# Stable sonoluminescence within a water hammer tube

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The sonoluminescence (SL) from the collapse of a single gas bubble within a liquid can be produced repetitively using an acoustic resonator. An alternative technique using a water hammer tube, producing SL from bubbles of greater size, is described here. A sealed vertical tube partly filled with a liquid and a gas at low pressure is subjected to vertical vibrations. The oscillation of the pressure within the liquid column, due to inertial forces, excites cavitation bubbles to grow and collapse. Rotation is used to confine the bubbles to the axis of the tube. Bright SL emissions were observed in a number of liquids. Repetitive emission was produced from bubbles in condensed phosphoric acid. Bubbles of 0.4 mm ambient radius (containing  $2 \times 10^{14}$  xenon atoms) were excited by vibration at 35 Hz. Approximately  $10^{12}$  photons were emitted per collapse in the range 400–700 nm (over four orders of magnitude greater than the brightest SL reported previously), corresponding to a 1% efficiency of the conversion of mechanical energy into light.

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# I. INTRODUCTION

The inertially limited collapse of a bubble [1] can result in the rapid compression of any gas within, leading to the emission of sonoluminescence (SL) [2]. A bubble trapped at the pressure antinode of a water-filled vessel, driven at resonance, may emit SL repetitively [3]. The single-bubble SL (SBSL) so produced has many remarkable properties [4]. In comparing the energy entering the system as sound to that leaving as light, it is found that SBSL concentrates energy by 12 orders of magnitude. This feature invites one to speculate about the ultimate limits of the phenomenon. Unfortunately, the conventional experimental technique devised for SBSL is not suitable for the investigation of the full parameter space of SL. In particular, it does not allow studies of bubbles that are considerably larger than a few micrometers ambient radius. An alternative method, which does not require an acoustic resonator, must be found. One promising idea is the use of a "water hammer" tube, as described by Su et al. [5]. The water hammer (or pipe hammer) effect is commonly encountered in domestic plumbing. When the motion of a liquid in a pipe is suddenly arrested by the closing of a valve, for example, a pressure pulse travels back along the liquid column. The magnitude of this pressure pulse P is equal to the product of the liquid's density  $\rho$ , its sound speed c, and the change of its velocity  $v(P = \rho cv)$ . Since the 19th century, evacuated glass tubes, partially filled with degassed water, have been used to demonstrate the phenomenon. When the tubes are shaken, a sharp metallic sound (similar to that of a hammer hitting a nail) is heard when the water hits one of the ends of the tube. These hammer pressures developed within the liquid are also capable of causing the collapse of any bubbles present within the liquid. This phenomenon may be produced in a repetitive manner if the tube is oriented vertically and subjected to vertical vibrations of low frequency. If the tube is accelerated downward, the inertia of the water opposes the acceleration of the tube, causing the pressure within the water to fall. The pressure at a distance hbelow the free surface is given by

$$P = P_0 + \rho h \left( g + \frac{d^2 z}{dt^2} \right), \tag{1}$$

where g is the acceleration due to gravity,  $P_0$  is the pressure above the free surface, and z(t) is the location of the bottom of the column of liquid. The modulation of the pressure is greatest at the bottom of the tube, and the pressure at that location will go negative if the downward acceleration of the tube exceeds  $(P_0/\rho H) + g$ , where H is the height of the liquid column. The tension within the liquid may be sufficient to cause it to cavitate spontaneously.

In the study by Su et al., a cylindrical tube (of 32 mm inner diameter, 50 cm length) was subjected to sinusoidal vibrations, at 10 Hz, with peak acceleration of up to 20 m s<sup>-2</sup>. The tube was partially filled with water and doped with xenon gas to a pressure of around 20 Torr. Under these conditions, cavitation activity was sometimes found to be initiated by the column of water separating from the base of the tube and flowing as a "plug". When the plug returned to impact the base of the tube, the water hammer pressure pulse traveled up the liquid column. On reaching the free surface of the liquid, the pulse was reflected, returning as a tensile wave. This tensile wave was sufficiently strong to cause many tiny cavitation bubbles to form. Once formed, the expansion and collapse of these cavitation bubbles was usually able to absorb the pressure changes due to the acceleration of the tube, in which case plug flow was not detectable. On other occasions, cavitation activity was initiated without the formation of a plug: if vibrations are applied to the tube, bubbles will become entrained within the liquid by the sloshing at the free surface. These bubbles experience a form of negative buoyancy, whereby they fall to the bottom of the tube [6]. Having arrived at the bottom of the tube, the bubbles may combine together and initiate plug flow. Alternatively, they may remain separate, forming a cloud. At high levels of drive, the cavitation behavior was chaotic. In the absence of the formation of a plug, the behavior of the bubbles is dominated by the continuous modulation of the pressure within the liquid due to the applied acceleration. By contrast, the behavior of the bubbles on the occurrence of plug flow is dominated by their response to the high impulsive pressures generated. Irrespective of the precise explanation for the cavitation behavior, Su *et al.* were able to detect subnanosecond flashes of light from some of the collapsing bubbles. The brightest flashes detected corresponded to emissions exceeding  $10^8$  photons, an order of magnitude greater than the brightest observed SBSL. However, the utility of the technique was severely limited: bubbles of differing sizes were present at different locations and it was impossible to predict which bubbles would emit light. Consequently, it was difficult to make detailed measurements.

