Precursor Luminescence near the Collapse of Laser-Induced Bubbles in Alkali-Salt Solutions

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A precursor luminescence pulse consisting of atomic line emission is observed as much as 150 nanoseconds prior to the collapse point of laser-created bubbles in alkali-metal solutions. The timing of the emission from neutral Na, Li, and K atoms is strongly dependent on the salt concentration, which appears to result from resonant radiation trapping by the alkali atoms in the bubble. The alkali emission ends at the onset of the blackbody luminescence pulse at the bubble collapse point, and the duration of the blackbody pulse is found to be reduced by up to 30% as the alkali-salt concentration is increased.

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The physics and chemistry involved in the production of luminescence from collapsing bubbles in water and other liquids is still not well understood. Luminescence has been observed from bubbles using a wide variety of techniques: bubbles driven at high acoustic levels (sonoluminescence) [1], laser-induced bubbles [2–4], bubbles created in electrical discharges [5], shake-table driven bubbles [6], and U-tube compression [7]. There is general agreement that the luminescence is connected with compressional adiabatic heating of the gas in the bubble, to temperatures of order 10 000 K, which results in a weakly ionized plasma. The details of the light emission process are poorly known however, such as why the duration of the luminescence pulse varies with the maximum bubble size, and yet does not appear to scale with the known dynamics of the bubble wall [8]. Also unresolved is the question of why in many cases the luminescence spectrum is that of a blackbody, even though that requires photon mean free paths in the hot spot to be less than 1 μm for the case of single-bubble sonoluminescence (SBSL). The problem in simulating this system is that the huge variation of temperature and pressure in the bubble takes place over a very short time scale, within the last microsecond from the collapse point, while the light emission duration can be shorter than nanoseconds.

In order to probe the dynamics of the compressional heating, we have undertaken a series of measurements with laser-induced bubbles in alkali-metal and alkaline-earth solutions [9]. The laser-induced bubbles are particularly useful for this purpose because the metal atoms are directly injected into the gas in the bubbles by the initial laser ionization of the liquid, unlike the case for SBSL, where no effects of salt are normally observed, since there is no mechanism to get the salt into the interior of the bubble. The salt lines have been seen in spectroscopic measurements in multibubble sonoluminescence [10] and in SBSL under certain special conditions [11], but the uncertain parameters of the cavitation in these experiments make time-resolved measurements difficult, and the continuous sonication leads to complicated chemical reactions that may be the source of the spectral lines.

With the ability to study in detail the time dependence of single isolated luminescence events, we have observed a new precursor luminescence pulse in alkali-metal solutions that arises from the alkali atomic transitions. This pulse begins as much as 150 ns before the main blackbody luminescence pulse at the bubble collapse minimum radius, and is found to be strongly dependent on the salt concentration. The precursor pulse should provide valuable information on the time dependence of the heating process in the collapsing bubbles, though a detailed theory of the process still needs to be formulated.

To create the bubbles a 6 ns pulse at 1064 nm from a Q-switched Nd:YAG laser is directed into a stainless steel cell containing the salt solution. An aspheric lens that serves as a cell window focuses the pulse to a spot size estimated to be about 10 μm at the center of the cell. The power level is adjusted to the threshold value to just create bubbles, about 150 mJ. Since the laser absorption is nucleated by a floating impurity that will vary with each shot, the maximum radius of the resulting bubbles also then varies considerably from shot to shot, and it is necessary to take many shots to accumulate data for a range of bubble sizes. The gas in the bubble is thought to be primarily the recombination products of the initial laser ionization hot spot. For an NaCl solution this would be atomic hydrogen, oxygen, sodium, and chlorine, and near the collapse point whatever water vapor is unable to recondense on the bubble wall. Since the bubble collapse times are generally less than 150 μs, and the gas density is very low over most of this time, it is unlikely that significant molecular recombination of the atomic species occurs.

The luminescence from the bubbles is monitored with two photomultipliers (Hamamatsu H6780-03 with 1.2 ns rise times) through quartz windows on opposite sides of the cell. One of the photomultipliers is fitted with an interference filter whose center frequency is chosen to selectively pass a strong alkali line (i.e., the 589 nm D lines for the case of sodium). The width of the filter passband is 10 nm. The other photomultiplier has both a neutral density filter that attenuates the light by a factor of 10 to avoid saturation of the photomultiplier, and a filter which only passes a

range in the blue from 250 to 450 nm. This photomultiplier is thus mainly only sensitive to the blackbody light from the bubble, while the other one detects primarily the alkali line emission, as well as the small amount of blackbody emission passing through the 10 nm passband of the interference filter. As also observed in Refs. [3,4,8], some fraction of the luminescence events are double pulses from bubbles that are unstable and have split into two bubbles (generally bubbles larger than 1 mm). These are readily detected as double pulses of 5–8 ns duration seen in both photomultipliers, and are excluded from the data here.

