*Scientific Paper*

# Determination of Optodynamic Excitation Mechanism Following Laser Pulse Absorption in $CuSO_4$ Solution

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## Abstract

Optodynamic phenomena in aqueous solutions of $CuSO_4$ were experimentally investigated for two different concentrations (0.025 M and 0.05 M). The solutions were irradiated with a pulsed Nd:YAG laser operating at 1064 nm, with pulse energy varied from 180 to 760 mJ. Optodynamic sources were formed at different distances from the liquid – air boundary inside the liquid and in the air. The propagating optodynamic waves were detected with a laser beam deflection probe inside the liquid. The possibility of identification of different optodynamic excitation mechanisms was investigated. Spatial nonhomogenity of the laser beam profile influences the absorption process at and near the liquid – air boundary. As a consequence of this influence the shape and characteristics of the optodynamic source were considered. It was found out that optodynamic amplitude analysis can be used to assess the light power density at which the transition from linear to nonlinear excitation regime occurs.

**Key words:** optodynamics, optodynamic generation mechanism, ultrasonic waveform, photoacoustic spectroscopy

## Introduction

In recent years interaction of pulsed laser radiation with liquids has been a subject of considerable amount of research. This is related to the prospects of its application in many areas, such as chemical analysis[1-3], technical[4], environmental[5-7], and medical[8,9] applications. A number of methods have been developed to characterize the processes of ablation and plasma generation in liquids[10–12] and at the surface of samples submerged in liquid environment applying single[13] or double pulse excitation[14–16]. Dynamic processes induced upon the light – matter interaction are studied within the field of optodynamics.[17-18]

In most cases quantitative analysis of experimental data is based on the assumption of spatially and temporaly ideal Gaussian beam profile. One of possible causes for disagreement between experiment and theory can be attributed to the departure of the spatial profile from the Gaussian shape. In this contribution we present the influence of spatial profile roughness on the thermoelastic and ablative processes involved in optodynamic generation in aqueous solution of $CuSO_4$.

## Experimental method

The experimental configuration designed for the detection of optodynamically generated ultrasonic waves in aqueous solutions of $CuSO_4$ is presented in Figure 1. A Nd:YAG laser with a wavelength of 1064 nm, pulse width 10 ns (FWHM), and pulse energy from 180 mJ to 760 mJ was used as the excitation laser to generate ultrasonic pulses in solutions. A small portion of the excitation beam was reflected to reach a photodiode that served to trigger the oscilloscope which was used to record the generated waveforms.

The laser beam with elliptical cross section (9x16 $mm^2$) was focused from above through a lens with focal length 100 mm into a glass container (140×100×100 $mm^3$) with liquid samples. The beam dimension in the focus was estimated to be 1x2 $mm^2$. The investigated liquids were 0.025 M and 0.05 M aqueous solutions of $CuSO_4$. Optodynamic transients induced by the laser pulse were detected in the liquid by a deflection of a continuous-wave He–Ne laser probe beam (wavelength 632 nm, power 10 mW), laying parallel to the liquid surface, 62 mm deep (Figure 1). The excitation laser and the probe laser beams laid in the same vertical plane and intersected at 90°.