## **II. EXPERIMENT**

In preliminary research to the present study, efforts were directed at improving the water hammer technique to render the bubble behavior (and hence the SL) more reproducible. Glass water hammer tubes of 16 mm inner diameter and 15 cm length were used. Starting from a 20 cm length of 1 mm wall borosilicate glass tubing, one end is closed to form a hemisphere, while 5 cm in from the other end the tube is constricted to approximately 5 mm diameter. After annealing, the tube is filled with tap water to a depth of about 10 cm and evacuated until the water boils freely at room temperature. At this stage, the tube could be isolated from the vacuum system, to permit the introduction of the gas of interest. However, the initial experiments were confined to tubes containing traces of dissolved air (0.1-10 Torr) remaining from incomplete degassing of the water. The tubes were then sealed at the constriction. Initially, the tubes were held in an aluminum sleeve, secured by a nylon bolt, the sleeve itself being screwed to the shaft of the vibrator. The vibrator (Goodmans Industries, type 390) was of moving coil design, and had a maximum stroke of 7 mm. It was driven by a sinusoidal oscillator via an audio amplifier (Quad 510). The system was able to provide peak accelerations exceeding  $70 \text{ m s}^{-2}$  to the tubes, within the frequency range 20-200 Hz.

The shorter tubes and higher frequency and higher acceleration of this system, compared with that used by Su et al., caused its cavitation behavior to differ. It was found that plug flow never arose spontaneously; the entrainment of bubbles was always necessary to initiate cavitation. In the subsequent behavior, plug flow was usually evident,<sup>1</sup> even at the highest driving amplitudes. However, there was a chaotic variation in the phase of the vibration at which the plug returned to the base of the tube. The signal from a photomultiplier (PM) (EMI 9781B) viewing the tube confirmed that, even without the addition of xenon, the SL from the bubbles could be detected. The correlation between the acoustic emissions (recorded by a nearby microphone) and the SL emissions confirmed that all the detected SL was excited by the water hammer pressure pulse resulting from plug flow [Fig. 1(a)]. When the PM signal was examined on shorter time scales



FIG. 1. (a) Signals from a PM (lower trace) and a microphone (upper trace) in response to the cavitation in a water hammer tube vibrated at 50 Hz. (b) PM signal in response to a single flash of SL, showing an instrument-limited rise time.

[Fig. 1(b)], it was found that the SL was emitted in bursts, each flash within the burst having a rise time indistinguishable from the single-electron rise time of the PM employed (2 ns). In other words, the individual SL flashes, corresponding to different bubbles, were all subnanosecond, as they were in the study of Su *et al.* 

# A. Glycerin

On substituting a tube containing glycerin<sup>2</sup> and air (at approximately 10 Torr), a remarkable contrast was found. The PM signal was found to be much more intense and there was little variation in the phase of the vibration at which the SL was emitted. Each cycle of vibration led to the emission of a single flash of light [Fig. 2(a)], rather than to a burst of separate flashes, as with water. A PM record of one of these flashes is given in Fig. 2(b). The rise time of the PM pulse is about 3 ns, which, assuming summation in quadrature, corresponds to a true SL flash width of about 2 ns. The tentative conclusion that the SL in glycerin was due to the repetitive emission from a single bubble was confirmed by imaging the SL from the tube using a high-gain image intensifier [7]. A bright spot was seen at a single location for many seconds (i.e., over several hundred cycles of vibration).

An intensifier, used in conjunction with a spectrograph [8], permitted the spectrum of the SL to be examined. An auxiliary condenser lens was used to form an image of the

<sup>&</sup>lt;sup>1</sup>Under these conditions, a large bubble could be seen at the bottom of the tube, so the plug motion can be attributed to the behavior of this bubble.

