03

Continuum pulse width in different multibubble sonoluminescence spectra regions determined by correlation method

© M.V. Kazachek, T.V. Gordeychuk

V.I. Il'ichev Pacific Oceanological Institute, Far Eastern Branch, Russian Academy of Sciences,
690041 Vladivostok, Russia

e-mail: tanya@poi.dvo.ru

Received May 30, 2023
Revised May 30, 2023
Accepted July 05, 2023

The time-correlated photon counting method was used for determining the width of light pulses in different spectral regions of multibubble sonoluminescence from water and NaCl, KCl, LiCl, $CaCl_2$ aqueous solutions of various concentrations. The pulse width has the same value for all wavelengths and for all spectra in those regions containing only continuum of emission. The result does not support black body emission as an immediate source of continuum emission. The observed comparability of continuum intensities for shortwave and longwavelength spectral regions also does not fit within the black body model.

Keywords: sonoluminescence, optical pulse width, correlation method.

DOI: 10.61011/EOS.2023.09.57345.5274-23

Introduction

Sonoluminescence (SL) is a weak optical emission accompanying nonlinear pulsations of vapor-gas bubbles in liquids subjected to ultrasonic irradiation. SL manifests itself in the form of short pulses correlated with the moment of bubble collapse [1]. Most SL spectra have the form of a broad continuum extending from the near UV region to IR (often with added molecular and atomic lines). The regime of stable SL of a single bubble has been discovered in 1989. Since the corresponding spectrum without lines was filled fairly well by a black body spectrum, it was hypothesized that the emission in this SL regime is thermal in nature. The authors of [2] were the first to measure the width of continuum pulses in the „red" and „blue" spectral regions for single-bubble SL by time-correlated photon counting. It turned out that the width values are equal: the difference for published spectra in the 300−650 nm range is $< 5\%$ at a pulse width of ~ 0.1 ns. This result, which was verified experimentally in [3,4], did not fit into the thermal SL model and, combined with other data, facilitated the development of models of non-thermal continuum emission mechanisms. Plasma emission, bremsstrahlung [5,6], molecular emission [7–9], and shocks [10] have been proposed as candidate SL continuum sources; such exotic phenomena as Casimir light [11] and a temperature dependence of absorption for correction of the black body mechanism [12,13] have also been considered. Ionized matter lines are observed in both single-bubble [14] and multibubble [15] SL spectra. We failed to find published data on the wavelength dependence of the pulse width for multibubble SL. In the present study, this dependence is examined by a correlation method. The results confirm that the continuum emission is non-thermal in nature in the case of SL from a bubble cloud.

Experimental

Multibubble SL of water and 4 M NaCl, 3 M KCl, 12 M LiCl, and 4.5 M $CaCl_2$ aqueous solutions under saturation with argon was studied. Salt solutions are convenient in providing a sufficient brightness of the examined continuum. The design of a flow-type ultrasonic cell and the diagram of the experimental setup were presented in [16]. A Sonics V750 generator (frequency: 20 kHz; power output: 20 W) was the source of ultrasound. The temperature of solutions was maintained at $10 \pm 1^\circ$C by a Julabo F12 thermostat; the static pressure increment in the cell was 0−0.4 atm. SL spectra were recorded by an MDR-23 monochromator with a resolution of 3 nm without correction for the spectral sensitivity of the „PMT + grating" system. FEU-79 photomultiplier tubes (PMTs) were used, and the grating blaze wavelength was 500 nm. The SL pulse width was measured with a correlation counter based on two FEU-79 PMTs operated in the photon counting mode, a RIGOL DS1104 digital oscilloscope, and a computer [17]. The time resolution of the correlation counter was made approximately two times higher. The correlation method works fine for both single-bubble and multibubble SL, since bubbles, which differ in size and are positioned differently, emit almost independently. The correlation method yields a mean pulse width in this case. Pulse width W was determined as the width at half maximum of a Gaussian curve approximating the correlation (see examples in Fig. 1). The duration of SL pulses may be calculated based on W by introducing corrections to intrinsic widths of PMTs and oscilloscope digitization circuits. According to the results of our calculations, each FEU-79 produces a contribution of < 1.1 ns, while the oscilloscope adds ~ 0.6 ns. Although these corrections are fairly large compared to the measured