Figure 1 shows single luminescence pulses detected by each photomultiplier for the case of NaCl solutions of different concentrations, at a hydrostatic pressure of 6 bars applied to the cell using dry nitrogen gas (previous measurements with the laser bubbles have shown that nitrogen pressurization is equivalent to hydraulic pressurization since the luminescence is found to be insensitive to the very low concentration of dissolved gas). The magnitude of the signal seen by the photomultiplier with the alkali interference filter is multiplied by a factor of order 10–20 to match the blackbody peak signals near $t = 0$. The precursor luminescence from the sodium D lines is readily apparent, becoming apparent at low concentrations as much as 150 ns from the collapse point. The signal reaches a maximum and then decreases prior to the collapse point. The D line signal becomes small past the collapse point, with barely any detectable amplitude above that point. It is apparent that the initial concentration of the liquid strongly affects the onset and duration of the precursor pulse, which is much longer at the lowest concentrations.

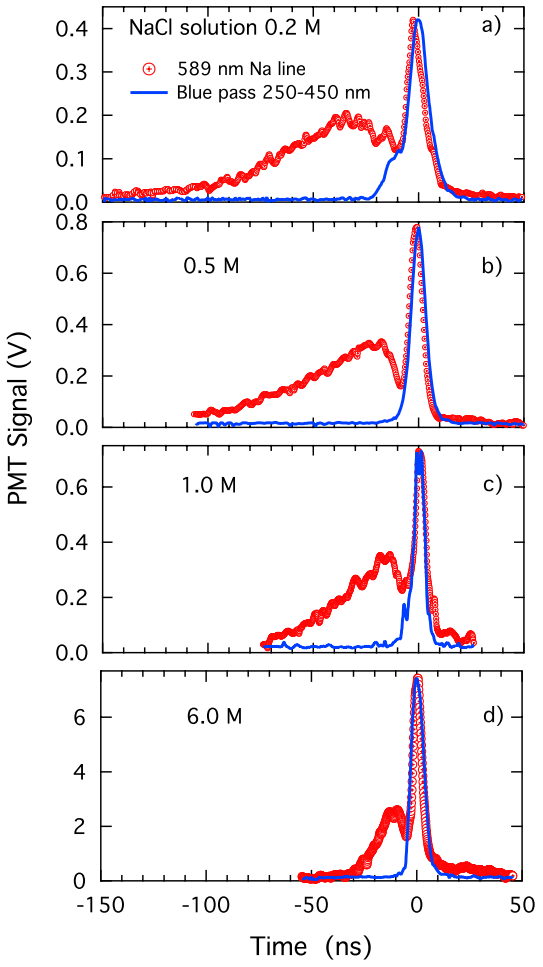

FIG. 1 (color online). Single luminescence traces observed near the collapse point ($t = 0$) of laser-induced bubbles in NaCl solutions with molar concentration between 0.2 M and 6 M, at a pressure of 6 bars. The maximum radii of these bubbles were (a) 0.83 mm, (b) 0.58 mm, (c) 0.40 mm, (d) 0.36 mm.

Figure 2 shows the duration of the precursor pulse as a function of the salt concentration and hydrostatic pressure. These data are averaged over 10–15 bubbles at each pressure and concentration, where the duration is taken from the first clearly detectable signal to the $t = 0$ peak of the blackbody signal. The precursor duration is affected by the hydrostatic pressure, increasing for the low NaCl concentrations by a factor of order 2 as the pressure increases from 1 to 6 bars. The duration did not appear to vary appreciably with the maximum bubble size; i.e., at 1 bar there was no consistent variation with maximum bubble radii in the range from 0.4 to 1 mm.

The time dependence of the precursor pulse gives information on the heating process in the bubble. Because the energy needed to excite the $3p$ levels of the alkali atoms is considerably less than the corresponding excited-state levels of the hydrogen or oxygen atoms, they should be the first to begin emitting as the temperature shoots up in the compressing bubble. The well-known yellow flame in Bunsen-burner sodium emission tests arises from temperatures in the flame of order 2000–2500 K. Using the simple model of the compressional heating in the laser-induced bubbles of Ref. [4], one finds for the bubble of Figs. 3 and 4 of that paper that the temperature at 100 ns from the collapse point is about 1/3 of the maximum temperature. Since the maximum temperature was found from the blackbody spectrum to be around 8000 K, the temperature at

