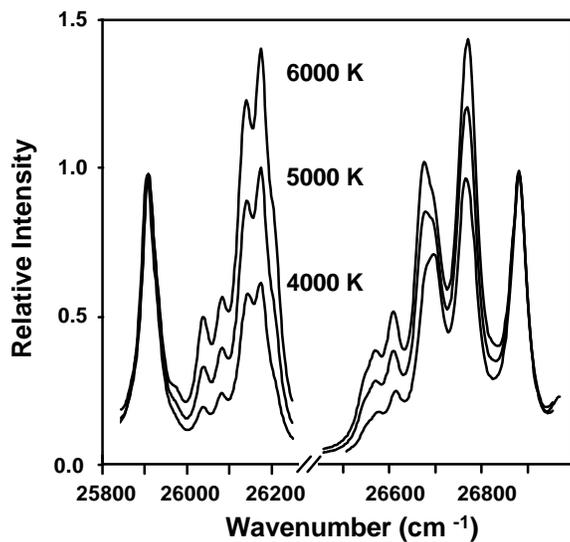


Figure 6. Calculated emission spectra of Fe atoms as a function of temperature.

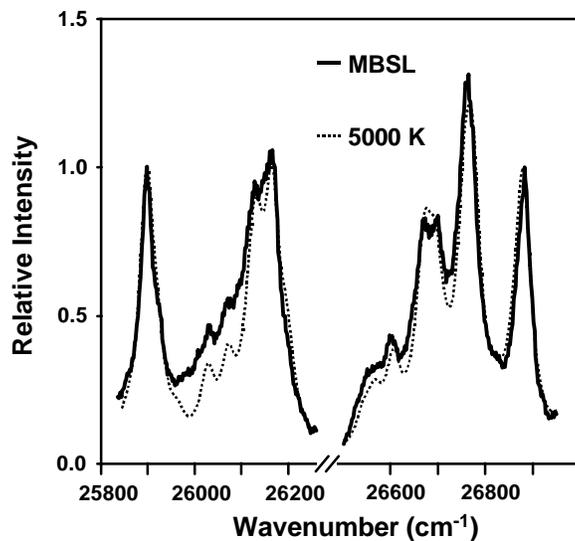


Figure 7. Sonoluminescence of excited state Fe atoms produced during sonolysis of $\text{Fe}(\text{CO})_5$ dissolved in silicone oil under Ar. Effective emission temperature is 5150 ± 300 K

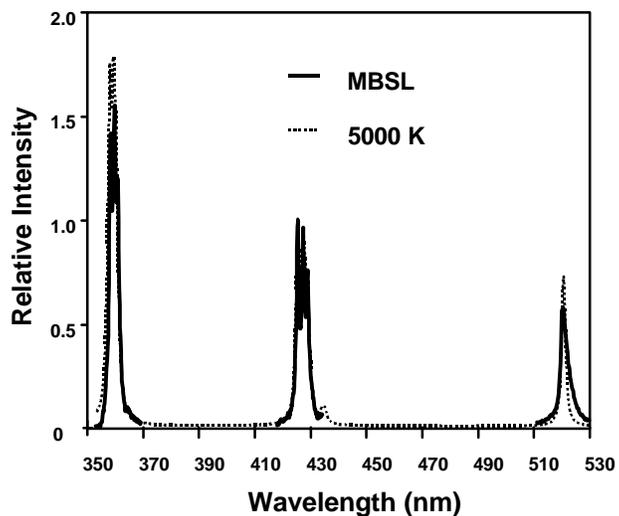


Figure 8. Sonoluminescence of excited state Cr atoms produced during sonolysis of $\text{Cr}(\text{CO})_5$ dissolved in silicone oil under Ar. Effective emission temperature is 4700 ± 400 K