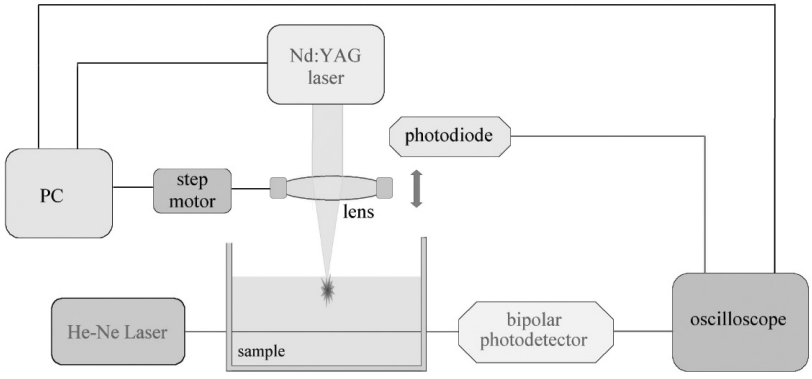


**Figure 1.** Experimental setup

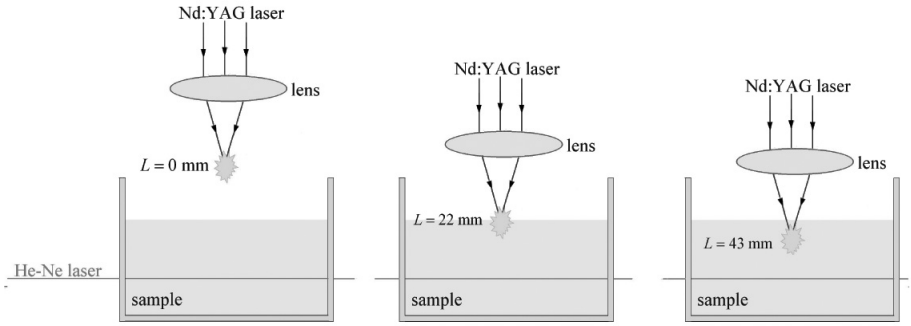


**Figure 2**. Notation concerning the position of the excitation laser focus with respect to the liquid surface. Three characteristic positions are presented.

The deflections of the probe beam were detected by a bipolar photodetector with 3 MHz bandwidth and digitized by an oscilloscope in single shot mode. The waveforms were transferred to a PC and averaged for 10 laser shots to improve the signal–to–noise ratio.

In one experimental series the lens holder was moved in 200 μm steps from the starting position where the focus was in the air, 22 mm above the solution surface, (Figure 2, $L$ = 0 mm), towards the liquid surface (position $L$ = 22 mm) and continuing to position $L$ = 43 mm where the focus was well inside the liquid. It should be noted that from the position $L$ = 22 mm on when the focus entered the liquid the 200 μm movement of the lens holder effects in 200·1.33 μm = 266 μm change of focus position, because of the refractive index of the liquid. The index was taken to be 1.33, equal to the refractive index of water. Nevertheless, the notation as depicted in Figure 2 is used, for simplicity. Series of waveforms were recorded for each solution at five different energies from 180 mJ to 760 mJ. Aditionally, at a few selected positions the waveforms were recorded at eleven different excitation pulse energies.

The excitation laser beam had a rough spatial profile, with several "hot spots". As an illustration of the meaning of the term "hot spot" Figure 3 shows a schematic 3D plot for a Gaussian beam intensity profile (left) and for a similar beam having just one "hot spot" (right).

