Properties of luminescence from laser-created bubbles in pressurized water

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The properties of the luminescence pulse from collapsing laser-created bubbles in pressurized water are studied for pressures between 0.25 and 15 bars. The duration of the light pulse is found to be linear in the maximum bubble size, but for a given bubble size it increases with the applied pressure p as $p^{0.38}$. The number of photons emitted increases quadratically with the bubble size, and increases approximately linearly with pressure. The spectrum of the luminescence is blackbody in form, with a temperature that increases somewhat with pressure, from 8100 K at 1 bar to 9400 K at 10 bars. At higher pressures the blackbody temperature drops, but this is primarily due to the rapid onset above 10 bars of a fission instability, where the bubbles split into two just before the collapse point.

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I. INTRODUCTION

The mechanism that gives rise to the emission of light from the center of a collapsing bubble in water is still poorly understood [1]. It is generally thought that strong heating of the gas in the bubble by adiabatic compression during the collapse phase is involved, but little is known about the details of exactly how the light is emitted. The problem is that very close to the minimum-radius collapse point the properties of the gas in the bubble become difficult to characterize due to the rapid changes in temperature, pressure, and density. It is known that the temperature becomes high enough that the gas is weakly ionized, and it is likely that the resulting bremstrahllung emission as the electrons scatter from the neutral atoms is the main source of the luminescence.

To try to understand better the dynamics of the emission process, we have studied the properties of the light emission from collapsing bubbles in pressurized water, where the bubbles are generated from a pulsed laser focused to a point in the water [2–5]. There are a number of advantages to using these laser-created bubbles to study the dynamics of the emission. The bubbles, with a maximum radius of up to 1 mm in the present work, are considerably larger than the bubbles of sonoluminescence [1] which typically have a maximum radius of order 50 μm. Due to this larger size the time duration of the luminescence pulse is of order 10 ns, whereas the sonoluminescence duration is much shorter, of order 200 ps [6,7]. The longer duration means that the pulse width can easily be directly measured with a fast photomultiplier, while much more involved indirect techniques are necessary for sonoluminescence [6,7]. Also, a wide range of bubble sizes can be generated in a single apparatus, in contrast to sonoluminescence where the bubble size can only be changed by large changes in the drive frequency [8].

The effect of external pressure on the bubbles has previously been studied in Refs. [3,5]. In the earlier work in our lab [3] we observed that the pulse width of the luminescence increased linearly with the maximum bubble size, and also noticed that the width increased somewhat with pressure, but no detailed measurements with pressure were carried out at that time. Wolfrum *et al.* [5] have studied the luminescence over the range of 1-3 bars, but found an instability onset in the bubbles for pressures above 3 bars. In the present measurements we have found that we are able to study the pressure range between 0.25 and 10 bars before the instabilities become a problem in our apparatus, with the highest pressures studied being 15 bars. We have studied the pulse duration and intensity of the luminescence over these pressures as a function of the maximum bubble radius between 0.2 and 1 mm. In addition we have measured the pressure dependence of the spectral properties of the luminescence at a fixed bubble size, which provides additional information on the nature of the luminescence.

II. APPARATUS

The pressure cell is a stainless-steel cuvette formed by boring three 40 mm diameter intersecting holes through a cubical block of sides 68 mm. The four side holes are fitted with millimeter-thick quartz windows 2.5 cm in diameter, which are attached with epoxy to stainless mounting flanges sealed with rubber O-rings. The bottom hole of the cell has a lens mounted in the same manner that is 30 mm in diameter and has a focal length of 35 mm. The lens focuses a 6 ns pulse at 1064 nm from a Q-switched Nd:YAG laser (Spectra-Physics INDI) into the center of the cell, with a spot size estimated to be about 10 μm. The cell is filled with 18 MΩ, 0.2 μm-filtered water at room temperature, 22 C. A fitting on the top hole of the cuvette allows the cell to be pressurized using a tank of high-purity dry nitrogen gas, monitored with a large Bourdon pressure gauge with an accuracy of about 1%. We assume that the nitrogen gas has no effect on the bubble luminescence, as observed earlier in our lab [3]. At the higher pressures of this work an increased fraction of nitrogen will be present in the bubbles, but is still estimated to be less than a part in 10^4 of the total gas at 10 bars. For measurements at pressures below 1 bar the cuvette

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is pumped with a small oil-free diaphragm pump.

