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Atomic Sodium Sonoluminescence Features during Bubble Collapse in a Cavitation Cloud by Time-Correlated Single Photon Counting

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Abstract—The pulse width of multibubble sonoluminescence flashes in an aqueous NaCl solution was measured by a correlation method for the spectral range of 300–800 nm. The flash pulse width had a maximum value of 21 ns in the spectral region adjacent immediately to the Na *D*-line peak (589 nm) and decreased to 2 ns with distance from the line peak. The measured dependence of the flash pulse width on the wavelength agreed with the dynamic Na line shape model proposed by us earlier, where the spectral line width and shift were governed by a fast change in the emitting medium density during bubble collapse. Using the correlation method, the sequence of metal and continuum flashes was determined to measure the relative delay between them. The results showed that Na emission takes a longer time as compared to continuum emission and occurred almost symmetrically in time around a continuum flash with a vanishingly small delay of 0.21 ns after the continuum flash. Using the same method for a $CeCl_3$ solution, a cerium line flash (350 nm) was revealed to occur after a continuum flash with a delay of 31 ns close to the Ce emission lifetime of 33 ns to be indicative of essential distinction between the mechanisms of Na and Ce emission under multibubble sonoluminescence.

Keywords: ultrasonic cavitation, sonoluminescence, optical spectra, flash pulse width, time-correlation method, Na, Ce

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INTRODUCTION

Sonoluminescence (SL) as a weak emission from liquids in an ultrasonic field is a multifactorial phenomenon associated with the ability of a cavitation bubble to concentrate sound energy up to 12 orders of magnitude. SL is manifested as a series of ultrashort flashes from the excited states of particles of different kind (atoms, molecules, ions) under nearly adiabatic collapse of bubbles. The pulse width and phase of separate SL components and the sequence of their emission are important for studying the formation mechanisms these excited states, which are still unclear in many respects. There are a number of papers listed in [1] on the flash pulse width under stable single-bubble SL. However, due to the broad recognition of ultrasonic technologies, of applied importance are multibubble systems when the collapse of individual bubbles is not correlated in time and space to complicate the above-listed data acquisition. We know of only one paper where the time-correlated single photon counting was used to determine the flash pulse width under multibubble SL of water [2]. The time-correlation method developed by us makes it possible to estimate the pulse width and sequence of photon pulses from SL spectrum components and the time shift between them by separating the pulses from a statistically average bubble from the total photon flux [1, 3–5].

In this paper, we have traced the evolution of emission from the Na *D*-line and the relation between the metal and continuum emission phases under SL from an aqueous NaCl solution. For comparison, the Ce line flash width and its delay after a continuum flash under SL from an aqueous $CeCl_3$ solution was studied.

EXPERIMENTAL

The scheme and method of the experiment are detailed in [1, 3, 4]. Solutions of 2–4 M NaCl (chemically pure grade) and 0.1 M $CeCl_3$ (pure grade) in distilled water were saturated with argon in a temperature-controlled flow cell for 1.5 h before and during the experiment. The ultrasound source was a Sonics VC750 generator with a frequency of 20 kHz and an output power of 20 W. The solution temperature was maintained at 10 ± 1°C with a Julabo F12 temperature control system. SL spectra were recorded with an MDR-23 monochromator with a resolution of 3 nm without correction for spectral sensitivity of the photomultiplier + grating system at a diffraction grating blaze maximum of 500 nm. A FEU-79 photomultiplier tube (PMT) with a sensitivity range of 300–830 nm was

