Measuring the Extreme Conditions Created During Cavitation

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Extreme temperatures and pressures are produced through acoustic cavitation: the formation, growth and collapse of bubbles in a liquid irradiated with high intensity ultrasound. Cavitation of single isolated bubbles have generally been assumed to give higher temperature conditions during compression than bubble clouds, but confirmation from the single bubble sonoluminescence (SBSL) emission spectra has been problematic because SBSL typically produces featureless emission spectra that reveal little about the intra-cavity physical conditions or chemical processes. Here we present definitive evidence of the existence of a hot, highly energetic plasma core during SBSL. From a luminescing bubble in sulfuric acid, excited state to excited state emission lines are observed both from noble gas ions (Ar^+, Kr^+, and Xe^+) and from neutral atoms (Ne, Ar, Kr, and Xe). The excited states responsible for these emission lines range from 8.3 eV (for Xe) to 37.1 eV (for Ar^+) above the ground state. Observation of emission lines allows for identification of intra-cavity species responsible for light emission; the energy levels of the emitters indicate the plasma generated during cavitation is comprised of highly energetic atomic and ionic species.

1 Introduction

A single gas bubble in a liquid can be acoustically levitated and driven into highly nonlinear oscillations. Within a certain parameter space, the nonlinear oscillations can result in subnanosecond flashes of light at the point of maximum implosion that are synchronous with the applied sound field [1,2]. This light emission from single acoustically driven bubbles, dubbed single-bubble sonoluminescence (SBSL), is generally featureless and has generally revealed little direct information about the physical conditions and complex chemical processes occurring during bubble collapse; for example, spectra obtained from water, the liquid used most often for SBSL experiments, consist of broad continuum emission extending from the near-UV to the near-IR [3]. Fitting of the featureless spectra to theoretical emission mechanisms such as blackbody and bremsstrahlung emission have led to model-dependent predictions of temperatures being upwards of 10^4 K with *opaque* core temperatures being much higher [4-6]. It is difficult, however, to determine the origin of and conditions responsible for the continuum emission in SBSL spectra, which could be due to a combination of emission mechanisms, which include blackbody, bremsstrahlung, and even overlapping contributions from multiple atomic and small molecule emitters arising from the sonolysis of water molecules. Though the currently accepted theories of SBSL predict at least a weakly ionized plasma, these theories, until very recently, lacked definitive experimental support [7].

Given the lack of features in the SBSL spectra from water, SBSL generated in other liquids could provide valuable insights into the physical and chemical processes occurring during single-bubble cavitation. In fact, SBSL spectra from organic liquids [8,9] have been previously reported. Most recently, we have found concentrated sulfuric acid (H_2SO_4) to be an extremely interesting and effective liquid for the study of SBSL [7]. In fact, SBSL from 85 wt% H_2SO_4 was much brighter, by more than a thousandfold, than SBSL from pure water under similar conditions. In addition, SBSL spectra from H_2SO_4 contain emission line and band features that provide valuable information about the excited state atoms, molecules, and ions emitters present. Here, we will discuss first the spectroscopic methods used to determine emission temperatures and how we have used these techniques to determine effective emission temperatures during multibubble sonoluminescence (MBSL). Next, we report on the conditions generated during single-bubble acoustic cavitation in sulfuric acid. More specifically, we will show proof of plasma formation

and discuss the temperatures reached by the analysis of the SBSL spectra from concentrated H_2SO_4. Finally, we will compare the conditions generated during SBSL in H_2SO_4 to those during MBSL in H_2SO_4.

