

MYSTERIES AND UNKNOWNNS OF SINGLE BUBBLE SONOLUMINESCENCE FROM VIEWPOINT OF PLASMA SPECTROSCOPY.

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1 Introduction

Sonoluminescence (SL) is one of the most exciting consequences of acoustic cavitation – the formation and non-linear oscillation of gas-vapor bubbles generated in liquids by ultrasound [1]. Fast collapse of bubbles lead to enormous local pressure and temperature, erosion of hard materials, chemical bond breakage and light emission (SL). Discovered in the early 1930s the phenomenon of SL observed in traditional experiments with cavitation clouds is often called as **multiple bubble sonoluminescence (MBSL)**. It is considered as a useful spectroscopic probe of the conditions inside bubbles during the collapse [1]. Light-emitting “hot spots” inside bubbles obtained in cavitation fields are known to be characterized with effective emission temperatures $\approx 5000\text{K}$ and pressures $\approx 1000\text{atm}$ [1]. Unfortunately, under those conditions, an investigator has to work with non-physical averaging of measured light intensities over time and space, because various bubbles have different size, appear-disappear at various moments and oscillate with different phases. It is important to underline that MBSL spectra consist of a continuum of unknown origin, atomic lines and molecular bands characteristic for species associated with host liquids [1].

Suddenly the situation in this traditional branch of non-linear acoustics has been changed dramatically after the discovery [2] of **single bubble sonoluminescence (SBSL)** – light emission of single, stable, oscillating bubble trapped by acoustic levitation inside an ultrasound resonator [3-6]. 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 [4] that every cycle consists of: 1) relatively slow growth of bubble radius up to $\approx 50\mu\text{m}$, 2) extremely fast implosive collapse to $\approx 0.5\mu\text{m}$, 3) damping in series of pulsation with much smaller amplitude and 4) waiting for the expansion phase of sound wave in so-called “dead mode” with constant radius $\approx 5\mu\text{m}$, corresponding to atmospheric pressure. SL appears as light flashes at the moment of the collapse. Further studies (see bibl. in [1-6]) have shown: 1) water being friendliest liquid for SBSL; 2) clock-like regularity of the flashes with $\approx 50\text{ps}$ stability; 3) abnormally short pulse duration ($\approx 50\text{ps}$); 4) featureless spectrum with the intensity increasing to UV up to photon energy $\approx 6\text{eV}$ (see Fig.1), which was fitted as a “tail of a blackbody spectrum” with abnormally high temperatures $T=25000\text{-}100000\text{K}$ [1,3,4]; 5) stimulating influence of heavy rare gases Ar, Kr, Xe; 6) absence of characteristic emissions associated with host liquid (in contrast with MBSL). Those peculiarities are often presented and discussed as mysteries and unknowns of SBSL (see i.e. [6]) 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” [5] are shown in Fig.2 (actually the conditions are sufficiently different, see below). Such observations are often interpreted as evidence that “these two phenomena are fundamentally different” (“sonochemistry” and “sonophysics” L.A.Crum, 1994). Unbelievably high temperatures “observed” in SBSL experiments were and are exciting most of all. 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” [4]. Time and numerous attempts to find X-rays and neutrons in experiments with deuterium and heavy water destroyed a wonderful dream of making controlled nuclear fusion in a boiling flask. The agiotage stimulated tremendous growth of speculations about the nature of SBSL. Dozens of mechanisms were proposed so far from traditional ones (quasiadiabatic compression, chemiluminescence, electric breakdown, imploding shock wave and others) up to such exotic as Schwinger's Dynamical Casimir Effect (extraction of energy from vacuum). Although most popular hypothesis is the *Bremsstrahlung* radiation of electrons in dense plasma (see i.e. [1,6]), 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 $\text{H}_2^*(a^3\Sigma_g^+)$ molecules (and possibly hydrides of rare gases like $\text{ArH}^*(A^2\Sigma)$) 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.

