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Conical bubble photoluminescence from rhodamine 6G in 1, 2-propanediol*

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A modified U-tube conical bubble sonoluminescence device is used to study the conical bubble photoluminescence. The spectra of conical bubble sonoluminescence at different concentrations of rhodamine 6G (Rh6G) solution in 1,2-propanediol have been measured. Results show that the sonoluminescence from the conical bubbles can directly excite Rh6G, which in turn can fluoresce. The light emission of this kind is referred to as conical bubble photoluminescence. The maximum of fluorescence spectral line intensity in the conical bubble photoluminescence has a red shift in relative to that of the standard photo-excited fluorescence, which is due to the higher self-absorption of Rh6G, and the spectral line of conical bubble photoluminescence is broadened in width compared with that of photo-excited fluorescence.

Keywords: cavitation, conical bubble sonoluminescence, conical bubble photoluminescence
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1. Introduction

Cavitation phenomenon involves the formation, growth, and collapse of microbubbles in a fluid. These processes may lead to the emission of light from the collapsing bubbles, and the light emission of this kind is referred to as sonoluminescence(SL).[1] The SL can be produced by a number of quite different means, e.g. the passage of ultrasound through certain liquids, which can induce multi-bubble sonoluminescence (MBSL)[2] and single-bubble sonoluminescence (SBSL),[3] laser pulse focused into a fluid,[4] high fluid tension imposed on a fluid, such as in a Venturi tube,[5] the tube arrest[6] or water hammer methods[7] and other processes.

Despite the fact that SL from a bubble field has been extensively investigated, there is still the argument about the mechanism of the light emission from bubbles. Noltink *et al* proposed that the SL originated from the blackbody emission of the heated cavity.[8] Electrical dischargey[9−11] inside the bubble has also been considered as the source of SL. In addition, the shock-wave model and hot-spot chemiluminescence model are also proposed. [12,13]

Ashokkumar and Grieser[14,15] reported a new type of emission referred to as sonophotoluminescence (SPL), where SL was absorbed to excite dissolved fluorescent solutes, leading to the emission of fluorescence associated with photoluminescence. Their study of SPL covered both cases of MBSL and SBSL. However, Hatanaka *et al* [16] negatived the possibility of SPL contributions in aqueous luminal solutions. In this paper, a new type of sonoluminescence apparatus, a conical bubble sonoluminescence (CBSL) device without any acoustic field involved, is used to study the SPL. Here, we refer to the SPL as the conical bubble photoluminescence (CBPL). The spectra of the luminescence in 1,2-propanediol solutions with different rhodamine 6G (Rh6G) concentrations have been obtained. Results show the CBPL exists in the light emission processes.

2. Experimental device

Figure 1 shows the schematic diagram of the conical bubble U-tube. Details of the apparatus have been

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given elsewhere.[17,18] Briefly speaking, when the argon inside the arms of the tube is evacuated to a desired pressure (the initial pressure is about 1000–1500 Pa), and then external argon (P=10^5 Pa) is introduced from the gas inlet valve to the left arm, exerting a pressure on the liquid. The liquid rapidly moves to the right arm. Thereby the gas in there is compressed and collapsed violently into the apex of the cone to generate luminescence.

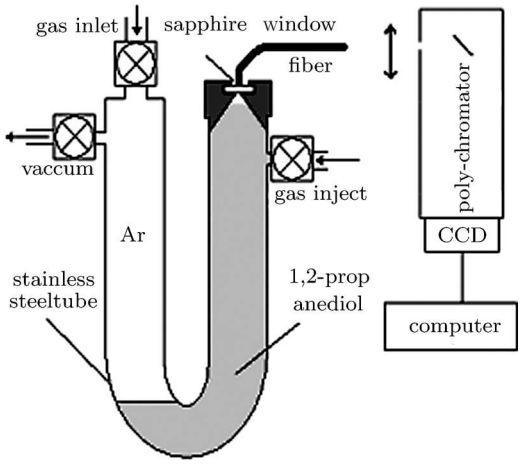


Fig.1. Experimental device with the stainless steel tube in U-shape (40 cm in height and 2.6 cm in inner diameter).

In the previous work, the strong luminescence produced by the U-tube in 1,2-propanediol has been obtained, which reached 1.4 mJ of the energy.[17] The shortest wavelength of CBSL is about 400 nm. In the present work, the CBSL is used as an internal light source to excite fluorescent solute. The fluorescent solute used in this experiment is Rh6G, which is a type of dye with well characteristic photophysical properties and is widely used in laser.

