Pis'ma v ZhETF, vol.70, iss.7, pp.428 - 433

SCENARIO OF THE ELECTRIC BREAKDOWN AND UV RADIATION SPECTRA AT SINGLE BUBBLE SONOLUMINESCENCE

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Submitted 5 April 1999

Resubmitted 2 September 1999

In a preceding paper we put forward a hypothesis that the single bubble sonoluminescence (SBSL) is caused by strong electric fields occurring near the surface of collapsing gas bubble because of the flexoelectric effect in water. Here we argue that these fields can indeed provoke an multiple electric breakdown in water, in a micron-size region near the surface of the collapsing gas bubble, and show that the main numerical characteristics of the SBSL can be naturally explained within this mechanism. The SBSL spectra are determined by radiation transitions between high-energy levels of noble gas atoms excited by hot electrons created by strong flexoelectric field in a "cold" water.

PACS: 43.20.+g, 52.80.Wq, 77.22.-d, 78.60.Mq

Sonoluminescence refers to the phenomenon of light emission during acoustic radiation of a liquid and is associated with cavitation bubbles present in the liquid. The most controllable and promising experimental data were obtained for the single bubble sonoluminescence (SBSL): picosecond UV radiation of single bubble pulsating in field of sound wave [1]. One of the specific features of SBSL is a decisive role of the noble gases soluted in water in the phenomenon. Recently a theory has been developed [2] which explains the very existence of stable pulsating of bubble by the soluted gas diffusion and chemical reactions in the bubble gas.

In this paper we argue that the noble gas atoms play a decisive role in the process of light emission for a bright SBSL. We assume, as well as in [3] that the flexoelectric effect [4], i.e., polarization of water due to gradients of pressure is essential for the SBSL. According to the estimations [3] the depolarizing field can achieve 10^7 V/cm, i.e. exceed the breakdown field of water. However, the breakdown scenario was far from being clear. Indeed, the mechanism of the breakdown in water involves "lucky electrons" whose acceleration in the electric field leads to developing of the avalanche (see, e.g.,[5]). At ambient temperature the concentration of free electrons in water is quite negligible and it is hardly probable to find a "lucky electron" in a small volume near the bubble surface, i.e. in the region of high electric field, during the short time of existence of this field. Moreover, the origin of optical radiation in the transparency window of water remained unexplained in [3]. The reason of a spectacular synchronization of the emission pulses [1, 6] was also uncertain. The aim of this paper is to answer these questions.

Let us describe shortly the proposed scenario of the breakdown and the radiation. At certain short time interval when the bubble radius is near its minimum the acceleration

of the bubble surface and the pressure gradient amounts to gigantic values (10^{14} cm/s^2 and 10^{14} dyne/cm^3 [1]). Because of the flexoelectric effect the field at the bubble surface can reach the value of 10^7 V/cm [3]. It is essential that in a certain time interval, $\tau_c \sim 1$ ns, when the bubble surface decelerates, the field is directed to the center of the bubble. The strong electric field is localized in a thin spherical layer, of about 1μm size, near the bubble surface and its value can exceed essentially the static breakdown field in water. However, the breakdown starts only if "lucky electrons" appear in the thin layer during the deceleration period. These electrons indeed appear because of sharp increase of temperature of the bubble gas and of a water layer very close to the bubble surface, up to at least several thousands K, when the bubble radius is close to its minimum value [7, 8]. The free electrons penetrate, due to their diffusion, into the thin water layer where the strong electric field is localized and is directed to the bubble center. Then they are accelerated up to the energies enough to generate additional free electrons as a result of the electric breakdown of water and to excite noble gas atoms. The light emission is determined mainly by intensive optical transitions between high-energy excited states of the noble gas atoms. Because of space-inhomogeneity of the strong electric field the radiation spectrum is continuous and resembles the black-body radiation spectrum with a temperature equal to effective temperature of the hot electrons. The characteristic time of the electric breakdown is much less than τ_c, i.e. the polarization can continue to change after the first breakdown and the electric field can reach once more the breakdown threshold value. As a result, several breakdowns can take place during the time interval τ_c. The multiplicity of the breakdowns determines both the energy of the SBSL pulse and its duration.

