

Hot Spot Conditions during Cavitation in Water

Yuri T. Didenko,[†] William B. McNamara III, and
Kenneth S. Suslick*

Department of Chemistry, University
of Illinois at Urbana-Champaign, 601 S.
Goodwin Avenue, Urbana, IL 61801

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Liquids irradiated with high-intensity ultrasound undergo acoustic cavitation—the formation, growth, and implosive collapse of bubbles. The energy stored during the growth of the bubble in the rarefaction phase of the acoustic field is released when the bubble violently collapses in the compression phase of the acoustic field, as acoustic noise, shock waves, chemical reactions, and the emission of light (sonoluminescence, SL).¹ This violent collapse is predicted to generate a hot spot of thousands of Kelvin within the bubble,^{1–5} but, to date, there have been only a limited number of experimental measurements of the temperature of this hot spot.^{6–10} Although the SL of water has been studied for more than 50 years,^{11–13} the effective hot spot temperature during aqueous cavitation remains unresolved. Given the importance of aqueous cavitation (sonography and bioeffects of ultrasound, sonochemical remediation of aqueous pollutants, synthetic applications of sonochemistry, etc.¹⁴), we decided to apply our previous spectroscopic analysis of SL of nonaqueous liquids to aqueous solutions doped with small amounts of hydrocarbons. We have collected and analyzed excited-state C₂ MBSL (multi-bubble sonoluminescence, light emission from the clouds of cavitating bubbles) spectra from mixtures of organic liquids in water at 20 kHz and find an effective emission temperature of 4300 ± 200 K.

To probe the conditions inside cavitation bubbles in water, the first requirement was to find substrates that would yield sufficiently intense C₂ emission for analysis. In addition, the substrate must lead to emission at very low concentrations so as not to change the motion of the bubble from that experienced in pure water. To this end, MBSL spectra were collected for dilute aqueous solutions of the following organic substrates as precursors for C₂ formation:¹⁵ pentane, cyclohexane, benzene, ethanol, *tert*-butyl alcohol, and acetone. All of the substrates led to weak C₂

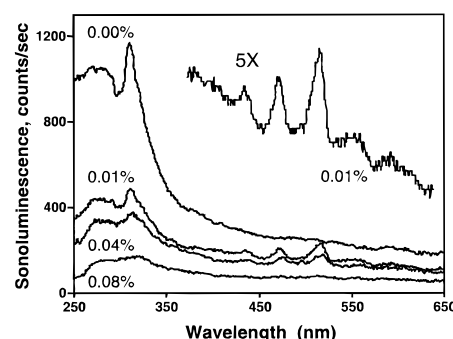
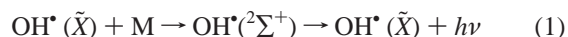


Figure 1. SL spectra of water–benzene mixtures at 278 K under Ar at 20 kHz and 50 W/cm². The spectra from top to bottom are for MBSL from pure water, 0.01% v/v benzene in water (also shown 5X expanded), 0.04% v/v benzene in water, and 0.08% v/v benzene in water.

emission and a significant decrease in the SL intensity of water when added to the solution.

The strongest C₂ emission among the substances studied arose from the irradiation of water–benzene mixtures, although it should be noted that the emission was very weak relative to C₂ emission from neat silicone oil or long-chain hydrocarbons. Figure 1 shows the representative case of the addition of small amounts of benzene to water. The intensity of SL decreases across the entire spectral region as the concentration of benzene is increased. It is interesting that the emissions from both C₂ (470 and 515 nm) and OH (310 nm) are significantly suppressed at benzene concentrations above 0.08%.

