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Time delays of alkali-metal atomic line flashes relative to spectral continuum flashes during multibubble sonoluminescence

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Flashes of alkali metal atomic lines during multibubble sonoluminescence are 10 ns in duration, while continuum flashes are less than 1 ns long. Using time-correlated photon counting, we have established that both processes occur almost synchronously with a delay in the intensity maxima of atomic line flashes relative to those of continuum flashes. The delay increases in sequence Na (589 nm), Li (670 nm), K (767 nm), Rb (780 nm from 0.1 to 0.8 ns, which correlates with a decrease in the excitation energy of the metal spectral line. The results confirm interrelation between the processes of the continuum and atomic lines emission. Temporal features of the continuum flashes are also discussed.

Keywords: multibubble sonoluminescence, alkali metals, flash duration, flash sequence, correlation method.

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Sonoluminescence (SL) arises under nonlinear pulsations of cavitation bubbles generated in liquid by ultrasound. This phenomenon combines different time scales: from microsecond bubble oscillations to picosecond light flashes. SL spectra include a continuum caused by high-energy processes taking place during the bubble collapse. Duration of the continuum emission is 0.25 ns [1], which corresponds to the phase of maximum compression and peak temperatures. Alkali-metal atomic lines observed against the continuum in the SL spectra of their salts' solutions are formed due to getting of metal ions/atoms in the bubble, e. g. with solution nanodroplets during the bubble surface deformation („injection model" [2]). Atoms may be excited at the temperatures lower than the peak ones. SL emission of atoms is longer; its duration increases with increasing atomic number and ranges from 5 to 40 ns [3]. Thus, the results of our studies have shown that the metal flash starts prior to the continuum flash and terminates after it. The mechanism for this behavior is unclear, as well as the reason for the revealed increase in flash duration with increasing atomic number of the metal.

The measurements were performed by the time-correlation method with the correlation counter described previously [3]. Under the multibubble SL, each collapsing bubble generates up to $\sim 10^4$ photons per flash. Due to restrictions imposed by the observation aperture and photocathode quantum efficiency, the counter detects a few single photons per flash. Detection of a small number of photons provides a more correct shape of the resulting correlation function (CF) than that in the case of a large pulse flow. Measurements of auto-correlations allow estimation of the flash duration by using Gaussian approximation of the correlation function.

The paper makes an emphasis on measuring cross-correlations whose analysis allows estimation of relative time shifts between different spectral components (metal lines and continuum). If different processes produce flashes at different wavelengths, they may be easily spectrally separated by using light filters or monochromator. If the processes correlate with each other, this will manifest itself in the obtained cross-correlation functions. The key technique consisted in measuring and comparing two CFs obtained in exchanging light signals entering two correlation counter channels [4]. Since the metal line occupies a narrow spectral range while the continuum covers the entire spectrum, the continuum contribution to the region isolated by the filter for the metal line distorts the correlation function. To correctly account for this effect, the two-Gaussian approximation was used.

The measurement accuracy depended on the following factors: hardware-induced errors (noise); digital errors due to the stepwise digitization of the signal; color effect of photomultiplier tubes (PMT) when the red photon induces a pulse later than the blue one, which results in an increase in the CF width due to scattering of the electron time-of-flight; dispersion of light in water. Estimation of the dispersion influence based on the water refractive indices for the red (1.33) and blue (1.34) light and optical path length (the distance from the emitter end to the cell output window is 10 cm) gave the delay of -0.003 ns (blue photons arrive later than red ones); this difference is insignificant. Accumulation of 100 correlations provides the accuracy of determining the correlation function peak position of 0.5 ns and that of determining the function width of 1.3 ns; for 1000 correlations, the respective values are 0.1 and 0.25 ns.

As the test objects, 3 M aqueous solutions of Na, Li, K, and Rb chlorides saturated with argon were used.

