Ultrabright cavitation luminescence generation and its time-resolved spectroscopic characterization

Qi-Dai Chen,[1] Li-Min Fu,[1,2] Xi-Cheng Ai,[2] Jian-Ping Zhang,[2] and Long Wang[1]
[1]*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*
[2]*State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
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The generation of intense cavitation luminescence flashes by the use of an improved U-tube apparatus is presented. The light flash was characterized by its high energy (~1.4 mJ) and long duration (~200 μs) that allowed the time-resolved spectrum to be measured for a single flash. The C_2 molecular vibrational band emission superimposed on a continuum background spectrum was observed and found to be delayed in time with respect to the background emission. The dependence of pulse width on the luminescence wavelength and the coincidence of the surface brightness with the blackbody radiation behavior suggest the blackbody mechanism of the luminescence.

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Cavitation luminescence, i.e., light emission from an imploding gas bubble in a liquid, is characterized by the great focus of energy. A widely used technique to create cavitation luminescence is to pass an acoustic wave through a liquid, which can induce multibubble sonoluminescence (MBSL) [1] or single-bubble sonoluminescence (SBSL) [2]. Observations of luminescence from the collapse of bubbles without any acoustic field involved have also been reported, such as the tube-arrest method, the venturi tube method, the cavitation induced by laser, and the electrical discharges method [1]. These types of cavitation luminescence were sometimes also called sonoluminescence (SL), irrespective to the way of cavitation creation.

The physics involved in the cavitation luminescence process is still in debate and several radiation mechanisms have been proposed [2,3]. Temporal and spectral characterizations of the cavitation luminescence events are essential for testing the proposed models for the cavitation generation. For example, if the luminescence were the blackbody radiation from an adiabatic compression of gas bubbles, one would expect that the luminescence pulse width is larger in the red than in the ultraviolet spectral regions. However, the pulses from SBSL, which are now extensively studied, are in general extremely weak ($\sim 10^6$ photons/flash) and very short lived ($\sim 10^{-10}$ s), this in addition to the 100 ps jitter in the synchronization electronics make the accurate measurements of the time-resolved spectra to be extremely difficult. Furthermore, the narrow allowance for the settings of driving parameters to ensure a stable SBSL has also impaired the attempt to obtain more intense pulses [4,5].

In this paper we present an experimental approach that is capable of generating a single flash that is intense enough for the time-resolved spectroscopic measurement. We adopted and improved the U-tube conical bubble device that was originally employed by Leighton *et al.* [6]. As shown in Fig. 1, a U tube was half filled with 1,2-propanediol, and empty space in both arms was charged with argon. A gas inlet valve was attached to the end of the left arm, whereas the other end of the tube was terminated with a hollow cone structure having a 60° angle. For optical detection a 1.5-mm-diam hole was opened at the apex, and was sealed by a quartz window. To ignite a luminescence flash, argon inside the arms was first evacuated to a desired pressure (the initial pressure P_0) before closing the regulation valves, external argon at 1 bar was then introduced from the gas inlet valve exerting a pressure on the liquid and moving it rapidly to the right. Gas in the right arm was thus compressed and collapsed violently into the apex of the cone to generate luminescence. In this way, a single flash is intense enough to be visible by naked eyes in a bright environment, and can even act as the flash to illuminate an object for taking ordinary photography.

The excitation method used in this experiment was quite different from conventional SL, hereafter, we would like to call it conical bubble luminescence (CBL). Compared with Leighton's work, the key improvement of the present experimental scheme is the larger volume of gas, i.e., about 120 ml in the right arm before the mechanical compression. Therefore, the strong light emission would possibly originate from the large quantities of inert gas. Furthermore, in Leighton's work, water was used as the working medium; the initial pressure of the bubble would be larger than 2000 Pa (the vapor pressure of water). In the present work, 1,2-

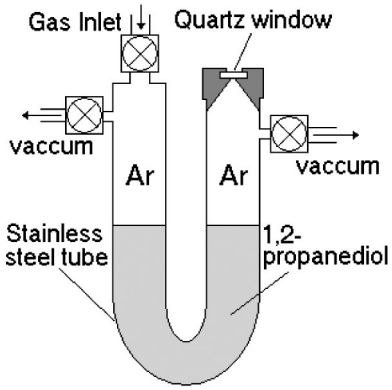

FIG. 1. Experimental setup. The stainless steel tube is U shaped, 40 cm in height, and 2.6 cm in inner diameter.