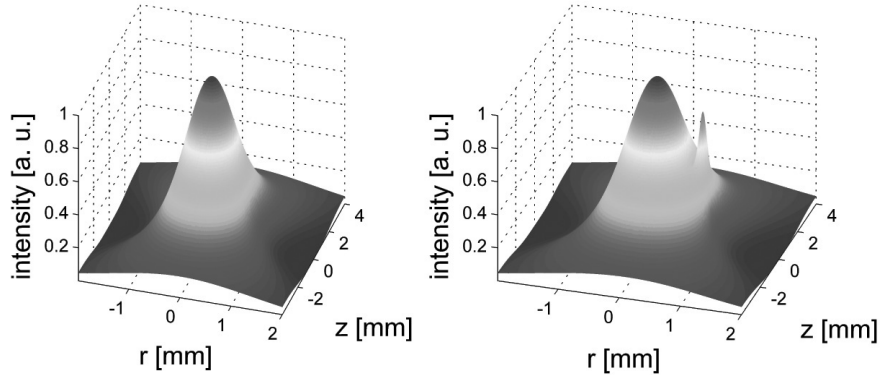


**Figure 3.** Schematic 3D plot for a Gaussian beam profile (left) and a similar beam having one "hot spot" (right).

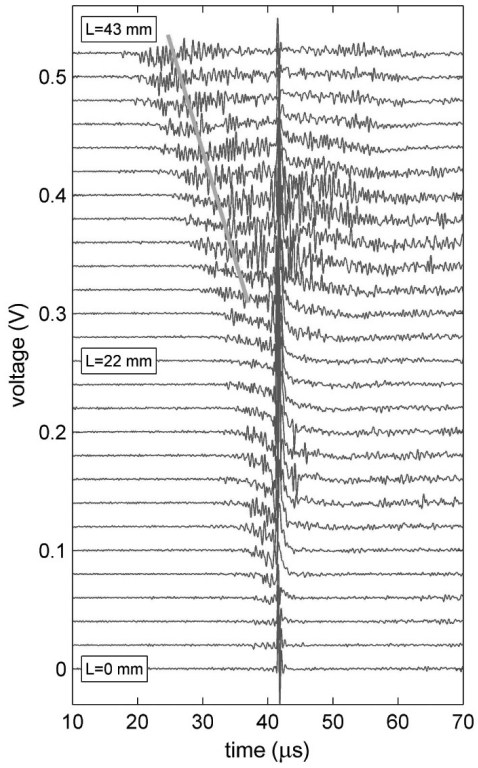


**Figure 4.** Some of the optodynamic waveforms induced in 0.025 M aqueous solution of $CuSO_4$ for 760 mJ excitation energy, at different positions of the excitation laser focus with respect to the liquid surface, from 0 mm (farthest in the air) to 22 mm (at the surface) and 43 mm (farthest inside the liquid). Waveforms at every fourth position are shown.

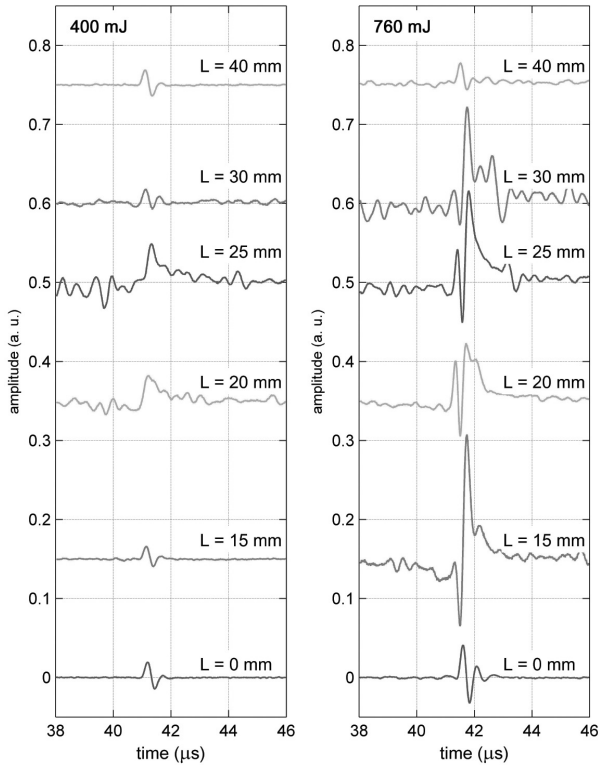


**Figure 5.** Examples of optodynamic waveforms induced in 0.025 M aqueous solution of $CuSO_4$ for two laser energies: 400 mJ (left) and 760 mJ (right), for different positions of the excitation laser focus with respect to the liquid surface.

## Results and discussion

We consider optodynamic waveforms generated at different positions of the excitation beam focusing lens with respect to air–liquid boundary. The different features of the waveforms are examined on different timescales. In Figure 4 some of the waveforms are presented for the case of 0.025 M $CuSO_4$ solution on a long timescale, up to 70 μs. The waveforms are offset by multiples of 20 mV for easier comparison. The reason to chose the offset value so small was to make obvious the existence of small amplitudes before and after the main signal. Consequently, the main signal itself which always occurs at around 41 μs can not be clearly seen. It is shown separately in more detail in Figure 5, for two different excitation energies, 400 and 760 mJ.

The waveforms of a particular series were put together to form a matrix and presented as a 3D plot, like the ones in Figure 6 where series of waveforms induced in 0.025 M (lower part) and 0.05 M (upper) aqueous solutions of $CuSO_4$ are presented, for 650 mJ (right) and 340 mJ (left) of excitation energy. Like in Figure 5, the time interval is chosen in such a way that the change of the main signal with respect to the excitation beam focus position can be observed.