To support the scenario let us first discuss the sign of the depolarizing electric field E at the bubble surface. It depends on the sign of the flexoelectric coefficient f defined by $E = f\nabla p = -f\rho a$ [3] , where p is the pressure, ρ is the mass density, $a = -d^2R/dt^2$, R is the radius of the bubble. The water molecules are highly asymmetric, so the negative oxygen ion tends to be located in the region of higher pressure while the positive hydrogen ions tends to be located in the region of smaller pressure. In other words, the polarization vector is directed opposite to the gradient and the depolarizing field is parallel to the gradient, i.e. $f > 0$ for water.

The most essential features of dynamics of the pulsating bubble are presented, e.g., in [1]. Within a short time interval $(1 \div 10)$ ns when the bubble radius R is close to its minimum value R_{min} the bubble surface first accelerates and then sharply decelerates, i.e. the velocity $v = -dR/dt$ first reaches its maximum and then goes to zero at the point $R = R_{min}$. That means that at R somewhat exceeding R_{min} the acceleration $a = = -d^2R/dt^2$ reverses its sign and achieves huge values. During the acceleration period the gradient of pressure $\nabla p = -\rho a$ is directed from the bubble center to its periphery so the field has the same direction. During the deceleration period, $\tau_c \sim 1$ ns, the arising flexoelectric field is directed to the bubble center.

As we have noted the field E can essentially exceed the static threshold field of breakdown of water E_{th} but the electric breakdown occurs only if "lucky electrons" which could provoke an avalanche are disposable. This situation resembles that of the laser breakdown [5]. The presence of the "lucky electrons" is practically discarded at ambient temperature within the time interval of interest, $\tau_c \sim 1$ ns, and the volume $(10^{-11} \div 10^{-12})$ cm^3. The source of the "lucky electrons" is, in our case, the bubble gas and a water layer very close to the bubble surface. These electrons are accelerated if the field is directed to the bubble

center. This situation, as we have shown above, is realized during the deceleration period when the bubble radius goes to its minimum value $R_{min} \simeq 1\,\mu$m [1]. Just when the bubble radius is close to R_{min} the gas temperature sharply increases [7, 8]. Even relatively moderate temperatures are sufficient to make sure the breakdown. Indeed, if we assume, as in [9], that the bubble gas has the temperature of 7000 K then the water layer of thickness of the thermal penetration length, $\delta_T \sim 0.1\mu$m, has the temperature about 3000 K. Water can be considered an amorphous semiconductor with the band gap $E_g \simeq 6.5$ eV [5, 10] and the effective density of states $N^* \simeq 10^{21}$ for $T > 3000$ K. The equilibrium concentration of conduction electrons at $T \geq 3000$ K is $n = N^* \exp(-E_g/2kT) > 3 \cdot 10^{15}$ cm^{-3} and settles in the thermal ionization time $\tau_T = (N^* \sigma v_T)^{-1} \exp(E_g/2kT) < 10$ ns where $\sigma \simeq 10^{-15}$ cm^{-2} is the cross-section of the free carrier recombination, v_T is the thermal velocity of conduction electron in water. Therefore the number of conduction electrons N thermo-generated within the time interval of interest, $\tau_c \sim 1$ ns, and in the surface layer of the volume $(10^{-11} \div 10^{-12})$ cm^3 exceeds $30 \div 300$. Note that a similar number of free electrons can be generated by thermal ionization of the bubble gas. Indeed, the gas temperature (7000 K) is about two times larger and the ionization energy both of the water vapor and Ar, Kr, Xe is about $(12 \div 16)$ eV, i.e. also about two times larger than E_g. Thus the SBSL flash is emitted in a well defined moment when during existence of high deceleration and strong electric field in cold water the bubble gas becomes very hot. This can explain the reason of synchronization of SBSL observed experimentally [1, 6].