3. Results and discussion

The photo-excited absorption and fluorescent spectra of Rh6G solution in 1,2-propanediol are measured by using the absorption spectrophotometer (U-3310) and the fluorescence spectrophotometer (F-2500, HITACHI), and the results are shown in Fig.2. It can be seen that the main absorption band ranges from about 440 nm to 570 nm, and no apparent absorption exists in the range of wavelength longer than 570 nm. The main fluorescence band is in a wavelength range from 520 nm to 630 nm and the maximum appears around 555 nm. Thus, it is possible to use the CBSL to excite the Rh6G to fluoresce in principle.

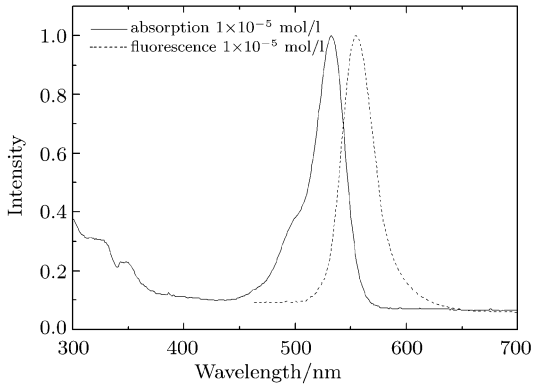


Fig.2. Absorption and fluorescence (λ_{ex}= 450 nm) spectra of Rh6G at 1×10^{-5} mol/L; the spectral line intensities are normalized.

Figure 3(a) shows the CBSL spectra in 1,2-propanediol at 0 mol/l, 1×10^{-5} mol/l and 1×10^{-4} mol/l Rh6G concentrations. As can be seen, the spectrum of CBSL in the absence of Rh6G (the line labelled as 0 mol/l) is quite a broad continuum ranging from 400 nm to 750 nm with a peak at 589 nm and a band at about 620 nm. The peak should be the resonance line of sodium. A tiny amount of sodium impurities from the 1,2-propanediol or the glass container should be the source of sodium. The band can be attributed to the red satellite bands ($A^2\sum^+ \rightarrow X^2\sum^+$) from the Na–Ar van der Waals molecule, which has been discussed elsewhere. [19]

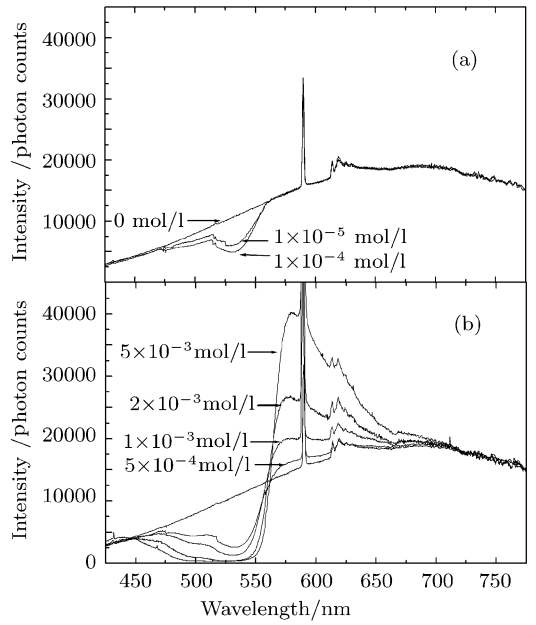


Fig.3. (a) CBSL spectra of 0 mol/l, 1×10^{-5} mol/l and 1×10^{-4} mol/l Rh6G solutions in 1,2-propanediol. (b) CBSL spectra of 5×10^{-4} mol/l, 1×10^{-3} mol/l, 2×10^{-3} mol/l and 5×10^{-3} mol/l Rh6G solutions in 1,2-propanediol.

When a tiny amount of Rh6G is added into the 1,2-propanediol, the CBSL spectral intensity falls

compared with that of CBSL in the absence of Rh6G in the 460 nm– 560 nm wavelength range. Furthermore, the intensity of CBSL spectral line decreases with the Rh6G concentration increasing in this range, as shown in Fig.3(a) by the lines labelled as 1×10^{-5} mol/l and 1×10^{-4} mol/l respectively.