The fact that the main signal is always found at 41 μs is somewhat surprising since the focus of the excitation laser is moved as much as 50 mm during one series. The distance that the ultrasonic pulse travels in 41 μs is 61.5 mm, taking 1500 m/s as the sound speed in the solution. Since the value corresponds to the distance between the probe beam and the solution surface, this suggests that the main signal always forms at the surface, irrespective of the position of the excitation beam focus. The reason for that is discussed below.

Regarding the main signal, there are common characteristics that are observed for all recorded series, for both solutions and all excitation energies. When the excitation focus is farthest from the surface, either in the air or inside the liquid, the amplitude is small and the shape of the signal is bipolar, suggesting thermoelastic excitation mechanism.[19] This mechanism is usually associated with excitation power densities which are so small that the absorption of light is followed only by temperature rise. With the focus of the excitation laser approaching liquid boundary ($L$ = 22 mm) the shape of

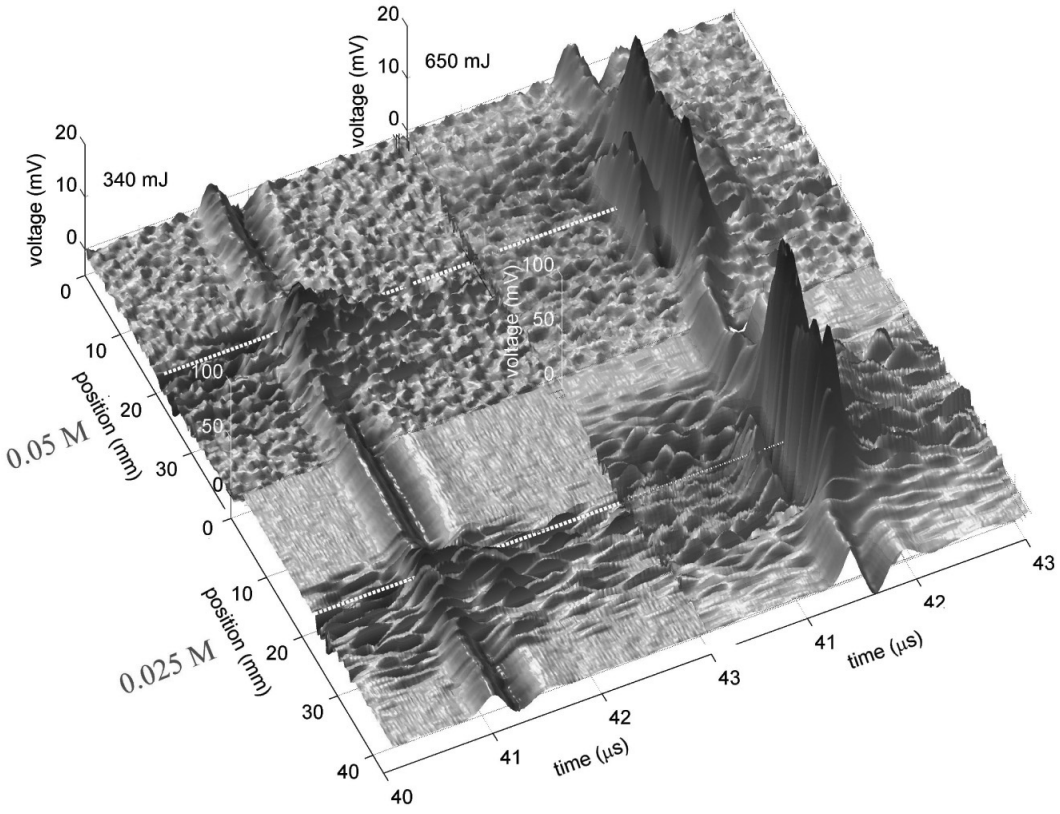


**Figure 6.** 3-D representations of four series of waveforms induced in 0.025 M and 0.05 M aqueous solutions of $CuSO_4$ for two laser energies: 340 mJ and 650 mJ, for different excitation laser focus positions. The white lines mark the air–liquid boundary.

the signal changes from a bipolar to a more complex one and the amplitude is increased considerably (Figures 5 and 6). The focus position at which the change occurs inside a paricular series depends on the excitation energy. The sharp increase of the ultrasonic amplitude suggests the onset of nonlinear generation mechanisms. Nonlinear absorption and optodynamic generation can have up to $10^3$ times greater light-to-mechanical conversion efficiency. They lead to material ablation and consequently different distribution and orientation of displacements within the liquid as well as greater amplitude compared to the thermoelastically generated displacements.[19]

Generally speaking, there are two characteristics of the generated waveform which point to the generation mechanism: the amplitude and the shape of the signal. A sharp change in signal amplitude and a change in signal shape indicate a change in optodynamic generation mechanism.