2 Temperature measurements by spectroscopic methods

Spectrometric methods of pyrometry are an extremely effective way of quantifying the temperatures generated during MBSL. These methods exploit the dependence of the internal (i.e., bound state) population distribution on temperature for thermally equilibrated systems; by comparing the relative intensities of emission lines from electronically excited atoms and molecules, one can determine an effective emission temperature. Indeed, this is the same technique employed to quantify the thermal conditions of high-temperature sources (e.g., plasmas and flames) and remote locations (e.g., stellar surfaces). Of course, this technique is limited by the simple necessity of observing discrete emission lines in the sonoluminescence spectra. MBSL spectra typically contain emission lines and therefore are amenable to this technique. We note that other spectrometric methods of pyrometry that use continuous radiative transitions rather than discrete transitions are highly model dependent (i.e., blackbody and bremsstrahlung).

The intensity of an emission line occurring from relaxation (induced as well as spontaneous) of an electronically excited atom can be described [10] by

$$ I_{nm} = \frac{bc}{4\pi} \cdot l \cdot \rho_0 \cdot \frac{g_n}{Q} \cdot \frac{A_{nm}}{\lambda_n} \cdot \exp(-E_n/kT) \quad (1) $$

Here, h is Planck's constant, c is the speed of light, k is the Boltzmann constant, l is the path length of the confining region, ρ_o is the atom number density, g_n is the degeneracy of the upper state n, Q is the partition function ($\sum_n g_n \exp(-E_n/kT)$), A_{nm} is the Einstein transition probability between states n and m, E_n is the energy of the upper state n, and T is the absolute temperature.

In principle, one can determine temperatures using so-called single-line radiance pyrometry, by comparing calculated calibration curves (i.e., I_{nm} versus T) and experimental spectral measurements of absolute line intensity for a specific transition (provided self-absorption

is not greater than ~1%). In addition to requiring careful measurements of line intensities, knowledge of path length, atom number density, and accurate spectroscopic constants, single-line pyrometry also has an effective temperature determination limit that is intrinsic to the species studied. Above a certain temperature specific to the transition studied, the radiance of the line no longer increases owing to the counterbalancing of the population of the excited state by ionization. For example, the temperature limit for the Ar 415.8 nm line is ~16,000 K [11].

Compared with the single-line method, the two-line radiance ratio method is simpler because it eliminates the need to know the path length and atom number density. Furthermore, one needs to know only the relative Einstein transition probabilities. This is a significant point because the absolute transition probabilities are typically known only to within ~20% for even the most rigorously studied atomic transitions. An obvious requirement for the use of this method is that the system studied must show a Maxwell-Boltzmann distribution. Gas temperatures are then determined by measuring the relative populations of two or more states and determining the least-squares fit to the data at a specific temperature. In addition to the two-line radiance ratio method, several other methods use this principle, such as atomic and molecular Boltzmann plots and the iso-intensity method [11].

We can derive the ratio of the intensities of two emission lines from Equation 1 and write it as

$$\frac{I_1}{I_2} = \frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_1} \exp\left[(E_2 - E_1)/kT\right] \qquad (2)$$

where the subscripts refer to the two spectral lines being compared. If the constants for a particular atom (i.e., g, A, λ, and E) are known fairly accurately, then one can determine an absolute temperature by measuring the relative intensities of two emission lines arising from transitions originating from different excited states (preferably well separated in energy). If the two lines used are from a neutral atom, the determined emission temperature reflects an atomic excitation temperature. In other words, the temperature corresponds to the equilibrium population among the excited states of the atom studied.

Our group has successfully used the two-line radiance ratio method in MBSL studies to determine the effective temperatures generated during acoustic cavitation. Sonication of solutions of volatile metal carbonyls in *n*-alkanes or silicone oil results in homolytic cleavage of the relatively weak metal-carbon bond resulting in free metal atoms [12]. Electronic excitation and subsequent radiative relaxation of the metal atoms produce intense and well-resolved emission lines in the MBSL spectra [13]. The relative ratios of these emission lines may be used to determine an effective MBSL temperature [14]. Figure 1 shows the emission lines observed from chromium atom excited states, which were populated during the sonication of a solution of $Cr(CO)_6$ dissolved in silicone oil saturated with Ar and irradiated at 20 kHz. By using the two-line radiance ratio method and comparing the MBSL emission with simulated emission spectra at various temperatures, we found the effective MBSL temperature to be 4700 ± 300 K. Using the same method for other metal carbonyls also

