Temperature Nonequilibration during Single-Bubble Sonoluminescence

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S *Supporting Information*

ABSTRACT: Single-bubble sonoluminescence (SBSL) spectra from liquids having low vapor pressures, especially mineral acids, are exceptionally rich. During SBSL from aqueous sulfuric acid containing dissolved neon, rovibronic emission spectra reveal vibrationally hot sulfur monoxide (SO; T_v = 2100 K) that is also rotationally cold (T_r = 290 K). In addition to SO, excited neon atom emission gives an estimated temperature, for neon, of several thousand Kelvin. This nonequilibrated temperature is consistent with dynamically constrained SO formation at the liquid−vapor interface of the collapsing bubble. Formation occurs via collisions of fast neon atoms (generated within the collapsing bubble) with liquid-phase molecular species in the interfacial region, thus allowing for a mechanistic understanding of the processes leading to light emission.
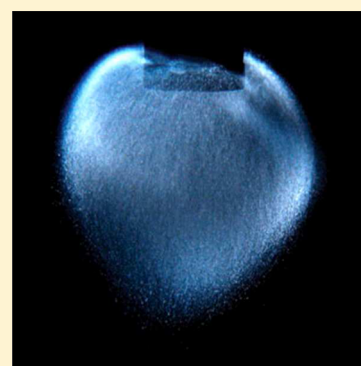
SECTION: Spectroscopy, Photochemistry, and Excited States

A single bubble can be levitated and driven into repeatable nonlinear oscillations by application of an acoustic standing wave to a liquid. Under certain conditions, a brief flash of light is emitted during the maximum implosion of the bubble, a phenomenon dubbed single-bubble sonoluminescence (SBSL).[1−4] In water, the known portion of the SBSL emission spectrum is typically featureless and broad-band, ranging from the UV to the near-IR.[5] From less volatile liquids, however, the spectra can be rich with lines from molecules, atoms, and ions. The relative intensities and profiles of such lines provide a means to quantify the intracavity conditions and processes.[4,6−8] These conditions can be extreme, at least in part, because of the relatively low number density of molecular species inside of the bubble. Thus, the compressional heating that arises during cavitation is generally expected to be more severe in less volatile liquids due to a reduction in endothermic processes.[9,10]

Previously, we reported that SBSL from sulfuric acid (H_2SO_4) containing dissolved neon shows emission from both atomic (neon) and molecular (sulfur monoxide, SO) species.[8] The emission bands from SO are due to transitions between several vibrational levels in the B $^3\Sigma^-$ excited state and X $^3\Sigma^-$ ground state, while neon emission occurs from the 3p−3s array, with the 3p states being over 18 eV in energy. From the SO bands, relatively modest vibrational temperatures (1500−3500 K, depending upon the acoustic driving pressure) were observed.[7] More recently, Xu and Suslick observed significantly higher vibrational temperatures of nearly 10 000 K

during SBSL from 65 wt % phosphoric acid (H_3PO_4) by comparison to simulated hydroxyl radical (OH) rovibrational emission spectra.[11]

For typical SBSL studies, the conditions determined from molecular and atomic lines are a spatiotemporal average of the entire observable emitting region. That is, the molecular and atomic emitters may not be uniformly distributed throughout the bubble interior and additionally may be emitting at different times during implosion.[7,12,13] Because emitting species are sensitive to the local environment, however, the line intensities and profiles may be used to develop a molecular-level mechanistic understanding of the conditions and processes associated with SBSL.

Here, we report the observation and quantification of nonequilibrated temperatures during sonoluminescence. For SBSL from aqueous H_2SO_4 under a partial pressure of neon, the vibrational temperature (T_v) of SO is found to be 2100 ± 300 K, while the rotational temperature is cold (T_r = 290 ± 30 K). Such nonequilibration between rotational and vibrational temperatures is evidence that the SO emission is not arising in the gas phase of the collapsing bubble. As discussed below in detail, we suggest that SO is instead being formed at the bubble vapor−liquid interface. The SO so formed experiences a dynamical constraint at the interfacial region that renders it

rotationally cold,[14] thus providing insight into the intracavity chemical processes occurring during cavitation.

