Luminescence Characteristics of Laser-Induced Bubbles in Water

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The luminescence characteristics of laser-created bubbles in water have been studied for pressures between 1 and 15 bars. A fast peak in the luminescence is correlated with the first collapse point of the bubble. The width of the light pulse is several nanoseconds, and increases with the bubble size. With increasing pressure two fast peaks are observed, separated by tens of nanoseconds; this is found to arise from an instability where the bubble splits into two at the collapse. The luminescence is independent of whether the water contains ambient dissolved air, is completely degassed, or is filled with 150 torr partial pressure of argon gas or 1 bar of xenon gas.

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The phenomenon of luminescence from bubbles in water has a long history, starting from multibubble sonoluminescence in water cavitated by strong acoustic fields [1], to the more recent discovery of single-bubble sonoluminescence (SBSL) from bubbles acoustically trapped in resonant cavities [2,3]. There have also been observations of luminescence from the collapse of single bubbles injected into the liquid without a sound field present, with the bubble being formed by different techniques such as electrical discharges [4], syringe injection of gas into a Venturi flow field [5], or the use of a focused laser beam vaporizing the liquid [6–8] or colloidal particle suspensions [9].

The physical origin of the luminescence is still not well understood. Early papers attributed it to the recombination radiation of metastable atomic and molecular states created in the bubbles [7,10]. In the more recent single-bubble sonoluminescence the most accepted models involve bremsstrahlung radiation from the plasma created by adiabatic compression [11–13] and then possibly further shock-wave heating of the gas in the bubble [12], although a number of other different mechanisms have also been proposed [13,14]. To better understand the nature of light emission from bubbles, we have studied the luminescence and oscillation dynamics of laser-created bubbles in water as a function of the static pressure and as a function of the gases dissolved in the water. We find similarities to SBSL, in that the emission at the bubble collapse is a fast pulse (nanosecond widths), but unlike SBSL there is no dependence on the dissolved gases. With the application of pressure the created bubbles are smaller and collapse more rapidly, allowing examination of the interplay between the luminescence from the recombining metastables and the luminescence at the collapse point. An unusual feature is that with pressure the fast pulse splits into two pulses separated by tens of nanoseconds; photographs show that this is due to an instability in the late stages of the collapse where the bubble splits into two.

The measurements use a focused Nd:YAG laser to create the bubbles. The Q-switched pulse at 1064 nm is 6 ns long and has a maximum energy of 0.6 J per pulse. The sealed sample cell has pressure and temperature sensors mounted in it, and the input window for the laser is made of a 25 mm diameter lens of focal length 3 cm. The surrounding three windows and a bottom window are borosilicate glass 3 mm thick, passing light at 300 nm and above. A beam expander and variable iris in front of the lens allows the tightness of the focal spot to be varied; in the present measurements the iris was left open, producing a relatively large spot size ($7-10\ \mu$m) that produced larger bubbles, up to 1 mm in radius. The tradeoff with the larger spot size is that the bubbles produced are slightly aspherical, as will be discussed later. The light emission from the bubble is monitored by a Hamamatsu H6780-03 photomultiplier, whose output is measured across the 50 Ω input of an HP 54820A oscilloscope. The bubble characteristics are observed with a long-distance microscope with about a 2 mm field of view at the focal point of the laser, which is in the middle of the cell, more than 30 mm from any solid surface. Backlighting the bubble with a cw laser (either a 10 mW He-Ne or 100 mW argon ion) pulsed with a width of 0.6 μs through an acousto-optic modulator allows photographing the bubble at various stages of its growth and collapse with a CCD camera at the microscope output, or alternately with steady laser backlighting the bubble radius versus time can be obtained from the variation of the signal of a photodiode also viewing the microscope output through a beam splitter.

The water in the cell is triple distilled and deionized, and has been passed through a 0.22 μm filter. For some measurements it is left with the ambient air dissolved in it; for other runs it is first pumped with a mechanical pump through a nitrogen cold trap for several hours while being circulated with a magnetic stirrer. It is then either left degassed, or a desired partial pressure of argon or xenon gas is introduced, and the water is then transferred with piping into the cell. The cell can be pressurized by expanding a stainless-steel bellows in the filling line with a hydraulic jack. The YAG laser power is adjusted to

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just above the threshold where the laser pulse creates a plasma hot spot at the focus; this threshold depends on the impurity content of the water, and is highest for the ambient triple-distilled water and lower for the degassed samples where inevitably more impurities are introduced during the handling process.