When the Rh6G concentration increases to 5×10^{-4} mol/l, the spectral line intensity rises compared with that of CBSL in the absence of Rh6G in the 560–650 nm wavelength range. Figure 3(b) shows the spectra of CBSL in a range from 5×10^{-4} mol/l to 5×10^{-3} mol/l Rh6G solutions. Their key features as follows: (1) CBSL is highly absorbed in the 460–550 nm wavelength range compared with that of Fig.3(a), and almost completely absorbed around 530 nm when the concentration reaches 2×10^{-3} mol/l. The spectral line intensity decreases with the increase of Rh6G concentration in this range. (2) A new emission spectral band appears, and the spectral line intensity increases with the increase of Rh6G concentration in this range. (3) Except for the two ranges mentioned above, the spectra of CBSL with and without Rh6G solutions are almost the same.

In order to clearly see the effect of Rh6G on the CBSL line intensity, the spectral line intensity of CBSL in the absence of Rh6G is subtracted from the spectral line intensity of CBSL in the presence of Rh6G, as shown in Fig.4, in which the emission line of sodium is ignored, because it is verified that the sodium has no effect on the CBPL.

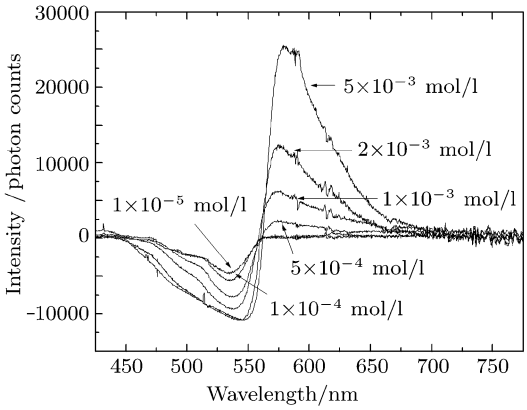


Fig.4. The CBSL spectral line intensities at different Rh6G concentrations, from which the spectral line intensity of CBSL in the absence of Rh6G is subtracted already.

Comparing Fig.2 with Fig.3 and Fig.4, it can be found that the wavelength range where the spectral line intensity decreases in Fig.4 corresponds to the absorption band, the new emission band corresponds to the fluorescent band of Rh6G solution, which suggests that the new emission band should be due to the fluorescence of Rh6G excited by the CBSL. However, the maximum spectral line intensity of the new emission spectra is located around 575 nm, and shifts about 20 nm towards the long wavelengths compared with that of the fluorescence spectrum in Fig.2; moreover, it has a weak red-shift in the maximum of spectral line intensity of the new emission spectra with the concentration of Rh6G increasing from 571 nm at 5×10^{-4} mol/l to 579 nm at 5×10^{-3} mol/l as shown in Fig.5. This can be explained by the Rh6G's self-absorption. It is seen from Fig.2 that the absorption spectrum and fluorescent spectrum overlap in the 510–570 nm wavelength range, which is the very range of both the longer wavelength absorption and the shorter wavelength fluorescent emission.

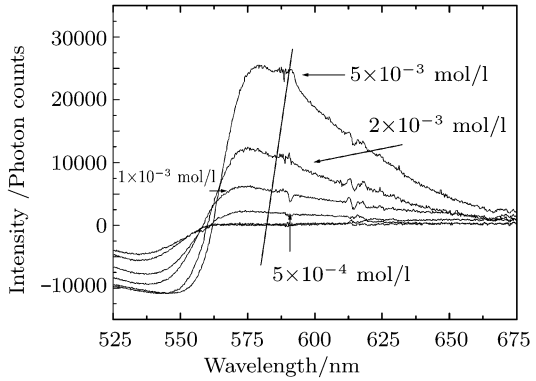


Fig.5. The weak red-shift of maximum of spectral line intensity of the new emission spectrum with the Rh6G concentration increasing. This figure is selected from Fig.4.

So the fluorescence emission will be affected and some fluorescence will be absorbed; moreover, these effects become more and more prominent with the increase of Rh6G concentration. Therefore, when the Rh6G concentration is 1×10^{-5} mol/l, the self-absorption has no apparent effect on the fluorescence emission, and the fluorescence peaks around 555 nm; this is the standard fluorescence spectrum of Rh6G, similar to the result in Ref.[20]. However, with the increase of Rh6G concentration, the fluorescence emitted in the 510–570 nm wavelength range can be strongly absorbed. The fluorescence emission in the range of wavelength longer than 570 nm is not affected by the self-absorption at all. As a result, the spectral line intensity of fluorescence spectrum in the range of wavelength longer than 570 nm is higher than that in the shorter wavelength range. Thus the fluorescence maximum appears around 575 nm as indicated in Fig.4. Meanwhile, because the self-absorption is more and more intense with the Rh6G concentration increasing, the maximum of the new emission shifts towards the red

