

Evidence for Gas Exchange in Single-Bubble Sonoluminescence

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In this Letter we describe measurements of the light emission evolution for single-bubble sonoluminescence. In particular, we show that the evolution of intensity for an air bubble depends on whether or not the bubble has previously been in a steady sonoluminescence state. Our results provide strong experimental evidence in support of the recent hypothesis that an air bubble undergoing single-bubble sonoluminescence in water transitions to an argon bubble. [S0031-9007(97)05098-9]

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When a small (nominally $5\ \mu\text{m}$ radius) air bubble is levitated by a standing wave in moderately degassed water under applied acoustic pressure amplitudes near 0.1 MPa, the bubble undergoes highly nonlinear radial pulsations. The bubble grows to several times its equilibrium radius during the tensile portion of the sound field, and then undergoes a violent and inertially dominated collapse during the compression phase. The collapse is so violent that light is emitted near the final stages of collapse of the bubble [1], yet the dynamics of the system repeat each acoustic cycle. This phenomenon has been called single-bubble sonoluminescence (SBSL) [2]. Several properties of the emitted light have been measured, including an extremely short emission duration [3,4], an energy spectrum without any observable peaks (at least for most gases) that increases into the ultraviolet (where the UV cutoff of water makes higher energy observations impossible [5,6]), and an unusual dependence of the light intensity on the relatively minor doping of noble gases [7].

Several theories have been proposed to explain the anomalous observations [8–14]. Although many of these theories purport to explain the emission lifetime and the spectral characteristics, very few theories attempt to explain the dependence on noble gas doping. We present here experimental evidence that appears to strongly support the “argon rectification” hypothesis [15] (including the recent calculations of Moss *et al.* [16]) which describes the sensitivity of noble gas doping as a process of gas exchange between the interior bubble contents and the dissolved gases in the host liquid. Although there currently exists experimental evidence that supports the argon rectification hypothesis, this evidence is principally circumstantial [15]. We show here that the intensity of SBSL depends directly on the time the bubble spends in the sonoluminescence state, and thus provides stronger and independent evidence that rectification does indeed occur.

The argon rectification hypothesis [15] infers that oxygen and nitrogen gases within a sonoluminescing air bubble are converted into chemically reactive species that are quickly and irreversibly transferred to the host liquid, while the nonreactive noble gases will remain within the bubble and provide a source for the electromagnetic

emissions. Thus, an air bubble, driven above the luminescence threshold, will eventually be converted to an argon bubble. Our goal was to test this hypothesis and to measure the time scales involved. In our experiment, we produced a rapid increase in the acoustic pressure amplitude from below the light-emission threshold to a value above the threshold, while we simultaneously monitored the bubble’s oscillations and light-emission intensity. We proposed that, if argon rectification was occurring, the transition time for light emission would be different, depending on whether the bubble had previously been in a sonoluminescing state. Our work improves upon earlier work [17,18] in that we were able to measure the instantaneous bubble radius and emission intensity, cycle to cycle. This real-time monitoring was necessary, due to the transient nature of the experiment.

Our experimental configuration consisted of a completely sealed 100 ml spherical levitation cell (driven at its fundamental resonance frequency of 30.0 kHz), filled with water and a gas concentration (measured as a partial pressure) of 110 mm hg for all gases studied, a photomultiplier tube (PMT) to monitor the light emission from the bubble, a laser-scattering system [19–21] to measure in real time the cycle-to-cycle radius-time profile of the bubble, and a fast digitizing oscilloscope (LeCroy 9384L) with 8 Mbyte of memory to collect the data. We use an optical bandpass filter and laser line filter, respectively, on our PMTs to collect the light emission and $R(t)$ profile. For most cases, the oscilloscope was configured to capture data at a resolution of 4 ns/point for a length of 8 ms (corresponding to approximately 240 consecutive acoustic cycles). In these experiments, we rapidly increased the acoustic pressure from approximately 0.10 to 0.14 MPa, corresponding to the pressure amplitude below and above the luminescence threshold, respectively (the rapid increase in the drive pressure resulted in a new equilibrium pressure after approximately 90 acoustic cycles, as measured with a needle hydrophone).