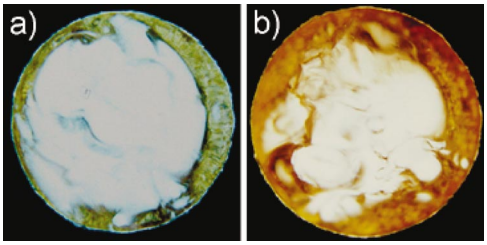

FIG. 2. (Color) Photographs of the luminescent conical bubbles generated at initial pressures 300 (a) and 1000 Pa (b), respectively.

propanediol, with a vapor pressure about 10 Pa was used, the initial pressure P_0 (300 or 1000 Pa) would be mostly due to inert gas and lower than that in Leighton's work. The relatively lower initial pressure would then induce a larger compression ratio and hence much stronger light emission.

When the apparatus was operated at an initial argon pressure of $P_0=1000$ Pa, a precise optical power meter (Yakowa 3292, Japan), whose detector is 10 mm in effective diameter and sensitive to the spectral range of 400–1100 nm, measured a single flash energy of 21 nJ. To avoid overexposure, the detector was 65 cm away from the observed window. Assuming a uniform distribution of the optical radiation in the solid angle of 4π, the light energy of a single flash is estimated to be 1.4 mJ. Taking an average photon energy of 2.0 eV the overall photon flux is then estimated to be $\sim 5 \times 10^{15}$ photons/flash, a value that is nine to ten orders of magnitudes higher than that of a typical SBSL pulse, i.e., 10^5–10^7 photons/flash [2].

The luminescent bubbles were photographed through the observation window, as shown in Fig. 2. The color of the CBL changes from orange red to bluish with decreasing the initial pressure. If the color of the luminescence represents the temperature of the gas, we are actually able to control the temperature in the cavitation bubble simply by changing the gas content in the bubble. In each photo the luminescent area holds a part of the observation window, and shows the bubble size at its maximum brightness. The viewed bubbles were in irregular shape and have certain structures. Obviously, the bubbles were neither simple single bubbles, nor bubble clouds consisting of many tiny bubbles. The diameter of the bright regions was about 1.3 mm, which was almost independent of the initial gas pressure.

Streak cameras have been used to measure the pulse shape of SBSL pulse [7]. In this paper, we use the streak camera combined with a polychromator to measure the time-resolved spectra of CBL. Figures 3(a) and 3(b) show two representative time-resolved spectra for two individual luminescence events at the initial pressure $P_0=300$ and 1000 Pa, respectively. Although the spectra extend from ultraviolet to infrared, only a limited range (445–557 nm) could be recorded for a single flash, owing to the limitation of the spectrometer. Three spectral bands superimposed on a continuum background are clearly seen in the spectral image, which are originated from the $d^3\Pi_g \rightarrow a^3\Pi_u$ transition of C_2 and referred to as the Swan bands [8], and are peaked at 470, 515, and 555 nm, corresponding to the vibrational manifold of $\Delta\nu=+1$, 0, and -1, respectively. Certain spectral lines of radical species such as CH, CN, and OH were also observed

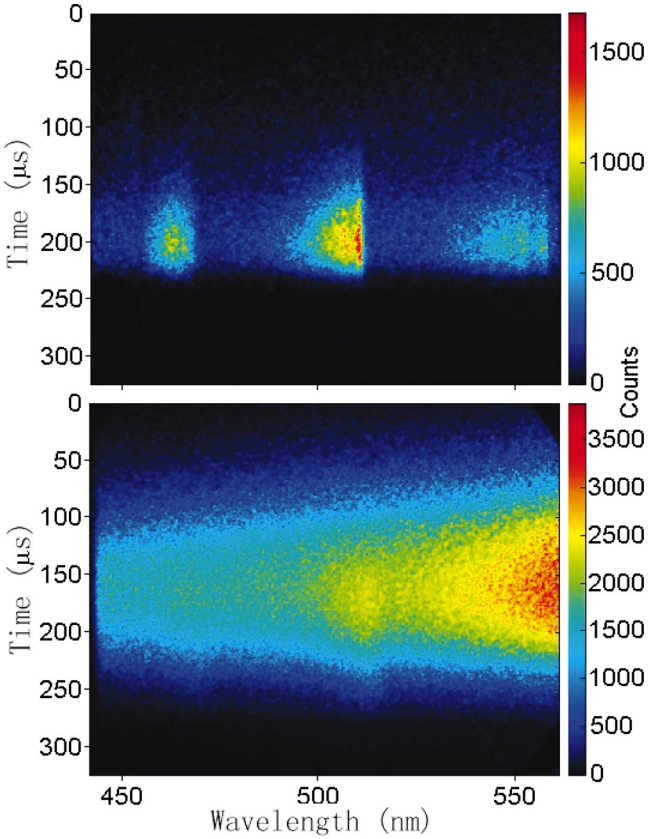

FIG. 3. (Color) Time-resolved spectra of two single luminescence events recorded with a streak camera (C2809/M1953, Hamamatsu Phonics) at initial pressures 300 and 1000 Pa, respectively. The emission was collected with a quartz fiber, and sent to a polychromator (Photonics C5094, Hamamatsu Phonics) before arriving at the photocathode.

in other spectral windows at under $P_0=300$ Pa. The typical duration of a CBL pulse is about 300 μs with a full width at half maximum (FWHM) of 150 μs. Comparing two cases of different initial pressure, it is clear that a higher initial gas pressure results in a stronger continuum and also a stronger total light intensity, while the Swan bands dominate the spectrum at a low initial pressure.

