Physics Letters A 379 (2015) 497–500

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Line emissions from sonoluminescence in aqueous solutions of halide salts without noble gases

Jinfu Liang [a,b], Weizhong Chen [a,*], Chao Zhou [a], Weicheng Cui [a], Zhan Chen [a]

[a] *The Key Laboratory of Modern Acoustics, Ministry of Education, Institution of Acoustics, Nanjing University, Nanjing 210093, China*
[b] *School of Physics and Electronic Science, Guizhou Normal University, Guiyang 550001, China*

ARTICLE INFO

Article history:
Received 25 June 2014
Received in revised form 19 November 2014
Accepted 24 November 2014
Available online 28 November 2014
Communicated by V.A. Markel

Keywords:
Sonoluminescence
Line emissions
Halide ions

ABSTRACT

Line emissions of trivalent terbium (Tb^{3+}) ion were observed from single-bubble sonoluminescence (SL) in an aqueous solution of terbium chloride ($TbCl_3$) that contained no noble gas. In addition, sodium (Na) lines were observed in multi-bubble SL in aqueous solutions of various halide salts that contained no noble gas. These observations show that the halide ions, such as Cl^-, Br^-, and I^-, help for line emissions as the noble gases. The intensity of a line emission depends on both the chemical species produced by cavitation bubbles and the temperature of SL bubble that responds to the driving ultrasound pressure. With the increase of driving pressure, some line emissions attached to the continuous spectrum may become increasingly clear, while other line emissions gradually become indistinct.

Sonoluminescence (SL), a kind of light emission, results from the extreme temperatures and pressures achieved during the violent collapse of cavitation bubbles in liquids that have been irradiated with high-intensity ultrasound waves [1–3]. SL can occur either from a cloud of cavitating bubbles [4] (multi-bubble sonoluminescence, MBSL) or from a single isolated cavitating bubble (single-bubble sonoluminescence, SBSL) [5]. For both MBSL and SBSL, spectroscopic observations are a major and effective experimental approach. In particular, measurements of characteristic line emissions that identify the illuminant inside the bubbles are currently receiving considerable attention in SL investigations.

In early experiments, the distinction between MBSL and SBSL was that the MBSL spectrum was supposed to be a broadband spectrum with some characteristic lines [6,7] (e.g., the OH-radical line), while the SBSL spectrum was presumed to be a featureless continuum [7,8]; however, this was before observations of the OH-radical line in dim SBSL [9]. In 2005, Flannigan and Suslick reported observations of argon (Ar) line emissions from moving SBSL in concentrated aqueous sulfuric acid (H_2SO_4) [10,11]. Then, line emissions of sodium (Na) and Ar were also observed from a stable SBSL in H_2SO_4 that contained both sodium sulfate (Na_2SO_4) and Ar [12]. More recently, OH line emissions were observed from SBSL in phosphoric acid (H_3PO_4) [13]. These observations show that the intrabubble processes of SBSL are similar to those of MBSL under some conditions.

As mentioned above, a line spectrum reflects characteristics of an illuminant, hence, measuring the line spectrum of a sample is a simple but effective approach for detecting its composition. Therefore, the discovery of line emissions from SBSL [9] opens a new opportunity for understanding the composition inside cavitating bubbles. Almost all experimental observations of line emissions from SL have been conducted on solutions containing a noble gas [6,8,10–15] except that Sharipov et al. observed the Tb^{3+} line emission from MBSL in the $TbCl_3$ aqueous solution with air [16]. For example, OH and PO line emissions from MBSL were observed in H_3PO_4 solutions saturated with helium [14], and the Ar atomic line emission of SBSL was measured in H_2SO_4 aqueous solutions containing Ar [10,12]. Pflieger et al. [15] observed the line emissions of the trivalent terbium (Tb^{3+}) ion in the terbium chloride ($TbCl_3$) aqueous solution containing 70 mbar (about 50 Torr) Ar. In 2007, Levinsen et al. reported that the intensity of SBSL spectrum without the presence of noble gases was much weaker than that of a stable argon bubble [17]. In this letter, we report observations of line emissions from SL in the aqueous solutions of halide salts that contained no noble gases.