Figure 1(a) shows the time dependence of the bubble radius and the accompanying luminescence emitted, for a completely degassed sample at ambient 1 bar pressure. The plasma flash is at $t = 0$, and the bubble subsequently expands, reaches a maximum, and collapses, with several smaller "afterbounces." This is well modeled by Rayleigh-Plesset dynamics [1,8] of free radial oscillations, and it can be shown that the maximum radius R_m is related to the time T_c from the bubble creation to the first collapse point by

$$R_m = 0.55\sqrt{\frac{p - p_v}{\rho}}\,T_c\,, \qquad (1)$$

where ρ is the water density, p the pressure, and p_v the water vapor pressure. Our photographic measurements of the bubble size are in good agreement with this equation. The composition of the gas in the bubble is not known, since it is formed from the recombination products of the water ionized in the initial plasma flash, but is probably dominated by atomic and molecular oxygen and hydrogen. There is a variation of about 50% in the bubble size from laser shot to shot, which may be due to variations in the nucleating impurity and how the laser energy is subsequently absorbed [15].

The luminescence signal in Fig. 1(a) has two components, a decaying signal following the plasma flash which lasts for less than 50 μs, and then a fast spike precisely at the minimum-radius collapse point. The fast signal is shown on an expanded time scale in Fig. 2(a), and also for comparison the signal from the same apparatus when viewing SBSL generated in a piezo-driven acoustic cell (150 torr xenon gas in water). The SBSL flash width is noticeably faster, and since that width is known [16] to be about 100 ps, the observed signal measures the response

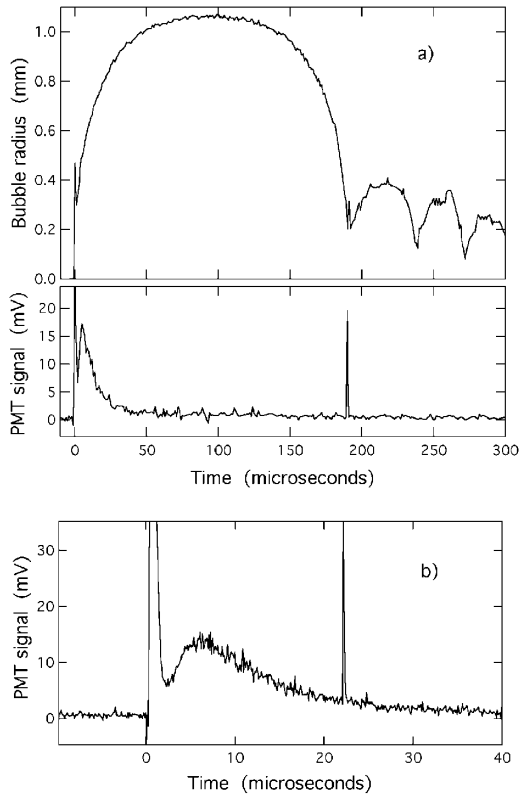

FIG. 1. (a) Bubble radius and photomultiplier output versus time in degassed water at 1 bar ambient pressure; (b) photomultiplier output at 10.3 bars.