<sup>&</sup>lt;sup>2</sup>Unlike water, glycerin cannot be made to boil at room temperature by a simple reduction of pressure. The tubes were heated to 100 °C to reduce the viscosity to a manageable level and then the tubes were vibrated while being evacuated to 0.1 Torr. The degassing was continued for at least half an hour, prior to gas readmission and sealing.



FIG. 2. (a) Signals from a PM (lower) and microphone (upper) for cavitation within a water hammer tube containing glycerin. (b) PM signal for a single SL flash. The rise time is longer than that due to the instrument response.

SL bubbles on the slit plane (the slits themselves having been removed). It was found that the spectrum was continuous in the range examined (400-600 nm). However, the addition of sodium chloride to the glycerin within the tubes did cause the SL spectrum to display the characteristic sodium lines at 589 nm. These lines were never evident when a bubble began to emit SL; instead, they appeared and grew in intensity over many cycles of vibration. This suggests that little or no sodium is present within the bubble prior to the emission of SL, and that a small quantity of sodium is transferred from the liquid to the bubble on each collapse that is sufficiently violent to cause the emission of SL. The reason for this transfer of sodium may be a (small) degree of asymmetry in the bubble collapse. It is known that the presence of salt has no effect on the spectrum of SBSL; however, if its symmetry is perturbed slightly, spectral lines may appear [9].

After a bubble ceased to emit SL—typically after 10 s there was usually a delay of some seconds before another bubble would begin to emit. After some minutes, the SL behavior of the bubbles began to change. As seen in the PM records (Fig. 3), a form of period doubling took place whereby a bubble would emit SL only on alternate cycles of vibration. This effect was accompanied by the formation of an extensive cloud of microbubbles near the bottom of the tube. As in water, bubbles in glycerin experienced negative buoyancy; however, this never led to plug flow. Viscous effects suppressed sloshing at the free surface, making it very



FIG. 3. PM and microphone signals after some minutes of cavitation within a tube containing glycerin. SL is detected on alternate cycles of vibration.

difficult to entrain bubbles in glycerin.<sup>3</sup> The high viscosity of glycerin is also responsible for the stabilization of bubbles [10] (against fragmentation, etc.), permitting them to emit SL over hundreds of cycles of oscillation. The only other physical property differing significantly between glycerin and water is vapor pressure. The vapor pressure of water is approximately 20 Torr at room temperature, whereas the corresponding value for pure glycerin is  $10^{-4}$  Torr. Thus, it is clear that the bubbles formed within glycerin contain a negligible quantity of vapor, unlike those in tubes containing water. It is probable that this difference contributes to increasing the SL intensity of gas bubbles in glycerin relative to those in water.

The brightest repetitive SL from air bubbles in glycerin corresponded to approximately  $10^7$  photons/collapse in the spectral range 400-700 nm. For a point source emitting a single instantaneous pulse of light uniformly in all directions, the threshold for detection by the unaided eye is about 10<sup>6</sup> photons per pulse. Consequently, the SL from the glycerin tubes should have been visible and, indeed, it could be seen with minimal dark adaptation. It was not necessary to use the vibrator to produce visible SL; it was sufficient to shake the tubes by hand in a particular manner.<sup>4</sup> Noting that this was by far the simplest method of producing visible SL, it seemed possible that someone might have observed the phenomenon previously. This did turn out to be true. Schmid [11] employed a water hammer tube to study cavitation bubbles, obtaining high-speed photographs of the bubble dynamics and shock wave emission on bubble collapse, etc. He also noted, in passing, that on replacing the water in his tube with glycerin he was able to see a SL flash on bubble collapse. He stated that the SL was bright enough to be seen in the presence of weak red illumination, but did not investigate the light emission any further.

The merit of glycerin, in the context of water hammer SL, is difficult to interpret. While a very low vapor pressure is

<sup>&</sup>lt;sup>3</sup>It was always necessary to entrain bubbles in the glycerin tubes, by swinging them around, prior to attaching them to the vibrator; the action of the vibrator alone was never sufficient. The same was true of tubes containing phosphoric acid (described later).

<sup>&</sup>lt;sup>4</sup>Holding the tube firmly in one hand, so that it is vertical, hit this hand (downward) from above with the other hand (i.e., fist), as if you were attempting to hammer your hand. Caution is advised as the tube may break.