As shown in Fig. 4, we analyzed the temporal behavior of the streak image for $P_0=1000$ Pa [Fig. 3(b)]. For the continuum of the light pulse, the quantitative fit to a blackbody spectrum is so good that one is tempted to conclude that CBL, at least for the rising part, is due to blackbody radiation. There is the possibility that CBL is a pseudoblackbody radiation. In this case, insight into the light-emitting mechanism cannot be obtained without additional information. The conditions to generate the blackbody require matter-radiation equilibrium. The 200 μs luminescent time and large inert gas volume in CBL seem better satisfied the conditions than that in SBSL, whose pulse width is about 10^{-10} s and luminescent radius is about 0.2 μs [9], which is comparable to the wavelength of visible light.

The dependence of the pulse width on optical wavelength had been studied for SBSL [9,10], in which no wavelength dependence was observed. This is contradictory to the blackbody emission model of adiabatic compression, which other-

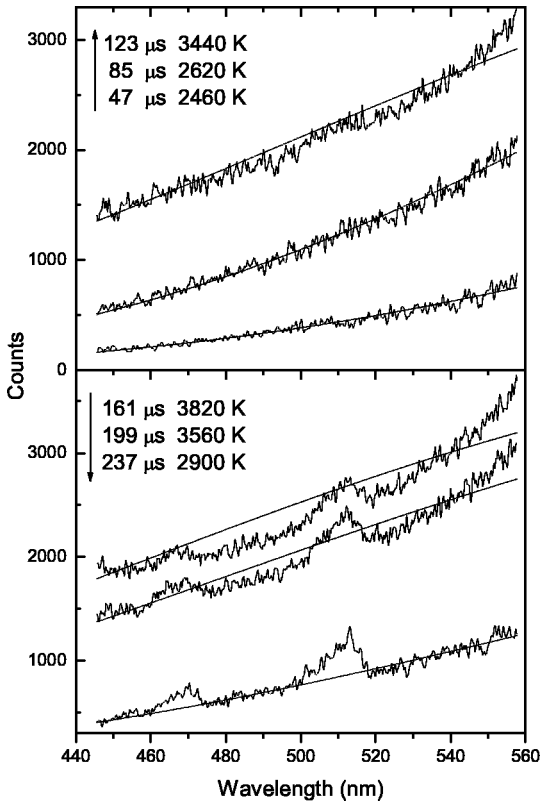

FIG. 4. Temporal evolution of the luminescence spectra extracted from the streak image in Fig. 3(b) along with the fitting curves based on the blackbody radiation formula.

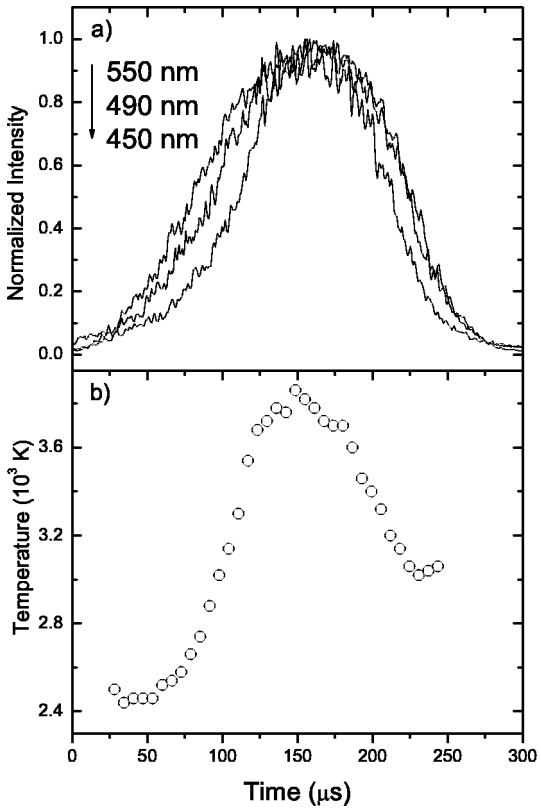

FIG. 5. (a) SL pulses at different probe wavelengths obtained from Fig. 3(b). (b) Calculated blackbody temperature as a function of delay time.

wise would result in an increase in pulse duration for a longer wavelength. The temporal evolutions of a single CBL pulse at three different wavelengths in Fig. 3(b) are displayed in Fig. 5(a), showing clearly such a wavelength dependence. Therefore, the analysis of the present experimental results based on blackbody theory would be reasonable and it is possible that the radiation mechanism of the CBL and SBSL is different.