The other features in the MBSL spectra of water have been analyzed in some detail¹³ and consist of both emission from the OH* radical at 280, 310, and 340 nm and a continuum background.^{12,13} The hot spot created during bubble collapse will excite water molecules into different rotational, vibrational, and electronic states via inelastic collisions. If enough energy is absorbed by a water molecule during such collisions, it will dissociate giving a hydrogen atom and a hydroxyl radical in the ground or excited state.¹⁶ Hydroxyl radicals in the ground state can also be directly excited by collisions to give an emission with its maximum at 310 nm:



We have found that almost all the organic liquids added to water exhibit weak C₂ emission as a feature of the MBSL spectra. At the same time, the overall intensity of SL decreases. This is most likely due to the consumption of H atoms and OH radicals through reactions with the organic species, thus decreasing the likelihood of radiative recombination, a possible source of the continuum. Another possibility is collisional relaxation of excited-state water molecules by the organic substrates and, consequently, a decrease in SL intensity. C₂* formation generally involves the intermediacy of C₂H* or CH*,¹⁷ which certainly can arise during the sonolysis of volatile organics. The complete set of possible reactions of organic substances inside the cavitation bubble, and in the solution after bubble collapse, is very complex.¹⁸

(15) MBSL were obtained with a thermostated stainless-steel cell with a quartz window mounted to an Acton Research 505F spectrograph with an intensified, UV enhanced, diode array detector (Princeton Instruments IRY-512 N). Ultrasound produced by a 0.5 inch diameter Ti horn (Heat Systems 375) at 20 kHz, 50 W/cm² at the horn surface, 278 K, with an Ar sparge. Solutions were made from Nanopure water (18 MΩ·cm) with high-purity organic liquids used as received. The optical system was calibrated with NIST-traceable standard lamps from 200 to 800 nm.

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* Corresponding author. Tel.: 217-333-2794. Fax: 217-333-2685. E-mail: ksuslick@uiuc.edu.

[†] Visiting Research Associate on leave from Pacific Oceanological Institute, Russian Academy of Sciences, Vladivostok 690041, Russia.

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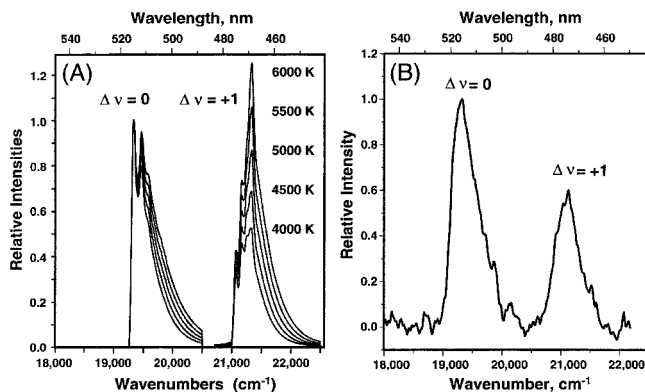


Figure 2. Emission spectra comparing the intensities of $\Delta\nu = 1$ to $\Delta\nu = 0$ bands of the $d^3\Pi_g - a^3\Pi_u$ transition (Swan bands) of C_2 ; (A) Calculated spectra; modified from ref 19. (B) Observed MBSL spectrum of 0.01% v/v benzene in water at 278 K under Ar at 20 kHz, with an estimated emission temperature of 4300 ± 200 K.

SL intensity decreases upon addition of small amounts of benzene to water. At benzene concentration above 0.08%, both C_2 emission and OH^\bullet emission disappear (Figure 1). A possible explanation of this effect is that, at high intrabubble concentrations of benzene, the concentration of OH^\bullet is insufficient to completely oxidize benzene to the short fragments required to produce C_2 emission. The reaction is limited to a few initial steps, OH^\bullet is consumed with no production of C_2 , and the intensity of both OH^\bullet emission and C_2 emission are consequently diminished. Note here that the absence of OH^\bullet emission at high concentration of benzene in solution confirms the importance of the reaction in eq 1 in the gross scheme of water SL.

The C_2 emission from water–benzene mixtures was used to estimate the temperature of cavitation following the method of Flint and Suslick.^{7,19} They compared the MBSL spectra of silicone oil saturated with Ar to synthetic spectra calculated using the well-understood theory of diatomic emission. Synthetic spectra for C_2 emission as a function of temperature were generated for the thermally equilibrated case, as shown in Figure 2; details of these calculations are given elsewhere.^{7,19}

The intensity of C_2 emission from water–benzene mixtures is much weaker than that from silicone oil, and we were limited to a comparison of the interband intensities of the $\Delta\nu = 0$ and $\Delta\nu = +1$ bands, as shown in Figure 2. This gives an effective emission vibrational temperature of 4300 ± 200 K. This is significantly lower than that observed from silicone oil (5080 ± 160 K),⁷ which is explained by the higher vapor pressure of water (6.6 Torr) compared with that of silicone oil (<0.01 Torr).