To create the bubbles the laser energy is slowly increased until the point where ionization of the water just begins to occur, noted by the visible flash from the cell. Although the laser energy only varies by less than 5% from shot to shot, we find that the maximum bubble size varies greatly with each shot. This is probably because a nucleating impurity is necessary to cause the initial water ionization, since the energy absorption of water alone is not sufficient for this purpose. Variations in the impurity size would considerably change the total energy absorbed, and hence the maximum bubble size. This is actually an advantage in these measurements, since a large range of bubble sizes are easily produced. Photographs of the light emitted by the ionization plasma [9] show a nearly spherical shape, with radii between 50-100 μm, and only a slight elongation in the direction of the laser beam is visible. The spectrum of the light is blackbody in form, with fits giving a temperature of about 17 000 K [4]. The initial plasma lasts for 50-100 ns before recombining, and the absorbed energy is then manifested in the expanding bubble. We find with this creation process that stable bubbles up to 1 mm in radius can be produced, at pressures up to about 10 bars. At higher pressures or larger radii, however, the bubbles rapidly become unstable due to a fission instability, where they split into two prior to the collapse point [3,4].

The composition of the gas being compressed in the bubble collapse is not known, but is most likely atomic hydrogen and oxygen resulting from the plasma recombination, and any water vapor that is unable to condense out on the bubble surface during the last stages of the collapse [10,11]. The 17000 K temperature of the initial plasma will certainly dissociate all molecules in the plasma volume, and since the bubble then rapidly expands the gas will be at very low pressure over most of its ≈ 100 μs lifetime, making molecular recombination unlikely to be appreciable.

The luminescence pulse emitted by the bubble is monitored with two photomultipliers. A slower tube with a rise time of about 10 ns is used to monitor the time T_c from the initial water ionization by the laser pulse to the collapse point of the bubble, and from this the maximum bubble radius R_m can be determined from the Rayleigh formula as in our previous work [3,4]

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

with p the applied pressure, ρ the liquid density, and p_v the water vapor pressure.

A faster photomultiplier tube (Hamamatsu H6780-03) is used to study the details of the luminescence pulse, with the signal analyzed on an Agilent 54820 oscilloscope. For the best rise time the tube is operated at a gain of 8×10^5, close to its maximum value. To protect the tube from the intense initial ionization luminescence a neutral density filter is used that reduces the signal by a factor of 1000. The measured width of the pulse Δt_m on the oscilloscope screen is taken to be the full width at one-half the maximum signal. To deconvolve this from the rise time of the photomultiplier and oscilloscope the impulse response half-width Δt_i is measured for a number of background single-photoelectron events, yielding an average value $\Delta t_i = 1.83$ ns. A good approximation for the observed pulses is to take their shape as Gaussian; this then gives the deconvolved pulse width as $\Delta t = \sqrt{\Delta t_m^2 - \Delta t_i^2}$. For most of the data here this is a small correction since Δt_m is generally considerably larger than Δt_i.

The photon number in the pulse is found using the integrated area under the pulse computed by the oscilloscope software. By measuring the pulse area of the background photoelectron events, using the known quantum efficiency of the tube, and extrapolating the tube area to a 4π solid angle, the total number of photons emitted in the bubble collapse can be computed. This is valid for the wavelength range between 250 to 600 nm where the efficiency of the tube is relatively constant; outside of this range the detection efficiency drops rapidly.

The spectrum of the luminescence is measured by collecting the light with paraboloidal mirrors, and focusing onto the slits of a 0.3 m spectrometer, as in our earlier work [4]. An intensified CCD detector reads out the light intensity over a 200 nm range for each bubble, with a resolution of about 1 nm. It is necessary to average over 25 bubbles to get a reasonable signal to noise ratio in the spectra, where only bubbles in a given range of radii (0.65 ± 0.05 mm in the present measurements) are included in the average. The measured spectra are divided by a calibration curve to account for the absorption in the optical path and the quantum efficiency of the detector, derived by illuminating a pinhole at the bubble position with quartz and deuterium lamps. There should be little optical change in the windows and the water as pressure is applied, and the same calibration curve is used for all the pressures.