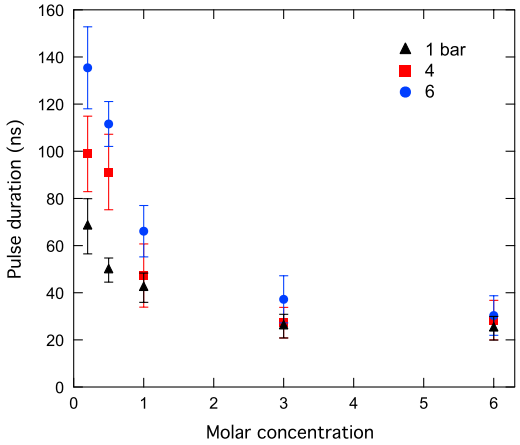

FIG. 2 (color online). Duration of the 589 nm emission line from bubbles in NaCl solutions as a function of concentration and pressure.

100 ns from the collapse would be about 2600 K, and this is roughly consistent with our observation for the lowest NaCl concentrations that the D line emission begins on the order of 100 ns prior to the collapse point, as seen in Figs. 1 and 2. Of course, the blackbody spectrum only gives the temperature of the surface of the hot spot; it is suspected that the interior temperatures may be higher, as suggested in recent SBSL experiments with sulfuric acid [12].

The observation that the onset and duration of the precursor pulse is such a strong function of concentration is a surprising result. It appears possible that this could be the result of resonant trapping of the Na emission line by the surrounding ground-state Na atoms in the bubble. Such resonant trapping is well-known in studies of Na atomic beams [13,14]. The effect of resonant trapping is to increase the effective lifetime τ governing the emission dynamics from the isolated-atom value of $\tau_0 = 16.1$ ns for the D lines [13]. The slower diffusion of the photons toward the bubble surface from the capture and reemission process would act to delay the onset of observable emission, as seen in our data. We note that only the gas-phase Na atoms inside the bubble need to be taken into account, since the Na^+ ions in the surrounding solution are not resonant at all at 589 nm, and the optical absorption of the solution in the visible range is practically independent of the salt concentration [15].

At 0.2 M the Na concentration in the gas will be about 0.12% of the total number of atoms resulting from the laser ionization of the water, if we make the reasonable assumption that the sodium atom concentration is the same as the initial water concentration. The theory of radiation trapping for this case of collision-dominated line broadening was formulated by Holstein [16] for a gas confined to a cylinder of radius R, where the lifetime ratio is given by $\tau/\tau_0 = \sqrt{\pi k_{\mathrm{Na}} R}$ with

$$k_{\mathrm{Na}} = \frac{\lambda^2}{2\pi}\frac{g_u}{g_l}\frac{n_{\mathrm{Na}}}{n}\frac{1}{\tau_0 k_c}, \tag{1}$$

where λ is the emission wavelength, g_u and g_l are the statistical weights of the upper and lower states, n_{Na}/n is the density ratio of the sodium atoms to the oxygen and hydrogen, and k_c is the collisional-broadening rate constant. To a fairly good approximation [17] this formula can also be used for confinement to a sphere of radius R, which we will take to be the bubble size. Experimental data for k_c exist for sodium collisions with hydrogen [18], and extrapolating these data to 2600 K gives an approximate value $k_c \approx 1 \times 10^{-14}$ m^3/s. Taking a bubble radius of 100 μm and $g_u/g_l = 1$ for the upper $P_{3/2}$ state at 589.6 nm gives values of τ/τ_0 ranging from 10 to 60 as the salt concentration increases from 0.2 M to 6 M. The $P_{1/2}$ state at 589.0 nm with $g_u/g_l = 2$ would have double this range of lifetime ratios. Though this is at best a very rough calculation, the fact that τ/τ_0 is substantially greater than one means that radiation trapping is an important factor, and the increase with salt concentration may account for the increasing delay in observing the precursor pulse seen in the data. A more quantitative description would also need to take into account that τ_0 itself would be decreasing from collisional deexcitation of the upper state as the overall density of atoms rises close to the collapse point.

The reason for the decrease in the precursor signal prior to reaching the collapse point is not entirely clear. In this regime approaching the maximal temperature there will be considerable ionization of the sodium atoms, since their ionization potential of 5.14 eV is less than half that of the hydrogen and oxygen. This may increase the optical thickness to the point where the sodium emission lines are redistributed in frequency enough that they no longer pass through our narrow-band filter. In fact about 10–15 ns prior to the collapse point we do observe additional signal in the blue passband filter, which may be upshifted photons from the precursor signal as it evolves into blackbody emission. This can be seen most clearly in the upper curve of Fig. 1. Just past the collapse point all of the sodium emission is rapidly extinguished; apparently all of the atoms are quickly brought back to the ground state by collisional deexcitation in the high density at the collapse point.