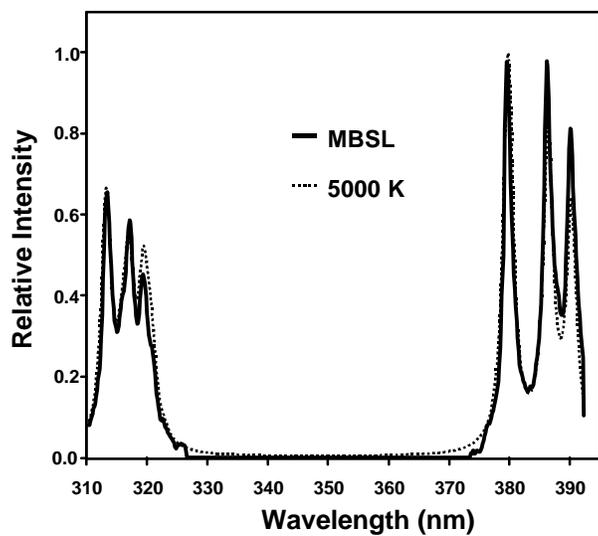


Figure 9. Sonoluminescence of excited state Mo atoms produced during sonolysis of $\text{Mo}(\text{CO})_6$ dissolved in silicone oil under Ar. Effective emission temperature is 4750 ± 400 K

We are also able to control the temperature within the cavitation bubble simply by changing the bubble contents. For example, upon addition of gaseous hydrocarbons (methane, ethylene, or propane), the observed emission temperatures from Cr atom excited states decrease dramatically, as shown in Figure 10. As polyatomic molecules are added to the bubble contents, the polytropic ratio of the gas in the bubble decreases, and so too does the expected temperature from adiabatic compression, as shown by Eqn. 2. The presence of the polyatomic gas simply provides vibrational and rotational modes that will divert much of the kinetic energy of collapse away from direct temperature increase. The effects of the addition of polyatomic gases to the observed cavitation emission temperature can be quantitatively modeled by simple adiabatic compression of a bubble during cavitation collapse. This simple model predicts pressures on the order of 10^3 Bar, which is quantitatively consistent with the linewidth broadening and small peak wavelength shifts observed in the metal atom emission.

$$T_{\max} = T_{\min} \left(\frac{R_{\max}}{R_{\min}} \right)^{3(g-1)} \quad (2)$$

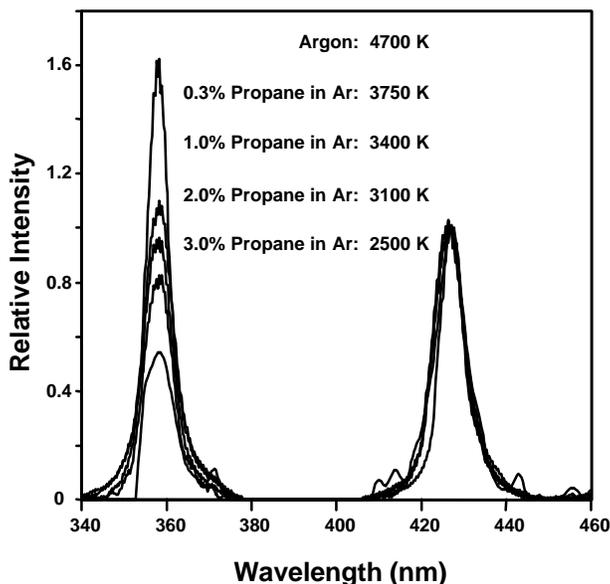


Figure 10. Control of cavitation temperature. Sonoluminescence of excited state Cr atoms produced during sonolysis of Cr(CO)₃ dissolved in silicone oil with increasing amounts of propane in Ar.

