ALT 12
Advanced Laser Technologies
2 – 6 September 2012, Thun, Switzerland

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c/o Bern University of Applied Sciences
Engineering and Information Technology
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DOI: 10.12684/alt.1.91

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Abstract

The photoacoustic (PA) pressure response of the absorbing liquid (water, ethanol) with free and confined surface to laser pulse with modulated intensity is studied. Modulation amplitude of the PA signal demonstrates non-monotonous behavior during laser pulse action which can be explained as interference between thermo-acoustic and vaporization mechanisms of pressure generation. The phase behavior of modulated part of PA signal also gives important information on processes in the irradiated matter. Doppler photoacoustic monitoring (DPM) is used to determine surface movement during laser irradiation (wavelength – 2.94 um, pulse duration ~ 200-300 ns, fluence ~ 0.3-1.6 J/cm^2). In the case of free surface this movement is possible into the upward and downward directions while for the constrained irradiated surface only one movement is supposed. This supposition is in agreement with the experiment. However the total behavior of PA response is more complicated due to probably vapor cavity formation between liquid and solid surfaces. In particular, despite the imposed constraint PA response behavior resembles the free surface case.

Introduction

The impact of laser pulses on absorbing condensed medium leads to pressure change in the irradiated zone, which in the form of acoustic disturbances propagates into the depth of the target and into the surrounding atmosphere and can be registered with broadband piezoelectric sensors or by other means. The generation of such signals can be considered as a generalized (nonlinear) case of the photoacoustic effect, which was first observed in the nineteenth century as a generation of acoustic waves in gas due to absorption of light with variable intensity.

Acoustic diagnostics has been used for almost half a century for the study of laser action on absorbing condensed media and using it (as well as some other techniques) many interesting results were obtained, in particular concerning the non-equilibrium behavior of matter and phase transitions in the irradiated zone. PA signal consisting of thermo-acoustic and vaporization components was first observed in Switzerland and USSR [1-3].

Additional information on the processes in irradiated matter can be obtained using laser pulses with periodically modulated intensity. At first we remind some theoretical and experimental results on PA-signal due to thermo-acoustic and vaporization mechanisms. Effect of laser intensity modulation on PA-signal is considered in the following sections and concluding remarks are given in the last section.

Thermo-acoustics and vaporization PA signals

Thermo-acoustic signal

Generation of pressure is associated with a change of state of matter under the action of laser radiation. This change may be quasi-equilibrium, i.e. be in accordance with the equation of state of the substance, or non-equilibrium, even for a nanosecond laser pulse of not too great intensity. An example of such non-equilibrium changes caused by non-thermal excitation of electron subsystem is the case of exposure of silicon to laser pulses with nanosecond duration and wavelength of 1.06 microns (see e.g. references in [4]). In this case the photoacoustic pressure signal is inverted in sign compared to that realized by conventional thermal mechanism of photoacoustic signal generation in absorbing media.

In the quasi-equilibrium case the mechanism of the pressure generation is described by a complete system of hydrodynamic equations, which for this problem in the linear approximation is reduced to the wave equation with a source, caused by absorption of radiation (see e.g. [4]):

$$\frac{1}{v_s^2}\frac{\partial^2 P}{\partial t^2}-\frac{\partial^2 P}{\partial z^2}-\frac{\beta}{c_p}\left\{\frac{\partial}{\partial z}\left[\kappa\frac{\partial}{\partial z}\left(\frac{\partial T}{\partial t}\right)\right]+\alpha\frac{\partial I}{\partial t}\right\}=0, \quad (1)$$

where v_s - sound velocity, β - thermal expansion coefficient, c_p - heat capacity, κ - thermal conductivity coefficient, α - coefficient of absorption, $I(t)$ - the intensity of absorbed laser radiation.

