Resolving Sonoluminescence Pulse Width with Time-Correlated Single Photon Counting

B. Gompf,[1] R. Günther,[2] G. Nick,[1] R. Pecha,[1] and W. Eisenmenger[1]
[1]*Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany*
[2]*Natural and Medical Science Institute, Eberhardstrasse 29, D-72762 Reutlingen, Germany*
(Received 17 April 1997)

The width of the short light pulses emitted from a single air bubble trapped in a resonant sound field in degassed water has been measured for the first time using time-correlated single photon counting. The pulse width at room temperature increases from about 60 ps at low gas concentrations and low driving pressures to more than 250 ps at high gas concentrations and driving pressures at the upper sonoluminescence threshold. The pulse shape is nearly Gaussian and is identical in the red and UV part of the spectrum. [S0031-9007(97)03852-0]

PACS numbers: 78.60.Mq, 43.25.+y, 43.35.+d

Single bubble sonoluminescence (SBSL), first observed by Gaitan *et al.* [1], is the phenomenon of light emission by a gas bubble trapped in the pressure maximum of a resonant sound field in water. The main difference of this phenomenon when compared to the light emission of transient cavitation bubbles known for the past 60 years is its high reproducibility and the enormous brightness, which makes SBSL a model system for investigating the fundamental physical mechanisms involved in energy concentration and sonochemistry. Until now one of the unsolved questions of this phenomenon is the width of the emitted light pulses. Barber *et al.* [2] estimated the pulse width from the response of a microchannel plate-photomultiplier tube (MCP-PMT) to the sonoluminescence (SL) pulse in comparison to a 34 ps laser pulse and found that the SL pulse is shorter than 50 ps. The authors also reported an increase of the rise time due to the ageing of the water, but they gave no quantitative values for the pulse width at higher gas concentrations. Moran *et al.* [3] estimated the SL pulse width of a single pulse from streak camera measurements to be less than 12 ps. In this experiment the air bubble was trapped in a 20% glycerine/water mixture at 10 °C and the emitted light was collected with a glass fiber connected to the entrance slit of the streak camera.

In this paper we demonstrate that time-correlated single photon counting (TC-SPC), normally used for fluorescence lifetime measurements [4], is an ideal method to investigate SBSL pulse width and shape even under extremely dim conditions.

To explain the principle behind this method we will first describe a normal TC-SPC experiment as it is used to determine fluorescence decay times. A short laser pulse, ideally much shorter than the decay time, excites the sample, and at the same time a fraction of this laser pulse acts as the start signal of a time-to-amplitude converter (TAC). With a fast multiplier, which stops the TAC, the time interval between the exciting laser pulse and the arrival of the first fluorescence photon is measured. This time is stored in a multichannel analyzer (MCA). Essential for this method now is that the intensity level must be adjusted so that in the average less than 0.01 fluorescence photon is observed for each laser pulse. If the intensity is too high the obtained decay time will be too short, because short time intervals are then statistically preferred. Remember that fluorescence emission is a random event. The probability of the emission of a single photon at various times reflects the time resolved decay for a large number of photons. That means measuring the time interval between the laser pulse and the arrival of the first emitted photon for a large number of events, typically 10^5, and storing each time in the MCA reproduces the time resolved decay. The advantage of this method is the good time resolution of about 10 ps, the low intensity one needs for the detection and the high dynamic range. Compared to streak camera measurements which allow single shot detection with higher time resolution (2 ps) but needs much more intensity, TC-SPC is a sampling technique, and therefore an essential condition is that the pulse width is stable within the measuring time of several minutes. In contrast to fluorescence lifetime measurements we start the TAC with a first photon from the SL pulse itself and stop it with a second photon from the same pulse. Because of the same statistical distribution of the start and stop pulses corresponding to the SL pulse shape one measures in this case the autocorrelation of the pulse shape. Because of the low intensity required in TC-SPC experiments it is possible to discriminate different pulse forms in different regions of a broadband optical spectrum. Time and frequency resolved measurements are, on the other hand, essential for testing the predictions of the theoretical models under discussion describing the light emission process in SBSL. If, for example, SBSL 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.