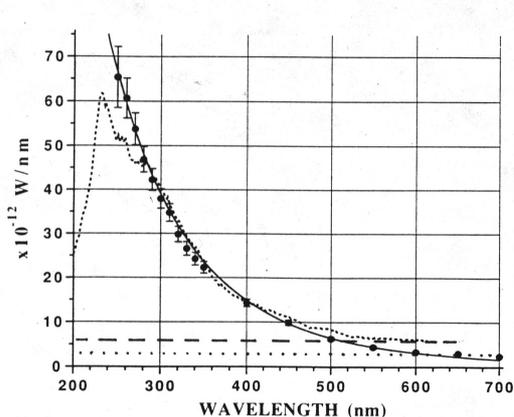


Fig.1 Spectral density of SBSL measured in [3] with two different light sources used for the absolute intensity calibration: the Deuterium lamp (dotted line) and the quartz tungsten halogen (QTH) lamp (points with error bars). The solid line represents blackbody spectrum for $T=25000$ K. The horizontal lines are the background levels proposed and used in present work.

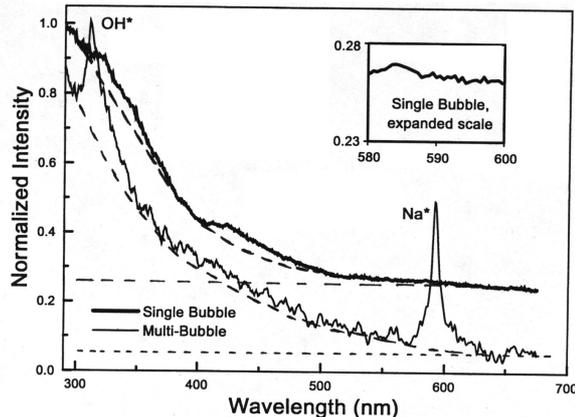


Fig.2 Spectra of SBSL and MBSL obtained in [5]. Solid lines are experimental results presented in [5]. Dashed lines were used in present work as the continuum intensities with the backgrounds shown by horizontal lines.

2 UV continua of SL observed in Hydrogen containing liquids

2.1 Radiative dissociation of $H_2^*(a^3\Sigma_g^+)$ and $ArH^*(A^2\Sigma)$ electronically excited molecules

Perhaps the most simple and natural explanation of the continuum radiation observed in SL spectra is spontaneous emission of radiative dissociation of $H_2^*(a^3\Sigma_g^+)$ and $ArH^*(A^2\Sigma)$ excited molecules. The famous hydrogen dissociation continuum appears 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 [7-10]). 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 [7,8]. **It is not directly connected with any translational temperature** (characteristics of velocity distributions) but is determined by a dynamic balance between excitation and deactivation of the $a^3\Sigma_g^+, v, J$ levels.

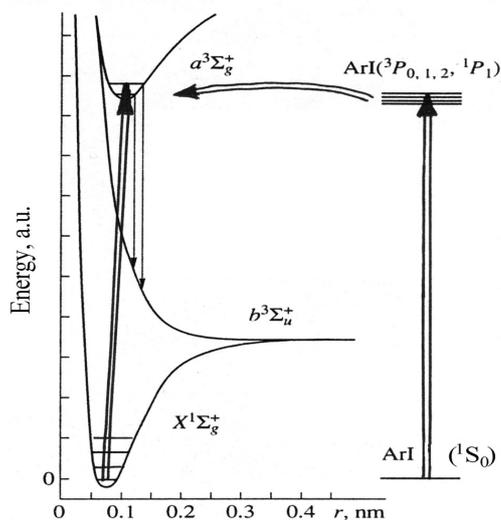


Fig.3 Grotrian diagram of the ground and lowest triplet excited electronic states of H_2 molecule and Ar atom.

Arrows indicate $a^3\Sigma_g^+, v=0,1 \rightarrow b^3\Sigma_u^+$ spontaneous emission transitions.

Double arrows show some processes of populating of the $a^3\Sigma_g^+, v$ vibronic states: electron impact excitation of atoms and molecules and $Ar^* \rightarrow H_2$ excitation transfer.