The cycle-to-cycle response of a bubble subject to a rapid pressure increase is shown in Fig. 1. Here, the individual $R(t)$ curves are shown as the bubble transitions to a different steady state. Near the 60th acoustic cycle,

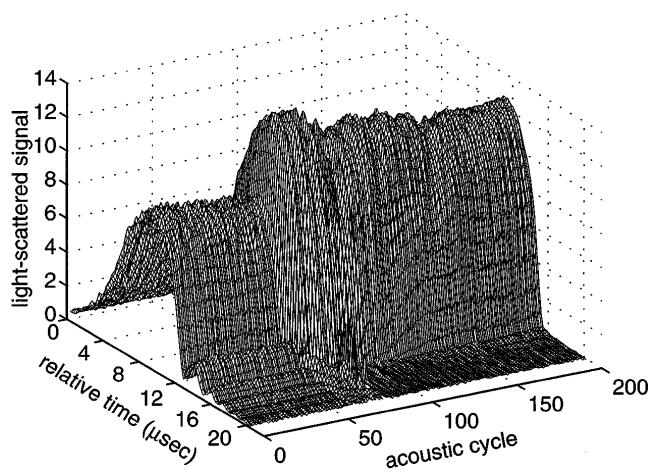


FIG. 1. The radius profile of a room-temperature air bubble as it transitions from a nonsonoluminescing state to a sonoluminescing state caused by an abrupt increase in the acoustic drive pressure. The increase occurs near acoustic cycle 60 in this figure. The bubble responds by collapsing at a later time, with a decrease in the rebound amplitude. The response time for the bubble (as well as the resonator) depends on the Q of the system; the pressure increase causes the bubble to overshoot initially before it settles down to a steady value after about 90 cycles. The highly irregular signal observed after the rapid increase in pressure is initiated is probably due in part to non-radial oscillations of the bubble.

the drive pressure is quickly increased to a level above the luminescence threshold. Note that these real-time measurements follow the bubble response to a rapid increase in the drive pressure amplitude. These measurements are not of steady-state bubbles at different drive pressures.

We were able to observe very low levels of SBSL emissions occurring soon after the pressure increase [Fig. 2(a)], provided we precooled the water (near 10°C). This low-level intensity gradually increased over a time scale of seconds until the PMT was saturated. At room temperature, we were unable to observe definitive light emission for a few hundred acoustic cycles.

With the liquid at room temperature, we allowed a bubble to stabilize for approximately 30 s in the SBSL state. Then, we quickly lowered the drive pressure to its original value below the luminescence threshold and then, after ≈ 90 ms (corresponding to ≈ 2700 acoustic cycles), we quickly returned the drive pressure back to its original value above the luminescence threshold. This time, the SBSL emissions were observed to occur almost instantaneously, and at a relatively intense level [see Fig. 2(b)]. The difference is that, in Fig. 2(b), the bubble was allowed to remain in a steady SBSL state for a period of time, before the rapid pressure change experiment was initiated, while in Fig. 2(a), the bubble was initially in a nonsonoluminescing state.