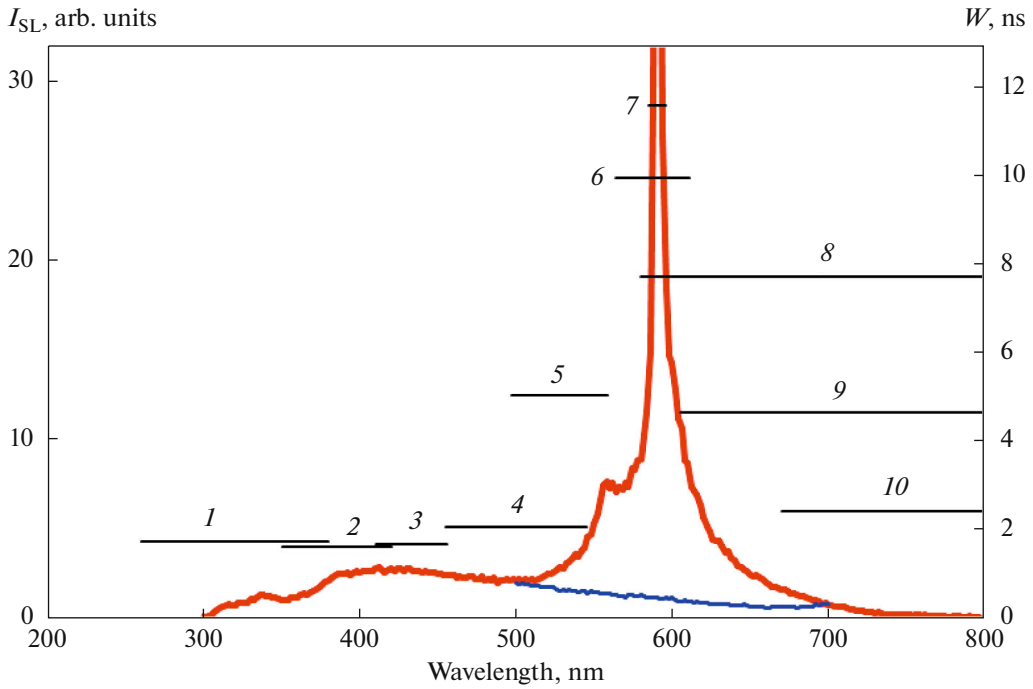

Fig. 1. SL spectrum of aqueous 3 M NaCl solution (solid line) and flash pulse width measured with ten different light filters. Wavelength range where the light filter transmission is more than 50% from maximum corresponds to location of intercept (*1*–*10*) along wavelength axis, and flash pulse width within the respective interval corresponds to the location of this intercept along axis *W*. Transmission spectra of filters are omitted to simplify the figure. SL spectrum is cut off on intensity scale for clarity. Fragment of SL spectrum of 3 M KCl solution (thin line) was used in calculations as continuum spectrum from 500 to 700 nm.

used. The flash pulse width and the delay between flashes of different type were measured by the correlation counter constructed on the basis of two PMTs operated in the photon counting mode, a RIGOL DS1104 digital oscilloscope and a computer [3, 5]. The correlation method is highly suitable for measuring the flashes of bubbles in a cloud, as they occur almost independently due to location and size spread. In this case, the correlation method gives the average pulse width with an average delay. The flash pulse width W was measured in the self-correlation mode when two PMTs received the emission passed through the same light filer. The width W was calculated by approximating the correlation peak with a Gaussian curve as the full width at half-maximum (FWHM). In some cases, dual Gaussian approximation was used as a sum of two Gaussian curves to separate the peaks. The required wavelength range was isolated by using broadband light filters or a monochromator and, in addition, a BP589 narrowband filter was used. The true flash pulse width can be estimated from measured W with consideration for the corrections introduced by each PMT and oscilloscope digitization circuits [5]. The pulse delay was measured in the correlation mode with installation of different light filters before two PMTs with further switching of their positions [1].

NA *D*-LINE

The Na line in SL spectra has a complicated structure as compared to the spectrum in flame. The line is strongly broadened, shifted to the red region, and has satellites (Fig. 1). The broad peak at ~560 nm from emission of excimer NaAr* molecules in the gas phase is called a blue satellite [6]. The broadened line part extended into the red region is called a red satellite. In high-resolution SL spectra against the broadened line background under certain experimental conditions, it is possible to observe narrow unshifted Na doublet peaks—lines at 589 and 589.6 nm, which are possible only from a low-density medium, so their appearance in the SL spectra is not distinct. The total spectral width of the Na line together with the satellites in the spectral region where the line brightness essentially differs from the brightness of the continuum is 200 nm and spans the range of 500–700 nm. The measured W values in different spectral ranges are shown in Fig. 1.