When analysing the waveforms one should have in mind that the probe beam deflection is not directly proportional to the pressure or displacement in the wave. For a plane wave probed parallel to the wavefront it is proportional to the density gradient.[20] In the case of different geometry the response is further complicated by geometrical considerations. In our case the probed wave is spherical. The central ultrasonic wavelength is in the range of one millimeter, therefore 60 mm away from the source a plane wave is a relatively good approximation. Nevertheless, obviously a detailed interpretation of the signal shape requires more analysis. For the purpose of the present analysis it was suficient to detect only the change of the shape, which can be done without the detailed knowledge of the real shape.

Another feature of the recorded waveforms are the random small amplitudes before and after the main signal. The length and the location of the interval where they appear depend on the location of the focal point (Figure 4). Roughly speaking, for the waveforms recorded with excitation focus inside the liquid (from position $L$ = 22 mm to 43 mm) the time between the center of the interval and the occurrence of the main signal corresponds to the distance from the focus to the liquid surface. The line in Figure 4 connects approximate positions of the centers of the intervals. The length of the interval is estimated to be up to 10-15 μs, corresponding to 15–20 mm distance in the liquid. Based on visual observations during the experiments this coincides approximately with the length of the region where many

little sparks of plasma are generated in the vicinity of the excitation beam focus. Each of these sparks acts as a small optodynamic source. All the signals are generated at the same time and, depending on the location of the source they arrive at the detector within the 10-15 μs interval. The amplitudes of these signals differ from the amplitude of the main signal for an order of magnitude. Concerning the other interval of small amplitudes, occuring after the main signal, we believe that they are reflections of the just described small pulses from the liquid surface. The reflections eventually also arrive at the probe beam, with an expected delay. Our belief is based on the results of similar experiments, described in more detail elsewhere,[21] which were performed with excitation laser beam having less energy but a very smooth Gaussian profile.

All the described characteristics of the waveforms, together with visual observations can be explained as follows:

When a laser pulse with a rough spatial profile containing many "hot spots" irradiates a liquid surface, the threshold for dielectric breakdown is first exceeded in the areas where the light intensity is high. This leads to plasma formation and even more light absorption in that areas during the laser pulse since plasma strongly absorbs in the UV, visible and IR part of the spectrum. This is the reason that the main signal, formed at the surface, is always present. As the rest of the light, which was not absorbed at the surface, travels inside the liquid and is being focused, the same effect happens on the way, i. e. each time when the threshold for dielectric breakdown is exceeded, plasma is formed in that area and it radiates an independent ultrasonic pulse. The volume in which plasma sparks randomly appear takes the shape of the excitation beam in the vicinity of the focus. It was speculated that possibly the existence of independent absorption centers could be attributed primarily to the light absorption by the impurities in the liquid. The possibility was ruled out after it was verified that the waveforms recorded in the same way with doubly distilled water and with tap water showed no noticeable difference concerning the described characteristics.

Regarding identification of different excitation mechanisms the dependence of the main signal amplitude on the laser radiation energy was examined. As expected the transition from the thermoelastic (linear) to the ablation (nonlinear) mechanism mainly depends on the incident light power density.

The main signal amplitude dependence on the energy of the exciting laser is shown in Figure 7 for 0.05 M aqueous solution of $CuSO_4$ for two focus positions: at 8 mm distance from the surface in the air (Figure 2, $L$ = 14 mm) and in the close vicinity of the surface ($L$ = 22 mm). The complex dependence of