III. RESULTS

Figure 1 shows the results of the pulse width measurements for several representative pressures. About 50 data points are acquired at each pressure, since each laser shot is different and it is necessary to average over the data. As found in our original measurements with smaller bubbles [3], the pulse width is linear in the maximum bubble size, as shown by the best-fit solid lines. In the fits we have assumed that there is no intercept at finite radius, and as can be seen this is a fairly reasonable assumption. We note that extrapolating the 1 bar data to small bubbles is at least roughly consistent with the pulse widths seen in sonoluminescing bubbles, which have a maximum bubble radius of about 0.05 mm and widths of order 200 ps. With increasing pressure the pulse width increases at fixed bubble size, although at higher pressures the rate of increase becomes smaller. This is illustrated in Fig. 2 where the slope of the best-fit line is plotted versus pressure for all of our data between 0.25 and 10 bars. The solid line in this plot is simply a fit of the data to a power law in the pressure, varying as $p^{0.38}$, with an uncertainty in the exponent of ±0.05.

The pulse width measurements were not extended above 10 bars since above that point a good fraction of the bubbles that are created become unstable and fission into two bubbles

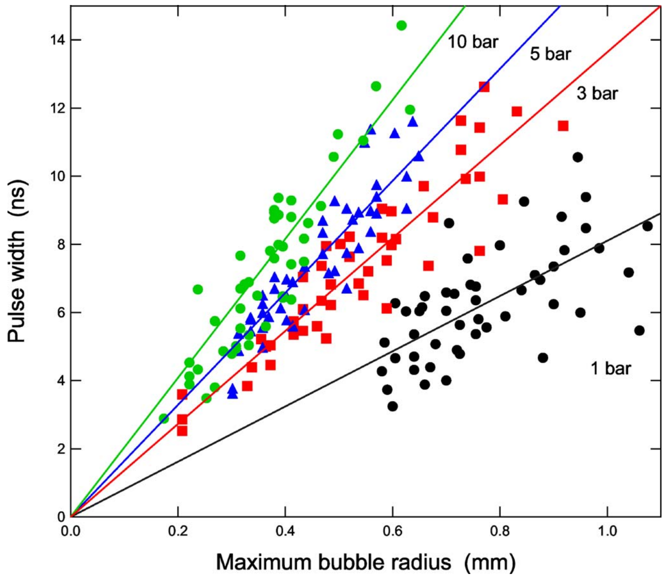

FIG. 1. (Color online) Duration of the luminescence pulse (full width at half-maximum) as a function of the maximum bubble radius and pressure. The solid lines are linear fits to the data.

prior to the minimum collapse radius. This is easily seen in the luminescence, which takes the form of two pulses separated by 20–40 ns, as each of the two bubbles collapse. Below 10 bars the double pulses are also occasionally observed, but these are rejected and only single pulses are included in the data set.

The photon number of the luminescence pulses is plotted in Fig. 3 for the same pressures shown in Fig. 1. The solid curves in this figure are fits to the square of the maximum bubble radius, and it can be seen that this is a reasonable representation of the data. A more detailed justification of this exponent is shown in Fig. 4, which shows the exponents obtained when fits were made allowing both the magnitude and power-law exponent to vary. Because of the scatter in the data there is some variation in the value of the exponent, but the average is 1.9 ± 0.2. Since the variation with pressure is not statistically significant, the curves are well characterized by the quadratic fits.

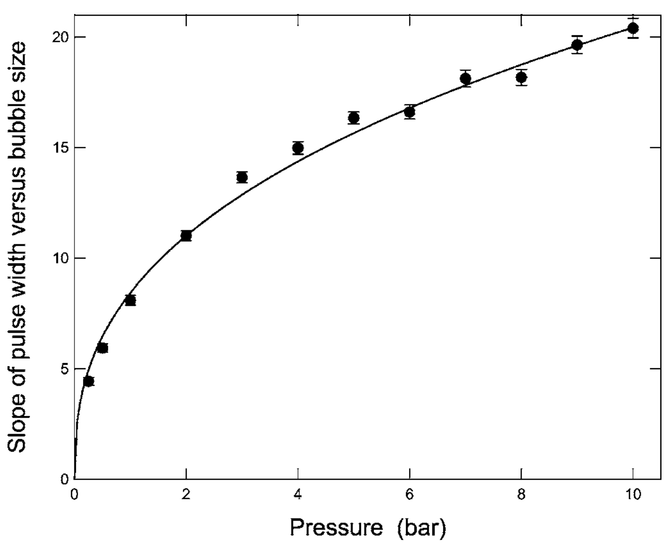

FIG. 2. Slope of the linear fit to the pulse duration versus bubble size, for different pressures. The solid line is a power-law fit to the data, found to vary as the pressure to the power 0.38.