revealed temperatures of ~5000 K: Fe gave 5100 ± 300 K, and Mo gave 4800 ± 400 K. MBSL temperatures determined in this manner compare well with the emission temperature of 5100 ± 200 K determined by simulating the C_2 emission bands observed during sonication of low-volatility *n*-alkanes [15,16].
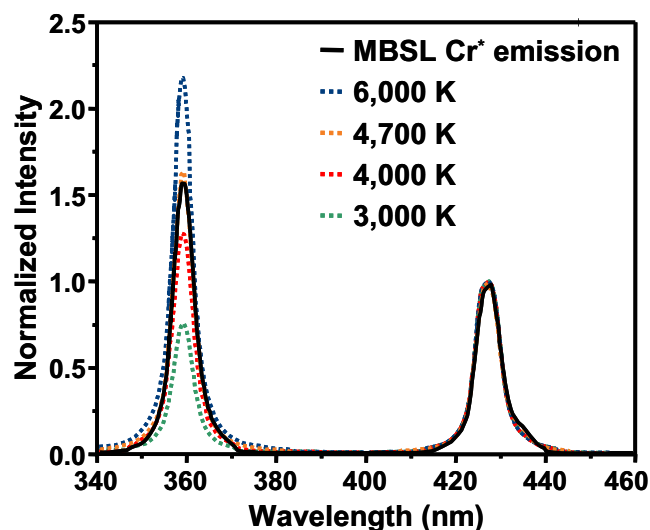

Fig. 1. MBSL from a solution of $Cr(CO)_6$ in silicone oil saturated with Ar gas, compared with a simulation of thermally equilibrated emission from Cr* atoms. The underlying continuum was subtracted from the MBSL spectrum for clarity, and all spectra have been normalized to the peak intensity of the convoluted triplet at 424 nm.

3   Condition during SBSL in sulfuric acid

The remarkable short lifetime of the SBSL flash, the phase-locking of the single-bubble dynamics, and the featureless emission spectra have made quantification of the conditions during bubble compression of wide interest. SBSL, however, is not as amenable as MBSL to the methods used for temperature measurements (i.e., kinetic or spectroscopic). First, a single bubble has a volume of only a few attoliters, so the concentrations of sonolysis products are very low and thus difficult to analyze [17]; second, the intensity of SBSL light emission is usually low, and the emission spectra are typically featureless, which makes spectroscopic analysis difficult. Although there have previously been a few hints of molecular emission during SBSL, these spectra were not of the quality suitable for quantitative analysis [9,18].

We recently discovered that the radiant power generated during SBSL from H_2SO_4 is several thousand-fold larger than that previously observed from any other liquid [7]. Spectral analyses of SBSL from H_2SO_4 revealed emission lines from atoms, molecules, and ions originating from the liquid and from gas dissolved in the liquid (Fig. 2) [19,20]. It also has been discovered that the most intense line emission relative to continuum emission during SBSL in H_2SO_4 occurs from a weakly driven bubble. Figure 3 shows the SBSL spectrum of a weakly driven bubble in H_2SO_4 partially regassed with Ar. Under these conditions, emission from Ar^+, O_2^+, and SO can clearly be observed.