We show results for an air bubble at two different liquid temperatures to emphasize that light emission does indeed occur soon after the transition, except that, at room temperature, the emission is apparently too weak to be observed until after some rectification occurs (with nitrogen

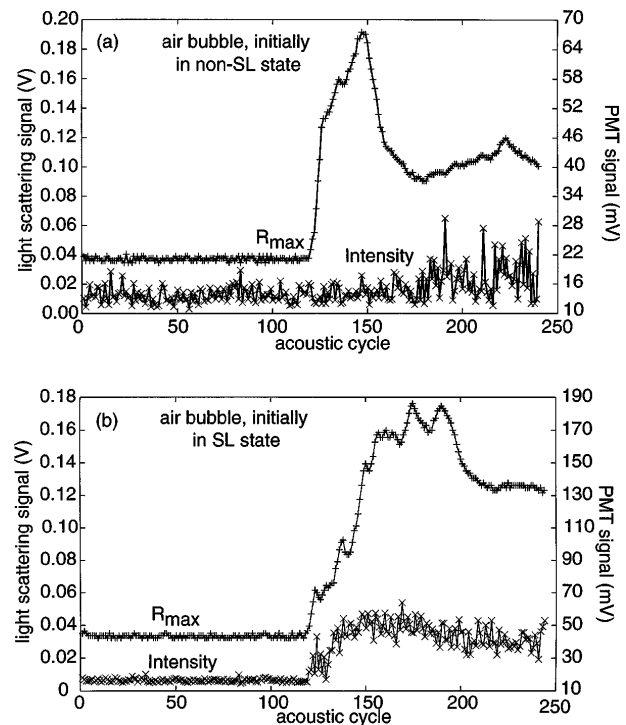


FIG. 2. The maximum radius (+) and sonoluminescence intensity (x) of an air bubble is plotted over approximately 240 consecutive acoustic cycles. The "radius" is actually a signal level, proportional to the square of maximum radius (assuming a geometrical optics limit for scattering from a sphere). (a) The bubble is initially below the light-emission threshold. The corresponding PMT signal level corresponds to noise. At approximately the 120th acoustic cycle, the drive pressure is rapidly increased to a value above the SBSL threshold. (b) For this case, the bubble is initially in a stable sonoluminescing state. The drive pressure is then rapidly reduced to a value below the light-emission threshold, and then quickly increased again after a time period of approximately 90 ms. In both (a) and (b), the drive amplitudes at the lower and upper values are the same.

bubbles, the emission remains weak). After the bubble has stabilized in a sonoluminescing state, the resulting sonoluminescence transition time is nearly instantaneous, *even* at room temperature. We have also observed that, if the pressure is reduced to below the luminescence threshold for longer than about 20 s, the resulting sonoluminescence transition time behaves similar to Fig. 2(a); that is, it again becomes an air bubble.

We also examined a bubble in water containing only nitrogen (again, cooled in order to observe the light emission), and in water containing only argon [at room temperature (see Fig. 3)]. These results are to be compared with Fig. 2 for an air bubble in water. In both the top and bottom portions of this figure, the acoustic pressure is rapidly increased from below the luminescence threshold to a value above it. We note that the relative light intensity of a (pure) nitrogen bubble [Fig. 3(a)] is similar to that of the (true) air bubble immediately after its transitions from below the threshold to above the threshold [Fig. 2(a)]. Similarly, the light intensity from the pure