Let us now elucidate the decisive role of the noble gases in the bright SBSL. In the typical situation the mean electron energy is about several eV (see below). There is some probability that an electron has the energy exceeding 10 eV what is about the lowest excitation energy of noble gas atoms and it excites these atoms. An important feature of the noble gas atoms is that their metastable states have life time up to milliseconds (see, e.g., [11]). So once excited the noble gas atom can remain in the metastable state during all the time interval of positive acceleration and multiple breakdowns, $\tau_c \sim 1$ ns, and, possibly, during many periods of the acoustic wave ($\sim 30\,\mu$s [1]). The hot electrons collide with these noble gas atoms in the metastable state and transfer them to higher excited states. The radiation transitions between high-energy excited states provide radiation in the transparency window of water ($h\nu < E_g \simeq 6.5$ eV) and govern the SBSL spectrum.

The energy distribution of the hot electrons with energy $\varepsilon < E_g \simeq 6.5$ eV is given by the Maxwell distribution. Indeed, in the strong electric fields an electron acquires, on average, an energy $qE\lambda >> \varepsilon_{ph}$, where λ is the electron energy relaxation length which for water is about $(20 \div 100)\mathring{A}$ and ε_{ph} is the characteristic energy of local oscillations in water which is practically equal to the energy of optical phonons in ice, $\varepsilon_{ph} \simeq$ $\simeq$ $(80 \div 100)$ meV [5]. Since in the process of the acceleration an electron radiate many optical phonons the electron energy distribution is nearly isotropic in the momentum space and is approximated by the Maxwell function with an effective electron temperature $kT_e = (eE\lambda)^2/3\varepsilon_{ph}$ [12]. In these conditions the effective thermal velocity of electrons $v_T = \sqrt{3kT_e/m_e}$ is much more the drift velocity $v_d = \sqrt{\varepsilon_{ph}/m_e}$. For $E \simeq (2 \div 10)10^6$ V/cm the effective electron temperature $T_e \simeq (2 \div 5)10^4$ K.

The high-energy excited states of the noble atoms because of the Stark effect in the strong electric field are spited. In addition the active region the electric field changes, at least, by several times (see below). The inhomogeneous broadening of all the lines is very strong and one can consider the density of the high-energy excited states as a constant. At every collision the hot electron transfers the metastable noble gas atom to a state with

energy ε, the reference point of energy being the energy of the metastable state (for our estimations we consider only one metastable state). The concentration of atoms excited during the breakdown time τ_b to energies within an interval $d\varepsilon$ reads

$$dn_n^{**} = n_n^*(\sigma_{ex} v_T n)\tau_b \exp(-\frac{\varepsilon}{kT_e}) \cdot \frac{d\varepsilon}{kT_e}, \tag{1}$$

where n_n^* is the concentration of the noble gas atoms in the metastable state, σ_{ex} is the cross section of the impact excitation of an atom from the metastable state to a state with energy ε. Atoms excited to the states with the energy ε go to the ground state preferably through intermediate excited ones radiating mainly phonons with energy $h\nu \simeq \varepsilon$ [11]. So the spectral density of energy per unit volume radiated in a single breakdown can be written as

$$\widetilde{P}(h\nu)d(h\nu) = h\nu w_r n_n^*(\sigma_{ex} v_T n)\tau_b \exp(-\frac{h\nu}{kT_e}) \cdot \frac{d(h\nu)}{kT_e}, \tag{2}$$

where w_r is the probability of the spontaneous radiation transition. Using that $w_r = = (4(2\pi)^4\nu^3/3c^3h)D^2$, where D is absolute value of matrix element of dipole moment of the transition [13] we find

$$\widetilde{P}(h\nu)d(h\nu) = \frac{4(2\pi)^4 D^2}{3c^3} n_n^*(\sigma_{ex} v_T n)\tau_b \nu^4 \exp(-\frac{h\nu}{kT_e}) \cdot \frac{d(h\nu)}{kT_e}. \tag{3}$$