The experimental apparatus and measuring method were similar to those described in previous studies [12,18,19]. The host liquids used for SBSL and MBSL here were aqueous solutions containing some solutes. The liquids were degassed for about 24 h at a vacuum of about 25 Torr (1 Torr ≈ 133.3 Pa), then they were regassed for the same period with selected gases at a pressure head

---

[*] Corresponding author.
E-mail addresses: liang.shi2007@163.com (J. Liang), wzchen@nju.edu.cn (W. Chen).

http://dx.doi.org/10.1016/j.physleta.2014.11.051

Table 1
Aqueous solutions used in the experiments on SBSL and MBSL.

SL	Solute	Concentration (mol/L)	Dissolved gas (100 Torr)
SBSL	$Tb(NO_3)_3$	0.15	no
	$Tb(NO_3)_3$	0.15	Ar
	$TbCl_3$	0.15	no
	$TbCl_3$	0.15	Ar
MBSL	$Tb(NO_3)_3$	0.15	Ar
	$Tb(NO_3)_3$	0.15	mixed gas[a]
	$TbCl_3$	0.15	mixed gas
	NaCl	1	mixed gas
	NaBr	1	mixed gas
	NaI	1	mixed gas

[a] The mixed gas is consisted of nitrogen (80%) and oxygen (20%).

of 100 Torr. We used the host liquids listed in Table 1. The SL spectra were acquired by a spectrograph (Acton Research SP-300i) and the slit width of spectrography was set at 0.20-mm. The experiments were conducted at a room temperature of about 15 °C.

We collected spectra from SBSLs of degassed aqueous solutions of terbium nitrate ($Tb(NO_3)_3$) containing no noble gas (Fig. 1(a)) and containing 100 Torr of Ar (Fig. 1(b)). Terbium (Tb) is a rare earth element, and the (Tb^{3+}) ion is a good green-light emitter. In Fig. 1(a), only featureless continuous spectra appear, while in Fig. 1(b) line emissions of Tb^{3+} appear in addition to the continuous spectra. This comparison shows that Ar helps the emission of line spectra during SL, as has been reported in many previous papers [10–15]. In the $Tb(NO_3)_3$ containing no noble gas, the Tb^{3+} line emissions are almost quenched by $NO_3{}^-$ and $NO_2{}^-$ formed by ultrasound treatment [20] ($NO_3{}^- \rightarrow NO_2{}^- + \frac{1}{2}O_2$) because there is no noble gas as protective gas.

However, when we performed a similar SBSL on a degassed $TbCl_3$ aqueous solution containing no Ar, the same Tb^{3+} line emissions were observed (Fig. 1(c)). Since there was no noble gas as protective gas in the aqueous solution, this result was beyond our knowledge. To clearly understand the line emissions of Tb^{3+}, we labeled four transitional peaks of Tb^{3+} from state $^5D_4$ to ^7F_J ($J = 6, 5, 4, 3$) by the letters A–D in Fig. 1(c). The corresponding wavelengths (λ) are given in Refs. [21,22]. Of course, the Tb^{3+} line emissions are also observed in $TbCl_3$ aqueous solutions containing Ar [15,23]. The phenomenon, compared with that in $Tb(NO_3)_3$ without noble gas, shows that the quenching of Tb^{3+} line emission by Cl^- is extensively less than that by $NO_3{}^-$ and $NO_2{}^-$ [24,25]. The Cl^- ions help for generating line emissions in SL. Similarly, it is reasonable to expect that other halide ions can also contribute to line emissions during SL.

To test the above concept, we measured MBSL spectra for the six aqueous solutions listed in Table 1. In Fig. 2(a), the Tb^{3+} line emissions from MBSL appear in both the $TbCl_3$ aqueous solution that contained 100 Torr of mixed gas (solid curve) and $Tb(NO_3)_3$ aqueous solution that contained 100 Torr of Ar (dashed curve); however, the spectrum for $Tb(NO_3)_3$ aqueous solution that does not contain noble gas (dot curve) is almost featureless. The Tb^{3+} excitation mainly occurs via collision of Tb^{3+} ions with "hot" particles at bubble–solution interface [15]. These "hot" particles such as OH radical, are generated during violent bubble collapse. Whereas the luminescence quenching of the Tb^{3+} line emission is a result of coupling between the electron excited state of Tb^{3+} and quenchers such as $NO_3{}^-$ and $NO_2{}^-$ by collision [24,25]. Fig. 2(b) shows Na line emissions at about $\lambda = 589$ nm in NaCl, NaBr, and NaI aqueous solutions that contained 100 Torr of mixed gas. These spectra show that line emissions of SL can be observed in aqueous solutions of halide salts that do not contain noble gases. Of course, the definition of Na line attached to the continuum spectrum is weaker than that in NaCl aqueous solution with noble gases [26–28].