Figure 1 shows the experimental setup used for the investigations. The air bubble was trapped in a 250 ml spherical quartz glass flask which was driven with two piezo disks at its resonant frequency at about 20 kHz. For the experiments we used filtered demineralized

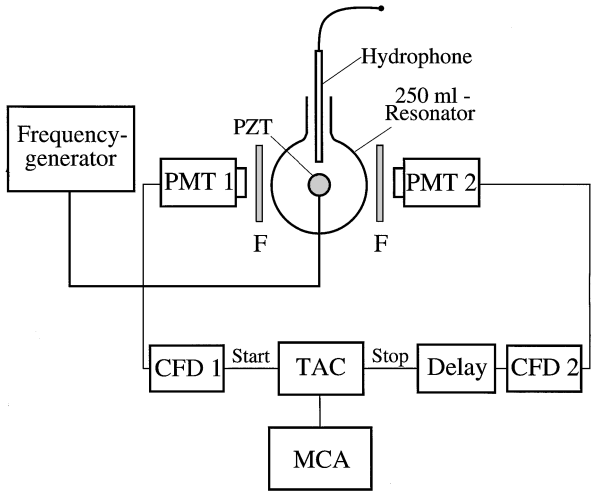

FIG. 1. Experimental setup for time-correlated single photon counting (TC-SPC). PMT: photomultiplier tube; CFD: constant fraction discriminator; F: optical filter; TAC: time-to-amplitude converter; MCA: multichannel analyzer.

water. The air concentration in the water was controlled by measuring the O_2 concentration with an oximeter. According to Henry's law an O_2 concentration of, for example, 1.8 mg/l corresponds to an air concentration of about $c_\infty/c_0 = 0.2$. The relationship between the air concentration which can be experimentally controlled and the equilibrium radius R_0 which is used in most calculations was first determined by Holt and Gaitan [5]. A theoretical treatment of this relationship is given by Hilgenfeldt *et al.* [6]. Both references also discuss the stability boundaries for SBSL in the gas concentration/driving pressure parameter space. The effect of noble gas doping on SBSL was investigated by Hiller *et al.* [7]. The amplitude of the driving pressure was determined with a fiber optic probe hydrophone [8]. This type of hydrophone is an absolute ultrasonic wideband reference standard with an accuracy of about 5%. The highest brightness at the upper SL threshold was about 3×10^5 photons/pulse in good agreement with literature values [9]. At the lower SL threshold we were able to determine the pulse width down to a brightness of about 3×10^4 photons/pulse.

For photon detection we used two fast MCP-PMT's (Hamamatsu R3809U-52) which are sensitive between 200–650 nm operating at the same sufficiently low count rate [4]. To avoid problems with the color dependence of the PMT response, all investigations were carried out with optical filters. The PMT's were connected to the start, respectively, stop input of the TAC (Ortec 457) via 1 GHz preamplifiers and two constant fraction discriminators (Canberra 2126) to achieve the lowest possible time jitter. The response of this experimental setup to a 300-fs 400-nm laser pulse was 49 ps (± 3 ps). This corresponds well to the autocorrelation of the time transit spread (30 ps) of the two MCP-PMT's as it is specified in the data sheets of the multipliers. Assuming that the sum of the squares of the real pulse width and the instrument response function is equal to the squared observed pulse width, a time resolution of about 20 ps can be estimated [Fig. 2(a)].

Figure 2(b) shows the result of a TC-SPC experiment at room temperature at about 1.2 bar driving pressure and a gas concentration of 1.8 mg/l O_2 measured with an UV filter in the range 300–400 nm. The two smaller peaks left and right of the main peak are due to reflections of the SL pulse at the glass-air interface. Subtracting these reflections and deconvoluting the result leads to the pulse shape shown in Fig. 3. For comparison additionally to the measured SBSL curve in Fig. 2 the forward convolution of Fig. 3 is shown. The SL pulse is nearly Gaussian with a slightly slower decrease at one side. Whether this side is the beginning or the end of the pulse cannot be decided from the experimental data alone, because of the symmetry of an autocorrelation function. Theoretical considerations discussed below lead to the pulse shape as plotted. The FWHM of the SL pulse in this case is 138 ps (± 10 ps). The dependence of the SL pulse width on the driving pressure at three different dissolved air concentrations in the liquid at room temperature is shown in Fig. 4. With constant