For the free irradiated surface and for not too rapid heating (characteristic time of heating corresponding to the laser duration τ is greater than the travel time of sound in the warm-up area: $\tau\alpha v_s > 1$), one obtains for the pressure in the area, whose dimension z^* exceeds the warm-up depth, but still is small compared to the characteristic acoustic wavelength:

$$P(z^*,t) = P(0,t) + \int_0^{z^*} dz' \int_{z'}^{z^*} \left(\frac{\partial^2 P}{\partial z^2} \right) dz = \quad (2)$$
$$= P(0,t) + \frac{\beta}{c_p} \left\{ \kappa \left(\frac{\partial T}{\partial t} \right)_{z=0} + \frac{1}{\alpha} \frac{\partial I_0}{\partial t} \right\}$$

where the temporal dependence of the surface temperature and its time derivatives is determined by the heat conduction equation:

$$\rho_0 c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right) + \alpha I \cdot \quad (3)$$

The pressure at the surface of the irradiated medium *P(0, t)* is determined by the boundary conditions, which depend on the particular physical problem. In the case of free surface without evaporation and the possibility of appearance of a plasma plume, *P(0, t) = 0*, so that the pressure signal with a relatively long laser pulse is completely determined by the last two terms in (2), each of which has both positive and negative phases.

Bipolarity of the pressure signal persists also for shorter laser pulses when $\tau\alpha v_s < 1$. In this case, the temporal dependence of the positive phase of the pressure signal in the linear approximation corresponds to the spatial distribution of the absorbed intensity in the irradiated material. This fact can be used to determine the absorption coefficient along the profile of the acoustic signal.

For the surface evaporation with a constant Mach number *M = 1* at the outside border of the Knudsen layer above the surface the value of *P(0, t)* is approximately half that of the saturated vapor pressure $P_s(T_0)$ for the given surface temperature T_0, and the temperature in the vapor flow T is about 0.67 T_0. The value of *P(0, t)* is determined by non-equilibrium gas-kinetic processes on the surface of evaporation and in the adjacent Knudsen layer. In contrast to the usual shock wave, the determination of the macroscopic relations at the evaporation jump cannot be obtained only on the basis of conservation laws with no consideration of its non-equilibrium structure. Investigations of such boundary conditions, that use some model assumptions on the explicit form of the non-equilibrium distribution function in the Knudsen layer, or a variety of numerical methods for solving the corresponding kinetic problem, continue for many decades (see references in [4]).

Pressure at the surface can also be determined by external reaction in the case of the loaded surface. If the irradiated surface is not free due to contact with another (transparent) medium, then the value of *P(0, t)* is determined by solving the dual problem for the two half-spaces (or layers) with a common boundary, where appropriate boundary conditions of continuum mechanics are formulated. In this case the temperature of the two media in the contact area may not coincide with each other due to the Kapitza jump. In the simplest case, when one can neglect the heat flow into the loading medium, one can obtain the following expression for the pressure at the surface of the irradiated material. Instead of (2) the following expression for the pressure can be obtained:

$$P(t, z=0) = \frac{I(t)\beta^* c_s}{(N+1)c_P}, \quad (4)$$

where $\beta^* = \beta\left(1 - 4c_t^2/c_s^2\right)$, c_s - transverse speed of sound, N - the ratio of acoustic impedances of loading and absorbing media: $N = \rho c_s / \rho_g c_g$, ρ - density of absorbing medium, ρ_g - density in transparent medium, c_g - longitudinal speed of sound in transparent medium.

Pressure signals in mercury confined by optical glass according to formula (4) at sufficiently low absorbed intensities of irradiation, were experimentally observed, for example in [5].

Vaporization signal

As noted above, in the case of the free irradiated surface the value of *P(0, t)* can be determined by the process of surface evaporation, the intensity of which very strongly depends on the surface temperature T_0 and increases rapidly with T_0 increasing. Evaporation pressure signals at the thermal photoacoustic background were observed in [1-4] and many other papers. Fig. 1 shows evolution of the evaporation peak (2) on the thermo-acoustic signal background (1) with about two-fold increase of laser intensity as it was observed in absorbing liquid (water) irradiated with erbium laser pulses (duration of 200 ns, the wavelength of 2.94 microns). It is seen that evaporation peak grows much stronger than photoacoustic signal amplitude which is approximately proportional to laser pulse intensity (note the voltage scale difference in Fig. 1 a, b.).