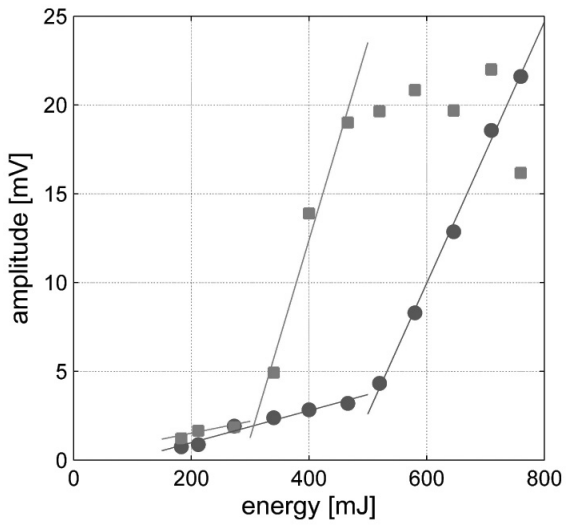


**Figure 7.** Optodynamic signal amplitude dependence on incident laser energy for two different focal positions: 8 mm above the air–liquid boundary ($L$=14, blue circles) and at the air-liquid boundary ($L$=22, red squares). Lines are linear fits.

the optodynamic signal amplitude with laser radiation energy is evident in both cases. The amplitude dependence can be divided into two regions: the one at lower energies where the amplitude increase with energy is slower (the two lines with gentle slope in Figure 7), and the one where the amplitude increase is faster (the two steeper lines). This points to the fact that the optodynamic signals in the first region are formed mainly via the thermoelastic mechanism while in the second region there is also a growing contribution of nonlinear mechanisms like plasma formation and ablation. The transition from thermoelastic to nonlinear regime occurs at different energies for the two cases. For focus position 8 mm above the liquid surface the thermoelastic region is wider, approximately 0–450 mJ, while for the focus position at the surface this region is only 0–300 mJ. In the second case there is also a third region, above 600 mJ of energy, where the amplitude becomes saturated and the last experimental point even exhibits a decrease. It should be noted that the shape of the signal is changed considerably for higher incident power densities. This change influences the signal amplitude, making it a less relevant parameter in that region.

Because of the pronounced roughness in the beam spatial profile only average fluence [mJ/mm$^2$] at the liquid surface can be estimated for the two cases. Nevertheless, from that estimation one can conclude that the transition from linear to nonlinear regime occurs at the same value in both cases, i. e. at around 70 - 80 mJ/mm$^2$.

The described waveform and amplitude characteristics were very similar for the both $CuSO_4$

solutions, indicating that the mechanisms of optodynamic generation were the same. The most pronounced difference between the two solutions was the amplitude of the signal which was up to seven times smaller in the case of 0.05 M solution. One of the reasons lies probably in the mechanisms of absorption of the excitation laser beam but it seems that a great contribution to such reduction is the absorption of the probe laser beam. Investigations are under way to determine the extent of this and other contributions.

It can be concluded from the described analysis that depending on the laser radiation energy and on the focal point location the method based on optodynamic amplitude analysis enables the distinction of the processes taking part in signal formation.

## Conclusion

Amplitude analysis of optodynamic signals can be used to distinguish excitation mechanisms in laser-liquid interaction. The existence of numerous smaller waves that are observed before the main signal in the optodynamic waveform is explained as the effect of roughness of the laser beam spatial profile. A detailed understanding of the generated waveforms is important in investigations of nonlinear optodynamic generation mechanisms.

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## Povzetek


Eksperimentalno so bili obravnavani optodinamski pojavi v 0.025 M in 0.05 M vodni raztopini $CuSO_4$. Kapljevina je bila obsevana z bliski Nd:YAG laserja z valovno dolžino 1064 nm in energijo posameznega bliska od 180 do 760 mJ. Optodinamski valovi so bili vzbujeni v zraku in v kapljevini na različnih razdaljah od gladine in detektirani z lasersko odklonsko sondo v kapljevini. Proučevali smo možnost identifikacije različnih vzbujevalnih mehanizmov z analizo optodinamskih signalov. Obravnavali smo vpliv, ki ga ima nazobčanost prostorskega profila žarka na absorpcijo na gladini kapljevine in v njeni neposredni bližini, s tem pa na obliko in karakteristike optodinamskega izvora. Ugotovili smo, da je možno z optodinamsko amplitudno analizo določiti območje intenzitet, kjer pride do prehoda iz termoelastičnega v ablativni režim optodinamskega vzbujanja.