The observation of emission lines from ions provides the first definitive experimental evidence for the generation of a plasma during SBSL. In addition, the observation of strong discrete emission lines provides a means to determine the intracavity temperatures in the same manner as we did for MBSL. The fact that SBSL is generated from a single solitary bubble provides a significant advantage over MBSL; the system is not complicated by volume emission or scattering, and the bubble motion is not perturbed by interactions with other bubbles or the container walls.
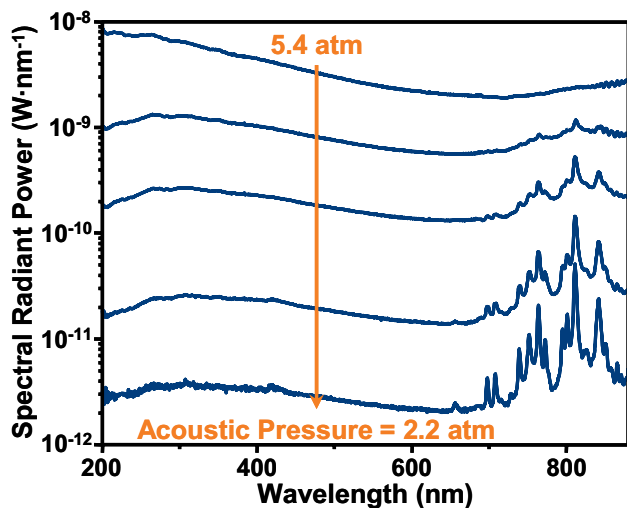

Fig. 2. SBSL as a function of P_a for 85 wt% H_2SO_4 partially regassed with Ar. The emission lines in the near infrared arise from excited state to excited state transitions within the Ar $4p - 4s$ manifold. The energies of the $4p$ levels range 12.9 to 13.4 eV, whereas the energies of the $4s$ levels range 11.5 to 11.8 eV.
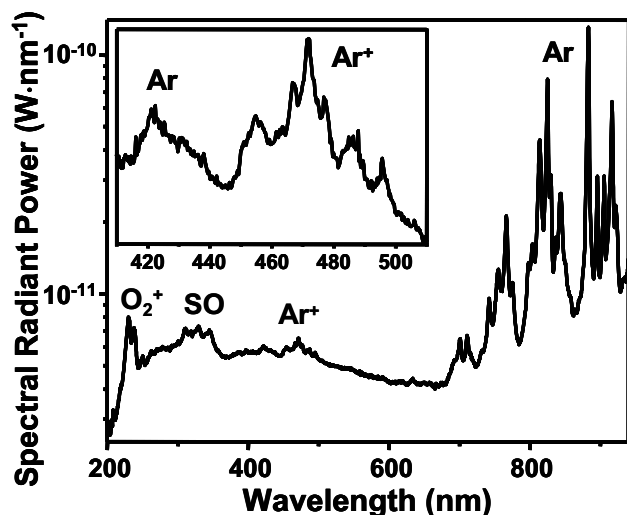

Fig. 3. SBSL spectra from 85% H_2SO_4 with 50 torr Ar and P_a 2.2 bar. The SBSL spectrum shows emission from Ar as well as Ar^+, O_2^+, and SO. (Insert) Enlarged region of the SBSL spectrum from 410 to 510 nm. The states in the $5p$-$4s$ manifold involved in emission of the Ar lines in the visible (410–450 nm) lie at 14.5–14.7 and 11.5–11.8 eV, respectively. The states involved in the observed Ar^+ emission (450–500 nm) are in the $4p$-$4s$ manifold; the Ar^+ $4p$ and $4s$ states lie at 35.0–37.1 and 32.4–34.2 eV above the Ar ground state ($3p^6$), respectively.

The gas contents of a bubble during SBSL are primarily a noble gas. Previous work has shown that by dissolving a noble gas into solution, the SL intensity is significantly increased relative to other gases such as N_2 or O_2 [3,21]. In addition, even if a small fraction of noble gas is mixed with a diatomic gas and dissolved into solution (or even air itself, which is 0.9% Ar), the SBSL from water behaves similarly to that observed from water containing the pure noble gas only. This is because the reactive diatomic gases are dissociated in the hot bubble interior and form soluble species (e.g., NO_x); the sonolysis products dissolve into the surrounding liquid, leaving only noble gas inside the bubble [17, 22-24]. The low thermal conductivities of the heavier noble gases as well as the high value of their polytropic ratio ($\gamma = 1.67$) also contribute to the observation of bright SL in the presence of these gases [25].