Mention that T_e in Eq.(3) is a function of the position because of $T_e \sim E^2$ (see above) and $E = E(r)$. To find approximately $E(r)$ one can consider water as incompressible liquid one where $\nabla p \sim r^{-2}$. As $E \propto \nabla p$, one has: $E \simeq E_s R_s^2/r^2$, where E_s is the field at the bubble surface. Integrating Eq.(3) we find approximately the spectral density of radiation of a single breakdown

$$P = \int \widetilde{P}(h\nu, r)dV = \frac{4(2\pi)^4 D^2}{3c^3 h} n_n^*(\sigma_{ex} v_T N_t)\tau_b \nu^3 \exp(-\frac{h\nu}{kT_{es}}), \tag{4}$$

where $kT_{es} = (eE_s\lambda)^2/3\varepsilon_{ph}$ and N_t is, practically, the total number of electrons participating in the breakdown. This number can be found taking into account that as a result of the breakdown the depolarizing flexoelectric field becomes screened. The total transmitted charge in process of the screening is

$$Q_t = PS = 4\pi R_s^2 \varepsilon_0 E_s = eN_t, \tag{5}$$

where we have used that in our case $D = P + \varepsilon_0 E = 0$, i.e., $P = -\varepsilon_0 E$.

The observed spectra are cut off in the shortwave region (at $h\nu \simeq E_g \simeq 6.5\,\mathrm{eV}$) because of absorption of water. Taking this into account we find the energy radiated in a single breakdown:

$$U_r = \int P w_r^{-1} d(h\nu) \simeq h\bar{\nu}(\sigma_{ex} v_T N_t)\tau_b n_n^* \geq h\bar{\nu}\frac{v_T}{v_d}(\sigma_{ex} R_s n_n^*)N_t, \tag{6}$$

where $h\bar{\nu}$ is the characteristic photon energy close to the energy of maximum of the observed spectrum, $h\bar{\nu} \sim (5 \div 6)\,eV$ in the case of strong electric field. In Eq.(6) we used that the breakdown time $\tau_b \simeq R_s/v_d$ (see below). For the considered electric fields $E_s \simeq 3 \cdot (10^6 \div 10^7)$ V/cm we find from Eq.(5) that $N_t \simeq (2 \div 10) \cdot 10^5$. Using $v_T/v_d = = eE\lambda/\varepsilon_{ph} = 20 \div 100$, $\sigma_{ex} \simeq 10^{-15}\,\mathrm{cm}^2$, $R_s \simeq 1\mu\mathrm{m}$, putting $n_n^* \simeq (10^{17} \div 10^{18})\ \mathrm{cm}^{-3}$,

what is one order of magnitude less than the concentration of the noble gas atoms close to the bubble [2], and assuming that there was about 10 breakdowns during the time interval τ_c (see below) we find from Eq.(6) that total photon number is $10^6 \div 10^8$ and the total energy $W_r = (10^{-13} \div 10^{-11})$ J. The observed energies of the bright SBSL pulses [1, 14, 15] are approximately equal to the energy of $10^6 \div 10^7$ photons with $\hbar\omega \simeq 5$ eV.

An estimation of the upper limit of the radiation energy because of a single breakdown can be made as well in another way. The energy of electric field in medium (water) is

$$U_t = \frac{\epsilon\epsilon_0}{2} \int_{R_s}^{\infty} E^2 dV. \tag{7}$$

Emphasize that not all this electric energy but only its certain part can be spend in principle for generation of the light. Indeed, the light arises because of excitation of the noble gas atoms by electrons accelerated by the flexoelectric depolarizing field. In other words the radiation is a part of the Joule power which is

$$W_J = \int_{R_s}^{\infty} jE dV = \int_{R_s}^{\infty} E(\frac{d}{dt}P)dV = \frac{\epsilon_0}{2}\frac{d}{dt}(\int_{R_s}^{\infty} E^2 dV) \equiv \frac{d}{dt}U_e, \tag{8}$$

where $j = dP/dt$ is the current of screening of the depolarizing field and we take into account that in our case $P = -\varepsilon_0 E$. From Eq.(8) follows that

$$U_e = \frac{\epsilon_0}{2} \int_{R_s}^{\infty} E^2 dV = \frac{1}{2} \int_{R_s}^{\infty} EP dV. \tag{9}$$

One can see that U_e is only energy of electric field created by the dipole moments. The difference of the energies $U_t - U_e$ is the free energy of ordering of the dipole moments. So only the part of total electric energy U_t can be transformed to the light.