The dependence of the SL flash pulse width on the Na line brightness fraction cut off by the light filter in Fig. 2 seems more informative to us. Each light filter transmitted some continuum and metal line fractions, and the sum of fractions was taken as 1. In this case, each filter can cover different emission regions in the Na line and its red and blue satellites. The flash pulse width W concerned the entire range cut off by a filter. The weighted average Na brightness fraction s trans-

mitted by each light filter was calculated from its transmission spectrum $T(\lambda)$, the NaCl solution SL spectrum $N(\lambda)$ containing the Na line and continuum, and the aqueous solution SL spectrum $K(\lambda)$, which had only the continuum in the region of 500–700 nm, by the formula $s = \Sigma\{T(\lambda)(N(\lambda)-K(\lambda))\}/\Sigma\{T(\lambda)N(\lambda)\}$, where summation was carried out over the wavelength λ with a step of 1 nm. For the light filters cutting the spectral regions, which do not cover the spectral range of the broad Na line (filters *1–3* in Fig. 1), W found by the correlation method attained ~2 ns and corresponded to the continuum flash pulse width, as found by us earlier, constant throughout the entire observed SL range [7]. The earlier estimated Na flash pulse width was ~10 ns [1]. Therefore, for the light filters transmitting both types of radiation (Na and continuum), a certain dependence of W on s should be expected. In the assumption of simultaneous emission from the line and satellites, modeling of W by a single Gaussian approximation with a curve comprising the sum of two Gaussian curves with widths of 2 and 10 ns gives the dependence of W on the broad Gaussian curve fraction s_g, which is shown in the inset to Fig. 2.

However, the results of Fig. 2 show that W quickly grows when s tends to 1. This casts doubts on the hypothesis about the synchronous flash of all the Na line components. The three right upper points in Fig. 2 (marked with circles) correspond to the BP589 narrowband filter (bandwidth, 11 nm; $W = 11.7$ ns) and the bands of 6 and 3 nm cut off by the monochromator around the wavelength of 589 nm ($W = 14.3$ ns, $W =$ 21 ns). Due to such a rapid growth in W, it may be expected that the central part of the Na line near 589 nm will have $W > 21$ ns. When the light filter transmits the peripheral part of the Na line (filters *4–5* and *9–10* in Fig. 1), W is much lower. Such a result is in remarkable agreement with our model, according to which the spectral Na line is broadened during bubble collapse and shifted by a varied inert gas (in our case, argon) density [8]. Peak medium pressure, density, and temperature values are attained in a bubble in much shorter time intervals as compared to lower pressure, density, and temperature values, which are still suitable for Na emission [1]. At the lowest medium densities close to the normal value (1 amg), the narrow unshifted Na line can be highlighted at 589 nm. For convenience, we discuss the density in Amagat units: 1 amg $= 2.6868\times10^{-19}$ cm^{-3} at normal temperature and pressure.

Under these experimental conditions, it is not possible to resolve the Na D-line doublet components at 589.0 and 589.6 nm and measure the pulse width of their flashes. The contribution of emission from the narrow components to the total brightness of the broadened Na line, being found from the line shape under SL, attains 5%, and the emitting medium density above 10 amg broadens them such that the doublet becomes unresolvable [8]. The fact of observing the narrow unshifted doublet peaks in the SL spectra can now be clarified by the experimental result that the Na flash time of ~21 ns proves to be comparable and may exceed the time of ~20 ns, for which a bubble exists in an adiabatic compression state [9].

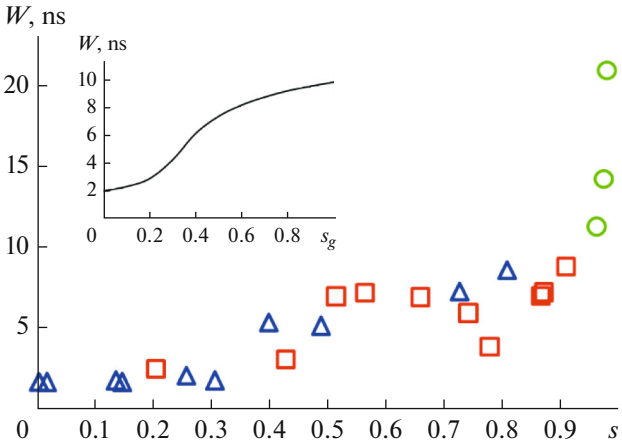

Fig. 2. Flash pulse width W versus weighted average Na line brightness fraction s for light filters cutting both continuum and, partially, Na line from SL spectral range in spectra of aqueous 3 M and 4 M NaCl solutions. Measurements by narrowband filter and monochromator near Na line center (circles), filters on short-wavelength side from Na line (triangles), and filters on long-wavelength side (squares). Inset: model dependence of W on the broad component fraction s_g in sum of two Gaussian curves.