Although the use of noble gases is nearly ubiquitous in SL studies, emission from electronically excited noble-gas atoms was not observed until our recent work in mineral acids [7,19]. The observation of emission lines from noble-gas atoms, especially Ne and Ar whose excited states are 10 to 20 eV above the ground state, strongly suggests that a plasma is formed and is at least partly responsible for the light emission. The formation of a plasma during SBSL was verified by the direct observation of relatively weak emission lines from noble-gas monocations (Ar^+, Kr^+, and Xe^+) [20]. By using the same technique as that employed for MBSL, one could then determine SBSL temperatures. By analyzing the relative intensities of the Ar* emission lines, we found temperatures of as high as 15,000 K were generated during single-bubble cavitation (Fig. 4). This temperature may not reflect the core temperature within the collapsing bubble: Plasma formation may lead to an optically opaque region within the bubble that is characterized by much higher temperatures and pressures; the observed temperature may well only reveal the conditions at the outer shell of the inner opaque core [6,7,26].
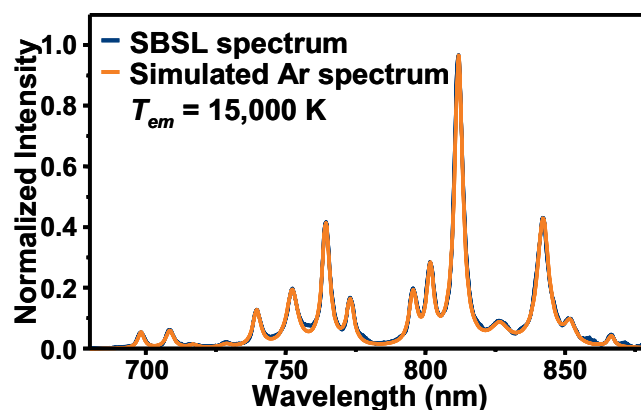

Fig. 4. SBSL from 85 wt% H_2SO_4 partially regassed with Ar. The emission lines arise from Ar* atoms. The SBSL emission is compared to a least-squares simulation of thermally equilibrated Ar* atom emission at 15,000 K. The underlying continuum has been subtracted for clarity.

4   MBSL in sulfuric acid

Having gathered a wealth of information about the conditions created during single bubble cavitation in H_2SO_4, we expanded our studies to MBSL in H_2SO_4 and discovered for the first time that there is also a plasma formed during MBSL [27]. The MBSL spectrum of H_2SO_4 under Ar, at relatively low acoustic power, consists of a broad continuum extending into the UV with sulphur monoxide (SO) and Ar emission lines on top of this continuum (Fig. 5). The Ar emission from MBSL in 95 wt% H_2SO_4 allowed for the determination of the cavitation temperature, just as earlier with Cr atom emission in silicone oil. Effective emission temperatures of ~8,000 K were measured; substantially greater than the ~5,000 K measured from MBSL in silicone oil. The main difference between the two liquids is the likely build-up of insoluble, polyatomic products produced by sonolysis of silicone oil, which effectively poison the cavitating bubbles and diminish the extreme conditions created during collapse. Sonolysis products from H_2SO_4, on the other hand, are more soluble in H_2SO_4, which permits for greater compressional heating in H_2SO_4. The temperature observed from MBSL in H_2SO_4 is less than the maximum temperature of 15,000 K observed from SBSL in H_2SO_4. In single-bubble cavitation, bubble collapse is less perturbed and more spherical than in a cloud of interacting bubbles, resulting in a greater temperature and pressure upon collapse.
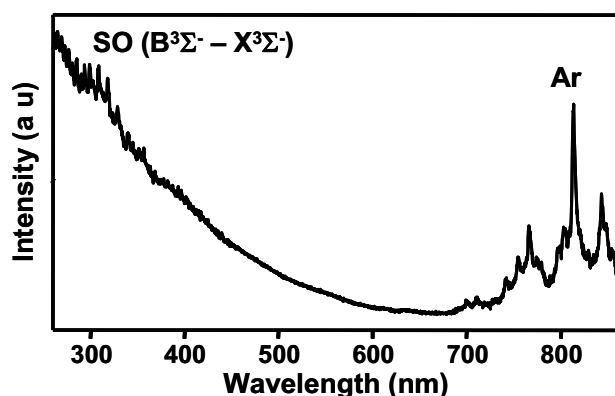