We have also found that the salt has an effect on the duration of the blackbody pulse emitted at the collapse point. The duration in pure water has been found to be linearly proportional to the maximum bubble radius and to increase with pressure [4,8]. Figure 3 shows the slope of the FWHM duration versus maximum bubble size from the blue-pass filter signal, from a linear fit averaging over 20–25 bubbles of differing size. The results for pure water are very similar to the previous data [8], but it can be seen that increasing the NaCl concentration leads to a decrease in the pulse widths by about 30% at the highest concentrations. The reason for this decrease is not particularly clear, but it could possibly also be related to the high ionization

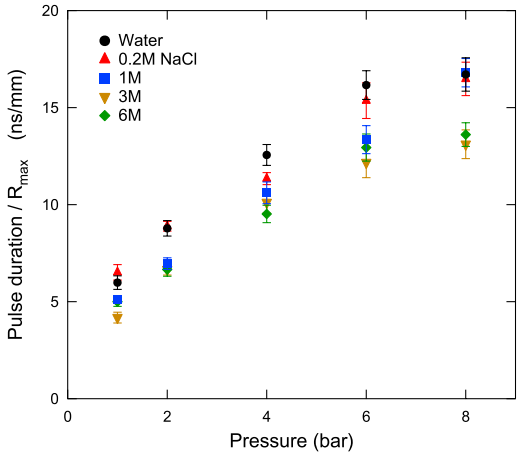

FIG. 3 (color online). Slope of the FWHM duration of the collapse point luminescence as a function of applied pressure and NaCl concentration.

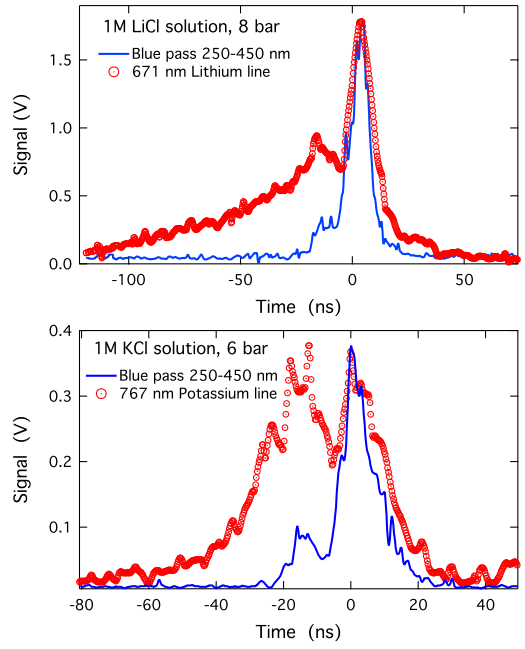

FIG. 4 (color online). Luminescence pulses from LiCl and KCL solutions.

levels of the sodium atoms, which will considerably increase the total overall ionization of the gas, since the ionization of the hydrogen and oxygen is thought to be very weak. The stronger electric fields could then affect the dynamics of the recombination process as the gas cools. The properties of the Cl atoms do not seem to play a major role, since we found a similar decrease of the pulse width in 1 M $NaCO_3$.

We have found a similar precursor luminescence pulse with other alkali-salt solutions, KCl and LiCl. Figure 4 shows the luminescence pulses in 1 M solutions, with again 10 nm bandpass filters centered on the respective D line transitions at 767 nm and 671 nm. The line emission is quite visible well before the collapse point, and the onset of additional structure in the blue-pass signal just before the collapse point is even more apparent, and appears to be correlated with the peak in the precursor signal.

Alkaline-earth solutions were also tried in these experiments, but no precursor luminescence could be observed. A 1 M solution of $MgCl_2$ was used with a 520 nm filter viewing the strongest neutral atomic lines of Mg at 517 and 518 nm, but no excess radiation other than the blackbody pulse could be detected. The same occurred for a 1 M solution of $BaCl_2$, when attempting to observe without success a neutral Ba line at 458 nm with a 460 nm filter. The alkaline-earth atomic lines are generally much weaker than the alkali-metal lines, and it is likely that we simply did not have enough sensitivity to detect them.

In summary, we have observed a precursor luminescence pulse in alkali-salt solutions, arising from the strong alkali atomic transitions as the gas in the bubble is heated by the bubble collapse. For low alkali concentration the onset of the pulse starts as much as 150 ns from the collapse point, but with increasing concentration the onset is delayed to much closer to the collapse point, and this appears to result from resonant trapping of the atomic-line photons in the bubble. This technique yields valuable information on the very rapid time-dependent heating in the bubble, though a more complete theoretical analysis will be needed to fully exploit it.

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