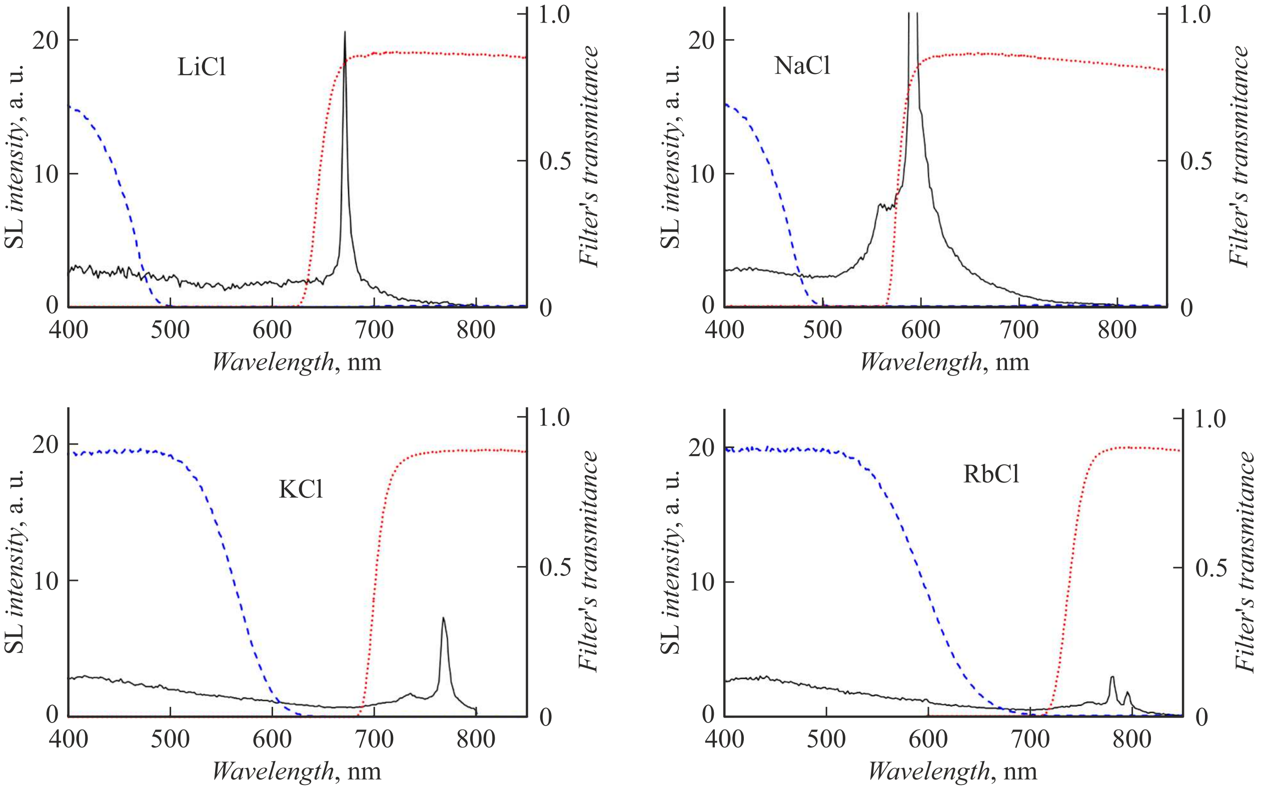

Figure 1. SL spectra of the Na, Li, K, and Rb 3M chlorides and transmission spectra of light filters. Solid lines represent SL spectra of metal chlorides. Dashed and dotted lines are transmission spectra of the filters used to isolate the respective spectral ranges during the correlation measurements.

The ultrasound frequency was 20 Hz. A detailed description of the experimental setup and measurement procedure is given in [3]. Signals were recorded with oscilloscope RIGOL MSO8104 in the delay measurement mode with the digitization step of 0.005 ns. The SL spectra and light-filter transmission spectra are shown in Fig. 1. In all the cases, one filter isolated only the continuum, while the other isolated predominantly the metal line.