SO ($B^3\Sigma^-$ – $X^3\Sigma^-$)

Ar

Fig. 5. MBSL spectrum from concentrated sulfuric acid under Ar. Sonication at 20 kHz (14 W/cm^2) with a Ti horn directly immersed in 95 wt % sulfuric acid, ~298 K.

While MBSL has been studied much longer than SBSL, no evidence of a plasma had previously been observed, though plasma formation had been postulated a number of times [28,29]. The observation of Ar ($4p$ – $4s$ manifold, with an effective emission temperature of 8,000 K) is the first indication of the presence of a plasma during MBSL. At 8,000 K, there would be no appreciable amount of Ar atoms thermally excited to the 13 eV states responsible for the observed emission, so they must be excited by another means; most likely electron impact from a hot plasma core.

Furthermore, we discovered that the MBSL of sulfuric acid has three distinct light emitting regimes, which are determined by the applied acoustic intensity (Fig. 6). At high acoustic intensity, where most MBSL has been studied, the luminescent bubbles are mostly at the horn tip and the Ar lines are not visible. At low acoustic intensity, the luminescent bubbles have more of a filamentous

structure extending into the liquid, in which case strong Ar lines are observed. Because most MBSL studies have been done at high acoustic intensity, the more complex spectra had gone unobserved.
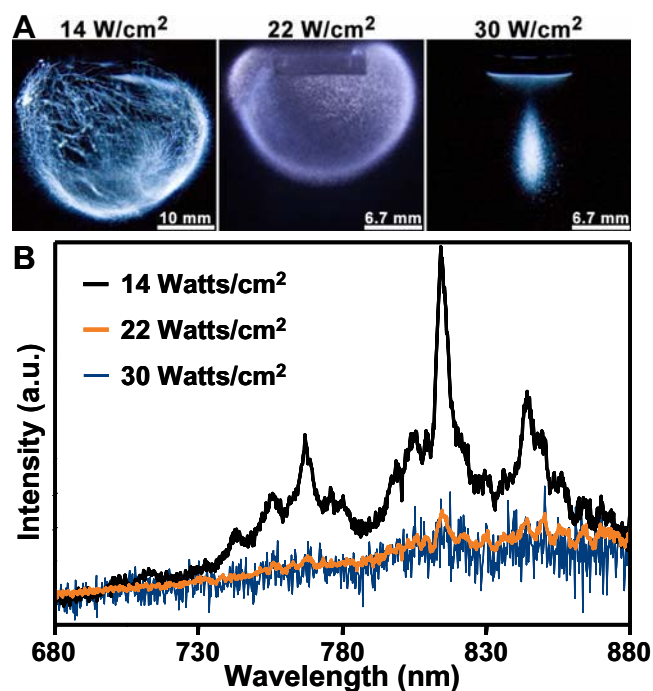

Fig. 6. MBSL of 95 wt % sulfuric acid at different acoustic powers. (a) Photographs of the different light emitting regimes of MBSL of H_2SO_4 increasing in acoustic intensity right to left. (b) MBSL spectra of 95 wt % H_2SO_4 at same acoustic intensities of the photographs. As acoustic intensity increases, the Ar lines become weaker.