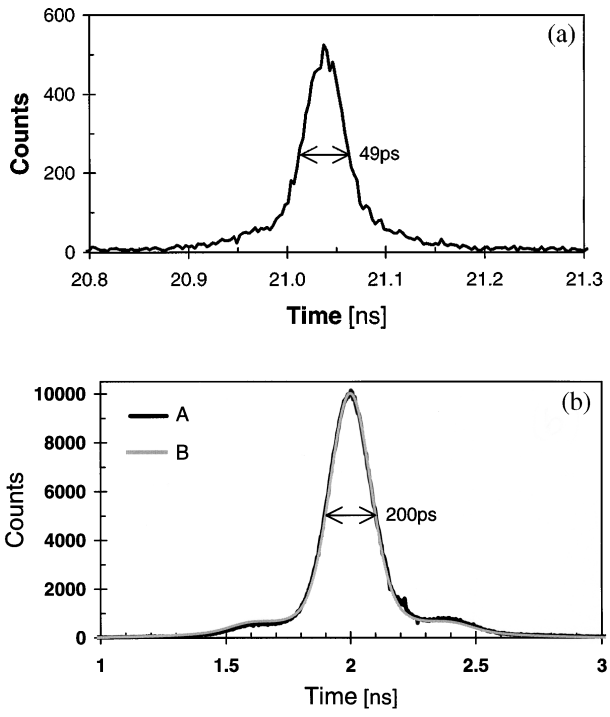

FIG. 2. (a) Response to a 300–fs 400-nm laser pulse. The response corresponds well with the convolution of the time transit spreads of the two multipliers. (b) curve A: SL pulse as measured with TC-SPC with a UV filter (300–400 nm). The two smaller peaks left and right of the main peak are due to reflections of the SL pulse at the glass flask. Curve B: Additionally to the measured SBSL signal the forward convolution of Fig. 3 is shown.

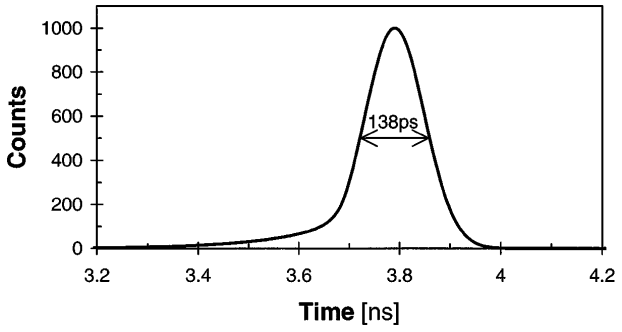

FIG. 3. SL pulse after subtraction of the reflections and deconvolution. The pulse shape is slightly asymmetric and its FWHM at 1.2 atm driving pressure and a gas concentration of 1.8 mg/l O_2 at 22 °C is 138 ps (±10 ps).

gas concentration the FWHM is shortest at the onset of the SL and increases monotonically with increasing driving pressure by nearly a factor of 2 at the upper SL threshold. The FWHM of the SL-pulse width also increases with the gas concentration. The shortest pulses of about 60 ps (±6 ps) we measure at the lowest possible air concentrations at the onset of the SL, the longest of about 250 ps (±10 ps) at the upper stability threshold of the air concentration and the driving pressure, respectively. The accuracy of the pulse width measurements is mainly limited by the accuracy with which the pressure and the gas concentration can be controlled. This accuracy is at the shortest pulses about ±10% and at the longest it is better than ±5%. In the unstable SL region, where the brightness is not stable, the pulse width varies and can therefore not be determined with TC-SPC.

To test the dependence of the SL pulse width on the observed wavelength we also measured with different optical filters. The result is shown in Fig. 5. The pulse width and shape does not show a significant difference in the UV (300–400 nm) and in the red (590–650 nm) part of the spectrum for all driving pressures and gas concentrations.