The distribution of points corresponding to long-wave and short-wave filters (respectively, squares and triangles in Fig. 2) indicates that the blue satellite flash has the same time regularities as the red satellite flash: the line is synchronously broadened to both directions.

SEQUENCE OF METAL AND CONTINUUM FLASHES

It is of interest to clarify the existence and value of the delay between Na and continuum flashes, preliminarily estimated in [1] as 0.5 ns. To compare the specific features of emission from different metals, an aqueous 0.1 M $CeCl_3$ solution was studied. Cerium is interesting in that, in addition to the characteristic continuum, the luminescent band of the Ce^{3+} ion with a maximum at 350 nm and a lifetime of 33 ns for luminescence emitted from a solution is observed in the SL spectrum of an aqueous solution of its chloride [10]. The water SL spectra and $CeCl_3$ SL and luminescence spectra are shown in Fig. 3. The photon correlation spectra (quantization time, 2 ns) under SL in Ce- and Na-containing solutions are shown in Fig. 4. The photon correlation spectra measured by using the time resolution improvement procedure [5] for the case of Na are given in Fig. 5, and the effective quantization time is 0.5 ns.

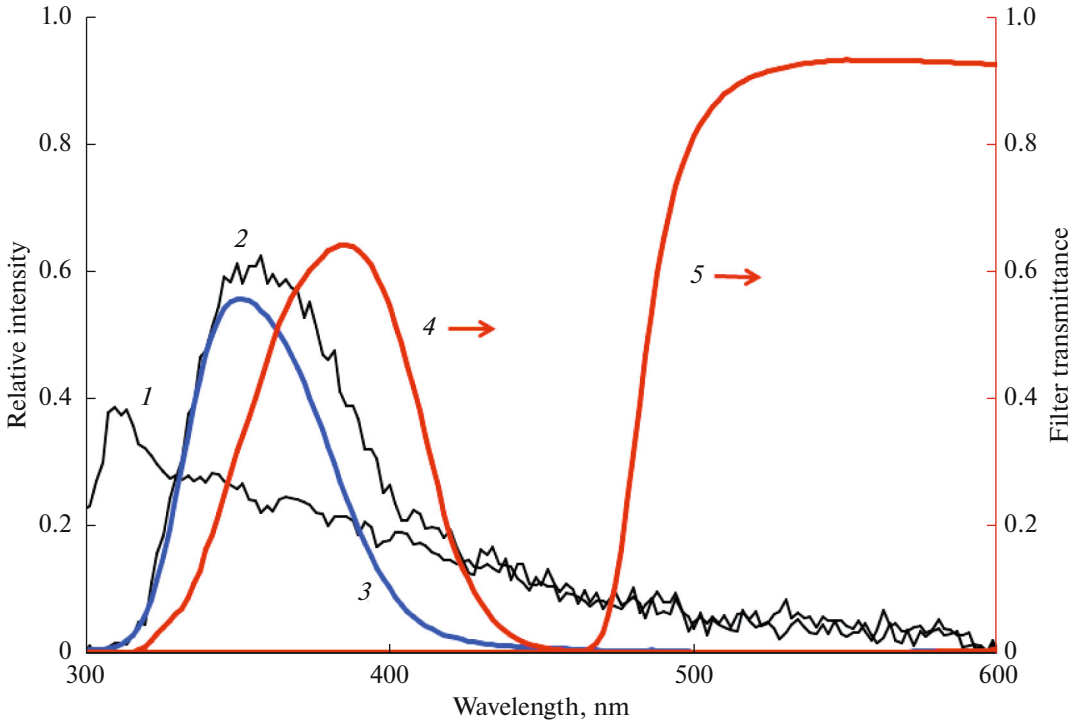

Fig. 3. SL spectra of (*1*) water and (*2*) 0.1 M $CeCl_3$, luminescence spectra of (*3*) 0.1 M $CeCl_3$, and transmission spectra of (*4*) violet and (*5*) yellow light filters.