To further examine the radiation mechanism in this experiment, the Stefan-Boltzmann law on blackbody radiation, $E=\pi\sigma R^2T^4\Delta t$, was used to estimate the CBL intensity. The time evolution of spectroscopic temperature obtained based on the time-resolved spectra [Figs. 3(b) and 4] is shown in Fig. 5(b). Taking an averaged temperature $T\approx 3000$ K, time duration $\Delta t\approx 100$ μs, and using the bubble diameter of 1.3 mm, which is roughly estimated from the photograph of the luminescent area (Fig. 2), as well as the Stefan-Boltzmann constant σ, we obtained a total energy of 2.4 mJ. Since the measured emission energy, i.e., 1.4 mJ, was contributed by the radiation in 400–1100 nm, it is in good agreement with the calculated value. Thus the radiation energy calculation also shows some consistency with the blackbody radiation mechanism for the high initial pressure case in the present work, and further suggests that the blackbody picture would be validity.

Didenko *et al.* suggested that both the molecular and the background continuum emission in MBSL are due to the emission from the small hydrocarbons species formed during the bubble collapse [11]. In the present case of CBL, however, the dependence of the intensity of the continuum radiation on the initial noble gas pressure and the relative delay of the molecular emission with respect to continuum suggest that the continuum is mainly generated from the noble gases. The featureless continuum associated with SBSL is generally believed to be originated from the hot inert gas, while the discrete bands with MBSL are from radical chemiluminescence. Therefore, the relative delay of the two different types of spectra resolved in a single flash event might provide a spectroscopic link between the SBSL and the MBSL.

It is interesting to ask why the molecular radiation delayed in time with respect to the continuum spectra. Generally speaking, organic liquid can be pyrolyzed into small hydrocarbons at about 3000 K. The time scale of generation and emission of excited state C_2^* is about 5 ns [12]. As shown in Fig. 4, the Swan bands do not appear until the inert gas blackbody temperature reached 3800 K, which was about 50 μs after the moment of 3000 K. Such a long delay in the appearance of C_2 bands could not be explained by the required chemical reaction time from the organic liquid vapor existed inside the bubble.

An alternative explanation is that the Swan bands were from the relatively cooler boundary layer near the bubble wall and the delay was caused by the time of the organic liquid near the wall to evaporate. However, the irregular luminescence shape shown in Fig. 2 reminds us of another possibility that the bubble near its minimal size breaks into sub-bubbles. It is then likely that the the organic molecules

enter the gas bubbles during the breaking process at this moment. This explanation can also explain the larger off track of the blackbody fit of the background continuum when the molecular emission appears (Fig. 4, 161 and 199 μs). In addition, the regression of the fit at 237 μs suggests that sub-bubbles reaggregated and then merged into larger bubbles again.

On the basis of molecular emission theory, the C_2 emission can be used to estimate the temperature of the luminescent bubbles generated in organic liquids [11]. In the case of $P_0=1000$ Pa, the calculated temperature by comparison of the interband intensities of the +1 and 0 vibrational bands is $\sim$4000 K at 237 μs, which is higher than the 2900 K blackbody emission temperature as estimated from the background continuum (Fig. 4). A possible explanation for the above temperature discrepancy is that chemical reactions inside the bubble broke the thermal equilibrium as they consume thermal energy.

The highest photon flux of a single cavitation luminescence pulse that has ever been achieved is 3×10^8 photons/flash as obtained by the use of the water hammer method [13]. The present method is similar to the water hammer method in a sense that both of them compress a volume of gas at cubic centimeter scale against a solid surface. However, in the process of water hammer action the gas to be compressed is extracted from the liquid and the amount is much less compared to that in the conical bubble scheme. Furthermore, before collapse, the bubble rapidly expands to its maximum, and thus the starting gas temperature would be much lower than room temperature under the adiabatic condition. To the opposite, in the conical bubble scheme the working gas was initially at its maximum volume and at room temperature, therefore both the amount of gas and the initial internal energy may contribute to the ultrabright luminescence.

In conclusion, a type of cavitation luminescence, with very different time scales, liquids, temperatures, geometries, and presumably physical processes has been reported. Compared with other kinds of cavitation luminescence, the present CBL generation merits in its brightness, which allows easier spectroscopic characterization, and in its versatility, i.e., the working media for the CBL test can be, in principle, any liquids and gases. Furthermore, parameters such as gas components, initial pressure, and temperature are all controllable; this would allow a significantly larger chemical reaction volume with adjustable conditions, which is ideal for the study of reactions under the extreme conditions.

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