Luminescence features from conical bubble collapse in 1,2 propanediol and its perturbation adding sulfuric acid

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Abstract. A summary of experimental findings on the luminescence from bubble collapse, CBL, varying the gas inert bubble content, the driving pressure and perturbing the liquid piston with small quantities of sulfuric acid is presented. The temporal, spectral, and spatial characteristics of the luminescence regarding with dynamic features of collapse are also examinees. CBL was reproduced using Argon gas, and 1, 2-propanediol as liquid piston. In general, the pulse shape exhibits a large variety of profiles. The luminescence intensity was increased two-fold and the pulse width decreased almost to half when the liquid was disturbed with sulfuric acid. Spectrally, the Swan, CH and CN lines were observed at low volume of Ar gas and low driving pressure, lines of OH°, Na*, K* always appear superimposed on an underlying continuum background. De-excitation of sodium at om at 589 nm and two satellites diffuse bands at ~554 nm and ~620 nm from alkali-metal-argon exciplexes was observed in both systems under certain conditions. All these findings point towards several sources of light emission that are generated during the compression time line, resulting in temporally and spatially inhomogeneous pulse. A mechanism for explain the bright CBL is broached.

1. Introduction

Cavitation, the rupture of liquids an its associated effects, can be defined as the formation, subsequent growth and collapse of cavities in a fluid resulting in very high energy densities on order of 1 to 10¹⁸ kW/m³ [1]. A large part of the available energy during the collapse is transferred and stored in a compression wave well before the inward motion is finally arrested [2]. The fundamental dynamics of this phenomenon was demonstrated very clearly by Rayleigh in his analysis of 1917 [3]. Refinements of this theory including compressibility of the liquid have been achieved by Gilmore [4], Hickling & Plesset [5], Ivany [6], Keller [7] and others in which the numerical models including chemical reactions and ionization gas and vapor inside the bubble [8-10].

These studies have permitted calculations of the extraordinary conditions inside the bubble (temperatures up to 15,000 K, pressures of 100 to 1000 bar; and heating/cooling rates > 10¹² Ks⁻¹) surrounded by a cold liquid. Earlier calculations have indicated values of ~ 10⁶ K while recent estimations converge to temperature values between 10,000 K and 20,000 K [11-12].

Under appropriate conditions, regardless of the method by which rapid bubble compression is achieved, a light flash is emitted during the final stages of collapse only if a small amount of noble gas...
is contained in the bubble [13]. One or more light emission mechanisms can be activated depending on the details of collapse. The intensity and shape of the emitted light depend not only on the initial gas pressure and the driving pressure but also on the physicochemical properties of the host liquid and substances dissolved in it. These are capable of penetrating into the cavity and of either enhancing or quenching the luminescence.

CBL implies the emission of UV-visible light generated by the violent collapse of a conical bubble driven by a liquid piston [14-24]. The advantages of the CBL procedure include that solid boundaries tend to stabilize the gas-liquid interface, the heat may be transferred between the system and its surroundings through the interface and/or solid boundaries, and also the centre of the collapse is well defined [20-21]. Furthermore, CBL renders it possible to control: the initial volume of the bubble, the inert gas volume in the bubble, the impurities in the liquid piston and the driving force.

According to radial dynamical models, the collapse time in SBSL and MBSL (~ 0.5 μs) is shorter than in CBL (~0.5 ms). This produces a large difference in both the pressure and temperature that are reached. However, a longer collapse time implies a greater interaction among atomic and molecular components with the inert gas. Hundred of chemical reactions can occur within the conical cavity during the timeline of the slow collapse, and the study of these reactions is more feasible in CBL. Most reactions may be chemiluminescent, which would explain the large and bright pulses from CBL compared to the flashes from SBSL and MBSL.

The present work describes the influence on the luminescence from CBL when the liquid piston is perturbed with small quantities of sulfuric acid. Temporal, spatial and spectral features of the luminescence for two cases: with (case II) and without acid sulfuric (case I).

2. Apparatus and instrumentation

A U-Tube apparatus was assembled based on the conical device originally employed by Kosky [19] and Hawtin [14] for studying the collapse of water vapor cavities, Leighton et al [17-18] for analyzing the dynamics of the collapse, Chen et al [19-20] for obtaining the spectroscopic features and others authors [21-24] that deepen on similar topics.