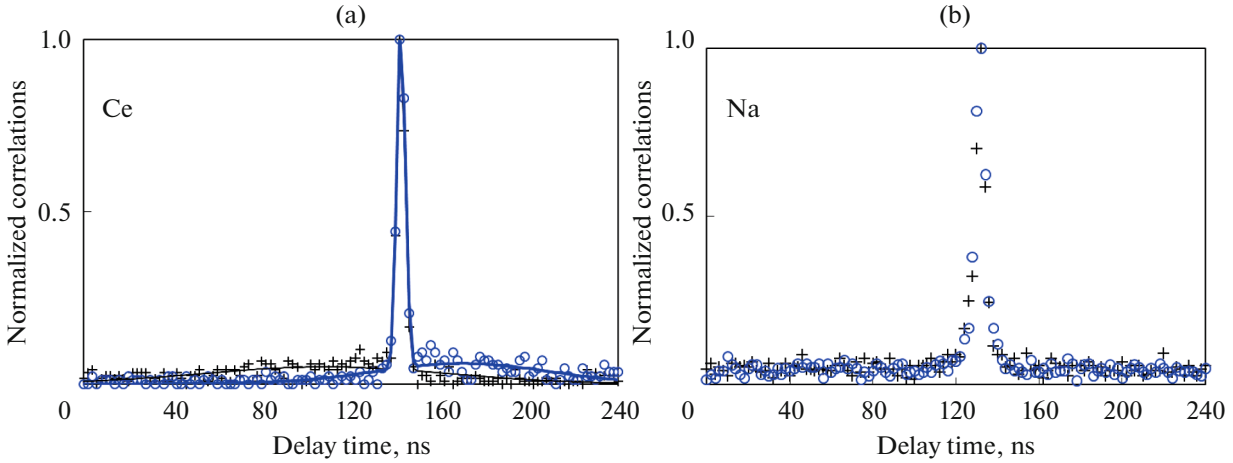

Fig. 4.(a) Photon correlation spectra (crosses, circles) and their dual Gaussian approximations (curves) for sonoluminescence in a 0.1 M $CeCl_3$ solution and (b) photon correlation spectra for sonoluminescence in a 2 M NaCl solution. Circles and solid line, "continuum–metal" correlations; crosses and thin line, "metal–continuum" correlations.

The continuum–metal and metal–continuum photon correlation spectra under SL in aqueous NaCl and $CeCl_3$ solutions were measured by installing different light filters in two pulse detection channels with further switching of their positions. The light filters used for the NaCl solution were orange (curve *8*, Fig. 1) with transmission fractions of 0.87 for Na and 0.13 for the continuum and blue (curve *2*, Fig. 1), which transmitted only the continuum in the region of 350–460 nm. For the $CeCl_3$ solution, they were violet (curve *4*, Fig. 3) with transmission fractions of 0.52 for Ce and 0.48 for the continuum and yellow (curve *5*, Fig. 3), which transmitted only the continuum in the region of 500–800 nm. The transmission fractions were found by calculation from the transmission curves of the filters and the SL spectra of the solutions. Therefore, one of the light filters transmitted only the continuum, and the other predominantly transmitted the metal line. We

called the obtained correlations "continuum–metal" when the continuum transmitting filter was installed in the first channel of the correlation counter and "metal–continuum" when such a filter was in the second channel. When the positions of the "continuum–metal" and "metal–continuum" spectral channels are switched, the relative shifts in time have opposite signs, so the shift between the peaks of photon correlation spectra correspond to the doubled delay between the photon pulses of different types [1].

The photon correlation spectra can be seen to have the components: narrow W_1 and broad W_2, which can be resolved by dual Gaussian approximation. The narrow peak is attributed to continuum flashes. It is present in the correlation spectra, as the continuum is partially transmitted by both filters and both channels and must have the same width as the pulse width of a continuum flash found from the self-correlation spectra. The broad correlation peak is related with metal flashes. Its width is caused by the convolution of metal and continuum flashes. The dual Gaussian approximations of photon correlation spectra are shown with solid lines in Figs. 4a and 5, and the full width at half-maximum (FWHM) was calculated for each Gaussian curve components: narrow W_1 and broad W_2. In the case of Na (Fig. 5), $W_1 = 1.8$ ns and $W_2 = 7.2$ ns were fixed (the values found from self-correlation spectra were used), and their amplitudes and shifts along the axes correlations and times were varied. The broad Na component is invisible in Fig. 4b due to the time axis scale. In the case of Ce (Fig. 4a), no shift along the axis of correlations was introduced, and $W_1 = 4.3$ ns and $W_2 = 110$ ns were obtained.