The relative delay between flashes of different SL components was calculated by a technique similar to that described in [4]. Fig. 2 presents cross-correlation functions for the KCl solution sonoluminescence. The experiment configuration is as follows: in the first correlation counter channel there was installed a filter transmitting the metal line (K), while in the second channel there was a filter transmitting only a part of the continuum spectrum (2430 accumulated correlations, Fig. 2, *a*); filters were exchanged between the channels (3967 accumulated correlations, Fig. 2, *b*). The Gaussian approximation does not convey the cross-correlation function (CF) shape because CF consists of two components: the narrow and broad ones. The narrow-component width is equal to that of the continuum flash obtained by the autocorrelation method because the continuum transmits only partly through both filters. The broad component gets formed due to convolution of the metal and continuum flashes. The analysis was performed by using the two-Gaussian approximation in which the narrow component width was fixed at 1.7 ns, while for the broad component values of 8.3 and 8.6 ns were obtained (Fig. 2, *a*, *b*). The results in Fig. 2, *a* show the broad component is located to the left of the narrow one, while in Fig. 2, *b* — to the right. The relative delay between the metal and continuum flashes was calculated as half the difference in the positions of the broad component centers in Figs. 2, *b* and *a*. In this case, the delay appeared to be 0.66 ns.

Insets to Figs. 2, *a* and *b* present curves simulating relative probability of the photon arrival during the flashes fed to the correlation counter inputs (the preset shift is $\sim$ 15 ns). The models are selected so that, being integrated, they reproduce the correlation functions shown in Figs. 2, *a* and *b*, respectively. The fitting parameter is the continuum brightness fraction in one of the input signals: 0.08 for Fig. 2, *a* and 0.41 for Fig. 2, *b*. The difference in those fractions may be associated with differences in the SL visible zones, photocathode spectral properties. The simulation showed that the CF shape depends on the ratio between the narrow and broad components but not on the signal amplitude. Even a small fraction of the continuum brightness getting in the metal line signal distorts the correlation function because of short duration of the continuum flash. This may hinder measurement of the duration and delay of emission from such elements as calcium whose spectral lines are poorly visible against the bright SL continuum.