Figure 1 shows a schematic of the U-Tube device with its measurement equipment. The conical end presented a right circular cone of 30 º terminated in a hole of 1.5 mm in diameter. The cone apex was sealed by a quartz window and was then used to record the spectra. Three photomultipliers (Hamamatsu, R5783-04 module, PMTs) were fixed around the apex cone to capture the luminescence. The signal from a dynamic force sensor (PCB Piezotronics, ICP 200B05, 75 MHz) on the top-plate provided data of dynamic oscillating forces from a pressure pulse that was caused by the bubble collapse. All signals were captured with a Textronix DPO7054 digital oscilloscope (500 MHz, 5GS/s).

Optical emission from the bubble was collected, on the vertical axis through a quartz window, by quartz optical fiber towards the entrance slit of a 50 cm focal length spectrometer (Princeton Instruments, SpectraPro 500i) equipped with a 150 lines/mm grating. The dispersed light was analyzed by a gated intensified charge couple device (ICCD) camera (Princeton Instruments, PI-MAX2 1020x1024) equipped with a pulse/delay generator. The wavelength was calibrated using an Hg lamp.

Two data acquisition systems were implemented; one to capture the spectrum and another to acquire the initial state (with pressure gauges, and thermocouples) and the transient response (PMTs, force transducers, and laser velocimeter). A signal of a pulse/delay generator (A) (Standford, DG535) controlled the opening of valve B and provided a trigger for two data acquisition systems.
3. Materials, optical characterization and experimental procedure

1, 2 Propanediol, (PD) and H₂SO₄ (98%), (SA) were used as provided. The spectra of Absorption, Raman and Fluorescence for both liquids shown that contain chromospheres molecules at ambient conditions. PD exhibited low absorption between 210-300 nm, and SA absorbed strongly at 280 nm. The fluorescence spectrum at 280 nm from both liquids contained high levels of impurities. SA contains several impurities including SO₄, SO₂ (absorption at 280 nm), As, Pb, Fe, Hg, Cl, K, NO₃, and NH₄, among others. Absorption, Raman and Fluorescence spectra of the neat liquids are shown in Figure 2.

3.1. Experimental Procedure

The U-Tube was partially filled with a degasified liquid (270 ±10 ml) at ambient conditions. Subsequently, the free and dissolved air was removed from the system, until a vacuum pressure around 1500 Pa was reached. Next, a small volume of inert gas was injected into arm 1 filling the free pipe volume and displacing the liquid in arm 2. This pressure was measured as a differential height, $\Delta h$. At some arbitrary zero time, valve B was opened thereby letting in air pressure in arm 2, $P_{\text{ext}}$, after which the liquid started to move until the gas collapsed on the conical end. The displacement air-liquid interface blocked two lines laser that were separated by 50 mm. These signals were used to calculate the velocity of the liquid in the cylindrical part, $V_0$. Compression, collapse, rebounds and re-expansion until equilibrium took approximately 100 ms, in which the remaining gas pocket and liquid were balanced by an external pressure.
When the liquid body had returned to its original position by vacuum, the gas and liquid underwent a turbulent mixing process and there remained a liquid layer on the surface of the tubular-conical cavity. Subsequently, the vacuum pressure was applied again in both arms during fifteen minutes, which caused desorption from the walls, ablation of the bubble–liquid interface or evaporation of microdroplets. As a result, the remaining gas composition was not the same as the previous one. To carry out the next collapse, fresh inert gas was injected into the conical chamber.

4. Model
The original model proposed by P. Hawtin et al [16] simulates the collapse of a vapor bubble under an applied pressure considering an adiabatic compression. This model was used to obtain the motion of the gas-liquid interface, as well as the pressures and temperatures of the gas. In the present case, a variation of the effective heat capacity, $\gamma$, was taken into account to simulate changes in the composition of gas.

The conical cavity conditions differed from those in models of a spherical bubble immersed in an infinite liquid; the rigid boundaries guided the collapse of the gas toward the rigid cone apex. The driving force depends on the pressure difference between surfaces of the liquid column. In this case, it did not exceed 4 atmospheres, and the experimental method to apply pressure to the liquid was not instantaneous. Consequently, $P_{ext}(t)$ was simulated by a ramp function to account for the time delay, $\Delta t$, associated with the response time of the electromechanical system and the subsequent filling of the pipeline. Figure 1 explains the geometry and Figure 3 displays the notation used to represent the theoretical and experimental parameters of the U-tube device. A detailed description of the model can be found in the references [15-16].