Evaporative peak first appears on the falling part of the thermo-acoustic pressure pulse near its zero value, when the surface temperature reaches its maximum during laser heating, and the process of thermal expansion gives way to contraction due to cooling. Such a difference in the behavior of the photoacoustic and evaporative pressure leads to the

characteristic features of the acoustic signal behavior in the case of periodic modulation of the laser pulse intensity.

In a quasi-stationary evaporation into a vacuum or gaseous medium with low pressure at the outer boundary of the Knudsen layer the Mach number $M = 1$ in vapor flow remains constant and pressure $P = P[T_0(t)]$ depends only on surface temperature T_0. The more general case with non-negligible back pressure when the value of M is less than unity and does not remain constant, requires the solution of the dual hydro-gas-dynamic problem for the condensed target material and the outer gaseous medium with the evaporation boundary conditions already mentioned above. Restriction of the free evaporation may be associated with the occurrence of plasma plume in the vapor flow. This can result in such a regime where under certain conditions the evaporation process is replaced by condensation [3-4].

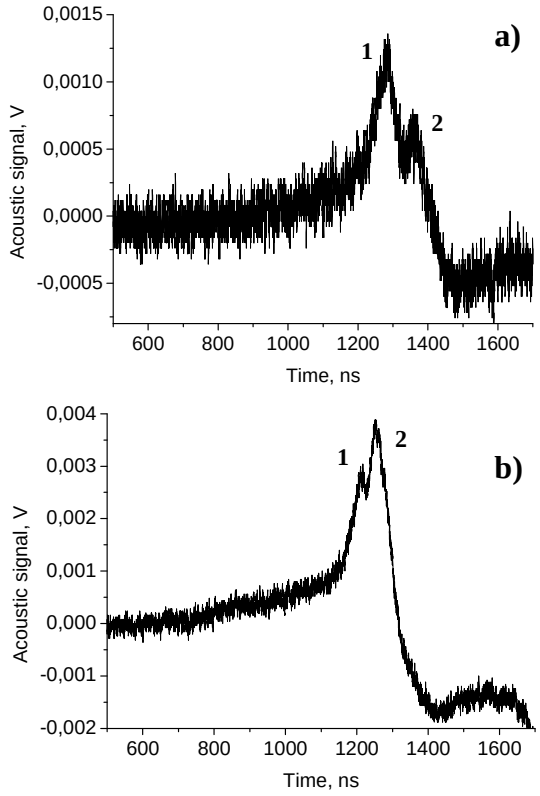

Figure 1: Thermo-acoustic (1) and surface evaporation (2) PA pressure signals at different laser intensities $I_b \sim 2I_a$

PA signals in the case of modulated laser intensity

Variation of light intensity is a necessary condition to produce photoacoustic pressure signals in absorbing media. This fact is also clearly evident from eq. (2) which contains time derivatives of light intensity and surface temperature of irradiated media. It is evident also that laser pulse intensity can have smooth envelope or can be periodically modulated (see, e.g., [1]). In this section two effects are discussed which were observed recently (see, e.g., [4]) in the case of modulated laser intensity.

PA modulation amplitude behavior

Fig. 2 shows the total modulated photoacoustic signal (a) and its decomposition to smooth (slow) and modulated (high-frequency) parts. According to (2), the envelope of the high-frequency signal component in Fig. 2 (b) approximately reproduces the shape of the smooth component of the laser pulse, and the modulation depth of the acoustic signal increases in comparison with laser intensity modulation depths in proportion to the ratio of the laser pulse duration τ_p to the modulation period τ_m. It should be noted here that the observed difference between amplitudes of slow and fast signals depends also on different acoustic extinction of these signals in water.