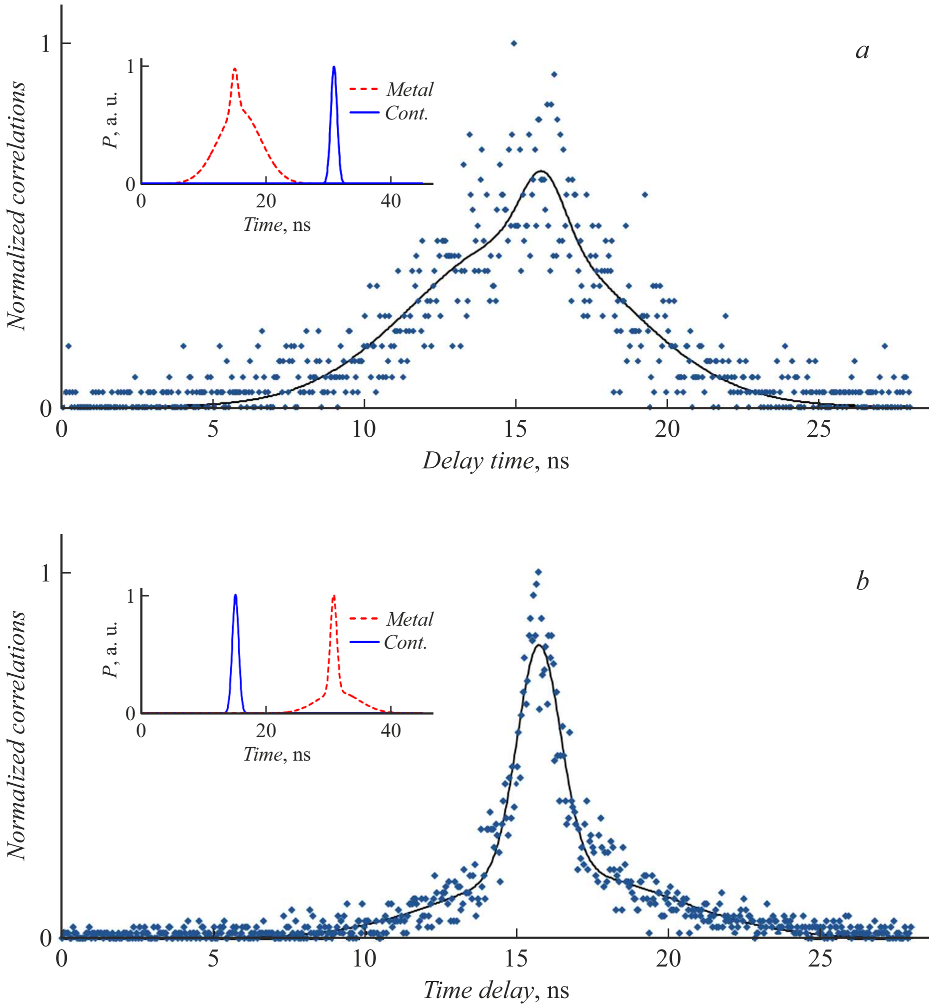

Figure 2. Cross-correlations (dots) under the 3M KCl sonoluminescence and two-Gaussian approximations (lines). *a* — potassium—continuum, *b* — continuum—potassium. The insets present simulated flashes at the correlation counter inputs; here *P* is relative probability of the photon detection during the flash.

Durations and relative delays of metal flashes under SL

Parameter	Spectral line			
	Na (589 nm)	Li (670 nm)	K (767 nm)	Rb (780 nm)
Metal atomic mass, g/mol	23.0	6.94	39.1	85.5
Spectral line excitation energy, eV	2.11	1.85	1.62	1.59
Number of accumulated correlations	5570	6698	11345	5898
Cross-correlation width, ns	9.04	8.36	8.68	9.81
Autocorrelation width, ns	9.02	8.62	11.6	14.5
Delay after continuum, ns	0.10*	0.37	0.64	0.80

*In the case of Na, the data should be supplemented by the delay of 0.21 ns obtained in [3].

Similar cross-correlation functions were obtained for SL of each alkali metal solution. In each case, a two-Gaussian approximation was performed; the metal luminescence delay with respect to continuum was determined from the shift of the broad component. The metal flash duration was determined as the full width at half maximum of the cross-correlation function broad component and, in addition, by autocorrelation measurements. The results are listed in the Table.

As a result, an increase in the metal flash center delay with respect to the continuum flash center is observed in the Na < Li < K < Rb sequence. The delay increase