Eq.(9) can be approximately rewritten as

$$U_e = \frac{\epsilon_0}{2} \int_{R_s}^{\infty} E^2 dV \simeq 2\pi R_s^3 \varepsilon_0 E_s^2 \simeq 2\pi R_s^3 \varepsilon_0 (f\nabla p)^2. \tag{10}$$

Here for estimation we used, as above, that $E \sim r^{-2}$. To estimate the maximum of U_e we put $E_s \simeq 10^7$ V/cm and $R_s \simeq 1\mu$m to find that $U_e \simeq (10^{-11} \div 10^{-10})$ J. The total Joule energy per SBSL pulse is higher because of multiplicity of the breakdown. This total Joule energy is much more than the observed energy of the SBSL pulse [1, 14, 15].

Emphasize that the spectrum given by Eqs.(4) resembles the black-body one but the role of the temperature is played here by the effective temperature of the hot electrons T_e in water which can be much higher than temperature of the bubble gas. Experimentally observed spectra can be fitted, in the wavelength interval $(200 \div 700)$ nm, to the black-body ones with temperatures $(2 \div 5) \cdot 10^4$ K [14]. As we have mentioned above such T_e are reached at electric fields $E_s \simeq (2 \div 10)10^6$ V/cm.

The pulse time is limited by the breakdown time. Its value is $\tau_b = R_s/v_d$ where v_d is the drift velocity of electrons which in the strong electric fields saturates at value $v_d = \sqrt{\varepsilon_{ph}/m_e} \simeq 10^7$ cm/s (see above). Assuming $R_s \sim 1\mu$m we find $\tau_b \sim 10$ ps. The whole deceleration period is about two orders of magnitude larger than $\tau_c \sim 1$ ns. Therefore, after the breakdown is finished and the depolarization field is screened the polarization continues to change, because of change in acceleration, and the field arises once more. As a result a new breakdown may take place. Such a situation can be repeated

several times. Effectively, it manifest itself in an increase of the pulse time. Therefore, within our scenario the more is the pulse duration the more is its energy. Analogous interrelation is observed in experiment [1, 16, 17]. Mention also that, within our scenario of SBSL, the pulse width does not depend on the spectral range of the radiation. This agrees with experiment as well [16].

Emphasize also that our mechanism of the SBSL displays in water near the bubble surface without any assumption about the extraordinary conditions but not in the bubble gas as it is considered in the most popular models of SBSL [1]. From our scinario it follows the answer to question [1]: "Why is water the friendlist liquid for the SBSL".

One sees from Eq.(6) that the radiation energy is proportional to n_n^*. The less is the excitation energy to the metastable level the more is n_n^*. This explains increasing of influence on the SBSL in the series He-Xe ([1]). Strong magnetic fields are known to hamper the heating of the electrons [18]. This might be the reason of decreasing of the SBSL intensity with magnetic field observed experimentally [19].

Above we neglected the water conductivity. It is justified because, as a rule, the dielectric relaxation time, τ_D, is much more than $\tau_c \simeq 1$ ns what is the maximal characteristic time of our problem. Increasing the ionic conductivity of water, by adding, for example, NaCl, one can, according to our estimations, decrease τ_D down to 0.1 ns. In such an electrolyte the mechanism of SBSL discussed in this paper might be less effective. Observation of this effect would support the mechanism of bright SBSL under discussion.

NG and VVO thank EU ESPRIT, the Spanish CSIC and NATO for Linkage Grant Ref. OUTRLG 970308. Also, APL thanks NATO for Linkage grant HTECHLG 971213.

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