Liquid	Vapor pressure(Torr)	Viscosity(cP)	Density (g/cm <sup>3</sup> )	Surface tension(mN/m)	SL intensity (photons/flash)
Water	20	1.0	1.00	74	106
Liquid paraffin BP	$10^{-3}$	20	0.85		$10^{6}$
Silicone oil (DC 704)	$10^{-8}$	39	1.07	37	$10^{7}$
Glycerin	$10^{-4}$	950	1.26	63	$10^{8}$
Ethylene glycol	$10^{-1}$	16	1.10	48	$10^{9}$
Dibutyl phthalate	$10^{-5}$	21	1.05	34	$10^{10}$
Sulfuric acid (100%)	$10^{-3}$	28	1.83	52	$10^{11}$
Phosphoric acid (100%)	$10^{-2}$	250	1.87	80	10 <sup>12</sup>

TABLE I. Physical and SL properties of a selection of liquids.

clearly advantageous, the merits of having a high viscosity are more ambiguous. The viscosity of glycerin is strongly dependent on temperature; therefore studying the SL emission as a function of temperature provides a means of examining the effect of viscosity. Although glycerin has a nominal melting point of 20°C, it is almost impossible to freeze. On cooling the glycerin, it was necessary to increase the amplitude of vibrator drive to maintain cavitation and SL. Below 5°C, no SL was evident, below 0°C cavitation noise was no longer heard, and below  $-10^{\circ}$ C the bubbles showed no detectable response to vibration. At elevated temperatures, the intensity of the emitted SL increased. However, the regularity of the cavitation behavior also declined; above 50°C repetitive emission from bubbles was no longer evident. Individual flashes at 80°C exceeded the brightest emissions at room temperature by an order of magnitude. These observations suggest that, while viscosity does have some role in stabilizing cavitation bubbles, it reduces the intensity of the emitted SL.

# **B.** Comparison of different liquids

At present, the water hammer SL has been studied only in molecular and hydrogen-bonded liquids. The specific liquids examined are listed in Table I. A selection of relevant room temperature physical properties is given, together with an indication of the SL intensity obtained from tubes containing xenon gas at a pressure of 20 Torr. The figures for the SL intensity indicate the approximate numbers of photons in the spectral range 400–700 nm emitted during the brightest flashes from single bubbles.

The data in the table show that the intensity of the SL is not directly correlated with any of the physical properties listed. Particularly noteworthy is the performance of silicone oil, which, despite having a very low vapor pressure, does not produce especially bright SL emissions. The cavitation behavior in silicone oil was also found to be exceptional. The liquid was exceptionally prone to "foaming," which may be explained, in part, by its low surface tension. However, tubes that had been sealed while highly degassed (i.e., without the addition of a gas) showed a distinct tendency to *evolve* gas bubbles when shaken. This tendency diminished after shaking had been continued for some time. It would appear that cavitation bubble collapse in silicone oil causes volatile substances to be formed. Presumably, the oil is decomposed by the high pressures and temperatures in proximity to collapsing cavitation bubbles. The room temperature properties of ethylene glycol are quite similar to those of glycerin at elevated temperatures, and this similarity extends to the SL behavior. Dibutyl phthalate displays some of the problems of silicone oil (foaming, evolving gas), but to a much lesser degree.

The SL properties of bubbles within sulfuric acid have come to be studied only recently. Sharipov et al. [12] studied multibubble SL from the ultrasonic cavitation of aqueous solutions of sulfuric acid and sulfur dioxide, saturated with air or argon. They found that a 90% solution of sulfuric acid gave SL that was 70 times brighter than water.<sup>5</sup> The high brightness of SL in sulfuric acid suggested the study of similar liquids, of which phosphoric acid is the only common example. Phosphoric acid<sup>6</sup> ( $H_3PO_4$ ) is exceptional in a number of respects. A single flash of the SL from a xenon gas bubble within phosphoric acid is easily visible in a well-lit room, and, under continuous vibrations, many bubbles will emit repetitively. Being a strongly hydrogen-bonded liquid, it has a relatively high viscosity and low vapor pressure, but what is particularly interesting is that the vapor of phosphoric acid consists of water molecules alone. Phosphoric acid does not boil; it dehydrates. Progressive heating of phosphoric acid gives a series of condensed phosphoric acids' that eventually volatilize at a very high temperature. In the context of SL, phosphoric acid may be regarded as a liquid whose only volatile decomposition product is water.

<sup>&</sup>lt;sup>5</sup>The authors attribute this enhancement to the presence of sulfur dioxide within the bubbles generated by decomposition of the acid. They claim that the broad spectral maximum at 450 nm, which they detected, was due to triplet-excited sulfur dioxide molecules. This spectral behavior was not found in the present experiments.