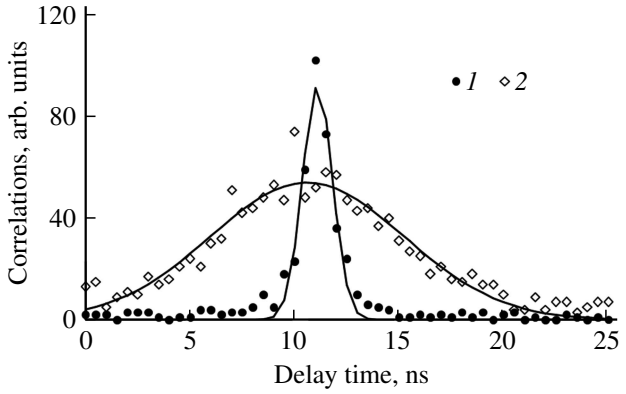

Figure 1. Correlation functions of continuum pulses (*1*) and line K (*2*), which were measured with the corresponding light filters for SL from a 3 M KCl aqueous solution, and their approximation with Gaussian curves ($W_1 = 1.69$ ns, $W_2 = 10.93$ ns).

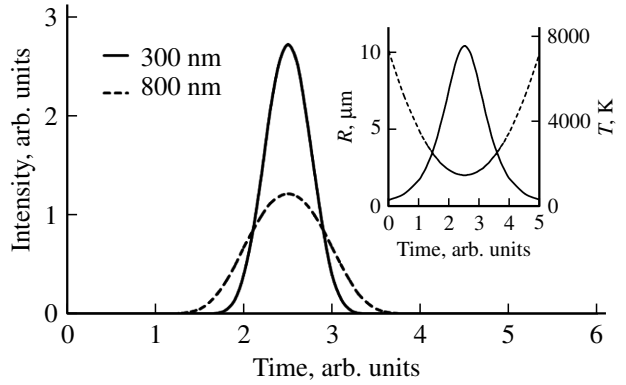

Figure 2. Intensity of a flash at the wavelengths of 300 and 800 nm in the black body radiation model. The set radius variation (dashed curve) and the calculated temperature variation (solid curve) are shown in the inset.

width, they remain constant, and the trends revealed in the study were reproducible. Correlation measurements of the pulse width for multibubble SL of water within the entire emission range (without discrimination between spectral regions) have been performed for the first time in [18]. The width determined under experimental conditions similar to the ones in the present study was 0.25 ns. This value may be used to calibrate the pulse duration measured by our instrument. Light filters were used to isolate spectral regions.

Contradictions of the black body model

It was noted in [2] that „If, for example, SL is simply an adiabatic compression followed by blackbody radiation, one would expect that the pulse width is much larger in the red than in the UV.“ A simple model is sufficient to validate this argument.

Let us assume that a bubble is subject to adiabatic compression $T = T_0(R_0/R)^{3(\gamma-1)}$, where T is temperature, $T_0 = 300$ K is the initial temperature (of the surrounding solution), $\gamma = 5/3$ is the polytropic index, R is the bubble radius, and R_0 is the initial radius. The maximum temperature in the bubble is $T_{\max}$, and the minimum radius is $R_{\min}$. The intensity of bubble emission at the chosen „blue“ ($\lambda = 300$ nm) and „red“ ($\lambda = 800$ nm) wavelengths is defined as $P = S\varepsilon(\lambda, T)$, where $S = \pi R^2$ is the apparent surface area of the bubble and $\varepsilon(\lambda, T) = 2\pi hc^2\lambda^{-5}/(\exp(hc/(\lambda kT)) - 1)$ is the Planck emissivity. Setting γ, $R_0/R_{\min}$, and the radius variation as model parameters, we find the temperature variation and emission intensities P_{300}, P_{800} (Fig. 2). Calculations reveal that the duration of the „red“ flash is approximately two times greater than the duration of the „blue“ one. The result changes insignificantly if the shape of the time dependence of radius is altered.

The power-law relation between γ and $R_0/R_{\min}$ imposes tight constraints on their possible values at which P_{300} and P_{800} are comparable. A small change of these parameters translates into a significant difference between $T_{\max}$, and a flash becomes either „red“ or „blue“ with P_{300} and P_{800} values integrated over the flash duration differing by more than an order of magnitude. At $R_0/R_{\min} = 5$ (Fig. 2), we find $P_{800}/P_{300} = 0.76$ and $T_{\max} = 7500$ K. At $R_0/R_{\min} = 10 - P_{800}/P_{300} = 0.06$ and $T_{\max} = 30\,000$ K; at $R_0/R_{\min} = 3 - P_{800}/P_{300} = 840$ and $T_{\max} = 2700$ K. In practice, $T_{\max}$ is limited by dissociation [9] and ionization processes. However, the range of measured and predicted $T_{\max}$ does not provide a sufficient explanation for the comparability of intensities in the „red“ and „blue“ regions.