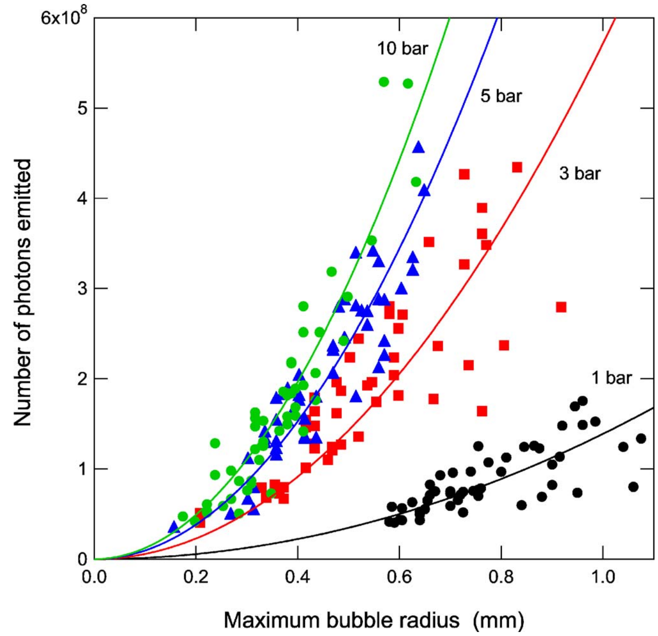

FIG. 3. (Color online) Number of photons emitted in the luminescence pulse, as a function of bubble size and pressure. The solid curves are quadratic fits to the data.

For fixed bubble size the photon number increases with pressure, as shown in Fig. 5 for the magnitude from the quadratic fits at a maximum radius of 0.6 mm. The increase is roughly linear with pressure up to 5 bars, and then increases more slowly, perhaps leveling off near 10 bars where the splitting instability becomes prominent. Although again this data involves selecting only single-pulse events, even the bubbles remaining intact may not remain completely spherical in the collapse.

Our data for the photon number versus pressure shows a much higher pressure range of bubble stability than seen in

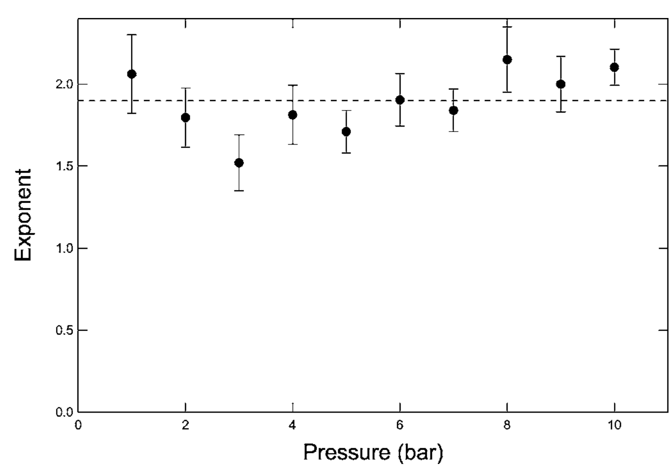

FIG. 4. Exponent resulting from fits to the photon number data when both the magnitude and exponent are allowed to vary. The dashed line shows the average value, 1.9 ± 0.2.

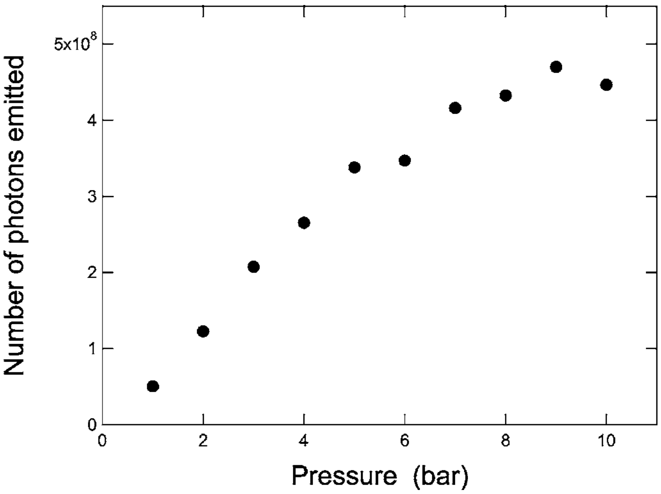

FIG. 5. Pressure dependence of the number of emitted photons, for a maximum bubble radius of 0.6 mm.