Figure 2. a) As-received absorption spectra from samples of PD and H$_2$SO$_4$; b) Raman spectra from samples of PD and H$_2$SO$_4$ vs. ethanol and SO$_2$ to emphasize their features; c) fluorescence spectra excited at 280 and 300 nm for PD, and d) fluorescence spectra excited at 280 nm for H$_2$SO$_4$.
Figure 3. Nomenclature and boundary conditions of the model.

Figure 4 shows the results of the model using experimental data. The displacement $H(t)$ and its first and second time derivatives are depicted, as is also the time evolution of pressure and temperature. The column graphs to the left correspond to the time evolution along the tubular section, i.e., $H_c < H(t) \leq H_0$. The column graphs to the right corresponds to conical portion ($0 < H(t) \leq H_c$). Simulation data: $\gamma = 1.3$, $\Delta h = 12$ mm, $H_c = 0.0229$ m, $H_0 = 0.256$ m, $dH(0)/dt = 0$ m/s, $L = 0.5$ m, $P_0 = 2700$ Pa, $P_{ext} = 248$ kPa (gauge pressure), $a = 2$ MPa/s, $\rho = 1036$ Kg/m$^3$.

The interface started moving soon after $P_{ext}(t)$ had been applied, and the liquid column reached the base of the cone at approximately 71.2 ms. Subsequently, the liquid was accelerated due to geometrical effects until the bubble reached its minimum volume. This process took 868 $\mu$s. The whole time to reach the compression of the gas pocket was $t_c = 72.078$ ms which is comparable in magnitude to the time registered experimentally by the force sensor $\approx 75.5 \pm 5$ ms, see figure 3. $V_0$ reaches $5 \pm 0.1$ m/s, and the current model predicted a velocity $|dH/dt| = 5.945$ m/s. The computed maximum pressure was $P_{gmax} = 28$ GPa and the temperature was $T_{gmax} = 12400$ K, and cooling rates were $\sim 10^8$ Ks$^{-1}$.

Figure 5 shows the calculated maximum temperatures at varying values of $\gamma$, when an initial polytrophic index $\gamma_0 \sim 1.3$ is assumed. The obtained experimental results indicated changes in the light pulse features as the number of experimental runs increased (see figure 10). Such changes were included considering variations of $\gamma$ within the range 1.15-1.35. The lower limit was calculated by considering a gas mixture with high volume fraction of liquid vapor (83 %) and Ar (17 %). The upper limit was calculated for low volume fraction of liquid vapor (10 %), Air (45 %) and Ar (45 %). These values were in agreement with experimental conditions. It should be remarked that $\gamma$ remains constant during gas compression for each experimental repetition; it only changes as a function of the gas composition.
Figure 4. From top to bottom, the behaviour as a function of time of the variables; $P_{\text{ext}}$, $H$, $dH/dt$, $d^2H/dt^2$, $P_g$ and $T_g$.

Accordingly, figure 5 indicates $T_{g\text{max}} \approx 3500$ to 10 000 K for $\Delta h = 40$mm and $T_{g\text{max}} \approx 2100$ to 9200 K for $\Delta h = 12$mm; these temperature ranges were too low to allow the molecular ionization mechanism. As it is well known, the preponderance of liquid vapor, water vapor and chemical reactions will tend to determine the local temperatures and pressures into the conical bubble.

Figure 5. Maximum temperatures as a function of $\gamma$ as computed with Hawtin’s model for two values of $\Delta h$; 40 and 20 mm.
5. Results

5.1. Temporal emission
Temporaly, single and multiple emissions were recorded under certain conditions; see Fig. 6(a). Emission signals acquired by increasing the inert gas pressure are given in figure 6(b). Examples of the pulse shapes obtained at various driving pressures and at identical inert gas content are shown in figure 6(c). Even for unchanged external experimental conditions, the amplitude, width and shape of the emission signal varied greatly. The luminescent pulse exhibited a large variety of profiles. Nevertheless, it always displayed a main maximum and up to two local maxima, one occurring before (precursor) the main maximum and one after. These local maxima resembled those generated by laser cavitation [25-26].