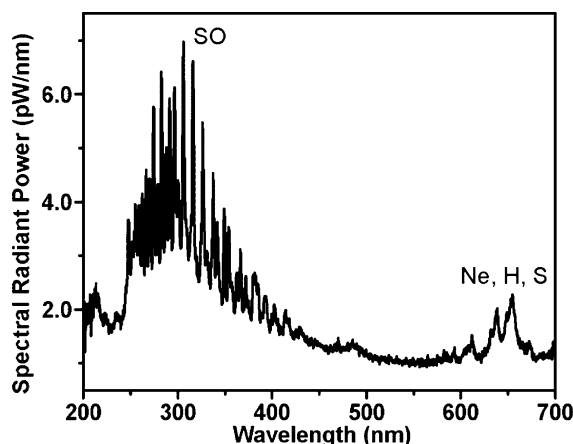Figure 1 shows the SBSL spectrum observed from 80 wt % H_2SO_4 under 50 Torr of neon. The spectrum in the UV region

Figure 1. SBSL spectrum from 80 wt % H_2SO_4 under 50 Torr of neon at a 4.7 atm measured acoustic pressure. Major features are labeled with the species responsible.

is dominated by emission from vibrational levels of the SO B $^3\Sigma^-$ excited state to various levels of the X $^3\Sigma^-$ ground state. There are also emission bands at longer wavelengths arising from neon, hydrogen, and sulfur atomic excited states. It is interesting to note that we did not observe any emission lines from atomic oxygen, though the 777 nm line has been seen in SBSL spectra from aqueous H_2SO_4 containing air.[15]

Figures 2 and 3 show expanded regions of the spectrum from Figure 1 compared to least-squares fit simulations. The
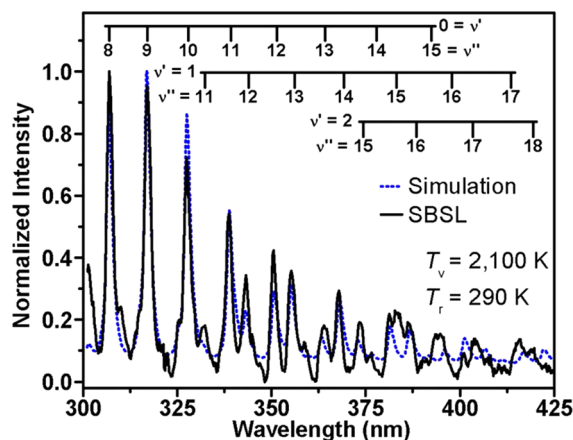

Figure 2. Expanded region of the SBSL spectrum from 80 wt % H_2SO_4 (underlying continuum subtracted) compared to a least-squares fit simulation of SO emission with T_v = 2100 K and T_r = 290 K. Transitions from the first three vibrational levels of the B $^3\Sigma^-$ excited state (ν' = 0, 1, and 2) to various levels of the X $^3\Sigma^-$ ground state (ν'') are labeled.

simulations were done using PGOPHER[16] and published molecular constants[17,18] and Franck–Condon factors[19] for the B and X states of SO. A striking observation from the simulations is that T_r for SO is not equivalent to T_v, as has generally been observed in prior sonoluminescence spectra.[4,11,20,21] Rather, T_r is found to be nearly equivalent to the
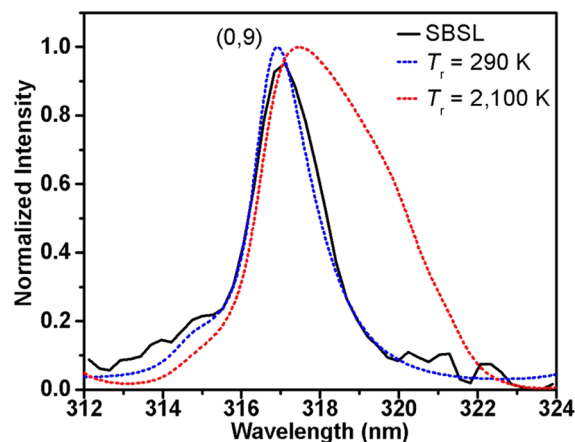

Figure 3. Higher-resolution region of the SBSL spectrum shown in Figure 2 compared to least-squares fit simulations with T_r = 290 and 2100 K. T_v = 2100 K for both simulations.

bulk liquid temperature (290 K), while T_v = 2100 K. To further illustrate that SO is rotationally cold, the (0,9) transition (B, ν' = 0 → X, ν'' = 9) was isolated at increased resolution and compared to simulations with T_r = 290 and 2100 K and T_v fixed at 2100 K (Figure 3). As can be seen, the experimental spectrum is well-matched by the rotationally cold simulation.