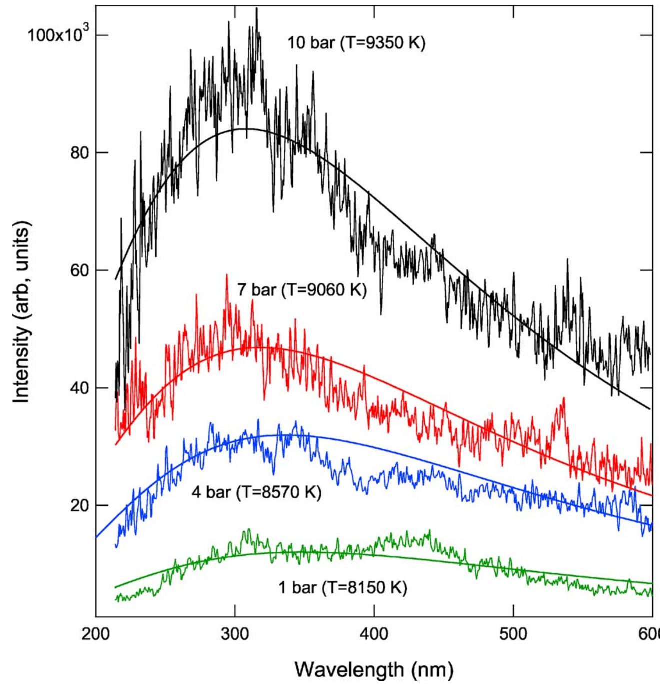

FIG. 6. (Color online) Spectrum of the luminescence for selected pressures between 1 and 10 bars, for a maximum bubble radius 0.65 ± 0.05 mm. The amplitude for each curve is scaled by an arbitrary amount to separate the different curves.

the measurements of Wolfrum *et al.* [5]. Their luminescence amplitude dropped off sharply above 3 bars, which they cited as due to the bubble splitting instability. This does not appear in our data until about 10 bars. The difference may be in the details of the initial bubble generation by the laser. Their more tightly focused laser pulse only generates bubbles of a single size, and to vary the parameters they increase the laser energy, so that they are always working well above the energy threshold for plasma creation. However, studies of the laser ionization process [12] show that the elongation of the plasma in the direction of the laser beam is greatly increased for energies above the threshold. This may lead to distorted initial bubbles that are then more susceptible to instabilities near the collapse point. In our case we operate at a constant laser energy just above the ionization threshold, and use a larger ionization volume. This results in a range of bubble sizes, but as noted earlier the ionization plasma appears to be nearly spherical, and the bubbles generated may remain more spherical and hence more stable at the higher pressures.

Figure 6 shows the spectra of the luminescence for four different pressures up to 10 bars. In these measurements only bubbles within a collapse-time window corresponding to a maximum bubble radius in the range of 0.65 ± 0.05 mm were selected, and also only single-pulse events were allowed. The solid lines show fits to a blackbody spectrum at the indicated temperatures. Although it is not clear that the blackbody formulation is entirely correct for the emission from these bubbles, the fits are reasonable, and we use the blackbody temperature to at least parametrize the data. The temperature appears to increase with pressure, from about 8150 K at 1 bar (consistent with our previous 1 bar results [4]) to 9350 K at 10 bars. Figure 7 shows the spectra for pressures of 12 and 15 bars, where split bubbles predominate and no attempt was made to discriminate between one and two-bubble events. The blackbody temperature decreases considerably in the 15 bar data, most likely due to the splitting instability. Figure 8 summarizes the variation of the fit temperatures with pressure.