The results show that the SL-pulse width ranges from 60 to 250 ps depending on driving pressure and gas concentration. This is a little bit more than the estimated pulse width by Barber *et al.* [2], but it differs significantly from the results obtained by Moran *et al.* [3]. The pulse width increase with increasing gas concentration is in qualitative agreement with Barber's observation, but he gave neither quantitative data for the observed increase of the rise time nor values for the gas concentration and the driving pressure. Also in the streak camera measurements of Moran, who used a 20% glycerine/water mixture at 10 °C, the corresponding data are not specified, so that a direct comparison of the different experimental results is difficult. For a criticism of the Moran experiment, which could explain the large difference to our results, see [10]. We cannot exclude that there is a regime of stable SL where the pulse width is shorter than 50 ps, but in the simple case of air bubbles trapped in clean degassed water at room temperature and at a driving pressure where the bubble can easily be seen with the unaided eye, our results clearly show that the pulse width is always larger than 100 ps. At low driving pressures where the pulses are shorter the SL emission is invisible for the unaided eye.

The large width of the observed light pulses in our case compared with known literature values can be discussed within a simple model. It is well known [11,12] that the Gilmore equation [13] represents a very accurate approximation for the collapse of the bubble under constant pressure. Even if the system investigated is driven by an alternating field, the dynamics of the collapse, especially near the instant of minimal radius, is well described by the constant pressure collapse that starts at the same maximum radius as the driven system. We have calculated the temperature inside the bubble by coupling this equation to the energy equation of the gas inside the bubble [14]. Using this model the SL-pulse width may be estimated by the width of the temperature peak shown in Fig. 6. As parameters for driving pressure P_0 and equilibrium radius R_0 the experimental values from Fig. 3 were used. From this temperature peak we estimate the SL pulse width under two assumptions: that

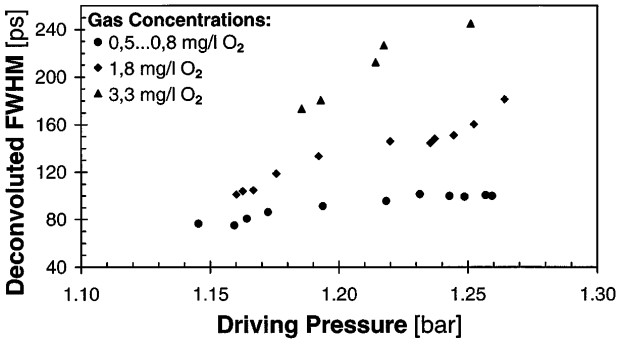

FIG. 4. Dependence of the FWHM of the SL pulse width on driving pressure and gas concentration at room temperature.

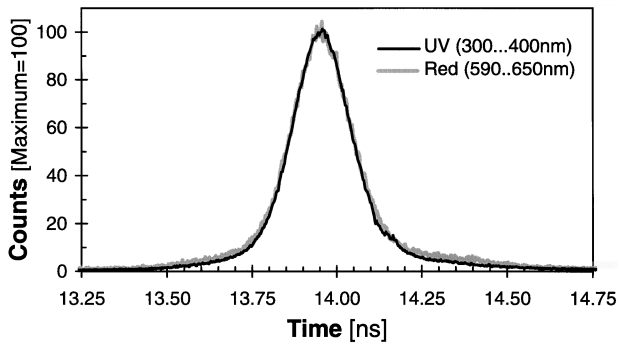

FIG. 5. SL pulse width measured at different parts of the spectrum. For the ease of comparison the pulses are not deconvoluted but without the glass wall reflections. (Red: 590–650 nm, UV: 300–400 nm).

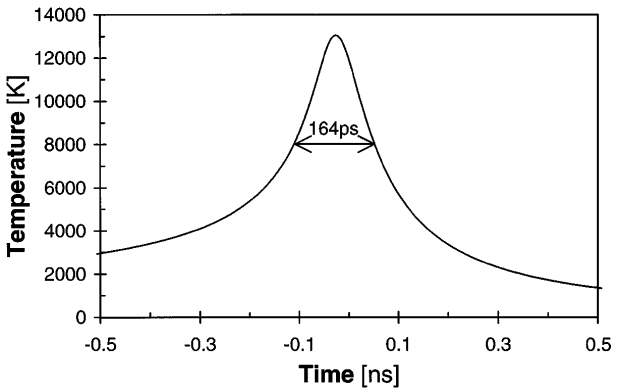

FIG. 6. Calculated temperature pulse. As parameters for driving pressure and equilibrium radius, the experimental values from Fig. 3 were used.

the light emitting process is either blackbody radiation or bremsstahlung from a plasma [15,16].