![Figure 6](image-url)

**Figure 6.** a) Multiple emissions plots, b) pulse shapes acquired by increasing the inert gas pressure, and c) pulse shapes registered at various external pressures and at identical gas content.

When the bubble collapses with a low pressure of inert gas, the main maximum and the precursor are of the same order. In this case, the light emissions detected by PMTs through three faces of the hexagonal box indicated that the pulse did not have axial symmetry. This behavior is illustrated in the Figure 7 for two directions, under conditions of $\Delta h = 40 \pm 2$ mm, $V_0 = 6 \pm 0.2$ m/s, $P_{\text{ext}} = 262 \pm 2$ KPa (gauge pressure). In addition, after repeating certain experimental runs, it was found that, the pulse intensity increased to high values, after which it became weak and wide. This decreasing amplitude can also be observed in Figure 7.
Figure 7. Waterfalls plot of the inverted PMT signal as a function of the increase of number of experimental runs. The signals were taken simultaneously in three directions. The results of two directions (a) and (b) are only deployed. The maximum of each curve has been shifted to $t = 0$.

The behavior described above was due to the repetitive compression process, which caused variations in the composition of the host liquid (chemical decomposition). This can be monitored by tracking of their optical properties. Raman and fluorescence spectra from solution I, taken before (1) and after (2) of the application of the repetitive compression, are shown in figure 8 (a) and (b), respectively. The spectra indicate the degradation undergone by the liquid during the iterative process of experimentation. There was an increase of the amount of fluorescent species and a shift towards longer wavelengths.

Figure 8. Solution I, a) Raman spectra, b) Fluorescence spectra. Before (1), and after (2) of the experimental runs.
5.2 Luminescence intensities

The intensity peak behavior associated with cases I and II are shown in Figures 9 (a) and (b), which illustrate how the pulse intensity varies as a function of the liquid solutions. The mean light intensity for solution II was two-fold higher that of, its counterpart case I. As can be seen, when the sulfuric acid was added up to a certain concentration the intensity grew in a nonlinear fashion. This was however not the case when the host liquid is used alone (case I): under such circumstances the intensity increased linearly.

The hydrodynamic behavior of the liquid piston was not substantially modified by addition of the substances at these concentrations to it. Moreover, the liquid density, collapse time and pressure pulse were not very affected to a large extent. However, large physicochemical changes were found. The H₂SO₄ is an oxidizing agent that accelerates the decomposition of the PD. It is known that the addition of high concentrations (1-2 mol L⁻¹) of metal salts to water enhances the luminescence continuum of the H₂O* molecules and the chloride ions inhibit the reactions of OH radicals. The physicochemical decomposition of liquid mixtures was followed by tracking their optical properties. Absorption and Raman spectra of the liquid before and after using it a liquid piston are illustrated in Figures. 10 (a) and 10(b). The absorption spectra of the solutions show a shift of the absorption band to longer wavelengths as opposed to the initial solution.

![Figure 9. Comparisons of the light pulse intensity as a function of the gas pressure and host liquid. a) Waterfall plots of the light emission from experimental runs for cases I and II in consecutive form. b) The maximum intensities are plotted and fitted with an exponential curve; a linear behavior was found when the liquid piston was used without adding sulphuric acid.](image)

Raman spectra (at 532 nm) displayed a large increase in fluorescence as a function of the added substances and repetition of experimental runs. These spectra indicate that a large number of chromospheres were generated during the experimental process and that they increased when perturbed substances were added. Obviously, the increase of chromospheres molecules in the host liquid and the compression procedure made the vapor and droplets of these species will be integrated into the gas composition. However, let us remember that after this increase in intensity (linear or not) a decrease of this one comes as it is observed in the Figure 7.
5.3 Spectral features

It is essential to understand the chemical processes that are initiated when the kinetic energy is absorbed by the species inside the bubble in order to elucidate the mechanisms that take place during the generation of light emission during CBL. This energy should be sufficient to produce molecular motions that affect the bonding configurations, which in turn influence subsequent chemical reaction pathways. The real sequence of the atomic and molecular processes that occur between the mechanical excitation of the collapse and the photonic emission still remains unknown. To ascertain the nature of the luminescent species, spectra from CBL were recorded and analyzed in the 280-880 nm wavelength range for the three cases. All spectra mentioned in this paper were acquired using a gate width of 20 ms in order to collect the entire emission from the CBL.