A remarkable feature of the curves in Fig. 2 (b) is a noticeable asymmetry between positive and negative parts of the smooth bipolar signal unlike the symmetric pattern for the high-frequency component. Such a difference can be caused by the fact that acoustic diffraction distortions of the signals depend on its characteristic frequency.

Indeed, the characteristic diffraction length of the acoustic signal $l = d^2 / \lambda_s$, where $\lambda_s \sim v_s \tau_p$ and v_s are the characteristic sound wavelength and the speed of sound, respectively. Under given conditions, at squared diameter $d^2 \sim 0.01$ cm^2, $v_s = 1.4$ km/s and $\tau_p = 200$ ns, the value $l < 0.1$ cm is smaller than the acoustic sensor thickness which gives main contribution to the diffraction distortions, but significantly exceeds it at $\tau_m = 5$ ns that is shorter than τ_p. In other words, the effect of acoustic diffraction distortions should be weak for a high-frequency signal component. Exactly this is observed in Fig. 2 where diffraction distortions of the bipolar signal are noticeable only for the smooth (long-wavelength) signal component.

An increase in the laser fluence significantly changes the high-frequency component of the measured signal, as is seen in Fig. 3, 4. It is believed that such a signal behavior is caused by the manifestation of the pressure generation mechanism due to surface evaporation which leads, in particular, to mutual suppression of high-frequency components of thermo-acoustic and evaporation pressures.

To realize the effect of mutual compensation of the high-frequency thermo-acoustic and evaporation signals, these signals should be out-of-phase, i.e.,

the mutual compensation depth depends on the proximity of the phase shift to π. Such a phase shift can result from the following reasons. Formula (2) shows that the thermo-acoustic signal, which is proportional to the time derivative of the laser intensity, is phase-shifted by $\pi/2$ with respect to the modulated intensity part. If it is further assumed that the evaporation signal is proportional to the temperature change whose derivative (according to Eq. (3)) depends on the laser intensity, the phase shift for this signal will also be equal to $\pi/2$ in magnitude, but with an opposite sign with respect to the thermo-acoustic signal.

As a result, the total relative phase shift is π, which just allows mutual compensation of the thermo-acoustic and evaporative signals, when their amplitudes become equal during an increase in laser fluence. In Fig. 3, such compensation occurs exactly near the maximum of the smooth evaporation signal. As the laser pulse intensity and corresponding evaporation signal further increase, two minima can be observed in the behavior of the high-frequency component of the total signal, which is shown in Fig. 4 b. The central maximum of the envelope of the modulated component in Fig. 4 is probably mainly due to surface evaporation mechanism while the other two maximum are mainly determined by thermo-acoustic response with no evaporation effect.

It should be mentioned that laser intensity increases from Fig. 2 to Fig. 4 while the amplitudes of signals in Fig. 2-4 do not reflect their real relative pressure values because the radiation spot in this case was not the same in these three cases.

We recall that the evaporation signal increases much more rapidly with the intensity than the thermo-acoustic signal due to the strong temperature dependence of the saturated vapor pressure, which is most pronounced under non-stationary evaporation conditions.

The evaporation signal is controlled by nonequilibrium gas-kinetic processes near the surface and surface evaporation kinetics which depends strongly, in particular, on the mass accommodation coefficient γ of vapor molecules to the liquid surface and other kinetic parameters. Experimental value of γ is not well determined [4] and more detailed quantitative experimental and theoretical investigation of, in particular, modulated photoacoustic response can help to solve this problem.