IV. DISCUSSION

Combining the results for the pulse width of Figs. 1 and 2 gives an emission time that scales with pressure and bubble size as $R_m p^{0.38}$. This scaling illustrates that the time dependence of the Rayleigh-Plesset (RP) equation [1] for the

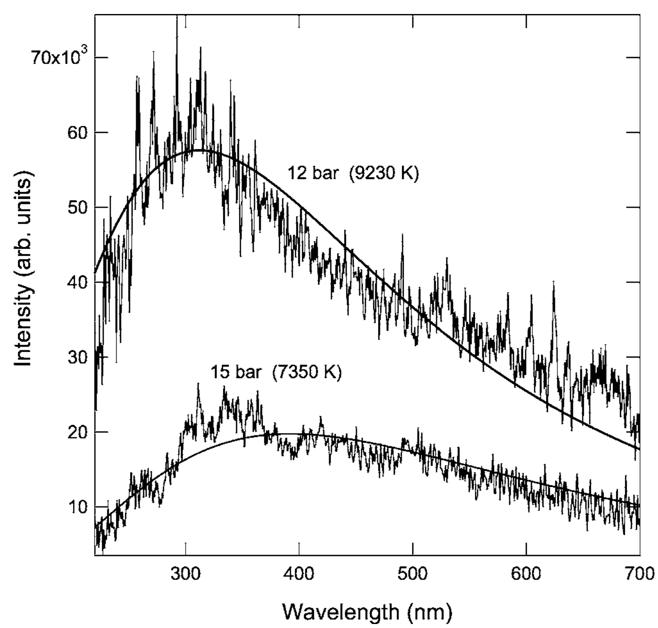

FIG. 7. Spectrum for 12 and 15 bars, primarily from bubbles undergoing the fission instability. The maximum bubble radius is 0.65 ± 0.05 mm, and the amplitude for each curve is scaled by an arbitrary amount to separate the curves.

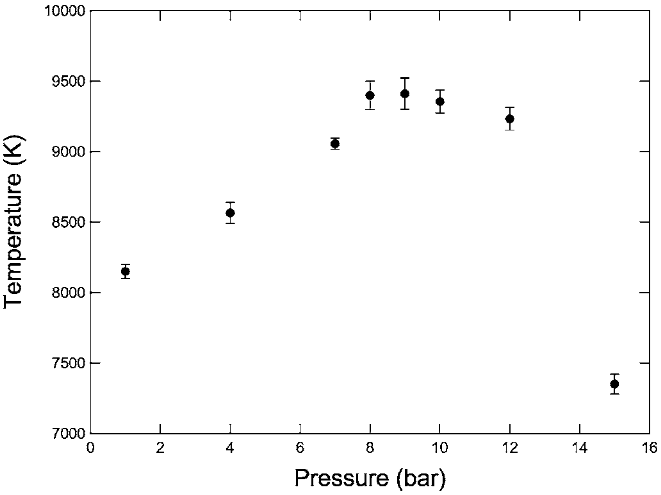

FIG. 8. Maximum bubble temperature for bubbles of maximum radius 0.65 ± 0.05 mm, from the fit to a blackbody spectrum. The fission instability becomes predominant above 10–12 bars.

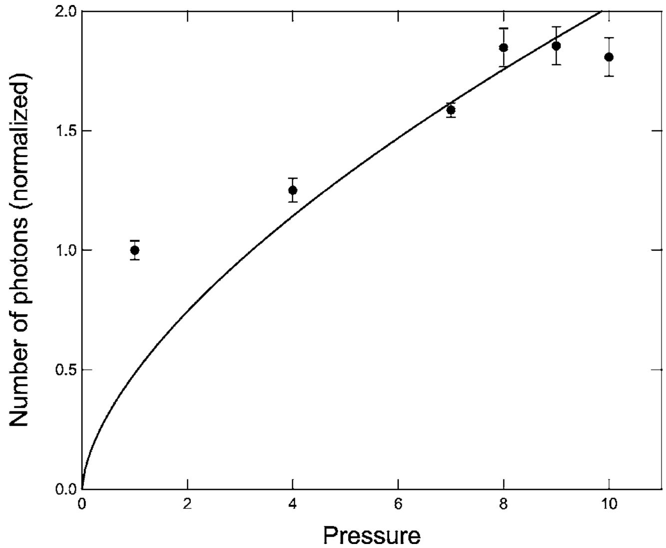

FIG. 9. Photon number derived from integrating the Planck spectrum at the temperatures given by Fig. 8 over the photomultiplier response, and normalized to the value at 1 bar. The line shows the fit to a variation as the pressure to the power 0.62.

bubble wall dynamics is not adequate to explain the dynamics of the emission process. The time variable in the RP equation scales with $R_m p^{-1/2}$ [as shown for example by Eq. (1)], and hence cannot explain the increase in the emission time with pressure that we observe.