The polytropic ratio of water is substantially lower than that of Ar, and the rotational and vibrational modes of water molecules inside the cavitating bubble serve as heat sinks. In addition, as the bubble is heated, dissociation begins to occur, and this endothermic process absorbs substantial energy. The energy consumed by all these processes is thus unavailable for raising the temperature of the bubble contents.

The interpretation of this spectroscopic temperature is not without complications. The temperature within an imploding bubble will have both a temporal and a spatial profile, and the emission spectra will thus vary as a function of time during collapse and the site of emission within the bubble. The overall emission will be dominated by the hottest portion of this cycle. The effective emission temperature obviously does not provide a unique parameter with which to describe this complex profile. Furthermore, C_2 is the product of a complicated set of chemical

reactions, and the initial distribution of states might reflect the thermodynamics of this chemistry rather than the conditions within the bubble. Unlike a flame, however, the contents of a cavitation bubble are subjected to high pressures and collisional frequencies. Thus, it is likely that C_2^* reaches thermal equilibrium during its lifetime, as previously discussed.²⁰

It has also been argued that the dissociation energy of C_2 provides an upper limit to its use for spectroscopic thermometry: since C_2 dissociates at temperatures not too much above 5000 K, this could be an upper limit to the temperature range for C_2 thermometry.²¹ Bernstein and Zakin speculate that the interiors of cavitation bubbles reach temperatures well in excess of 5000 K.²² Recent work in this laboratory, however, has confirmed the 5000 K temperature in low volatility solvents using metal-atom emission, which is not prone to dissociation effects.²³ Even more importantly, the spectroscopic temperatures for cavitation in water reported here are well below those required for dissociation of C_2 .

There have been few prior attempts to estimate cavitation temperatures in water. Seghal and co-workers used MBSL from aqueous alkali metal salt solutions in an attempt to probe the temperature and pressure inside a cavitation bubble.⁸ In particular, they used the broadening and shift of Na and K lines in the SL spectra of water–salt solutions with the implicit assumption that adiabatic compression of the bubble begins at 1 atm and 285 K. The initial temperature and pressure at the point of adiabaticity during bubble collapse, however, are unknown;³ thus, no accurate estimates of hot spot conditions are possible from their work. In addition, their method for determining line widths and shifts was erroneous because of line asymmetry and insufficient spectrometer resolution. For these reasons, the report by Seghal et al.⁸ must be viewed with skepticism.

Another, more reliable approach was taken recently by P. Riesz and co-workers, who analyzed isotope effects in the formation of radicals during aqueous sonolysis.⁹ In particular, they used spin traps to study the relative rates of O–H and O–D bond cleavage during ultrasonic irradiation of Ar-saturated H_2O – D_2O mixtures. Unfortunately, there are intrinsically substantial error limits in this technique. They found that the temperature inside the bubble was between ~ 2000 and ~ 4000 K, depending on the spin trap. In addition, Hoffmann and co-workers have recently estimated the interfacial temperature during remediation of nitrophenols,¹⁸ but this does not probe the gas phase of the collapsing bubble.

We conclude that the effective emission temperature during cavitation in water is 4300 ± 200 K. The concentration of benzene in solution is very low ($\sim 0.01\%$), and the vapor pressure of benzene inside the bubble should be negligible compared with that of the water. It is therefore unlikely that the presence of benzene would perturb the bubble dynamics relative to that of pure water. We also note that the kinetic isotope effect studies of Riesz and co-workers,⁹ while giving only a broad range of possible cavitation temperature (2000–4000 K), are in reasonable agreement with our results, despite the vastly different techniques employed.

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