<sup>&</sup>lt;sup>6</sup>Phosphoric acid has a nominal melting point of 42 °C; however, it readily supercools. The phosphoric acid used in this study [ortho-phosphoric acid, about 100%  $H_3PO_4$  (contains some pyrophosphoric acid)] was supplied by Fisher Scientific (U.K.).

<sup>&</sup>lt;sup>7</sup>Two molecules of (ortho)phosphoric acid ( $H_3PO_4$ ) may combine to produce a molecule of pyrophosphoric acid ( $H_4P_2O_7$ ), eliminating a molecule of water. Similarly, *n* molecules may combine to give  $H_{n+2}P_nO_{3n+1}$ , yielding, in the limit of large *n*, metaphosphoric acid HPO<sub>3</sub>. Further dehydration may occur, but the limit of  $P_2O_5$ cannot be attained owing to azeotropic behavior.



FIG. 4. Apparatus for simultaneous rotation and vibration of a water hammer tube e, consisting of a subwoofer speaker a, a cutdown funnel b, an induction motor c, tapped cylinders d, and a heavy steel base f.

### C. Stabilization of bubbles

In order to stabilize a bubble against fragmentation during collapse and rebound, it is necessary, but not sufficient, to preserve the symmetry of the flow of liquid in its immediate environment. The presence of other bubbles, or solid surfaces nearby, destroys this symmetry. To stabilize bubbles in a water hammer tube, therefore, one can minimize the influence of solid surfaces by confining the bubbles to the central axis of a cylindrical tube. Fortunately, this is easily accomplished by rotating the tube about its axis. As all the bubbles present within the tube will be confined to the axis by this means, one is left with a line of bubbles, rather than a threedimensional distribution. In order to test the idea of using rotation to stabilize bubbles during vibration, various models were constructed, leading ultimately to the design illustrated in Fig. 4. A 450 W subwoofer speaker (MacAudio, Mac Fire) was used as the vibrator. The induction motor from a small fan was attached to the cone of the speaker via a spacer (a cut-down plastic funnel). The motor had to be modified to limit the degree of its axial play. The spacer was necessary to raise the motor to a level where the view of the bottom of the tube would not be obscured by the chassis of the speaker. To the center of the motor was glued a short aluminum cylinder, with a hole drilled down its axis, tapped to accept a screw. A similar cylinder was glued to the base of each water hammer tube, with the aid of a jig, to ensure axial centering. The tubes were fixed to the motor by means of a grub screw between the aluminum cylinders. The choice of materials was dictated, in part, by the need to minimize the oscillating mass. The motor was driven by an ac power supply, adjusted produce a rotational speed of approximately to 20 revolutions/s.

The initial experiments involved continuous vibration of tubes. The rotation of the tube, in the absence of vibration, caused the free surface of the liquid to assume the familiar parabolic form. This form was perturbed slightly, during vibration, by the change in the volume of the cavitation bubbles. However, the free surface always remained intact, even for low-viscosity liquids such as water. The suppression of sloshing at the free surface succeeded in eliminating the entrainment of bubbles, which dramatically improved the stability of the cavitation behavior. The confinement of the bubbles to the axis of the cylinder also resulted in a substantial reduction in the fragmentation of bubbles; in the higherviscosity liquids, such as glycerin, the vibrations could be sustained for an indefinite period without the formation of clouds of microbubbles. Nevertheless, although the bubbles were confined to the axis, they were not confined vertically; the bubbles generally sank due to negative buoyancy, as before. This problem could be minimized by avoiding the use of continuous vibrations. It is possible to correct for the net downwards motion of a bubble, over a cycle of vibration, if the next cycle is delayed to allow the bubble to rise the same amount under gravitational buoyancy. However, this solution required continuous adjustment of the delay, as the equilibrium was inherently unstable.

Similar behavior on the application of impulsive vibrations with simultaneous rotation was also found in phosphoric acid, although the behavior on continuous vibration was different. The lower viscosity and higher surface tension of phosphoric acid caused the bubbles that sank to the bottom of the tube to coalesce. The large bubble at the bottom was, in some way, associated with the vertical stabilization of the remaining bubbles in the column above.<sup>8</sup> Furthermore, these bubbles emitted bright and stable SL, at comparatively modest accelerations (30 m s<sup>-2</sup> peak, at 35 Hz). Some bubbles persisted in a sonoluminescing condition for up to 30 min. The loss of SL emission from a bubble was usually due to the development of unstable behavior in the bubble at the bottom of the tube. It seemed probable that the water hammer pressure pulse, generated on the collapse of the bottom bubble, was exciting the bubbles above to SL. This conclusion is supported by the observation that the SL from the bubbles commences only after some bubbles have fallen to the bottom of the tube. When this occurs, a characteristic water hammer noise (the sound of the water hammer shock) is emitted by the tube, and bubbles begin to emit SL. Another observation is that even bubbles at the top of the liquid column (i.e., those within a few millimeters of the free surface) can emit SL. It is obvious that the pressures developed due to the inertial response of the liquid are not sufficient, at such small depths, to cause cavitation behavior.