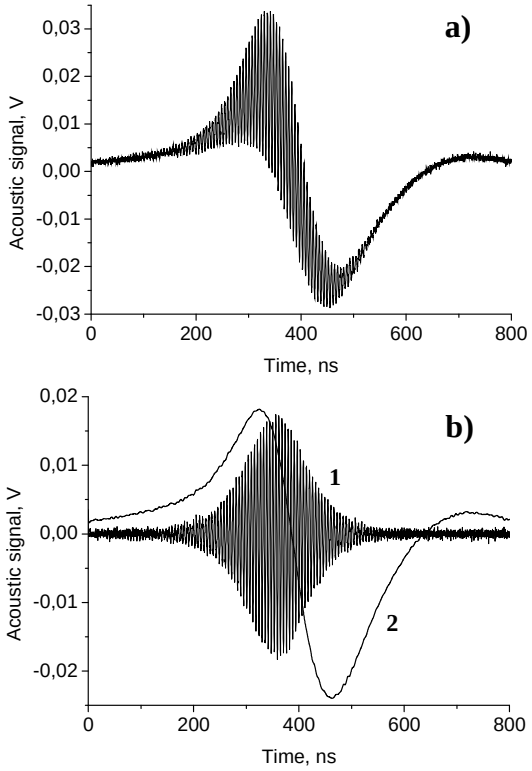

Figure 2: Pressure response to modulated laser pulse: a – total pressure signal, b – modulated pressure component (curve 1) and slow pressure component (curve 2)

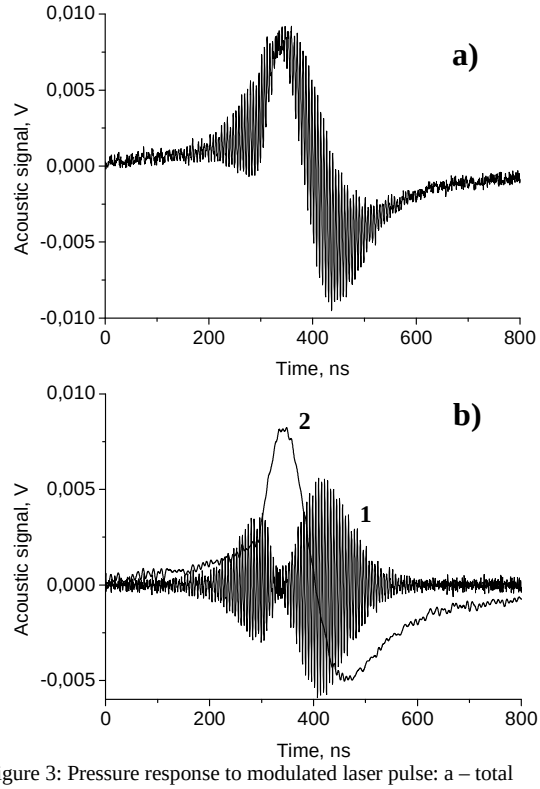

Figure 3: Pressure response to modulated laser pulse: a – total pressure signal, b – modulated pressure component (curve 1) and slow pressure component (curve 2)

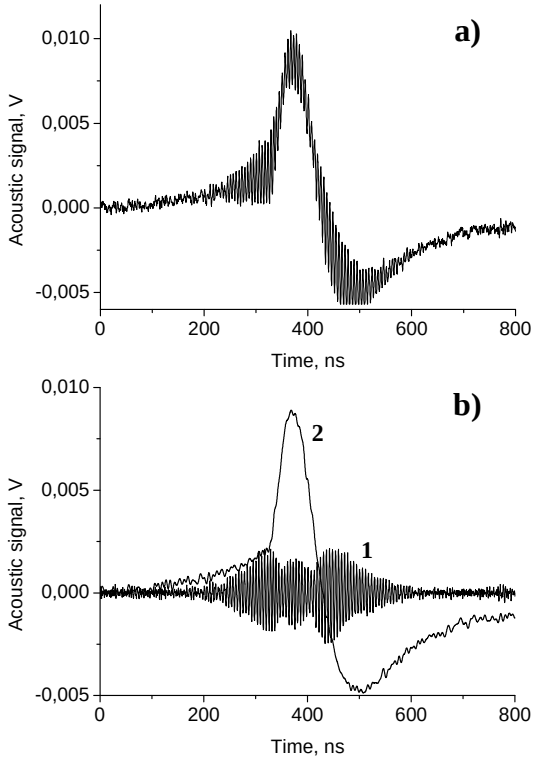

Figure 4: Pressure response to modulated laser pulse: a – total pressure signal, b – modulated pressure component (curve 1) and slow pressure component (curve 2)