5   Conclusion

Acoustic cavitation provides a unique method to drive chemical reactions. Spectrometric methods of pyrometry have proven particularly effective for temperature determinations during MBSL and SBSL. By employing the two-line radiance ratio method to relative intensities of emission lines from electronically excited metal atoms, we have determined an MBSL temperature of ~5,000 K for transient cavitation in long chain alkanes and silicone oil. By simulating thermalized Ar lines, the effective MBSL temperature in H_2SO_4 was found to be ~8,000 K.

Cavitation in a single, isolated bubble is generally assumed to be more intense than in a dense cloud of bubbles, owing to the sphericity of collapse and the lack of perturbation by other bubbles and the resonator walls. The recent observation of emission lines from electronically excited Ar atoms in SBSL from nonaqueous liquids permits the determination of SBSL temperatures in much the same manner as was done for MBSL. By comparing relative intensities of Ar* lines, we can determine emission temperatures and control them as a function of driving acoustic pressure and thermodynamics properties of the intracavity gas and vapor up to 15,000 K. These temperatures were determined at modest acoustic pressure. At elevated acoustic pressures, the Ar lines become severely broadened and indistinguishable from the

underlying continuum, and temperatures can be expected to be significantly higher as a result of the increased ferocity of bubble collapse.

These measured conditions may only hint at what occurs in the core of a collapsing bubble. Emission during single-bubble cavitation originates from noble-gas excited states as much as 20 eV above the ground state and from plasma emission from Ar^+, Kr^+, and Xe^+ as much as 40 eV above the ground state. These results reveal (for at least some liquids under some conditions) the hidden presence of a transient, optically opaque core of still higher energy.

Acknowledgments

References

1. D. F. Gaitan, A. Crum Lawrence, C. C. Church, A. Roy Ronald, "Sonoluminescence and Bubble Dynamics for a Single, Stable, Cavitation Bubble", *J. Acoust. Soc. Am.* 91, 3166-3183 (1992)

2. B. Gompf, R. Gunther, G. Nick, R. Pecha, W. Eisenmenger, "Resolving Sonoluminescence Pulse Width with Time-Correlated Single Photon Counting", *Phys. Rev. Lett.* 79, 1405-1408 (1997)

3. R. Hiller, K. Weninger, S. J. Putterman, B. P. Barber, "Effect of Noble Gas Doping in Single-Bubble Sonoluminescence", *Science* 266, 248-250 (1994)

4. W. C. Moss, D. A. Young, J. A. Harte, J. L. Levatin, B. F. Rozsnyai, G. B. Zimmerman, I. H. Zimmerman, "Computed Optical Emissions from a Sonoluminescing Bubble", *Phys. Rev. E:* 59, 2986-2992 (1999)

5. S. Hilgenfeldt, S. Grossmann, D. Lohse, "A Simple Explanation of Light Emission in Sonoluminescence", *Nature (London)* 398, 402-405 (1999)

6. C. Camara, S. Putterman, E. Kirilov, "Sonolumine-scence from a Single Bubble Driven at 1 MHz", *Phys. Rev. Lett.* 92, 124301/124301-124301/124304 (2004)

7. D. J. Flannigan, K. S. Suslick, "Plasma Formation and Temperature Measurement During Single-Bubble Cavitation", *Nature (London)* 434, 52-55 (2005)

8. K. Weninger, R. Hiller, B. P. Barber, D. Lacoste, S. J. Putterman, "Sonoluminescence from Single Bubbles in Nonaqueous Liquids: New Parameter Space for Sonochemistry", *J. Phys. Chem.* 99, 14195-14197 (1995)

9. Y. T. Didenko, W. B. M. McNamara, III, K. S. Suslick, "Molecular Emission from Single-Bubble Sonolumi-nescence", *Nature (London)* 407, 877-879 (2000)

10. J. D. Ingle Jr., S. R. Crouch, *Spectrochemical Analysis*, Prentice-Hall: Upper Saddle River, NJ, (1988).

11. R. H. Tourin, *Spectroscopic Gas Temperature Measurment: Pyrometry of Hot Gases and Plasmas*, Elsevier: New York, (1966).