wavelength with the concentration increasing. The above proposition can be verified from Fig.6: these spectra are the photo-excited fluorescence spectra at 1×10^{-5} mol/l, 1×10^{-3} mol/l and 5×10^{-3} mol/l, measured by using the fluorescence spectrophotometer (F-2500, HITACHI). It can be found that the maximum of fluorescence spectral line intensity shifts towards the red wavelength with the concentration increasing, which indicates that the fluorescence in the 510 nm - 560 nm wavelength range is absorbed. The maximum of fluorescence spectral line intensity is at about 579 nm at 5×10^{-3} mol/l, which is similar to the maximum of spectral line intensity in the band where the spectral line intensity increases at 5×10^{-3} mol/l in Fig.4.

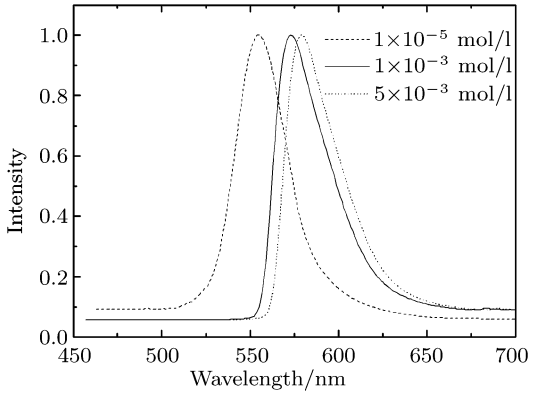


Fig.6. The photo-excited fluorescence of Rh6G at different concentrations, measured by using the fluorescence spectrophotometer (F-2500, HITACHI, λ_{ex}=450 nm)

Figure 7 directly shows the comparisons between spectral line intensity of the spectrum in the range where the spectral line intensity decreases at 1×10^{-5} mol/l in Fig.4 and that of the absorption spectrum at 1×10^{-5} mol/l in Fig.2, and between spectral line intensity of the spectrum in the range where the spectral line intensity increases at 5×10^{-3} mol/l in Fig.4 and that of the photo-excited fluorescence spectrum at 5×10^{-3} mol/l of Rh6G solution. In Fig.7, the maximum of spectral line intensity of the absorption spectrum is on the same scale to the maximum of spectral line intensity of the spectrum in the range where the spectral intensity decreases at 1×10^{-5} mol/l, and the maximum of spectral line intensity of fluorescence spectrum is also on the same scale to the maximum of spectral line intensity of the spectrum in the range where the spectral line intensity increases at 5×10^{-3} mol/l. So the two types of spectra can be compared conveniently. It can be seen clearly that the spectral line intensities of the absorption spectrum and the fluorescent spectrum are in good agreement with those of the spectrum in the range where the spectral line intensity decreases and of the spectrum in the range where the spectral line intensity increases in CBSL, respectively. This verifies that the new emission band should be due to the fluorescence emitted from Rh6G and the decrease in spectral line intensity should be attributed to the absorption of Rh6G. This suggests that the CBPL exists in the process of CBSL.

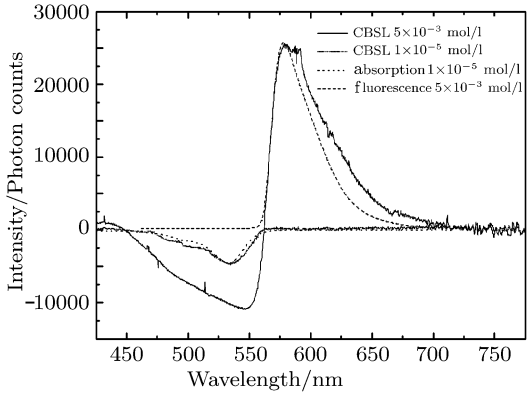


Fig.7. Comparisons between the spectral line intensities of the CBSL at 1×10^{-5} mol/l and the absorption spectrum at 1×10^{-5} mol/l, and between the spectral line intensities of the CBSL at 5×10^{-3} mol/l and the photo-excited fluorescence (λ_{ex}= 450 nm) spectrum at 5×10^{-3} mol/l Rh6G solution in 1,2-propanediol. The maximum of absorption spectral line intensity is on the same scale to the maximum of spectral line intensity of the spectrum in the range where the spectral line intensity decreases at 1×10^{-5} mol/l, and the maximum of the fluorescence spectral line intensity is also on the same scale to the maximum of spectral line intensity of the spectrum in the range where the spectral line intensity increases at 5×10^{-3} mol/l.