The brightness of the SL from repetitively emitting bubbles was related to their size. Stroboscopic photography

<sup>&</sup>lt;sup>8</sup>The attractive forces between the bubbles (in the liquid column) caused them to coalesce. Bubbles that were separated by more than about 1.5 cm were able to avoid coalescence. The only microbubbles within the tube that do not coalesce were located within the bottom 2 cm of the liquid column. The stable SL emissions described here originate from isolated single bubbles.



FIG. 5. Photodiode signal in response to a single flash (of approximately  $10^{12}$  visible photons) of the repetitive SL produced by a bubble of xenon in a water hammer tube containing dehydrated phosphoric acid.

was used to measure the maximum radius attained by a stable SL bubble. As an example, a bubble of ambient radius 0.4 mm (measured with the vibrator off) and located at a depth of 5 cm below the free surface attained a maximum radius of 1.0 mm, for a peak acceleration of 30 m s<sup>-2</sup>. The filling pressure of xenon was 20 Torr. The growth of the bubble occurs due to free surface reflection of the water hammer shock produced by the collapse of the bubble at the bottom of the tube.9 It is possible to make an estimate of the potential energy of the SL bubble. Equation (1) indicates that the hydrostatic pressure in the liquid adjacent to the SL bubble is 60 Torr when the bubble is at its maximum radius. This pressure remains largely constant during the expansion and collapse of the bubble produced by the reflected shock wave. The potential energy is given by the product of the hydrostatic pressure and the maximum volume of the bubble, i.e.,  $3 \times 10^{-5}$  J.

The temporal properties of the SL were measured with the aid of a silicon p-i-n photodiode (Centronic AEPX65, rise time 1 ns). Figure 5 shows a typical oscilloscope record. In contrast to the very short duration of SBSL emissions, the stable SL from xenon bubbles in phosphoric acid was emitted in flashes lasting hundreds of nanoseconds. It was also found that the brightness and duration of the flashes were positively correlated.<sup>10</sup> However, if the tubes were excited impulsively at high amplitude, without a bubble at the bottom of the tube, the bubbles would emit SL flashes of considerably shorter duration (tens of nanoseconds). In this case, the intensity of the flashes was less well correlated with the flash width (the ratio of the brightness to the flash width typically exceeded that of the bubbles excited by a water hammer shock). These results are not confined to phosphoric acid. Of all the liquids listed in Table I, water is the only one



FIG. 6. Image (in negative) of two SL xenon bubbles simultaneously emitting in phosphoric acid. Light from the bubbles was dispersed horizontally by a diffraction grating to show spectral behavior. Emission lines (arrowed) are seen in the spectrum of the upper bubble at wavelengths of 825, 895, and 940 nm.

that does not appear to produce long flashes when the SL is induced by a water hammer pressure pulse.

## **D.** Spectral studies

The spectral behavior of the SL in phosphoric acid was quite unusual. When bubbles were not stabilized by rotation, differences in the color of the SL from different bubbles were evident on visual inspection. For tubes that had been degassed at a temperature below 60°C, prior to introduction of xenon and sealing, the SL was either blue or red in color. The blue bubbles were intense point sources, whereas the red emissions were weak, diffuse, and extended, sometimes over a millimeter in size. Blue bubbles often decayed into red bubbles, but rarely, if ever, did a red bubble turn blue. It was found that the emission of red SL was suppressed in phosphoric acid that had been degassed<sup>11</sup> at 100°C. These observations suggest that the red SL is associated with a small, but finite, quantity of water vapor within the bubbles. The differences in the emission spectrum of different bubbles made it necessary to measure the spectra of different bubbles independently. This is most readily achieved by use of dispersive imaging, e.g., the use of a spectrograph without slits. The SL was sufficiently bright to be recorded by an ordinary monochrome charge-coupling device video camera (sensitivity 0.02 lux).