12. K. S. Suslick, S. B. Choe, A. A. Cichowlas, M. W. Grinstaff, "Sonochemical Synthesis of Amorphous Iron", *Nature (London)* 353, 414-416 (1991)

13. K. S. Suslick, E. B. Flint, M. W. Grinstaff, K. A. Kemper, "Sonoluminescence from Metal Carbonyls", *J. Phys. Chem.* 97, 3098-3099 (1993)

14. W. B. McNamara, III, Y. T. Didenko, K. S. Suslick, "Sonoluminescence Temperatures During Multi-Bubble Cavitation", *Nature* 401, 772-775 (1999)

15. E. B. Flint, S. Suslick Kenneth, "The Temperature of Cavitation", *Science* 253, 1397-1399 (1991)

16. K. S. Suslick, E. B. Flint, "Sonoluminescence of Non-Aqueous Liquids", *Nature* 330, 553-555 (1987)

17. Y. T. Didenko, K. S. Suslick, "Energy Efficiency of Formation of Photons, Radicals & Ions During Single-Bubble Cavitation", *Nature* 418, 394-397 (2002)

18. J. B. Young, J. A. Nelson, W. Kang, "Line Emission in Single-Bubble Sonoluminescence", *Phys. Rev. Lett.* 86, 2673-2676 (2001)

19. D. J. Flannigan, K. S. Suslick, "Molecular and Atomic Emission During Single-Bubble Cavitation in Concentrated Sulfuric Acid", *Acoustics Research Letters Online-ARLO* 6, 157-161 (2005)

20. D. J. Flannigan, K. S. Suslick, "Plasma Line Emission During Single-Bubble Cavitation", *Phys. Rev. Lett.* 95, 044301/044301-044301/044304 (2005)

21. B. P. Barber, C. C. Wu, R. Lofstedt, P. H. Roberts, S. J. Putterman, "Sensitivity of Sonoluminescence to Experimental Parameters", *Phys. Rev. Lett.* 72, 1380-1383 (1994)

22. D. Lohse, M. P. Brenner, T. F. Dupont, S. Hilgenfeldt, B. Johnston, "Sonoluminescing Air Bubbles Rectify Argon", *Phys. Rev. Lett.* 78, 1359-1362 (1997)

23. K. Yasui, "Chemical Reactions in a Sonoluminescing Bubble", *J. Phys. Soc. Jpn.* 66, 2911-2920 (1997)

24. D. J. Flannigan, K. S. Suslick, "Plasma Quenching by Air During Single-Bubble Sonoluminescence", *J. Phys. Chem. A* 110, 9315-9318 (2006)

25. F. R. Young, "Sonoluminescence from Water Containing Dissolved Gases", *J. Acoust. Soc. Am.* 60, 100-104 (1976)

26. W. C. Moss, D. B. Clarke, D. A. Young, "Calculated Pulse Widths and Spectra of a Single Sonoluminescing Bubble", *Science* 276, 1398-1401 (1997)

27. N. C. Eddingsaas, K. S. Suslick, "Evidence for a Plasma Core During Multibubble Sonoluminescence in Sulfuric Acid", *J. Am. Chem. Soc.* 129, 3838-3839 (2007)

28. Y. T. Didenko, T. V. Gordeychuk, "Multibubble Sonoluminescence Spectra of Water Which Resemble Single-Bubble Sonoluminescence", *Phys. Rev. Lett.* 84, 5640-5643 (2000)

29. K. Yasui, "Temperature in Multibubble Sonolumi-nescence", *J. Chem. Phys.* 115, 2893-2896 (2001)