5.3.1 $OH A \, ^2\Sigma^+ \rightarrow X^2 \Pi$ transitions

The hydroxyl radical ($^\cdot$OH) is the most important free radical species in oxidation processes, it is a primary chain carrier in flame chemistry, and the main actor in water-solvent-based “advanced oxidation processes” [27-29]. It is a primary product of water radiolysis with ionizing radiation, photolysis with UV photons, or even bubble collapse in sonolysis in which the consecutive reactions keep on producing $^\cdot$OH even after collapse. Also the $^\cdot$OH self-recombination is a primary source of corrosive hydrogen peroxide and oxygen molecules.

An excited OH relaxes toward the X(0) state and such OH molecules can exist for very long times (several tenths of microseconds). There are many studies of its reactions in the gas phase and in aqueous solution.

In MBSL and SL for water, the main collapse is associated with a rapid generation of OH$^\cdot$ radicals once the temperature exceeded 4000 K [8]. Even so, near 2600 K, 10% of water molecules are thermally dissociated at atmospheric pressure [30].

$^\cdot$OH radical spectra acquired from the two cases are presented in Figure 11. As can be seen, there was a red shift associated to II with regard to I. The system II exhibited a featureless component that started near to 315 nm and extended up to 350 nm. According to Sehgal et al. [31] the featureless continuum below 315 nm was due to the presence of another molecular system, as can also be
observed in OH radicals generated by laser-excitation in the presence of inert gas. The latter are due to the electronic de-excitation of OH-Ar complexes. In case I, the Na* line was also observed.

The observation of OH A-X transitions in present CBL experiments, as well as MBSL and SL, was in complete agreement with the detection of OH(X) radicals in acoustically cavitating aqueous solutions [27-29]. The interpretation of the electronic OH $A^{2} \Sigma^{+} - X^{2} \Pi_2$ transitions are detailed in reference [28].

Within the temperature and pressure range predicted by the model and according to the features spectra, the all above reactions can occur in the conical bubble collapse. Because the conditions needed to generate the reactions were achieved. For example: the temperature to produce homolytic cleavage of the molecules precursors is within the minimum range 600 $\beta \ T \ \beta \ 8000 \ K$, [8, 10] this temperature range is reached after passing the liquid-gas interface of the cone base.

If it is consider that the production of radicals is not a direct consequence of the temperature, but rather of the pressures, the model predict that during the latest stage of the collapse is reached at least on the average 4 GPa.

As is well known, the kinetic energy transmitted directly by the liquid piston, through the interface, to the bubble components is very small, however, at the molecular level is sufficient to activate and/or excite species molecules or atoms that are in an unstable state.

Accordingly, we consider that the kinetic energy absorbed directly by the molecular and atomic species in an unstable state is the trigger for that various mechanisms are coupled to produce light emission. As collapse progress, the electron excitation energy is increased due to inelastic collisions. The interaction time among species is very long since -the collapse time- is slow (~ 0.5 ms).

Figure 11. Spectral features in the 280-350 nm wavelength range associated with OH transitions from the both cases. The continuum below 315 nm can be associated to the OH-Ar excimers. Apparently, the continuum emission was larger for case I, which also presented a peak associated to the emission of a sodium atom.
5.3.2 Swan bands

The emission of blue-green Swan bands is one of the oldest observed with molecular electronic spectra $C_2 \left( d^3 \Pi - a^3 \Pi \right)$. This type of emission has been observed and reported in a wide variety of conditions, including flames, shock tubes, shock pyrolysis, plasmas, laser ablation, IR multiphoton photolysis, and low-temperature discharge [32-33]. It was discovered in MBSL using dodecane in 1987, by Suslick et al [34-35]. Also, Swan bands have been observed in previous CBL experiments [20, 22].

Figure 12a shows the presence of $C_2$ bands (2, 0), (1,0), (0,0), and (0,1) of $d^3 \Pi_g \rightarrow a^3 \Pi_u$ were seen and a strong peak at 431 nm was identified as a CH system. When the external pressure exerted on the gas volume exceeded a certain threshold, (in the present case; 45 kPa gauge) for the case I, a strong continuum emission emerged and there was also a stronger total light intensity, see Figure 15.