The delay between continuum and metal flashes, if it exists, is equal to a half the time shift between the broad peaks. In the case of Ce, the time shift of 62 ns is well visible, whence we obtain the average delay of 31 ns between Ce and continuum flashes. In the case of Na, this shift is small to be at time resolution limit, and the delay estimate is ~0.21 ns. The sequence of metal and continuum flashes is determined from the order in which the correlation peaks follow each other. In the case shown in Fig. 4a, the continuum flashes much earlier than Ce, and in the case of Fig. 5, the continuum flashes a bit earlier than Na.

Let us compare the cases of Ce and Na. Bubbles flash to give a broadband continuum with a pulse width less than 1 ns in both cases [2, 7]. Ce gives ordinary luminescence [10], but the matter for Na is still unclear. The line at 350 nm ($5d \rightarrow 4f$ transition) is attributed to Ce^{3+} ions present in the solution surrounding the flashing bubbles. The ions are excited by short-wave SL continuum flashes and highlighted according to the natural excited state lifetime of 33 ns [10, 11], which is very close to the delay of 31 ns measured here. Flashes occur by a descending exponent, so the application of Gaussian approximation to the broad peak is not quite correct here, but only estimative. From the correlation spectra, it is possible to obtain the luminescence quenching curve [11]. The mutual arrangement of the continuum–cerium and cerium–continuum correlations (Fig. 4a) shows a correct sequence of flashes: first, a bubble flashes and, later, cerium. This is the case of classic luminescence.

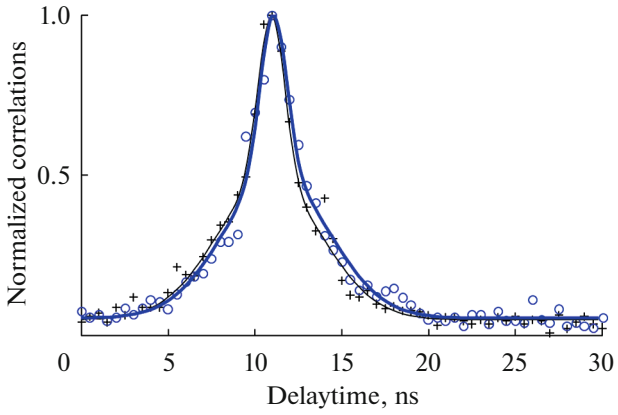

Fig. 5. Detailed photon correlation spectra and their dual Gaussian approximations for sonoluminescence in a 2 M NaCl solution. Circles and solid line, "continuum–metal" correlations; crosses and thin line, "metal–continuum" correlations.

The line at 589 nm is a neutral Na atom line ($3p \rightarrow 3s$ transition). In solution, the metal exists in the form of Na^+ and cannot emit the line at 589 nm. It is presumed that Na enters a bubble together with nanodroplets of solution, where salt molecules sustain homolytic dissociation with the further excitation of a neutral atom [12]. The lifetime of the excited Na state (17.5 ns) is of the same order as for Ce and, if Na flashed by the same mechanism as for Ce, the correlation pattern would be similar. The measured pulse width found for Na flashes for SL from self-correlation spectra is ~10 ns (depending on the wavelength), and the measured delay of 0.21 ns is much shorter than the excited state lifetime. Hence, Na emission occurs on average at the same time as for the continuum, but is more prolonged and surrounds the continuum flash symmetrically in time.

It is customary to classify cavitation bubbles into sonoluminescent (emit the SL continuum) and chemiluminescent (responsible for lines and bands in spectra) [12, 13], but it follows from the results that bubbles exist that yield both types of emission [1]. The conclusion about a synchronous character of Na and continuum flashes concerns such bubbles. In precisely these bubbles, the correlation between metal and continuum flashes can be given by two components in the Na correlation spectrum. If the bubbles could be undoubtedly classified into two types and flash independently from each other, no broad component would be observed in the correlation spectra in Fig. 5 at all. Analysis of the distribution of the number of

correlations in terms of the delay times makes it possible to estimate the number of bubbles belonging to different types, such as sonoluminescent, chemiluminescent, and mixed [4]. According to the method [4], the number of bubbles that flash for the period of ultrasound to give only the continuum, only Na, and both types of emission in SL spectra is approximately 100, 150, and 200, respectively.