The spectra obtained from the blue bubbles were continuous and without any trace of spectral lines in the visible. However, spectral lines were sometimes evident in the infrared. The spectrum of a stable blue bubble would often develop lines between 800 and 1000 nm after some minutes of repetitive emission. The maximum intensity, which these lines attained, was related to the degree to which the phosphoric acid was dehydrated. Figure 6 illustrates the spectra of two stable bubbles that were simultaneously present in a tube of dehydrated phosphoric acid ("106%" H<sub>3</sub>PO<sub>4</sub>). The upper

<sup>&</sup>lt;sup>9</sup>The amplitude of the tensile wave was, however, insufficient to cause spontaneous cavitation within the liquid column.

<sup>&</sup>lt;sup>10</sup>This correlation was observed over wide limits by changing the pressure of the gas. An increase in gas pressure resulted in an increase in the brightness and duration of the flashes. However, it was not possible to produce repetitive SL from tubes that had been filled at pressures much above 20 Torr.

<sup>&</sup>lt;sup>11</sup>Degassing at elevated temperatures results in the dehydration of phosphoric acid. This reduces its vapor pressure and increases its viscosity, etc. The composition resulting from degassing for 1 h at  $100^{\circ}$ C/0.2 Torr is about "106%" phosphoric acid, i.e., 76.7% P<sub>2</sub>O<sub>5</sub> in H<sub>2</sub>O.



FIG. 7. Corrected spectrum of a repetitively emitting xenon bubble in phosphoric acid (jagged curve) and a blackbody fit (7000 K). The spectrum of individual bubbles changed over time; the temperature of the best blackbody fit declined from 8000 K at the start of repetitive emission to about 6000 K after several minutes. The dip between 410 and 650 nm could be explained by spectral absorption or wavelength-dependent emissivity.

bubble had been emitting for more than five minutes, whereas the lower bubble was only one minute old. It can be seen that the upper bubble has at least three spectral lines in the near infrared; the wavelengths corresponding to these lines are approximately 825 nm, 895 nm, and 940 nm. Some less prominent lines are also present between the latter two wavelengths. These lines can be correlated with vibrational transitions in water vapor. Although it was not possible to obtain the spectrum of the bubbles that emitted red SL, it is likely that the red coloration resulted from vibrationally excited water molecules [13]. In order to obtain the true form of the blue SL spectrum, use was made of a conventional spectrograph (EG&G 1235, intensified). The spectra<sup>12</sup> from repetitively emitting bubbles gradually changed over time. Each spectrum obtained could be fitted to thermal emitter with a temperature in the range 6000-8000 K (the effective temperature declined over time). Figure 7 shows the spectrum of a bubble that had been emitting for two minutes, and a blackbody fit of 7000 K. Within the range 410-650 nm, less radiation was detected than would be expected from the blackbody fit. The ratio of the measured radiance to the radiance of the blackbody was a function of wavelength alone; it did not depend on the temperature of the blackbody. This behavior could be produced by a simple spectral absorption, although it is unclear how such absorption could arise transiently. Alternatively, the spectra could be attributed to a thermal emitter with an emissivity of 0.83 between 500 and 580 nm, rising "linearly" to unity at 410 and 650 nm.

### **III. DISCUSSION**

The present study has demonstrated that the water hammer tube technique allows for a substantial upscaling of SL if certain liquids are used. The liquids that give the best performance are those that have a low vapor pressure and a high degree of stability against decomposition. This study has also identified a technique for the stabilization of bubbles within a water hammer tube. The use of rotation, to confine the bubbles to the axis of the tube, results in a vast improvement in the reproducibility of the phenomenon. It achieves this by suppressing bubble entrainment at the free surface, eliminating bubble-wall interactions, and minimizing bubble-bubble interactions. However, satisfactory results have been obtained only with liquids of moderately high viscosity. It is unclear if the technique can be improved to accommodate liquids in which viscous stabilization is comparatively weak. Parasitic, nonaxial vibrations cause significant bubble jitter in the more inviscid liquids. Some improvement is obtained by increasing the speed of rotation; however, this is achieved at the expense of the descent of the bottom of the meniscus, as it assumes a sharper parabolic profile. The better solution would be to minimize the parasitic vibrations.