It also can be found from Fig.7 that the width of fluorescence spectral line in CBPL has a broadening compared with that of the photo-excited fluorescence spectral line. This should be due to the pressure broadening. This can be explained by use of the uncertainty principle: $\Delta E \times \Delta t \approx \hbar$. Any process that reduces the lifetime of the radiating species broadens the energy distribution (line width) of the emission. In the CBSL process, the pressure is higher than that of the photo-excited fluorescent process,[17] and the intermolecular interaction is strong. Therefore, the lifetime of the emission decreases due to the increase in number of the collisions per unit time and the spectral line width of the fluorescence also increases.

The self-absorption has an effect on the CBPL emission, but is not apparent in the range of wavelength longer than 570 nm. The fluorescence spectral line intensity of the CBPL against Rh6G concentration at 579.5 nm is plotted in Fig.8, where the inten-

sity at each of the selected concentration is measured eight times. It can be seen that the intensity is approximately linear with the concentration of Rh6G solution in the range of concentration less than 2×10^{-3} mol/l; however, the increasing rate of spectral intensity decreases in the range of concentration larger than 2×10^{-3} mol/l. This is because the absorption is saturated at about 530 nm in wavelength and larger than 2×10^{-3} mol/l in concentration of Rh6G solution as shown in Fig.3(b).

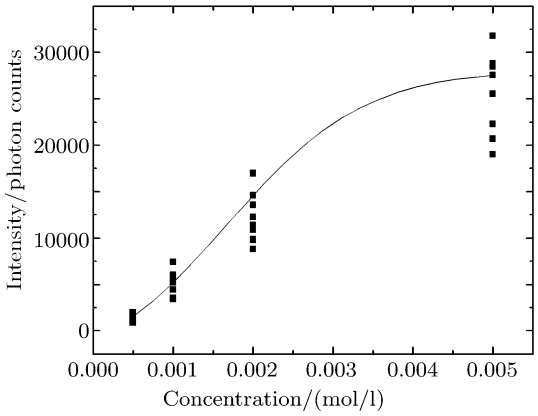


Fig.8. The spectral line intensity of CBPL as a function of concentration of Rh6G solution at 579.5 nm.

In order to confirm that it is CBSL but not some thermal activation from heat leaking from collapsed bubbles that excites Rh6G, the following experiment is carried out. The experimental condition is the same as the above, except for the pure water rather than 1,2-propanediol being used. The previous results[18] show that the spectrum of sonoluminescence in pure water appears at wavelengths longer than 700 nm, so if the fluorescence is excited by CBSL, the light emitted in this condition should have no enough energy to be able to excite the Rh6G to fluoresce. Results show that the absorption and fluorescence (photoexcitation λ_{ex}=450 nm) spectra of Rh6G solution in pure water have similar characteristics to those in 1,2-propanediol. However, the spectra in pure water with the addition of Rh6G are the same as those in pure water without any addition of Rh6G. This indicates that there is no CBPL because of the absence of appropriate light source.

Finally, two points should be noted. From Fig.3(a) it can be seen that the decrease in spectral line intensity is apparent, but no fluorescence emission can be observed. This is because the bubble motion is very acute in the process of CBSL, most of absorbed energy may be consumed by being converted into heat energy or chemical energy, so the energy is not enough to excite Rh6G to fluoresce, and the fluorescence spectral line intensity is too weak to be observed. Second, when the fluorescence in the CBSL has appeared, whether the CBPL can be clearly observed in the spectral diagram lies in the intensity ratio between fluorescence and CBSL to some extent. When the Rh6G concentration is very low, this ratio is very small. So the difference between the spectral line intensities in the absence and that in the presence of Rh6G cannot be clearly seen in the fluorescent emission range. However, the intensity of fluorescent emission spectral line increases with the increase of Rh6G concentration, and the intensity ratio rises, thus the fluorescence of CBPL can be clearly seen. This point can be verified from Fig.3.

4. Conclusions

The U-tube conical bubble sonoluminescence apparatus has been used to study the CBPL. The CBSL spectra at different concentrations of Rh6G solution have been measured. Meanwhile, the photo-excited absorption and fluorescence spectra are also obtained. The results show that CBSL can lead to direct excitation of Rh6G, which in turn can fluoresce. The maximum of fluorescence spectral line intensity in the CBPL process has a red-shift because Rh6G has a strong self-absorption at higher concentrations, and the line width of CBPL has a pressure broadening compared with that of photo-excited fluorescence. The intensity is approximately linear with the concentration of Rh6G solution in the range of concentration less than 2×10^{-3} mol/l.

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