In addition, Figure 12b shows the CN* peaks at 386 y 416 nm, the CN violet system ($B^2 \Sigma^+ \rightarrow X^2 \Sigma^+$), these bands were only observed for case I. As can be seen, there is a relationship between the intensity and width of light pulse with gas pressure. Considering the solution I as liquid piston, the light emission was wide with a weak intensity at low gas pressure and low external pressure. However, in the corresponding spectrum, the $C_2$, CH, CN, Na-Ar, Na, and K transitions were well distinguished, which was not the case when other substances were added to the liquid, cf. case II. When using solutions II as liquid piston, the intensity increased, but the pulse width decreases, as shown in Figure13.

**Figure 12.** Emission spectrum for the case I. a) $C_2$ emission bands at 438, 473, 516, and 563 were distinguished. The peaks at 431 nm and 588.9 nm were associated to the transitions of CH and Na, respectively. b) Continuum emission and overlapping peak at 416 associate to the CN transitions was also observed. The light pulse associated to each spectrum is plotted along them.
Figure 13. C₂ emission bands acquired from cases I, and II, and light pulse corresponding to each spectrum.

5.3.3. Na*, K*, and complex Na-Ar, K-Ar van der Waals molecular transitions in CBL

CBL emission spectra were recorded in the vicinity of the resonance lines (2P-2S transitions) of the alkali metals. Figure 14a illustrates the spectra of CBL between 520-670 nm for the three cases. The spectrum for case I, which contained small amounts of sodium impurities and water, revealed the same features as that of case II, to which had been added sulfuric acid. One can notice the blue and red complex Na-Ar van der Waals molecules. The normalized intensity of emitted light is show in Figure 14b.

As is well known, the line asymmetry, line shift, line broadening and the presence of the blue satellites accompanying the resonance lines are reminiscent of the disturbance by foreign neutral atoms on atomic emitters and thus implies a gas phase (see refs. 28, 36-37); for a more detailed explanation.
Figura 14. Spectra and light pulse emissions from solutions between 520-670 nm. a) Na resonance lines \( ^3P \rightarrow ^3S \) transitions. Obvious differences can be seen: for cases I and II, blue and red Na-Ar complexes can be distinguished. b) A comparison among the shapes of the pulse light.

5.3.4. Weak and diffuse emission lines from Ar atom in the near-IR region

Figure 15 shows weak and diffuse emission lines from an Ar atom in the near-IR region next to resonance of the K atom. The right side of each spectrum displays the light pulse acquired by the photomultipliers and the colored bars indicate the temperature and pressure calculated from the cone base. In the both cases the collapse time is around \(~0.5\) ms and the compression ratio is about 12, both considered from base to apex of the cone.

These values were obtained using the experimental data. For cases I and II, the bands appeared under the conditions indicated in the figure legend. The observed K* emission arose from the well-known doublet of potassium lines: 766.5 nm \((P_{3/2})\) and 769.9 nm \((P_{1/2})\).

The blue and red satellite bands around the potassium were not detected in the performed CBL experiments. This was to the fact that no potassium chloride was incorporated in the case I or II. On the other hand, the blue and red satellite bands around Na were observed both cases, even when the sodium chloride was found as an impurity.

The simultaneous observation of Na* and Ar* emissions at low external pressure with or without sulfuric acid, with little or much inert gas, suggested that the emitted species were formed at various times during collapse, as well as at different spatial locations as shown by the pulse shapes (in which the “precursors” appear or not).

The closeness between the predicted values of maximum temperatures and pressures for the three cases indicates that the hydrodynamic behavior of the liquid piston and the thermodynamics of gas compression were not substantially affected. Nevertheless, the pulses for each case showed very obvious differences, suggesting a cascade of physicochemical changes directly producing the diverse shapes and features of the pulses and spectra.
Figure 15. From case I and II, weak and diffuse emission lines from Ar* near-IR next to the K atom resonance were detected. The temperature and pressure reached during the compression process, and predicted by the model, are given next to each spectrum, as well as the acquired light pulse.