A number of the features of the SL studied are unusual. The emission of red SL from some bubbles in phosphoric acid has many interesting aspects. The most intriguing of these is that the size of the emitting region is of macroscopic extent. While Rayleigh's analysis [1] suggests the possibility of interesting phenomena arising on a bubble attaining its minimum size, it provides no explanation for the diffuse patches of light observed. Although it has been suggested that molecules of water vapor are responsible for the emission, this does little to clarify the matter, other than to position the emitting region within the bubble rather than the condensed phase (the phosphoric acid). It is reasonable to expect that the inertial collapse of a bubble could excite the vibrational energy levels of water molecules within; however, such emissions are not generally observed (e.g., in SBSL). It would also appear that the emission from water vapor requires the presence of another gas within the bubbles (typically xenon), implying that energy transfer from other molecules is required. The discovery of SL emissions with flash widths extending up to a microsecond (or even longer, for some liquids) would appear to be unprecedented. While this form of emission has not been observed in water, the differences between the liquids in which it has been observed suggest that the phenomenon is general. That these liquids should also sustain bubbles that emit on far shorter time scales is equally interesting.

It has been shown that the spectrum of repetitively emitting bubbles in phosphoric acid resembles the radiation from a thermal source. Vazquez *et al.* [14] showed that the similarity of blackbody emission to the light emission in SL was not limited to the spectral behavior. Using the instantaneous intensity of the SL flashes, they were able to show that the effective size of the light-emitting region, calculated using Planck's formula, was similar to, but slightly smaller than, the minimum size attained by the bubbles. Similar estimates can be made for the SL from a water hammer tube. A repetitively emitting xenon bubble (of 0.4 mm ambient radius, in 106% phosphoric acid) gives  $8 \times 10^{11}$  photons in the range 400-700 nm over 250 ns. This means that the peak intensity is  $3.2 \times 10^{18}$  photons per second, or in terms of power, 1.2 W. The total emissive power of a blackbody at 8000 K in

<sup>&</sup>lt;sup>12</sup>The intensity correction was determined with the aid of a lamp calibrated for a color temperature of 2856 K by the National Physical Laboratory (U.K.). The corrections in the visible region due to the variation in the transmission of the tube and the phosphoric acid were negligible.

the range 400–700 nm is  $8.9 \times 10^7$  W m<sup>-2</sup>. Combining this with the peak power of the SL, the radius of the emitting surface (assumed spherical) is about 30  $\mu$ m. Experiments on SBSL have shown that the collapse of a bubble is arrested when the bubble volume reaches the van der Waals excluded volume of the gas. For xenon, the excluded volume corresponds to a gas density of 434 amagats. This suggests that, for xenon bubbles at 30 Torr hydrostatic pressure, the ratio of the ambient radius to the collapse radius is 22. Thus, for a 0.4 mm bubble, the collapse radius would be 20  $\mu$ m. Such a bubble contains  $3 \times 10^{-10}$  moles of xenon. If the entire potential energy of the bubble ( $3 \times 10^{-5}$  J) were used to compress this quantity of gas adiabatically, then a temperature rise of approximately 8000 K would result. It is also noteworthy that the efficiency of the conversion of the bubble energy to visible light is as high as 1%. There are considerable problems in scaling up conventional SBSL apparatus to study larger bubbles, the problem being the physical size of the resonator required. This restriction does not apply to the technique described here.

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- [1] Lord Rayleigh, Philos. Mag. 34, 94 (1917).
- [2] A. J. Walton and G. T. Reynolds, Adv. Phys. 33, 595 (1984).
- [3] D. F. Gaitan, L. A. Crum, C. C. Church, and R. A. Roy, J. Acoust. Soc. Am. 91, 3166 (1992).
- [4] B. P. Barber and S. J. Putterman, Nature (London) 352, 318 (1991); S. J. Putterman and K. R. Weninger, Annu. Rev. Fluid Mech. 32, 445 (2000).
- [5] C.-K. Su, C. Camara, B. Kappus, and S. J. Putterman, Phys. Fluids 15, 1457 (2003).
- [6] H. Hashimoto and S. Sudo, AIAA J. 18, 442 (1980).
- [7] A. J. Walton, PACT 6, 524 (1982).

- [8] A. J. Walton and N. C. Debenham, Nature (London) 284, 42 (1980).
- [9] W. Winiarczyk and K. Musiol, Opt. Commun. 172, 93 (1999).
- [10] Y. Hao and A. Prosperetti, Phys. Fluids 11, 1309 (1999).
- [11] J. Schmid, Acustica 9, 321 (1959).
- [12] G. L. Sharipov, A. M. Abdrakhmanov, and R. Kh. Gainetdinov, Russ. Chem. Bull. **52**, 1966 (2003).
- [13] T. I. Quickenden and C. F. Vernon, J. Phys. Chem. 93, 6682 (1989).
- [14] G. Vazquez, C. Camara, S. Putterman, and K. Weninger, Opt. Lett. 26, 575 (2001).