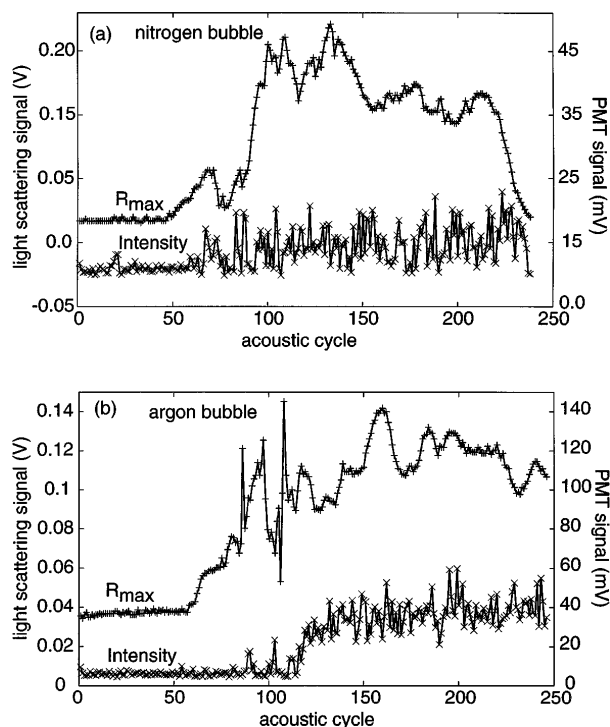


FIG. 3. The maximum radius (+) and sonoluminescence intensity (x) of (a) a nitrogen bubble and (b) an argon bubble are plotted over approximately 240 consecutive acoustic cycles. In both cases, the acoustic pressure has initially been below the light-emission threshold. The pressure is then rapidly increased to a value above the threshold (same values as in Fig. 2).

argon bubble [Fig. 3(b)] is similar to that of an (presumably, but not actually) air bubble that was initially sonoluminescing, then driven below, and then (90 ms later) quickly returned to above the luminescence threshold. We have also performed these pressure-increase experiments with neon and helium and found in all cases that the light emission occurs soon after the pressure is increased above the SBSL threshold, with an emission intensity similar to that for argon.

Our results show some variability in the maximum radius, light intensity, and onset delay time for light emission. The degree of variability changes from run to run. The variability in the radius is due in part to the increased noise level from light scattering when the bubble is near its maximum size, in part to bubble motion when the pressure increase is initiated, and in part to instabilities in the bubble dynamics during and immediately after the pressure increase. Our technique of capturing the transient behavior precludes the use of averaging to smooth out these variations.

The onset delay time for light emission may be due in part to gas diffusion, although diffusion time scales are typically much longer than the observed delay of milliseconds. A more probable delay mechanism is the induced shape instability of the bubble. We believe that the sharp spikes in the maximum radii seen in Fig. 3(b), for example, are a result of nonradial oscillations of the

bubble [a deformed bubble can reflect and refract incident light in such a manner as to cause focusing at different locations (see also Fig. 1)]. These instabilities would serve to limit the energy concentration of a collapsing bubble, and thus limit the light emission intensity. (Note that, as a control, we kept the gas concentration constant throughout. Changing the gas concentration of argon may stabilize the radial pulsations; the light emission is still strong.)

In summary, these experiments provide strong evidence that a sonoluminescing bubble is a “chemical reaction chamber,” as proposed by Brenner *et al.* [15]. It rapidly converts the nitrogen and oxygen present in air into chemically active species that irreversibly leave the interior of the bubble and eventually stabilizes with mostly argon (and water vapor) inside the bubble. (We note for reference that, at room temperature and pressure, the molecular binding energies of diatomic nitrogen and oxygen are 9.41 and 4.98 eV, respectively, and the first ionization energy for argon is 15.7 eV.) An air bubble that is driven below the SBSL threshold remains truly an air bubble; however, when it is driven above the SBSL threshold, the transition time for argon replacement appears to be on the order of a few seconds. Once the bubble is driven above the luminescence threshold, and argon rectification occurs, reducing the driving pressure to below the luminescence threshold and then returning it back above the threshold gives us a unique and novel probe to determine this rectification time. We shall report on these rectification times for a variety of gases as our experiments continue. Parenthetically, we note that our experiments utilize the luminescence threshold in order to quantify the time scales for argon rectification. The dissociation of nitrogen and oxygen and the luminescence threshold may or may not be correlated.

Argon rectification may also be a major factor that influences comparisons between SBSL and MBSL (multibubble sonoluminescence): It takes several thousand acoustic cycles to rectify the argon, and MBSL bubbles probably do not survive for more than a few cycles [22]. Our results also show that the acoustic storage mechanism proposed by Brenner *et al.* [23] is unlikely to be involved, since the light emission occurs almost immediately after the pressure increase. Finally, this unique and robust system may provide an exciting laboratory for sonochemistry.

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