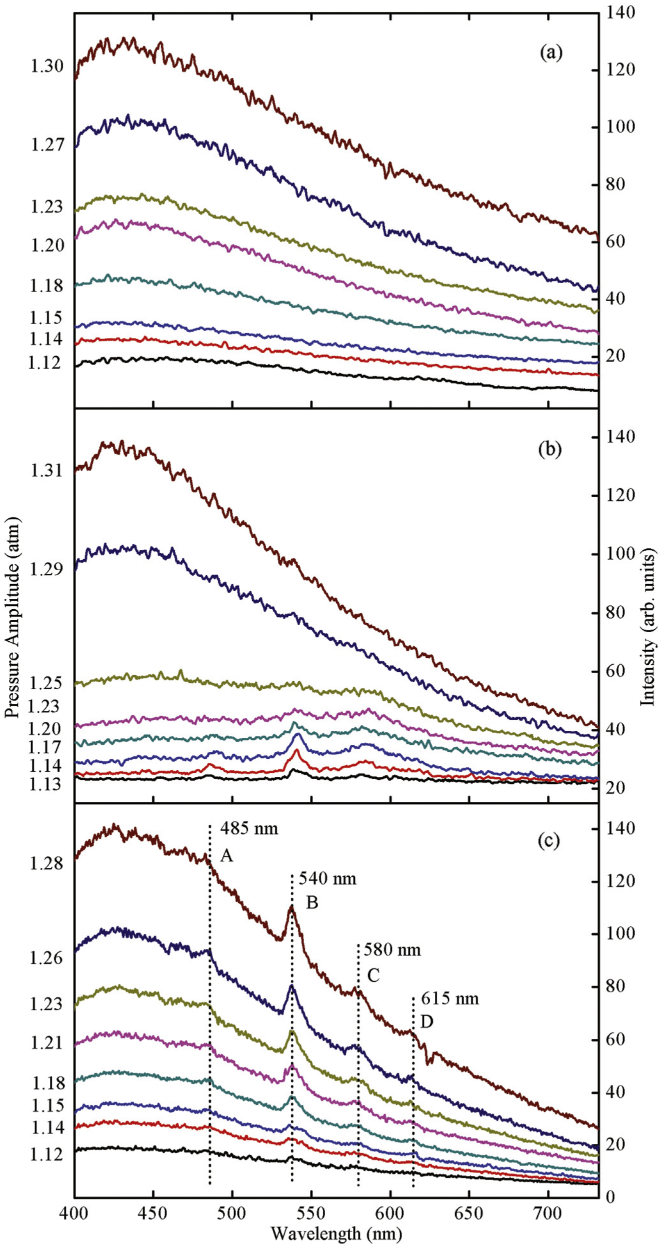

Fig. 1. (Color online.) SBSL spectra from (a) degassed $Tb(NO_3)_3$ aqueous solutions, (b) $Tb(NO_3)_3$ aqueous solutions containing 100 Torr of argon and (c) degassed $TbCl_3$ aqueous solutions. The vertical dotted lines show four central wavelengths of spectral peaks labeled by A, B, C, and D.

The intensities of line emission depend on both the chemical species formed by ultrasound treatment and the intra-bubble's temperature that responds to the driving sound pressure. For example, the intensity of Tb^{3+} line emissions in Fig. 1(b) and (c) increases with the driving pressure, especially at $\lambda = 540$ nm. Which can be explained with the theory of energy level transition. Eight outer electrons in a Tb^{3+} ion are in the 4f shell, which yields its ground state ^7F_J ($J = 6, 5, \cdots, 0$), the first excited state $^5D_4$, second excited state $^5D_3$, and so on (Fig. 3). When a ground state Tb^{3+} ion absorbs an energy ΔE and jumps to the excited state $^5D_4$, the lines for $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, \cdots, 0$) are spontaneously emitted [22,29]. The energy absorbed ultimately comes from the ultrasound field. For a suitable driving pressure, the collapsing cavitation bubble supplies an appropriate energy ΔE to make the ion jump to $^5D_4$ with high probability, leading to a bright line emission of $^5D_4 \rightarrow {}^7F_J$. For a weaker driving pressure corresponding