Acoustic monitoring of irradiated surface movement in the case of free and confined cases

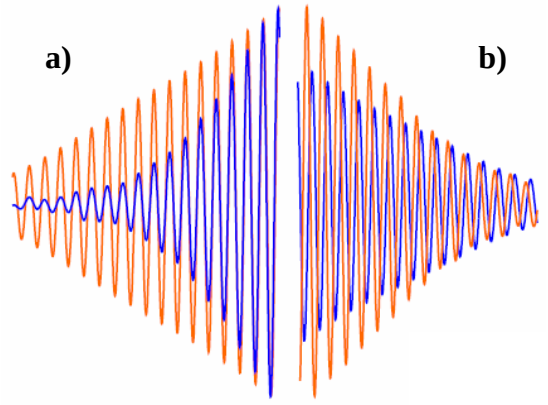

Figure 5: Superimposed laser (orange) and acoustical (blue) modulation signals at the beginning (a) and at the end (b) of the pulse (initial and final part of Fig. 6 b)

Important information about processes in the irradiation zone can be inferred also from the behavior of the acoustic signal modulation period. This period, in contrast to the laser intensity modulation period, varies during laser pulse action giving rise to relative time displacement of laser and acoustical modulation signals that is seen from Fig. 5. It means that the zone of acoustic signal generation changes its position with respect to the transducer surface (Doppler effect). First observation of this effect in the case of periodically modulated nanosecond laser pulses was reported recently in ref. [6]. Behavior of modulated components of laser and acoustic pulses are shown in Fig. 5 which demonstrate clearly the difference between laser and acoustic modulation periods that increases to the end of the pulses.

To calculate variation of the acoustic signal modulation period, the authors [6] used the expression for the time delay $t_f = t_n - n\Delta t$, which is the difference between the real-time position t_n of the nth zero point of the signal modulation component and its extrapolated value $n\Delta t$ with some fixed half period Δt determined, e.g., in the acoustic pulse beginning where the laser heating effect is small. Instead of $n\Delta t$, one can use the real positions of zero values in the laser pulse modulation component.

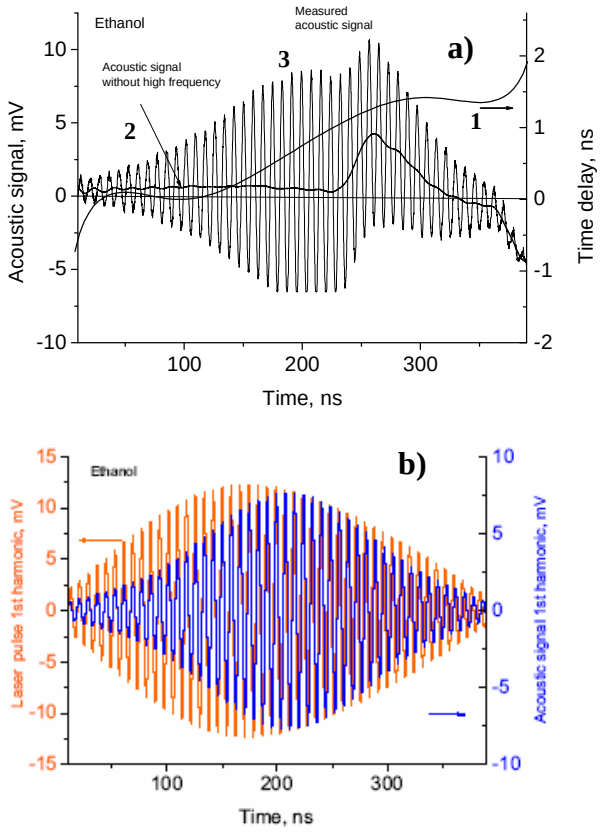

Figure 6: PA response to modulated laser pulse and delay time behavior (ethanol) a: curve 1 – time delay, 2 - slow pressure component, 3 – total pressure signal; b: superimposed modulated components of laser (orange) and acoustic (blue) pulses