DISCUSSION

Let us consider the possible Na emission mechanisms in the context of the pulse width and delay of flashes. The chemical reactions of recombination between radicals were proposed as an excitation mechanism for Na atoms under SL [6]. In this case, the pulse width of a Na flash must be much longer than the observed one, as the lifetime of radicals is several microseconds [14]. Inelastic collisions with neutral particles may lead to transitions into excited states, but these processes must be accompanied by nearly equiprobable reverse transitions (the radiationless deactivation of an excited state). Inelastic collisions with ions must give a very short excitation time and a low flash probability, as the phase of ionization in a bubble is short in time. Resonant continuum excitation by light with a wavelength of 589 nm is also lowly probable, as continuum emission at 589 nm is weak, short in time, and cannot explain the observed Na line intensity and flash pulse width. The electrical discharge hypothesis implies flashes at the bubble expansion phase due to the formation of zeta-potentials [15]. In this case, the continuum must coincide with Na emission in time, but the Na line should not have any broad satellites, and only narrow components should be observed in the doublet. Some other SL mechanisms were also considered [16]. In all the cases, there must be a delay between Na excitation and emission, which depends on the lifetime of its excited state. This delay may decrease if there is an efficient channel of quenching for the excited state. Indeed, free sodium atoms are chemically active and must be bonded immediately after their appearance. The time of chemical reactions (the time for which atoms move along the reaction coordinate) is several picoseconds. The "continuum–Na" delay of ~0.21 ns measured here may mean the time for which excited Na states are deactivated due to collisions or chemical bonding. In the case of cerium, the excited states of its ions in a solution are subjected only to their own lifetime of ~33 ns without any other quenching channels. Therefore, in addition to the excitation and quenching mechanisms, the mechanism of the generation and preservation of free Na atoms in all bubble life phases associated with SL is very important. Homolytic dissociation explains the appearance of free Na atoms only at hot moments related with the maximum collapse of bubbles. An experimental result of this study is the detection of a long-term Na flash, which is nearly symmetric in time with respect to the continuum flash. This result would be explainable if there were neutral metal atoms in a bubble both before and after the moment of collapse. Hence, the Na SL mechanism remains many questions.

According to the obtained data, Na emission under SL evolves as follows. At the expansion phase and for the majority of the collapse phase, a bubble does not luminesce. The bubble collapses to start adiabatic heating and, while its density is still low, the central Na SL line part begins to emit; in particular, the narrow components of its doublet become resolvable. While the density and temperature grow, the Na doublet merges into a single visible line, which is broadened and shifted to form satellites. When the density and temperature are maximal, the continuum flashes and quenches. The bubble expands, the density and temperature decrease, the Na line becomes narrow again, the flash is terminated by quenching in the central Na line part, and, simultaneously, the doublet again becomes resolvable.

CONCLUSIONS

Experimentally, using the self-correlation method, we have ascertained that the pulse width of a flash from the central Na *D*-line part (589 nm) under SL in a NaCl solution (21 ns) is much longer as compared to its peripheral part (2 ns). This agrees with the dynamic model proposed by us earlier for the integral Na line shape under SL. The mechanism of the appearance of narrow components in the Na *D*-line doublet under SL has been clarified, as the pulse width of their flash (>21 ns) proves to be longer than the time for which a bubble exists in a collapsed state. Using the correlation method, it has been confirmed that there exist bubbles that emit both Na and the continuum in the same flash. It has been calculated that their number is comparable with the number of bubbles emitting only Na or only the continuum. With the correlation method, it has been determined that a continuum flash occurs approximately in the center of a long-term Na flash with a vanishingly small delay of 0.21 ns (Na after the continuum). Under SL in a $CeCl_3$ solution, the delay of a flash from the Ce^{3+} line (350 nm) after a continuum flash (31 ns) has been measured by the correlation method to match the luminescence lifetime (33 ns) and the model of Ce^{3+} emission from a solution and accentuate the distinction from the mechanism of Na emission under SL.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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