These simple considerations have two important corollaries. If one relies on the black body model, (1) the duration of a „red“ flash should be greater than the duration of a „blue“ one, and (2) the intensities of „red“ and „blue“ flashes may differ considerably. In contrast, (1) the durations of continuum pulses measured experimentally at different wavelengths are equal both for a single bubble [2–4] and for a multibubble system (see below), and (2) the continuum intensities measured at different wavelengths (with the spectral sensitivity of instruments taken into account) are comparable, remaining within one order of magnitude of each other. These two contradictions suggest that the black body mechanism should not be applied to SL continuum emission. Note also that an optically transparent bubble should not, according to the Kirchhoff's law, emit anything at all. Plasma emission with its spectrum following the Kramers formula and the pulse duration being governed by ionization and recombination may be a fitting model for the examined continuum.

Color dependence of the PMT response

Let us consider the problem of color dependence of the PMT response. This involves calculating the time of flight of an electron from a photocathode to the first dynode and finding out how this may affect the measurements.

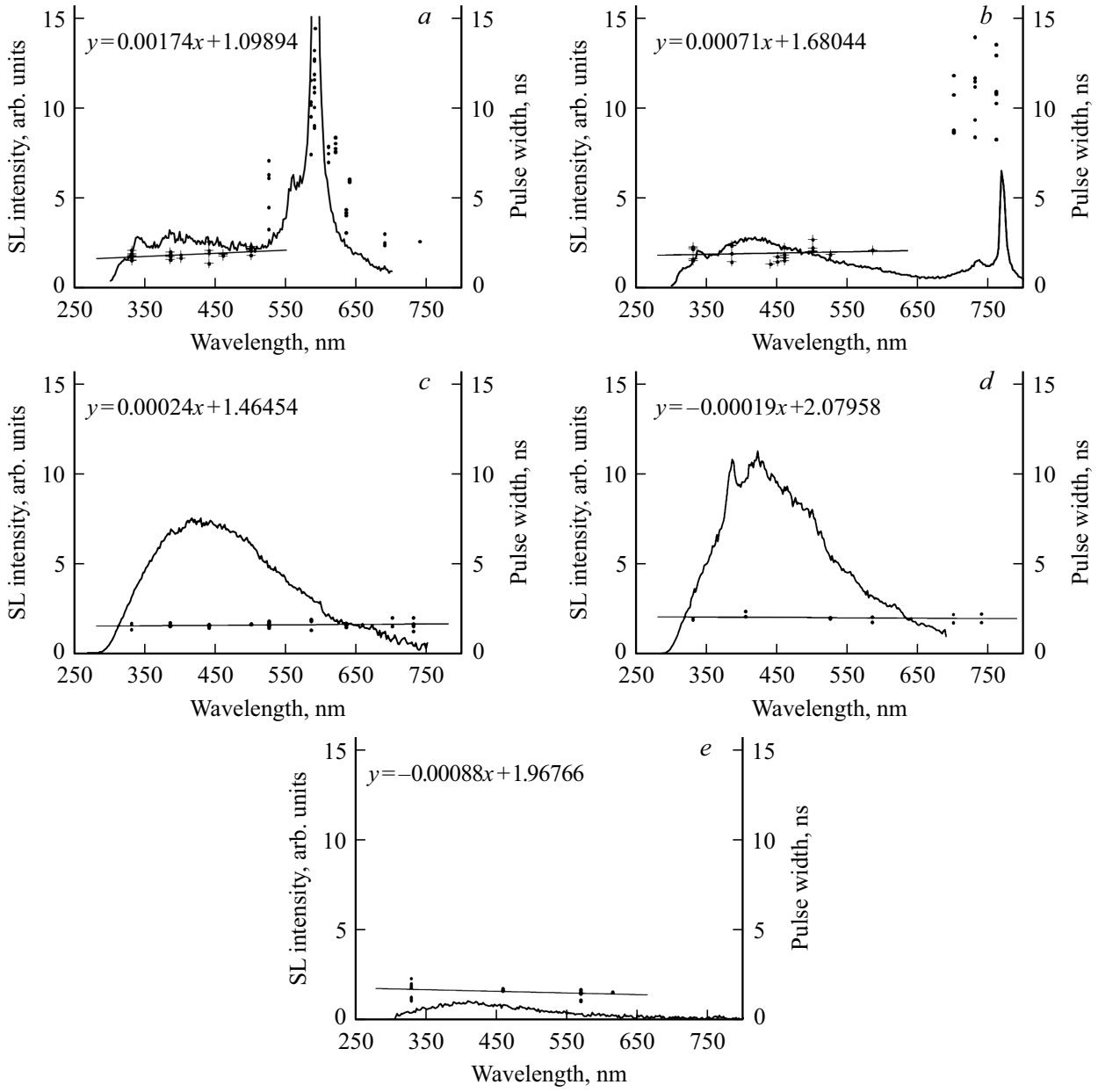

Figure 3. SL spectra without spectral correction (solid curves) and spectra of pulse widths (dots) for 3 M NaCl (*a*), 3 M KCl (*b*), 12 M LiCl (*c*), and 4.5 M $CaCl_2$ (*d*) aqueous solutions and water (*e*). The wavelength coordinates of dots in width spectra correspond to tentative center transmission wavelengths of light filters (in the case of red filters, the PMT limit is taken into account). Linear trends are plotted by points corresponding to SL continuum emission (denoted with crosses in panels *a* and *b*), and their equations are indicated.

The initial velocity imparted to an electron knocked out from the PMT photocathode depends on the energy of an absorbed photon that exceeds the work function. Let us assume that the work function corresponds to the red PMT sensitivity limit (800 nm). Electrons knocked out by photons with $\lambda = 800$ nm and $\lambda = 300$ nm then have an initial velocity of 0 and $\sim 10^6$ m/s, respectively. The distance from the photocathode to the first dynode is set to 1 cm. Elementary calculations yield that an electron moves to the first dynode with a constant acceleration of $\sim 10^{15}$ m/s^2, which is induced by the applied potential difference of ~ 150 V, and reaches it in 2.5 ns. The difference in times of flight from the photocathode to the first dynode for electrons knocked out in the dynode direction by photons with $\lambda = 300$ nm and $\lambda = 800$ nm is ~ 0.4 ns. Therefore, the apparent pulse stretching due to the statistical variability of flight times is ~ 0.2 ns. This effect is negated at the second and subsequent PMT dynodes, since secondary electrons are knocked out by primary ones acquiring an energy that is well above the work function. Thus, the PMT may introduce wavelength-dependent pulse stretching.

Results

