Novel Mechanism for Single Bubble Sonoluminescence

Boris P. Lavrov
Faculty of Physics, St.-Petersburg State University, 198904, Russia
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Careful re-examination of typical experimental data made it possible to show that the UV continua observed in multi-bubble (MBSL) and single-bubble (SBSL) sonoluminescence spectra have the same physical nature - radiative dissociation of electronically excited H₂*(a³Σ⁺) molecules [and probably hydrides of heavy rare gases like ArH*(A²Σ)] due to spontaneous transitions between bound and repulsive electronic states. The proposed mechanism is able to explain all available spectroscopic observations without any exotic hypothesis but in terms usual for plasma spectroscopy.

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Sonoluminescence (SL) is one of most exciting features of acoustic cavitation - the formation and non-linear oscillation of gas bubbles generated in liquids by ultrasound. Bubble collapses lead to enormous local pressures (about 1000 atm and more) and temperatures, erosion of hard materials, chemical reactions and light emission (SL). Discovered in early 1930s the SL observed in cavitation clouds is called multi-bubble sonoluminescence. MBSL spectra consist of a continuum of unknown origin, atomic lines and molecular bands of species connected with host liquids. Atomic and molecular emissions give effective temperatures \( \approx 3000–5000 \) K.

Suddenly the situation in this traditional branch of non-linear acoustics has been changed dramatically after the discovery of single bubble sonoluminescence - light emission of a single, stable, oscillating bubble trapped by acoustic levitation inside an ultrasound resonator. Such eccentric change in the performance of SL experiment provided unique opportunity to study the dynamics of oscillating bubble, obviously masked in MBSL. It was shown that every cycle consists of: 1) relatively slow growth of bubble radius up to \( \approx 50 \) \( \mu \)m, 2) extremely fast implosive collapse to \( \approx 0.5 \) \( \mu \)m, 3) damping and waiting for the expansion phase of sound wave in so-called “dead mode” with constant radius \( \approx 5 \) \( \mu \)m, corresponding to atmospheric pressure. SL appears as light flashes at the moment of the collapse. Further studies (see bibl. in [1,3,5–7]) have shown: 1) water being friendliest liquid for SBSL; 2) clockwise regularity of the flashes with \( \approx 50 \) ps stability; 3) abnormally short pulse duration (\( \approx 50–350 \) ps); 4) featureless spectrum with the intensity increasing to UV (see Fig. 1), which was fitted as a “tail of a blackbody spectrum” with abnormally high temperatures \( T = 25000 – 100000 \) K; 5) absence of characteristic emissions associated with host liquid; 6) stimulating influence of Ar. Those peculiarities are often presented and discussed as mysteries and unknowns of SBSL (see i.e. [5,7]) not only in respected scientific journals, but also in popular ones and newspapers as well.

Spectra of MBSL and SBSL measured “under similar experimental conditions” are shown in Fig. 2 (actually the conditions are sufficiently different, see be-
Such observations are often interpreted as evidence that “these two phenomena are fundamentally different” (“sonochemistry” and “sonophysics”) [6]. Unbelievably high temperatures “observed” in SBSL experiments were so exciting that the mechanism of highly spherical imploding shock wave in SBSL was even considered as “the key to reaching temperatures and densities sufficient to realize the fusion of these hydrogen nuclei to yield helium and neutrons” [5]. The stir stimulated tremendous growth of speculations about the nature of SBSL. Many mechanisms have been proposed so far from traditional ones (quasi-adiabatic heating, chemiluminescence, electric breakdown, shock wave and others) up to such exotic as Schwinger’s Dynamical Casimir Effect. Although most popular hypothesis is the Bremsstrahlung radiation of electrons in dense plasma (see i.e. [1,7,9]), the real nature of SBSL is still an open question [1].