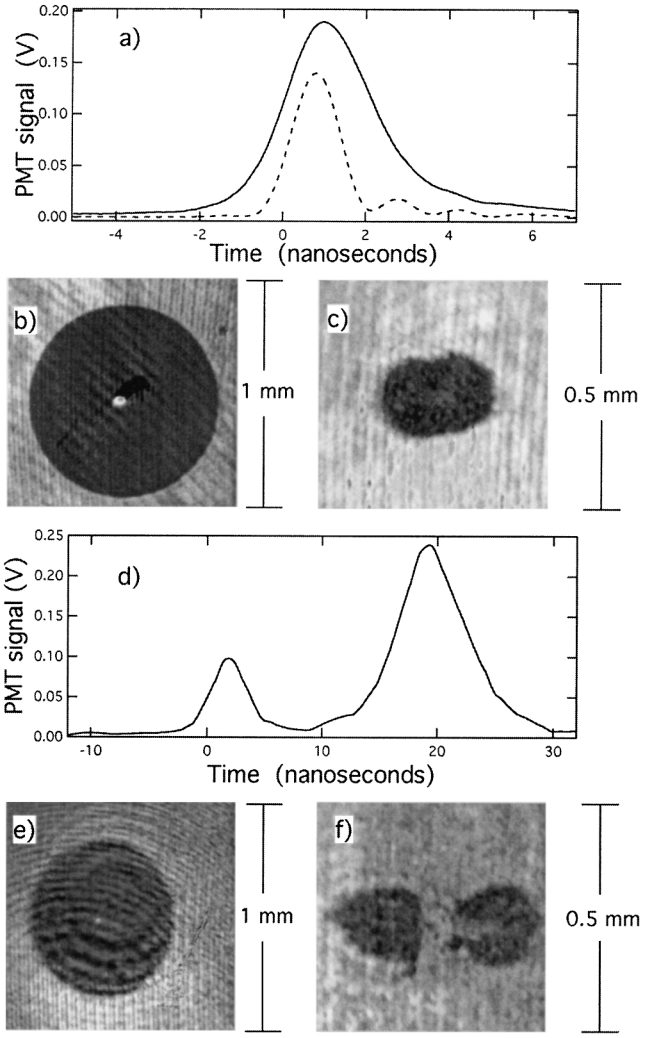

FIG. 2. (a) Fast pulse at the collapse point (solid line) for a bubble in degassed water at 1 bar, compared with the signal observed from a SBSL cell (dashed line). (b) Photograph of a bubble at 1 bar near R_m ($t = 75$ μs, $T_c = 113$ μs) and (c) near the collapse point ($t = 90.0$ μs, $T_c = 94.14$ μs). (d) Double pulse observed at 9 bars. (e) Photograph of a bubble at 10.3 bars near R_m ($t = 15$ μs, $T_c = 30$ μs) and (f) near the collapse point ($t = 38.0$ μs, $T_c = 38.89$ μs).

function of our oscilloscope-photomultiplier combination. By deconvolving the two signals we find that the pulses from the laser-induced bubbles are a few nanoseconds in width, increasing linearly with bubble size, as shown in Fig. 3. The increased widths compared with SBSL may be due to the fact that these bubbles have a considerably larger maximum radius than those in SBSL, leading to correspondingly slower Rayleigh-Plesset dynamics near the collapse point.

Figure 2(b) shows a photograph of a bubble at 1 bar pressure near the maximum radius, which appears to be spherical to within our 1% resolution. However, near the collapse point the bubbles evolve to become quite nonspherical, more like the quadrupolar shape of 2(c), and some are even much more distorted and yet still give off the fast light pulse as in 2(a). The growth of shape instabilities near the collapse point is a known feature of laser-induced bubbles [17], probably arising from anisotropy in the initial plasma [15].

When the cell is pressurized the bubbles become smaller and have a shorter time period to collapse, as shown in Fig. 1(b) for a pressure of 10.3 bars. By averaging over a number of laser shots at each pressure, we find between 1 and 15 bars that the average maximum radius scales with pressure as $p^{-1/3}$. This is the variation expected from energy conservation, since for the same energy deposited by the laser the product of the pressure times the maximum bubble volume must be constant.

The luminescence from the smaller bubble under pressure in Fig. 1(b) is similar to that of the larger bubble of 1(a), but with the difference that the fast pulse at the collapse point now overlaps the decaying luminescence from the plasma flash. The fact that this decaying luminescence continues to vary smoothly through the collapse point shows that it is unaffected by the bubble motion, and it does not appear to originate from the interior of the bubble. It is likely that this luminescence arises from metastable atomic and molecular states injected into the water during or just after the plasma flash, which then recombine relatively slowly. If instead the metastables were inside the bubble it would be expected that their population would be strongly affected by the compression to high densities at the collapse point. However, as Fig. 1(b) shows we see no detectable change in the decaying luminescence at that point.

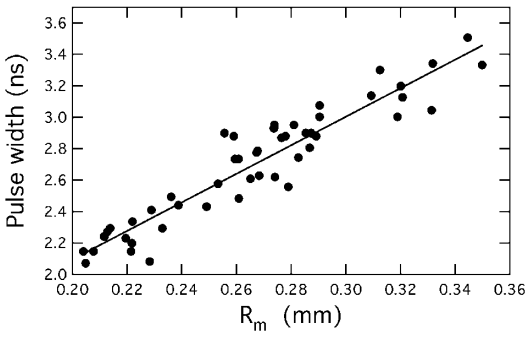

FIG. 3. Full width at half maximum of the luminescence pulse as a function of the maximum bubble radius. The solid line is the best-fit straight line.

An unusual feature seen with the smaller bubbles under pressure is that in a large fraction of the laser shots for pressures above 3–4 bars the fast peak at the collapse is found to split into two peaks, separated by times of order 20 ns, as shown in Fig. 2(d). Both the separation time and the relative amplitudes of the peaks varied considerably from shot to shot. Photographs of the bubbles taken near the collapse point showed that this is the result of the initial bubble splitting into two bubbles a few μs prior to the collapse point, as shown in Figs. 2(e) and 2(f) for 10.3 bars pressure. At this pressure the bubbles near R_m already display a quadrupolar distortion of about 5% [Fig. 2(e)], which continues to grow until the breakup into two bubbles very close to T_c in Fig. 2(f). Each of the two split bubbles also shows strong surface distortions, but both still radiate light. The growth of the shape instability that leads to the splitting of the bubbles appears to be strongly enhanced with the application of pressure. This may be due to the smaller average bubble size, which increases the surface curvature, or it could also be associated with greater initial anisotropies in the initial plasma/bubble creation process under pressure.