Under certain conditions, SL spectra of salt solutions contain intense lines of the corresponding metals. We have already found in [1] that sodium SL pulses in an aqueous solution of NaCl (~ 10 ns) are significantly wider than continuum pulses (~ 2 ns). One light filter isolating the continuum emission region (350−430 nm) and another light filter transmitting mostly the emission of Na in the 590 nm region were used in [1]. Since the aim of the present study was to compare the width of continuum pulses at different wavelengths, narrow spectral bands needed to be isolated. Unfortunately, the low SL intensity made a monochromator useless in this regard. This is the reason why we used a series of 15 light filters with only one of them (an interference filter for 590 nm) having an 11-nm-wide transmission band. The other filters had transmission regions extending for several tens or hundreds of nanometers; each filter had either a transmission peak or (red, orange, and yellow filters) a cutoff wavelength. The width of light pulses corresponded to the entire range isolated by a filter. We picked a certain wavelength close to the transmission peak of a filter and associated it with the obtained SL pulse width. In the case of red light filters that have a cutoff wavelength only, a certain wavelength within the transmission region of a filter was selected with regard to the fact that the red PMT sensitivity limit is around 800 nm. Dependence $W(\lambda)$ of the pulse width on the center transmission wavelength of a filter was obtained this way (dots in Fig. 3). Let us call this dependence a pulse width spectrum.

Since the spectra of salt solutions contain emission lines of metals, the width of pulses in the vicinity of lines in such spectra is specified by a certain combination of the intensity of lines and the continuum. Therefore, the pulse width should vary over the spectral range (see the data for 3 M NaCl and 3 M KCl solutions in Figs. 3, *a, b* for a clear illustration of this). Intense lines make it more difficult to determine the width of continuum pulses. However, the widths of pulses measured at different wavelengths lying far from lines in spectral regions dominated by continuum emission turned out to be identical (within the accuracy of measurements) and equal to $W = 1.8 \pm 0.2$ ns in all the examined salt solutions and water. The same invariability and the same value of W have been observed in [19] in the SL spectra of high-concentrated 12 M LiCl and 4.5 M $CaCl_2$ salt solutions (where metal lines are lacking or very weak for certain reasons). The trend lines of pulse width spectra in these cases were near-horizontal (Figs. 3, *c, d*). The value of W in water spectra also had no wavelength dependence (Fig. 3, *e*).

The slope coefficients of linear trends plotted by points corresponding to the continuum were close to zero. The weighted average of all the obtained trends (with the exception of NaCl) was 0.000063 ns/nm. Thus, the continuum pulse width increases by ~ 0.03 ns within the range from 300 nm to 800 nm. This insignificant growth may be attributed to the above-discussed color dependence of the PMT response. The trend slope for NaCl is more noticeable due to the fact that an intense broadened Na D emission line, which is located in the „red“ half of the spectrum, contributes to the SL continuum spectrum range (Fig. 3, *a*).