In the case of blackbody radiation this simple model can explain the pulse width in the UV, the increase of the pulse width with increasing driving pressure and increasing gas concentration, and the total amount of radiated power in the observed spectral range within a factor of 2. But it leads to a much larger pulse width in the red than in the UV and can therefore not explain the results shown in Fig. 5. In the case of bremsstrahlung the model additionally can explain the identical pulse width in the red and UV, but in this case it cannot explain the total amount of radiated power. The mean temperatures during the collapse under this uniform pressure assumption reach only $(1-2) \times 10^4$ K, which is about a factor of $2-3$ too low to account for bremsstrahlung of the observed intensity. This can be an indication that the assumption of a uniform pressure inside the bubble, which neglects the local temperature rise [17], underestimates the temperature in the bubble. We stress the fact that using the Rayleigh-Plesset equation instead of Gilmore's equation leads to a 2 times larger pulse width, an effect being due to the neglect of the dependence of sound velocity on the pressure in the liquid.

In conclusion, our results show that TC-SPC is an ideal tool for characterizing the SL pulse width and shape in dependence of the many parameters influencing the SL brightness. In the parameter range investigated in this study the pulse width increases from about 60 ps at low gas concentrations and low driving pressures to over 250 ps at high gas concentrations and high driving pressures. The pulse is identical in the red and UV parts of the spectrum and is nearly Gaussian with a slightly slower increase. A comparison of the experimental values with a simple model exclude that SL is blackbody radiation, but corresponds with the assumption that bremsstrahlung could be the underlying light emitting process.

We thank H. Port, T. Hirsch, and T. Stümpfig for many helpful discussions on the TC-SPC and for the opportunity to measure at their fs-laser system. We gratefully acknowledge financial support by the Bundesministerium für Forschung und Bildung.

[1] D. F. Gaitan, L. A. Crum, C. C. Church, and R. A. Roy, J. Acoust. Soc. Am. **91**, 3166 (1992).
[2] B. P. Barber, R. Hiller, K. Arisaka, H. Fetterman, and S. Putterman, J. Acoust. Soc. Am. **91**, 3061 (1992).
[3] M. J. Moran *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **96**, 651 (1995).
[4] D. V. O'Connor and D. Phillips, *Time-correlated Single Photon Counting* (Academic Press, New York, 1984).
[5] R. G. Holt and D. F. Gaitan, Phys. Rev. Lett. **77**, 3791 (1996).
[6] S. Hilgenfeld, D. Lohse, and M. P. Brenner, Phys. Fluids **8**, 2808 (1996).
[7] R. Hiller, K. Weninger, S. J. Putterman, and B. P. Barber, Science **266**, 248 (1994).
[8] J. Staudenraus and W. Eisenmenger, Ultrasonics **31**, 267 (1993).
[9] R. Hiller, S. J. Putterman, and B. P. Barber, Phys. Rev. Lett. **69**, 1182 (1992).
[10] B. P. Barber, R. A. Hiller, R. Löfstedt, S. J. Puterman, and K. R. Weninger, Phys. Rep. **281**, 122 (1997).
[11] A. Prosperetti, J. Acoust. Soc. Am. **83**, 502 (1986).
[12] E. A. Neppiras, Phys. Rep. **61**, 159 (1980).
[13] F. R. Gilmore, California Institute of Technology Hydrodynamics Laboratory Report No. 26-4, 1952.
[14] K. Yasui, J. Acoust. Soc. Am. **98**, 2772 (1995).
[15] L. D. Landau and E. M. Lifschitz, *Lehrbuch der theoretischen Physik IV* (Akademie-Verlag, Berlin, 1980).
[16] C. C. Wu and P. H. Roberts, Phys. Rev. Lett. **70**, 3424 (1993).
[17] Detailed numerical and analytical calculations taking into account the temperature, pressure, and density variations inside the bubble will be published elsewhere.