Another possible scaling variable in the problem is the total mechanical energy of the bubble, $E=4\pi R_m^3(p-p_v)/3$. Our observed scaling of the pulse width would be at least approximately consistent with a variation as $E^{1/3}$. However, we are unaware of any theoretical justification of why the exponent should take the value of $1/3$.

The results of Figs. 3 and 5 can be combined to give the scaling of the number of photons emitted as $R_m^2 p$, at least for pressures below 5–6 bars. Since the number of photons involves the time integral of the luminescence pulse, we expect that as a first approximation the number of photons will be proportional to the pulse duration. This would account for a portion of the observed scaling, a factor $R_m p^{0.38}$ from the pulse duration results of Figs. 1 and 2. The changes in the blackbody temperatures in Fig. 8 will also affect the photon number. Even small changes in the blackbody temperature can give rise to appreciable intensity changes, a consequence of the Stephan-Boltzmann law. Figure 9 shows the results of integrating the Planck spectrum for the photon number over the spectral response function of the photomultiplier, for the temperatures shown in Fig. 8. The results are normalized to the value found at 1 bar. Also shown as the solid line is the power law $p^{0.62}$. The 1 bar data point does not fit, but the higher-pressure data is at least crudely consistent with this variation.

There are at least two further possibilities that could account for the additional factor of R_m in the photon number. It is possible that the blackbody temperature could increase with bubble size, and only relatively small changes in temperature would be needed. We have not yet been able to measure any changes in temperature with bubble size to check this, since bubble sizes smaller than 0.6 mm yield too little light to take a spectrum, while the spectra of bubble sizes larger than 1 mm are complicated by the onset of the bubble instabilities and the OH^- line at 310 nm [4], which obscures the spectrum near the blackbody peak where the fits are most sensitive.

A further factor is that the area of the hotspot that is emitting the photons may increase as the maximum radius increases. Measurements of the diameter of the light-emitting region [13] were initially interpreted as showing such an increase. However, in a later paper [11] it was noted that this data may only indicate the minimum bubble size, since the emitted light illuminates the bubble surface at the collapse point. The photograph of the emission spot in [4] from a bubble with $R_m=0.8$ mm shows a central bright region with a radius of about 12-13 μm, which may be the emission radius, and then dimmer light up to about 35 μm, possibly marking the minimum bubble radius. Further photographic studies of the emission region as a function of bubble size and pressure will be necessary to resolve the contribution of the emission spot size to the photon number.

Several groups have attempted to model the dynamics of laser-induced bubbles, though only for the case of ambient 1 bar pressure, and usually only for a single bubble size. In the work of Baghdassarian *et al.* [3], experimental data on the variation of the bubble radius very near the collapse point was analyzed using the simplest form of the RP equation to at least crudely model the time dependence of the temperature and ionization in the bubble. For a bubble with $R_m=1.2$ mm the fit parameters gave an estimate of 9×10^{13} atoms of hydrogen and oxygen gas in the bubble, with the water vapor ignored. The calculated temperature pulse attained a maximum value of about 30000 K, with a half-width time of order 500 ns. The ionization pulse calculated from the Saha equation was found to have a much shorter width of order 40 ns, using the hydrogen ionization potential of 13.6 eV. The maximum temperature and ionization pulse width are both about a factor of four larger than the 1 bar data of Figs. 1 and 8. The higher values are possibly the result of assuming that the collapse is adiabatic for the entire compression, whereas it is probably more nearly isothermal until just a few microseconds from the collapse point. It would be of interest to extend this type of measurement to the higher pressures used in the present measurements, although the bubble radius measurements become more challenging with the shorter bubble collapse times at high pressure.