In low-pressure gas discharges, the spectral intensity distribution of the continuum may be calculated not only in relative (H_2, D_2) [8a], but even in absolute scale (H_2) [8b] being in rather good accordance with experimental data. In the H_2+Ar mixtures the $Ar^*(4s) \rightarrow H_2(X^1\Sigma_g^+)$ excitation transfer from long living (metastable and resonant) levels of Ar [9] 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 [7,10]. 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 H_2 (D_2) continua shape in dense plasma with temperature higher than 1000K is impossible just because the transition probabilities are available only for rotationless molecule [7]. 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. 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 [7]. 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.

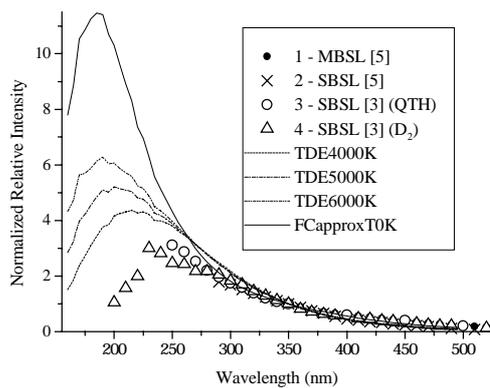


Fig.4 The comparison of recalculated experimental SL continuum spectra [3,5] with those calculated for the TDE conditions with $T=4000, 5000$ and $6000K$ (dash-dot lines). Solid line corresponds to the case of direct electron impact excitation and spontaneous decay of $a^3\Sigma_g^+, v$ levels of H_2 [7].

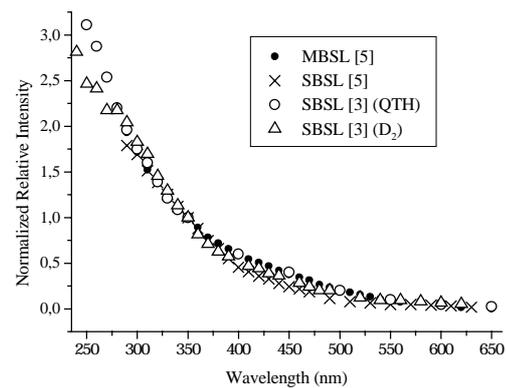


Fig.5 Relative continuum intensity obtained from SBSL and MBSL spectra [3,5] (Fig.1,2) after the subtraction of the background and renormalization for unity at the background wavelength $\lambda=350nm$.

Better calculations should be based on certain quantitative, non-stationary model of plasma formation in collapsing bubble. Only then it would be possible to understand what are the main volume and surface processes responsible for the generation of $H_2^*(a^3\Sigma_g^+)$ excited molecules from the great variety of known processes (electron impact, electron-ion and ion-ion recombination, associative three-particle collisions, photo and/or collisional fragmentation, etc). Two main depopulating processes are for sure: spontaneous emission and radiationless collisional quenching.

On the other hand, the experimental data are not free from criticism. For brief analysis of the continua shape (relative intensity distribution), it is enough to mention four most important points:

1) Intensity calibration should take into account re-absorption in plasma and transparency of plasma-liquid boundary neglected in [3,5]. Thus the curves presented in Fig.1,2 may be underestimated for the $\lambda \approx 365$ nm – threshold of stepwise photo ionization of H. (Observed difference in UV cutoffs of SBSL and MBSL [1] may be due to higher re-absorption in the latter case, because light emitted by one bubble has to pass through others.)

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. (Note that it is common practice to use double monochromator when you work with low signals and need to measure a continuum emission.) Moreover, a “spectral distribution” of scattered light is not necessarily constant. Nevertheless, for the rough estimations I used the lines shown in Fig.1,2. The huge difference between backgrounds of SBSL and MBSL curves is caused by use of two different optical systems in [5]. 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 2π solid angle (much bigger than the instrumental aperture) was able to enter the spectrograph and partly be detected as scattered light.

3) The separation of the continuum intensity from the total signal of a detector is also a rather delicate and unambiguous deal. For example the peculiarities on the SBSL curve of Fig.2 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. (Normalization of MBSL and SBSL curves to unity at maxima occurring at different wavelengths has absolutely no sense, just because the intensities have obviously different origins: UV bands of OH and the continuum.)