The main goal of the present work is to propose and consider electronically excited $H_2^∗(a_3^3\Sigma^+_g)$ molecules [and possibly hydrides of rare gases like $ArH^∗(A^2\Sigma)$] as light emitters responsible for continua observed in both MBSL and SBSL experiments with hydrogen-containing liquids. This provides new sight on the well known “mysteries and unknowns” of the SBSL phenomenon.

Perhaps the most simple and natural explanation of the continuum radiation observed in SL spectra (never even considered previously) is spontaneous emission of hydrogen dissociation continuum appearing due to the $a^3\Sigma^+_g, v, J \rightarrow b^3\Sigma^+_u$ transitions ($v, J$ - vibrational and rotational quantum numbers) between lowest triplet bound (upper) and repulsive (lower) states (Fig. 3). It is a well-known spectral feature of hydrogen-containing plasmas widely used in UV spectroscopy (see bibl. in [10]). The shape of the continuum is determined by the distribution of population density among vibro-rotational levels of the upper $a^3\Sigma^+_g$ electronic state [11]. It is not directly connected with any translational temperature but is determined by a dynamic balance between excitation and deactivation of the $a^3\Sigma^+_g, v, J$ levels.

In low-pressure gas discharges, the spectral intensity distribution of the continuum may be calculated not only in relative [1], but even in absolute scale [12] being in rather good accordance with experimental data. In the $H_2+Ar$ mixtures the $Ar^+(4s) \rightarrow H_2(a^3\Sigma^+_g)$ excitation transfer from long living (metastable and resonant) levels of $Ar$ [13] may play important role as well as the formation of excited $ArH^∗$ excimer molecules and $A^2\Sigma \rightarrow X^2\Sigma$ spontaneous emission due to bound-repulsive transitions [14][15]. The $ArH$ continuum overlaps that of $H_2$ being located in the same wavelength range. The energy of $He^*$ and $Ne^*$ metastables is too high to participate in an excitation transfer leading to populating of the $a^3\Sigma^+_g$ state. However, $Kr^*$ and $Xe^*$ can do the job in three-body collisions with two $1S$ hydrogen atoms.

Correct calculation of the continuum shape in plasma with temperature higher than 1000 K is impossible just
because the transition probabilities are available only for rotation-less molecule [10]. On the other hand, it needs development of certain model of microscopic excitation-deactivation processes and certain values of plasma parameters determined by macroscopic dynamics of collapsing bubble. Two main de-populating processes are for sure: spontaneous emission and radiationless collisional quenching [13]. But there is a great variety of competitive volume and surface processes responsible for the generation of $H_2^+$ ($a^3\Sigma_g^+$) excited molecules (electron impact, electron-ion and ion-ion recombination, associative three-body collisions, photo and/or collision-induced fragmentation of water, etc.). Nevertheless, very rough estimations can be made by neglecting the rotational structure of $a^3\Sigma_g^+$, $v$ levels in two simple cases: 1) thermodynamic equilibrium (TDE) populations of $a^3\Sigma_g^+$, $v$ levels relative to ground $X^1\Sigma_g^+$, $v$=0 vibronic state; 2) direct electron impact excitation and spontaneous decay of the levels [10]. The results are shown in Fig. 4. One may see that calculated spectra are in accordance with experimental observations at least qualitatively. They have “featureless structure” with the intensity rising to UV cutoff $\lambda \approx 250$ nm. In the range of observation, they may be fitted as “blackbody spectrum” with “enormous temperatures”.

Experimental data are also not free from criticism:

1) Intensity calibration should take into account re-absorption in plasma and transparency of plasma-liquid boundary neglected in [3,8].

2) Determination of the background level is not so simple, because light scattered inside a flask and a spectrometer overlaps dark signal of a detector. The huge difference between backgrounds of SBSL and MBSL curves is caused by use of two different optical systems in [8]. The emission of MBSL was focused on the entrance slit of the spectrometer by a lens. In the case of SBSL, no collection lens was used. The entrance slit was placed close to the side of the levitation cell being 2.25 cm from the bubble. It means that all light coming from within $2\pi$ solid angle (much bigger than the instrumental aperture and that for radiation directly coming from the bubble) was able to enter the spectrograph and partly be detected as a background.