To rationalize the observed SBSL spectra, it is useful to know the vapor- and liquid-phase compositions of H_2SO_4. The vapor phase above aqueous H_2SO_4 solutions is mainly comprised of H_2O, SO_3, and H_2SO_4. At room temperature, the partial pressures of H_2SO_4 and SO_3 above 80 wt % H_2SO_4 are 6 and 12 orders of magnitude lower than that of H_2O, respectively; the vapor composition is comprised mainly of H_2O and whatever inert gas is dissolved in the solution.[22] Thus, if the vapor phase was the location for the formation and excitation of the emitting species, one would expect to see spectra dominated by OH rather than SO in the near-UV. Therefore, SO must be formed and excited via processes that do not involve isolated precursor molecules in the vapor interior of the bubble.

The two-site model of sonochemical reactivity indicates that a hot interfacial liquid–vapor shell, distinct from the interior vapor phase and the relatively cold bulk liquid, is conducive to radical formation and light emission.[23−25] This interfacial shell is the most likely location for SO formation and excitation. Note that for the liquid–air interfacial region of aqueous H_2SO_4 solutions, the overall surface composition matches that of the bulk,[26,27] though the molecular orientations and hydrogen bonding structure differ significantly.[28,29] The hydrogen bonding that occurs between molecules in the liquid means that the surface of 80 wt % H_2SO_4 has few free OH groups protruding into the vapor phase; the surface is dominated by S=O groups oriented away from the bulk liquid.[28] These surface SO groups are mainly from HSO_4^- of bisulfate/hydronium ion pairs and from H_2SO_4 at the interface.[27]

Under our experimental conditions, the vapor phase of a collapsing bubble in 80 wt % H_2SO_4 is dominated by neon atoms (0.14 Torr of H_2O vapor versus 50 Torr of Ne). Thus, the formation and excitation of SO at the liquid–vapor interface is likely initiated via collisions with energetic gas-phase neon atoms. As a useful analogy, collisions of energetic neon atom beams with H_2SO_4 solutions results in significant energy

transfer to the surface molecular species via atom trapping/desorption.[30−32] These collisions lead to vibrational excitation, heating, and dissociation of interfacial molecular species. Further, the species released from such fast atom collisions with H_2SO_4 surfaces do not show thermalized Boltzmann behavior.[30]

The observation of low SO T_r indicates a dynamical constraint during formation that results in little torque, and thus low T_r, on the escaping diatomic molecule. In the case of H_2SO_4 surfaces, the dynamical constraints arise from the OH groups being tightly bound in a crystalline-like hydrogen bonding network, which reduces the tumbling and minimizes the recoil of the parent molecules during formation of SO. Indeed, H_2 molecules, which are sterically undemanding and without any dipole, have been observed to be rotationally cold when leaving hot silicon surfaces due to low torque during desorption.[14]

Through the process of energetic atom impact on a H_2SO_4 surface, one would expect T_v of SO to be no greater than the translational temperatures of the impacting neon atoms due to high collision rates and rapid thermal equilibration at the interface. That is, the bulk solution (100 cm³) acts as a massive heat sink compared to the cavitation hot spot (~1 μm³). Figure S1 in the Supporting Information shows a simulation of the section of the SBSL spectrum obtained from 80 wt % H_2SO_4 that contains neon atom lines. All lines of neon, hydrogen, and sulfur having known constants were included in the simulation,[33] and the temperature-dependent electronic partition functions were determined for each.[34] Lines for atomic oxygen and the monocations of each atom were also included in initial simulations, but this did not produce better agreement with experiment. The least-squares fit simulation indicates a temperature of between 5000 and 10 000 K for neon, which is above T_v for SO (2100 K). Further, the relative number density of gas-phase neon is found to be many orders of magnitude higher than that of hydrogen or sulfur. Thus, collision of energetic neon atoms with interfacial species is the most probable event.

In conclusion, analysis of SBSL spectra from aqueous H_2SO_4 solutions with neon shows the formation and excitation of nonthermal SO. The significant difference in the SO rotational and vibrational temperatures rules out its formation in the vapor phase of the collapsing bubble. Rather, the formation of SO likely arises from the impact of energetic neon atoms (formed during compressional heating of the vapor within the collapsing bubble) with the vapor−liquid interface. Thus, the SO is serving as a local molecular probe of the conditions and processes occurring at the liquid−vapor interfacial region of the collapsing bubble.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details, one data table, and one figure about the SBSL SO and Ne spectra simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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