Experimental data of [3,5] may be 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 [3,5] are in good agreement as well as intensity distributions obtained by MBSL [5] and SBSL [3,5].

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 $a^3\Sigma_g^+, v, J \rightarrow b^3\Sigma_u^+$ spontaneous emission of H_2 molecule (Fig.4) are in semi-quantitative agreement good enough to propose $H_2^*(a^3\Sigma_g^+)$ molecules to be responsible for the continuum emission.

2.2 Considerations about the nature of SBSL

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 more than an order of magnitude bigger than that used in SBSL (≈ 0.5 atm). Therefore in MBSL the action should be much more powerful and destructive for bubbles (necessity of effective cooling system is an evidence of that). The widely distributed opinion that SBSL is a stronger phenomenon is based mainly 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.

Most important is qualitatively different gas contents of bubbles in those two types of SL experiments. MBSL bubbles are mainly air-filled with small amount of water vapor. Dissociation of N_2 , O_2 , H_2O during the collapse leads to formation of very aggressive species (like HN_3 , HNO_3 , N_2O_2 , N_2O_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 Ar (1% in air) as it has been proposed by Lohse *et al*, Moss *et al* in 1997, but molecular hydrogen as well. The hydrogen molecule in its ground state has almost the same electronic structure as that of He atom – its united atom analogue (two 1s electrons with anti-parallel spins). Thus, H_2 itself has low chemical activity in great contrast with hydrogen atom. The solubility of H_2 in water is much smaller than that of radicals made from N, O and H atoms.

Therefore, stable-oscillating bubble in SBSL mode actually consists of an H_2+Ar gas mixture with periodically changing amount of water vapor (increasing during the expansion and decreasing in the collapse). These additional H_2O molecules disappear in the collapse and serve as an engine (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 (see figure on p.34 of [4]);
- 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 (see figure on p.35 of [4]).

Clockwise regularity of SBSL flashes synchronized with acoustic wave 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_2O .

The abnormally short duration of SBSL light flashes ($\approx 50ps$) may be explained by extremely high rise of both the rate of excitation of atoms and molecules 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 favourable conditions could not be achieved at all. 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_α 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 [11] gives $\approx 1ps$ (being 4 orders of magnitude smaller than the radiative lifetime of $a^3\Sigma_g^+, v$ states ≈ 10 ns).

The positive influence of heavy inert gases Ar, Kr, Xe 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 probably caused by effective radiationless deactivation in the presence of protons, atomic and molecular hydrogen.

3 Conclusion

UV continua observed in MBSL and SBSL spectra of hydrogen-containing liquids have the same physical nature – $a^3\Sigma_g^+, v, J \rightarrow b^3\Sigma_u^+$ radiative dissociation of electronically excited $H_2^*(a^3\Sigma_g^+)$ molecules (and possibly hydrides of heavy rare gases like $ArH^*(A^2\Sigma)$). In the case of SBSL of “air bubbles” in water with dissolved Ar the oscillating bubble actually consists of a H_2+Ar mixture with periodically changing amount of water vapor. The proposed mechanism is able to explain all available spectroscopic observations without any exotic hypothesis but in terms usual for plasma spectroscopy. Moreover, it is common practice in optical emission spectroscopy that an investigator should find proper answers for three questions:

- 1) Who is the emitter of the emission? (Which quantum transition is responsible for it?);
- 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 certain 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” have no much sense. On the other hand, the present paper may give the answer on the first question only and provide some ideas about the second one. The highly dynamic, non-linear and probably non-equilibrium phenomenon of SBSL may be considered as a prospective tool for generation and studies of extremely dense plasmas having unique properties up to formation of contemporary crystal-like structures.

P.S. The story of SBSL is not the first (and probably not last) proposition to obtain fusion temperatures in dense plasma based on incorrect interpretation of spectroscopic data. Electron temperatures as high as 1000000K have been “achieved” in [12] due to treating of measured continuum as *Bremsstrahlung* radiation. Correct explanation of the “phenomenon” as the recombination continuum and L_α far wing see in [13].

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