3) The separation of the continuum intensity from the total signal of a detector is also a rather delicate and ambiguous deal. For example the peculiarities on the SBSL curve of Fig. 3 may be interpreted as some additional emissions at $\lambda \approx 310 - 360$ nm (OH bands) and $\lambda \approx 400 - 500$ nm (NaH bands or $H_2$ continuum in the second order of the grating), or as absorptions at $\lambda < 320$ nm (OH) and $\lambda \approx 350 - 420$ nm (NaH).

4) Proper normalization of experimental curves is necessary for a comparison of their shapes.

Experimental data of [3,8] have been treated taking into account what is written above. Results of such recalculations are presented in Fig. 4 & 5. One may see
that the results of two independent SBSL experiments \[3,8\] are in good agreement as well as intensity distributions obtained by MBSL \[8\] and SBSL \[3,8\].

Taking into account experimental errors and the uncertainties in the data processing we have to come to the following conclusion. After proper treating the experimental data show: 1) The continua emitted by SBSL and MBSL (Fig. 5) have identical spectral intensity distribution, therefore they may have the same nature; 2) Measured spectral intensity distributions and those roughly calculated for the \(a^3\Sigma^+\rightarrow b^3\Sigma^+\) spontaneous emission of \(\text{H}_2\) molecule (Fig. 4) are in semi-quantitative agreement good enough to propose \(\text{H}_2^*\) \((a^3\Sigma^+)\) molecules to be responsible for the continuum emission. “Enormous temperatures” of SBSL reported so far have no physical meaning being the result of incorrect fitting (unproper treated experimental data were approximated by unproper analytical expression – Planck formula).

There is actually a great difference between MBSL and SBSL experiments even if they are carried out with the same chemical solutions: 1) The amplitude of sound wave in MBSL (10 atm) is about one order of magnitude bigger than that used in SBSL (\(\approx 1.3\) atm). Therefore in MBSL the action of ultrasound should be much more powerful and destructive for bubbles. The widely distributed opinion that SBSL is a stronger phenomenon is based only on the “observation” of “enormous temperatures”, not more. 2) MBSL experiments are made with 100% air saturation of a solution, while SBSL experiments are performed with degassed water.

Thus, the bubbles have qualitatively different gas contents in those two types of SL experiments. MBSL bubbles are mainly air-filled with small amount of water vapor. Dissociation of \(\text{N}_2, \text{O}_2, \text{H}_2\text{O}\) during the collapse leads to formation of very aggressive species (like \(\text{HN}_3, \text{HNO}_3, \text{N}_2\text{O}_2, \text{N}_2\text{O}_3\), etc.) which disappear by chemical reactions with water boundary. In the expansion phase a bubble (if it would be able to survive!) is again filled with air due to 100% air saturation. New bubbles are definitely generated as air-filled.

An absolutely other situation should occur in the case of SBSL when the action of acoustic waves is much more gentle and water is degassed. The SBSL bubble can accumulate not only \(\text{Ar}\) (1% in air) \([16]\), but molecular hydrogen as well. The hydrogen molecule in its ground state has almost the same electronic structure as that of \(\text{He}\) atom - its united atom analogue (two 1s electrons with anti-parallel spins). Thus, \(\text{H}_2\) itself has low chemical activity in great contrast with hydrogen atom. The solubility of \(\text{H}_2\) in water is much smaller than that of radicals made from \(\text{N}, \text{O}\) and \(\text{H}\) atoms. Therefore, a stable-oscillating bubble in SBSL mode actually consists of a \(\text{H}_2+\text{Ar}\) gas mixture with periodically changing amount of water vapor (increasing during the expansion and decreasing in the collapse). These additional \(\text{H}_2\text{O}\) molecules disappear in the collapse and serve as an en-
gine (and fuel) for the transformation of the translational energy of collapsing liquid-gas boundary into the energy of light emission. This mechanism explains: 1) Why the light flash appears only at the first collapse but not at the second one in the series of damping oscillations in spite of almost the same compression [5]; 2) Why the average radius of a bubble generally increasing with a rise in acoustic amplitude suddenly shrinks when the onset of SL is reached [5]; 3) Great rise of SBSL with a decrease of water temperature [5].