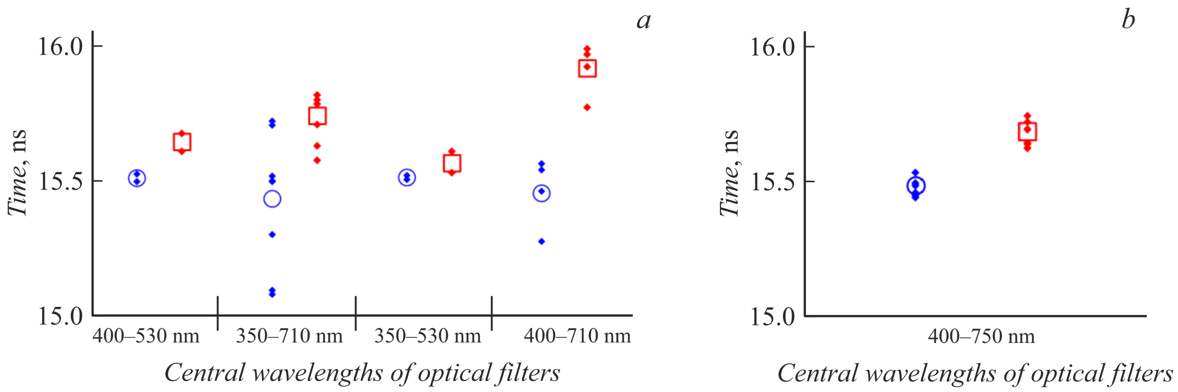

Figure 3. Time positions of the correlation function peaks for different light filters used in the correlation counter channels for water (*a*) and 12 M LiCl (*b*). Dots represent data of individual measurements, symbols demonstrate averaged values: circles — „red" filter in the first channel, „blue" filter in the second channel; squares — „blue" filter in the first channel, „red" filter in the second channel.

correlates better with a decrease in excitation energy of the metal spectral line than with an increase in the metal atomic mass. This may be associated with time asymmetry of bubble heating and cooling: heating is faster, cooling is slower. Particles with lower energy are expected to follow this asymmetry for a longer time. The metal flash duration correlates better with the metal atomic mass [3]. The mechanism of metal atoms excitation in reactions with the H and OH radicals [5] may also play an important role in understanding the obtained results, since these radicals get formed at the short hot phase of collapse and may be retained in the bubble until the next collapse. Replenishment of the number of radicals at the moments of collapse may be a source of the revealed delay of metal flashes with respect to those in continuum.

Let us dwell on the PMT color effect, since emission of metal atoms lies in the red spectrum range, while that of continuum lies in the blue range. In [6] we have estimated the difference in the time of electron arrival from the photocathode at the first dynode (0.4 ns at wavelengths of 300 and 800 nm) and respective increase in the time dispersion (0.2 ns). The increase in the measured flash width should comply with the increase in arrival time spread; the increase in the measured delay should match the difference in arrival times. If the continuum flash is synchronous over the entire spectrum range, then the delay at different wavelengths should match only the difference in the time of electron arrival at PMT. Estimates, as well as measurements, have errors; however, the measurement error may be contributed by the SL effects. As shown by data obtained by the streak camera method, in the case of single-bubble SL in sulfuric acid the continuum spectral peak shifts from the red range to the blue one by ~ 5 ns [7]. Our measurements performed in solutions exhibiting continuum-dominated spectra (water and 12 M LiCl solution) showed that the red continuum flash follows the blue one with the delay of ~ 0.1 ns. The CF peaks' time positions at different wavelengths are shown for these fluids in Fig. 3. Each graph point was obtained by analyzing ~ 500 correlations.

The delay was determined as half the difference in the CF peak positions. Though the delays are visible against the scattered experimental data, the difference in them for the two studied fluids is insignificant. The average delay normalized to $\Delta\lambda = 500$ nm is 0.23 ns for water and 0.14 ns for LiCl solution. If the effect depends on the experimental conditions, e. g. on the fluid composition, then it should be attributed to the SL nature; otherwise, it should be related to the measuring devices, namely to the PMT color effect. Comparing the data given in the Table and Fig. 3, we can see that, even if the color effect does contribute to the increase in the continuum–metal flashes delay with increasing atomic line wavelength, this effect is insignificant. Since the metal emission in all the cases lies in the red spectrum range while the blue SL spectrum range is for the continuum, the measured delay values should be reduced by 0.1 ns.

Delays in the Li, K and Rb atoms' flashes relative to the continuum flash (maximum intensity of the metal atom flash after the continuum flash maximum) were measured under sonoluminescence for the first time. The delays were found to increase in the Na < Li < K < Rb sequence from 0.1 to 0.8 ns following the decrease in excitation energy of the metal spectral line. In addition, the delay of the red-spectrum continuum flash with respect to that in the blue range was estimated and appeared to be 0.23 ns at $\Delta\lambda = 500$ nm for water and 0.14 ns for the concentrated LiCl solution.

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Conflict of interests

The authors declare that they have no conflict of interests.

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