Akhatov *et al.* [11] solved the Rayleigh-Plesset equation including thermal conduction in the gas and evaporation effects at the bubble surface. They assume that the gas being compressed is primarily the water vapor that is unable to condense on the bubble surface once the temperature is above 647 K. For the case of only pure vapor they find that for a bubble with $R_m=1.0$ mm the temperature reaches a maximum value of about 10000 K with a half-width of about 20 ns. They also added a small fraction of "noncondenseable" gas (modeled as air molecules), for concentrations between 1 to 10% of the water vapor being compressed. This caused the maximum temperature to decrease to about 5000 K at the 10% concentration. We note that the question of whether the water vapor plays a significant role in the luminescence can be probed experimentally by varying the temperature of the water, since near 0 C the vapor pressure becomes very small.

Byun and Kwak [14] have modeled laser bubbles starting from the initial laser ionization event. They employ the Keller-Miksis form [1] of the RP equation, and also model thermal conduction and evaporation effects. For a 1 mm bubble they find a maximum temperature of about 7000 K, with a half-width of about 20 ns. The gas in the bubble does include water vapor, but the exact composition of the gas is not given. They also show an ionization pulse with a half-width of 11 ns, but it is unclear what ionization potential was used, and it is puzzling that this is only a factor of two smaller than the temperature half-width.

In further modeling it will be important to characterize the composition of the gas in the bubble, and to extend the parameters so that the bubble size and external pressure can be varied. This would allow a more detailed comparison with the experimental results presented here. The origin of the linear dependence of the emission pulse width with bubble size of Fig. 1, for example, is still not understood. For such calculations it will also be necessary to carefully characterize the photon emission process that is connected with the weak ionization of the gas, and check whether blackbody emission is a reasonable approximation.

V. CONCLUSIONS

We have measured the pressure dependence of the emission photon number, pulse widths, and spectra of the luminescence from collapsing laser-created bubbles in water. The pulse widths are found to increase with both the bubble size and with pressure, scaling as $R_m p^{0.38}$ up to 10 bars in pressure. The photon number also increases with bubble size and pressure, scaling approximately as $R_m^2 p$. The spectra are found to have blackbody temperatures that increase about 20% between 1 and 10 bars. We would hope that this data can be useful to theorists studying the physics of light emission from collapsing bubbles. The relatively large laser-created bubbles studied here have slower dynamics, and lower temperatures and pressures at the collapse point than the smaller bubbles of sonoluminescence. A successful modeling of the emission from these bubbles may then allow a better perspective for understanding the more complicated case of sonoluminescence.

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[1] M. Brenner, S. Hilgenfeldt, and D. Lohse, Rev. Mod. Phys. **74**, 425 (2002).

[2] C. D. Ohl, O. Lindau, and W. Lauterborn, Phys. Rev. Lett. **80**, 393 (1998).

[3] O. Baghdassarian, B. Tabbert, and G. A. Williams, Phys. Rev. Lett. **83**, 2437 (1999).

[4] O. Baghdassarian, H.-C. Chu, B. Tabbert, and G. A. Williams, Phys. Rev. Lett. **86**, 4934 (2001).

[5] B. Wolfrum, T. Kurz, O. Lindau, and W. Lauterborn, Phys. Rev. E **64**, 046306 (2001).

[6] B. Gompf, R. Gunther, G. Nick, R. Pecha, and W. Eisenmenger, Phys. Rev. Lett. **79**, 1405 (1997).

[7] R. A. Hiller, S. J. Putterman, and K. R. Weninger, Phys. Rev. Lett. **80**, 1090 (1998).

[8] C. Camara, S. Putterman, and E. Kirilov, Phys. Rev. Lett. **92**, 124301 (2004).

[9] O. Baghdassarian, Ph.D. thesis, UCLA, 2001.

[10] W. C. Moss and D. A. Young, J. Acoust. Soc. Am. **103**, 3076 (1998); B. D. Storey and A. J. Szeri, Proc. R. Soc. London, Ser. A **456**,1685 (2000).

[11] I. Akhatov, O. Lindau, A. Topolnikov, R. Mettin, N. Vakhitova, and W. Lauterborn, Phys. Fluids **13**, 2805 (2001).

[12] F. Doccio, P. Regondi, M. Capon, and J. Mellerio, Appl. Opt. **27**, 3661 (1988).

[13] C. D. Ohl, T. Kurz, R. Geisler, O. Lindau, and W. Lauterborn, Philos. Trans. R. Soc. London, Ser. A **357**, 269 (1999).

[14] K. Byun and H. Kwak, Jpn. J. Appl. Phys., Part 1 **43**, 621 (2004).