6. Remarks and discussion

Under the present experimental conditions:

1. According with numerous authors [2-10, 17-18, 25-26 and 38-41], one or more light emission mechanisms can be activated depending on the details of collapse.
2. The energy stored in the compressed gas is released almost exclusively through emission of sound waves, as described in [2 and 17].
3. The maximum temperature and pressure predicted were 10000 K and 12 GPa, respectively. The collapse time was of order of 0.5 ms.
4. Only homolytic bond cleavage can be considered under above considerations, thus in CBL, the average emission will tend to enhance the molecular relative to the continuum one.
5. The intensity and shape of the emitted light depends on the initial gas pressure, driving pressure and physicochemical properties of the liquid piston and substances dissolved in it. It is clear that the intensity and pulse width do not depend directly on the maximum temperature reached in the
collapse, but whether on the duration at which the mean temperature is kept above of the temperature at which the non-equilibrium chemical reactions are activated.

6. The physicochemical properties of the liquid piston varying as a function of the number of experimental runs by liquid degradation process. Similar affirmations have been described in [22-23].

7. Adsorption and desorption processes (by vacuum) from liquid-gas interface and walls are involved in how the atomic and molecular species have penetrated into the cavity, either enhancing or quenching the luminescence.

8. As the collapse proceeds beyond the molecular emission regime, the temperature becomes not sufficiently high to ionize the inert gas.

9. According with the experimental data and the spectral features the luminescence arose from several chemical pathways as a result of different local temperatures that emerge spatially and temporally along the collapse-rebound time line.

10. The simultaneous observation of OH-Ar and Na-Ar complexes as well as Ar* emissions applying low external pressure, with or without sulfuric acid, at low or high-inert gas pressure-, suggested that other mechanisms can be involved in the excitation processes such as: photonic absorption and/or multiphotonic [42].

Considering the above-mentioned, the molecular luminescence arises from chemiluminiscent reactions.

Under the present experimental conditions, during the collapse-rebound, the continuum growth of temperature and pressure induced only dissociation and numerous kinds of chemical reactions which took place inside bubble. A large number of these reaction products were oxidants and chromophore molecules, which were dispersed and mixed when the liquid bulk returned to its original position. In the cavity remained a liquid layer, and when the vacuum was applied, desorption and ablation from both the walls and the bubble–liquid interface occurred. So, the cavity became partially filled with vapor and droplets, which carried solid impurities. These new species were mixed with the injected inert gas to integrate the new bubble for the next collapse. Consequently, the intensity, shape, width and the spectral features of the emitted light were affected.

In other words, the luminescence features depends on the experimental sequence (repetition), in which some cumulative processes [43] could be developed into the conical chamber.

The mechanism, which resulted from a combination of spectroscopic data, pulse characteristics, changes in the host liquid, dynamic features of collapse and temperature predicted from the model, involved the following sequence:

Generation of excited species by homolytic cleavage (dissociation only) by either temperature or kinetic energy, (steam, air, vapor and droplets of host liquid, inert gas and other species as atoms or molecules in an unstable state under environmental conditions). Inelastic collisions of the fist order (or more) produce excited states as OH*, C3H*, and there are also formation of M-Rg*, and H2O*•Rg states (M= Metal, Rg = inert gas). The de-excitation of many of these species produces UV-VIS emission, which excited the new reaction products (chromospheres molecules) by absorption and/or multiphoton absorption processes. The chromophore emissions are overlapping of the whole detected emission [44-45].

7. Conclusions
A summary of experimental findings on the luminescence from conical bubble collapse, CBL are presented and discussed, including: spatial, temporal, and spectral characteristics, as well as comparisons with a thermodynamical model.

In the experimental runs, Ar gas and two liquid media (1,2-Propanediol, 1,2-Propanediol+H2SO4) are used. Single and multiple light emission events are recorded. The line emissions of OH*, Na*, K*, and Swan lines are observed as a function of the injected inert gas pressure and the driving pressure. A comparison between the temperature and pressure predicted by the model as well as the experimental
findings revealed that the emission intensity of CBL was not directly related to the maximum temperatures reached in the collapse. Instead, the intensity of the emitted light depended on the impurities in the bubble and could be due to the large number of physical and chemical reactions (homolytic) and collisions. The above take place at different local temperatures that emerge spatially and temporally along the collapse-rebound time line. Also, the presence of Ar emission lines, as well as OH-Ar and Na-Ar complexes might be explained as a result of collision coupling with multiphotonic absorption.

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