The fact that such highly distorted bubbles are still able to give off luminescence pulses is rather surprising. The theories of SBSL which rely on shock-wave heating of the gas [12,13] in the bubble assume that the shock is launched when the spherical bubble wall reaches Mach 1. It has been estimated [18] that an asphericity of only 5% in the bubble wall would be enough to disrupt the energy focusing and prevent light emission. Our laser-induced bubbles are clearly much more distorted than this a few μs from the collapse point, and it appears the instabilities are still growing. If this continues to hold to the final stages of the collapse where the shock would be launched, our observation that light is still emitted from these bubbles would suggest that the shock wave is not an important heating mechanism in producing the luminescence.

We have found that the results described above appear to be independent of the presence of gases dissolved in the water. The triple-distilled water straight from the source, fully saturated with ambient air, gave just the same results as the degassed water. Adding 150 torr of argon or 1 bar of xenon to the degassed water also had no effect. This is unlike SBSL, which is quite dependent on very small amounts of dissolved noble gases [3,19]. Figure 4 shows the integrated intensity of the fast luminescence at the collapse point for the degassed, ambient air, and xenon-added samples at 1 bar pressure, taking 110 shots for each sample that span a range of bubble sizes. The photon number over the range 300–600 nm is determined by calibrating the photomultiplier with its dark-current pulse

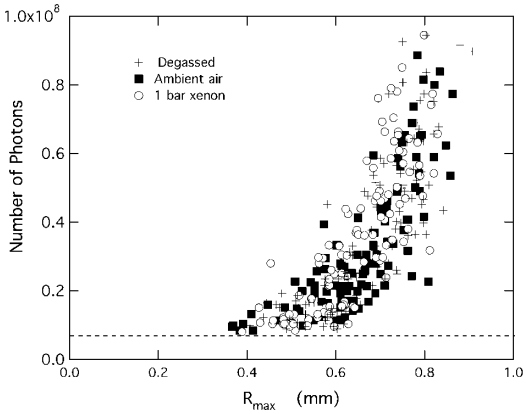

FIG. 4. Integrated light output versus maximum bubble size for samples at 1 bar that are either completely degassed, or have 1 bar ambient air or xenon dissolved in them. The dashed line indicates the trigger threshold to ensure that noise spikes are not counted.

heights, taking into account the subtended solid angle and the quantum efficiency of the photocathode. There is no observable difference in the data from the three samples, and even the shot to shot variability is about the same for the three. The maximum observed amplitude of 10^8 photons is about an order of magnitude larger than the maximum seen in SBSL [3], which is perhaps consistent with the order-of-magnitude longer pulse width we observe compared with SBSL.

The lack of sensitivity to dissolved gases can be understood from a simple argument involving the time needed for the gas to diffuse into the bubble. The focal spot size of the YAG beam is estimated to be $7-8\ \mu$m, and so a conservative estimate of the amount of gas in the bubble is the mass in a water volume $(5\ \mu\text{m})^3$, which is about 7×10^{-11} g. The mass of dissolved gas which can diffuse into the bubble during the time $0.5T_c$ while the bubble radius is roughly its maximum is [1]

$$\Delta M = \pi D C_\infty R_m T_c\,, \qquad (2)$$

where D is the diffusion coefficient of the dissolved gas and C_∞ its concentration far from the bubble. Using values for 1 bar partial pressure xenon in water, $D \approx 2 \times 10^{-5}$ cm^2/s and $C_\infty \approx 2 \times 10^{-5}$ g/cm^3 give an estimate $\Delta M \approx 3 \times 10^{-14}$ g. This is 3 to 4 orders of magnitude smaller than the mass in the bubble; there is simply no time for any appreciable amount of gas to diffuse in. The only xenon in the bubble will be that initially vaporized with the water, which is only a fraction 10^{-5} of the total, which as seen in Fig. 4 is not enough to have any observable effect on the luminescence pulse. The difference with SBSL is that in that case the gas can build up over many thousands of acoustic cycles [19], eventually becoming dominant.

The longer pulse widths and increased brightness compared with SBSL that we observe in these laser-created bubbles are consistent with the trends observed in these quantities with the smaller bubbles of SBSL [16]. To further check if the mechanism of the light emission is the same for the two cases, it will be necessary to measure the spectrum of the light from the larger bubbles. It will also be of interest to apply the laser-creation technique to other liquids where SBSL is difficult or impossible to study.

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