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2.3. SINGLE-BUBBLE SONOLUMINESCENCE SPECTRA

The spectra of MBSL and SBSL are dramatically different and the interpretation of SBSL spectra is much less clear. MBSL can be observed in essentially all liquids, whereas SBSL has been observed primarily in aqueous liquids. While MBSL is generally dominated by atomic and molecular emission lines (e.g. excited states of OH^\bullet in water and of C_2 in hydrocarbons), SBSL is an essentially featureless emission that increases with decreasing wavelength. Unusual effects on the intensity of this featureless SBSL emission are observed when the gas contents of the bubble are changed [22, 23, 31, 32]. Furthermore, the SBSL spectra show no evidence of OH emissions, and when He and Ar bubbles are considered, continue to increase in intensity even into the deep ultraviolet. For example, the MBSL spectrum of an aqueous solution of NaCl is dominated by strong bands from excited states of both OH^\bullet and Na; however, the SBSL spectrum of an identical solution shows no evidence of these peaks [21]. Similarly, the MBSL spectrum falls off at low wavelengths, while the SBSL spectrum continues to rise, at least for most noble gases [22, 23].

Early work on SBSL stirred intense interest due primarily to the exceptionally short duration of the sonoluminescence flash. The initial reports by Putterman et al. placed the emission lifetimes well below 50 ps [23], but more recent studies by Gompf [33] have shown that the emission is generally longer, ≈ 200 ps. The standard hydrodynamic models of adiabatic collapse of a single bubble could not have explained emission lifetimes below 50 ps, which generated a wide range of quite speculative (and often just plain silly) theories on the origin of SBSL. The consensus appears to be settling on intense adiabatic compression, with sonochemical reaction and rectification into the water of reactive gases (e.g., O_2 and N_2 from air filled bubbles) [31], and with some ionization occurring in the last stages of bubble collapse [34, 35]. There may also be a convergent shockwave within the single bubble, although this remains an open issue.

The difference between SBSL and MBSL spectra appears likely to be related to the sphericity of collapse. In SBSL, where bubble collapse is more spherical and the extent of compression greater, sufficient temperatures are reached (probably above $\approx 20,000$ K) to form a plasma and the primary emission becomes electron-ion or electron-atom bremsstrahlung [34,35]. In such a plasma, the temperatures will ensure dissociation of all molecules and will broaden, through Stark and pressure effects, any remaining molecular or atom emission beyond recognition [35]. The issue of a spherically convergent shockwave remains an open question. There continues the possibility of extraordinarily high energy conditions (up to and including those needed for inertial confinement fusion!) at the center of the bubble (which would be shielded from direct observation by the opacity of the surrounding plasma) [34, 36].

4. Conclusion

Sonochemistry and sonoluminescence are closely related phenomenon, both of which derive from acoustic cavitation. Bubble collapse in liquids results in an enormous concentration of energy from the conversion of the kinetic energy of liquid motion into heating of the contents of the bubble. The enormous local temperatures and pressures so created provide a unique means for fundamental studies of chemistry and physics under extreme conditions. A diverse set of applications of ultrasound to enhancing chemical reactivity has been explored, with important applications in mixed phase synthesis, materials chemistry, and biomedical uses. Many of these are discussed throughout this monograph.