Conclusion

The results of measurements with our correlation counter demonstrated that the widths of SL continuum pulses in the examined aqueous salt solutions of various concentrations are approximately the same (1.8 ± 0.2 ns) and have no dependence on wavelength. The indicated value needs to be corrected for the instrument function in order to determine the pulse duration. However, the obtained trends are reproducible. The lack of a wavelength dependence of the width of continuum flashes of multibubble SL, which is similar to single-bubble SL in this regard, is a compelling argument against direct application of the thermal mechanism in the study of SL continuum. The comparability of continuum intensities at different wavelengths also contradicts the thermal mechanism. Molecular emission and/or plasma emission are viable SL continuum mechanisms, since ionization does indeed occur. The dependence of width of flashes on the concentration and the type of salt and the width of flashes of emission lines of different metals will be examined in future studies.

Funding

This was carried out under the state assignment, registration number: AAAA-A20-120021990003-3.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] T.V. Gordeychuk, M.V. Kazachek. Opt. Spectrosc., **128** (10), 1602 (2020). DOI: 10.1134/S0030400X20100124.
[2] B. Gompf, R. Gunter, G. Nick, R. Pecha, W. Eisenmenger. Phys. Rev. Lett., **79** (7), 1405 (1997). DOI: 10.1103/PhysRevLett.79.1405
[3] R.A. Hiller, S.J. Putterman, K.R. Weninger. Phys. Rev. Lett., **80** (5), 1090 (1998). DOI: 10.1103/PhysRevLett.80.1090
[4] M.J. Moran, D. Sweider. Phys. Rev. Lett., **80** (22), 4987 (1998). DOI: 10.1103/PhysRevLett.80.4987
[5] M. Brenner, S. Hilgenfeldt, D. Lohse. Rev. Mod. Phys., **74**, 425 (2002). DOI: 10.1103/RevModPhys.74.425
[6] J. Rooze, E.V. Rebrov, J.C. Schouten, J.T.F. Keurentjes. Ultrason. Sonochem., **20**, 1 (2013). DOI: 10.1016/j.ultsonch.2012.04.013
[7] K. Yasui. Phys. Rev. Lett., (**83** (21), 4297 (1999). DOI: 10.1103/PhysRevLett.83.4297
[8] Y.T. Didenko, T.V. Gordeychuk. Phys. Rev. Lett., **84** (21), 5640 (2000). DOI: 10.1103/PhysRevLett.84.5640

[9] Y.T. Didenko, W.B. McNamara III, K.S. Suslick. Phys. Rev. Lett., **84** (4), 777 (2000). DOI: 10.1103/PhysRevLett.84.777
[10] V.Q. Vuong, A.J. Szeri. Phys. Fluids, **8** (9), 2354 (1996). DOI: 10.1063/1.869131
[11] J. Schwinger. In: Proc. Natl. Acad. Sci. USA, **90**, 958 (1993).
[12] W.C. Moss, D.A. Young, J.A. Harte, J.L. Levatin, B.F. Rozsnyai, G.B. Zimmerman, I.H. Zimmerman. Phys. Rev. E, **59**, 2986 (1999). DOI: 10.1103/PhysRevE.59.2986
[13] S. Hilgenfeldt, S. Grossmann, D. Lohse. Nature (London), **398**, 402 (1999). DOI: 10.1038/18842
[14] D.J. Flannigan, K.S. Suslick. Phys. Rev. Lett., **95**, 044301 (2005). DOI: 10.1103/PhysRevLett.95.044301
[15] T.V. Gordeychuk, M.V. Kazachek. Photonics Russ., **17** (1), 72 (2023). DOI: 10.22184/1993-7296.FRos.2023.17.1.72.76.
[16] M.V. Kazachek, T.V. Gordeychuk. Tech. Phys. Lett., **46** (3), 263 (2020). DOI: 10.1134/S1063785020030232.
[17] M.V. Kazachek, T.V. Gordeychuk. Instrum. Exp. Tech., **62** (1), 26 (2019).
DOI: 10.1134/S0020441219010081.
[18] I. Ko, H.-Y. Kwak. J. Phys. Soc. Jap., **79** (12), 124401 (2010). DOI: 10.1143/JPSJ.79.124401
[19] T.V. Gordeychuk, M.V. Kazachek. Russ. J. Phys. Chem., **97** (5), 902 (2023).
DOI: 10.1134/S0036024423050102.

Translated by D.Safin