Clockwise regularity of SBSL flashes should not be so surprising and does not need unusual mechanisms because the experimental setup used in SBSL experiments is essentially a resonant system. The stability of this regularity means that after each collapse in the “dead mode” the bubble contents returns to the initial one - 98% of (H$_2$+Ar) mixture and 2% of H$_2$O.

The abnormally short duration of SBSL light flashes may be explained by extremely high rise of both the rate of excitation and the rate of collisional quenching of excited states. Thus the conditions suitable for spontaneous emission may be realized only in rather limited period of time. The situation is obviously different for different excited species. For some of them the favorable conditions could not be achieved at all (this explains also the existence of upper threshold of SBSL). The quenching may lead to a dissociation of molecules and to emission of vacuum UV radiation being out of the range of observation. The dim luminosity cloud surrounding a hot spot most probably is the fluorescence induced by L$_{\alpha}$ atomic line and/or Lyman and Werner bands of H$_2$. The estimation of the characteristic time of H$_2$(a$^3\Sigma_g^+$) collisional quenching with cross sections from [15] gives $\approx$1 ps.

The positive influence of heavy inert gases Ar, Kr, Xe (in contrast to He, Ne [17]) may be connected with the excitation transfer from their metastables and with formation of excited hydrides like ArH$^+(A^2\Sigma)$. Absence of characteristic emissions of Na$^+$ and OH$^+$ in SBSL is caused by better evacuation and/or quenching of upper states in hydrogen-dominated contents of the bubble.

It is common practice in plasma spectroscopy that an investigator should find proper answers for three questions: 1) Who is the emitter of the emission? 2) What are main processes of excitation and deactivation of the upper state of the transition? 3) How the population density of the upper level(s) can be related to plasma parameters? Only when all three are answered the emission may be used for plasma diagnostics (spectroscopic determination of temperatures, particle densities etc.). From such point of view any speculations around abnormally high temperatures “observed” in SBSL and “the opportunity” to make one more “cold fusion” are meaningless.
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FIG. 1. Spectral density of SBSL measured in [3] with two different light sources used for the absolute intensity calibration: the Deuterium lamp (dotted line) and the quartz tungsten halogen (QTH) lamp (points with error bars). The solid line represents blackbody spectrum for $T=25000$ K. The horizontal lines are background levels used in present work.

FIG. 2. Spectra of SBSL and MBSL obtained in [8] (solid lines). Dashed lines were used in present work as the continuum intensities with backgrounds shown by horizontal lines.
FIG. 3. Grotrian diagram of the ground and lowest triplet excited electronic states of H$_2$ molecule and Ar atom. Arrows indicate $a^3\Sigma^+_g(v \rightarrow b^3\Sigma^+_u)$ spontaneous emission transitions. Double arrows show some processes of populating of the $a^3\Sigma^+_g(v$ vibronic states: direct excitation of atoms and molecule and Ar$^* \rightarrow$ H$_2$ excitation transfer.

FIG. 4. The comparison of recalculated experimental SL continuum spectra [3,8] with those calculated for the TDE conditions with $T = 4000, 5000$ and $6000$ K (dash-dot lines). Solid line corresponds to the case of direct electron impact excitation and spontaneous decay of $a^3\Sigma^+_g(v$ levels of H$_2$ [10].
FIG. 5. Relative continuum intensity obtained from SBSL and MBSL spectra [3,8] (Fig. 1, 2) after the subtraction of the background and renormalization for unity at $\lambda = 350$ nm.