5. Acknowledgments

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6. References

1. Suslick, K.S., ed. (1988) *Ultrasound: Its Chemical, Physical, and Biological Effects*, VCH Publishers, New York.
2. Suslick, K.S. (1990) *Science*, **247**, 1439.
3. Mason, T.J., Lorimer, J.P. (1988) *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*, Ellis Horwood, Ltd., Chichester, U.K.
4. Leighton, T.G. (1994) *The Acoustic Bubble* Academic Press, London, pp. 531-551.
5. Suslick, K.S.; Crum, L.A. (1997) "Sonochemistry and Sonoluminescence," in *Encyclopedia of Acoustics*; Crocker, M. J., ed.; Wiley-Interscience, New York, vol. 1, ch. 26, pp. 271-282.
6. Crum, L.A. (1994) *Physics Today*, **47**, 22.
7. Putterman, S.J. (1995) *Scientific American*, **Feb. 1995**, 46.
8. Lord Rayleigh (1917) *Philos. Mag.*, **34**, 94.
9. Richards, W.T. Loomis, A.L. (1927) *J. Am. Chem. Soc.*, **49**, 3086.
10. Flynn, H.G. (1964) "Physics of Acoustic Cavitation in Liquids," in *Physical Acoustics*, ed. by W.P. Mason, Academic Press, New York, Vol IB, p. 157.
11. Margulis, M.A. (1992) *Ultrasonics* **30**, 152.
12. Lepoint, T., Mullie, F. (1994) *Ultrasonics Sonochem.*, **1**, S13.
13. Suslick, K.S.; Kemper, K.A. (1993) *Ultrasonics* **31**, 463-465.
14. Suslick, K.S.; Dokytcz, S.J.; Flint, E.B. *Ultrasonics* **1990**, **28**, 280-290.
15. L.A. Crum, *J. Acoust. Soc. Am.* **95**, 559 (1994).
16. B.P. Barber and S.J. Putterman, *Phys. Rev. Lett.* **69**, 3839 (1992).
17. Putterman, S. J.; Weninger, K.; Barber, B.P. *Phys. Rev. Lett.* **1997**, **78**, 1799-180.
18. Suslick, K.S.; Hammerton, D.A.; Cline, Jr., R.E. (1986) *J. Am. Chem. Soc.* **108**, 5641.
19. Henglein, A. (1993) *Adv. Sonochem.*, **3**, 17.
20. Frenzel, H. Schultes, H. (1934) *Z. Phys. Chem.* **27b**, 421.
21. Matula, T.J.; Roy, R.A.; Mourad, P.D.; McNamara III W.B.; and Suslick, K.S. (1995) *Phys. Rev. Lett.* **75**, 2602.

K.S. Suslick, W.B. McNamara III, Y. Didenko; "Hot Spot Conditions During Multi-Bubble Cavitation" in *Sonochemistry and Sonoluminescence*, Crum, L. A.; Mason, T. J.; Reisse, J.; Suslick, K.S., eds. Kluwer Publishers: Dordrecht, Netherlands, 1999, pp. 191-204.

22. Cheeke, J.D.N. (1997) *Can. J. Phys.* **75**, 77-98.
23. Barber, B. P.; Hiller, R.A.; Lofstedt, R.; Putterman, S.J.; Weninger, K.R. (1997) *Phys. Rep.* **281**, 65-143.
24. Didenko, Y.T.; Pugach, S.P. (1994) *Ultrasonics Sonochemistry* **1**, s10-s12.
25. Didenko, Y.T.; Nastich, D.N.; Pugach, S.P.; Polovinka, Y.A.; Kvochka, V.I. (1994) *Ultrasonics* **32**, 71-76
26. Flint, E.B.; Suslick, K.S. (1991) *J. Phys. Chem.* **95**, 1484.
27. Flint, E.B.; Suslick, K.S. (1989) *J. Amer. Chem. Soc.* **111**, 6987.
28. Suslick, K.S.; Flint, E.B.; Grinstaff, M.W.; Kemper, K.A. (1993) *J. Phys. Chem.*, **97**, 3098-3099.
29. Flint, E.B.; Suslick, K.S. (1991) *Science* **253**, 1397.
30. Jeffries, J.B.; Copeland, R.A.; Flint, E.B.; Suslick, K.S. (1992) *Science* **256**, 248.
31. Lohse, D.; Brenner, M.P.; Dupont, T.F.; Hilgenfeldt, S.; and Johnston, B. (1997) *Phys. Rev. Lett.*, **78**, 1359-1362.
32. Barber, P.; Hiller, R.; Arisaka, K.; Fetterman, H. and Putterman, S.J. (1992) *J. Acoust. Soc. Am.* **91**, 3061.
33. Gompf, B., Günther, R.; Nick, G.; Pecha, R.; Eisenmenger, W. (1997) *Phys. Rev. Lett.* **79**, 1405.
34. Moss, W.C.; Clarke, D.B.; Young, D.A. (1997) *Science* **276**, 1398-1401.
35. Bernstein, L.S.; Zakin, M.S.; Flint, E.B.; Suslick, K.S. (1996) *J. Phys. Chem.* **100**, 6612-6619
36. Barber, P.; Hiller, R.A.; Lofstedt, R.; Putterman, S.J.; Weninger, K.R. (1994) *Phys. Rev. Lett.*, **72**, 1380.