Evolution of discrete values of t_f during laser action on ethanol is described in Fig. 6a by continuous curve 1 a. Positive value of the time delay means that the liquid effective surface where the pressure signal is generated moves away from the transducer. It is believed that this movement is due to heat expansion of the irradiated liquid. The effective surface displacement $h = v_s t_f$ with ethanol sound velocity v_s = 1.2 km/s and t_f = 1.5 ns amounts to a rather large value of h ~1,8 μm. From Fig. 6b it can be also seen that modulated part

of acoustic signal is practically unaffected by vaporization pressure represented by slow part of acoustic signal (curve 2 in Fig. 6a). Difference in modulation amplitude behavior of laser and acoustic pulses visible in Fig. 6b is probably due to nonlinearity of the thermo-acoustic response.

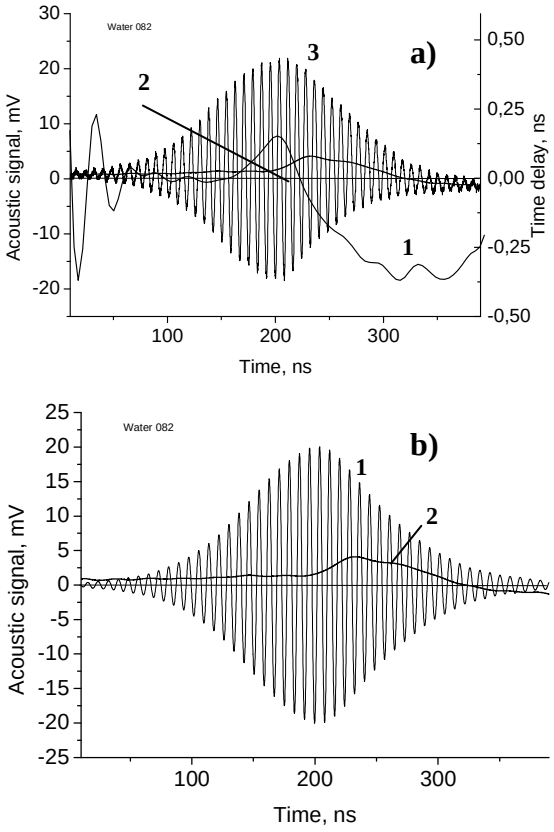

Figure 7: Pressure response to modulated laser pulse and delay time behavior (water) a: curve 1 – time delay, 2 - slow pressure component, 3 – total pressure signal; b: 1 – modulated pressure component, 2 – slow pressure component

Behavior of the time delay for irradiated water in Fig. 7a is different (curve 1). The time delay t_f (and corresponding displacement $h = v_s t_f$, v_s = 1.4 km/s) changes its sign from positive to negative at the moment when the vaporization pressure (curve 2) begins to rise. For this reason, one can suggest that the effective surface displacement towards the transducer is due to a vaporization process. However, at this intensity the vaporization process does not affect the behavior of the modulated part of the acoustic signal, as is seen from Fig. 7b.

At higher laser intensities the vaporization process diminishes the modulation amplitude of the acoustic signal in water (Fig. 8 b). Here the effective surface displacement $h = v_s t_f$ is about 3 μm in contrast to h ~ 0.4 μm in Fig. 7a.

Experimental setup is shown at Fig. 9 for both free and confined irradiated surface of liquid layer placed on $LiNbO_3$ piezotransducer.

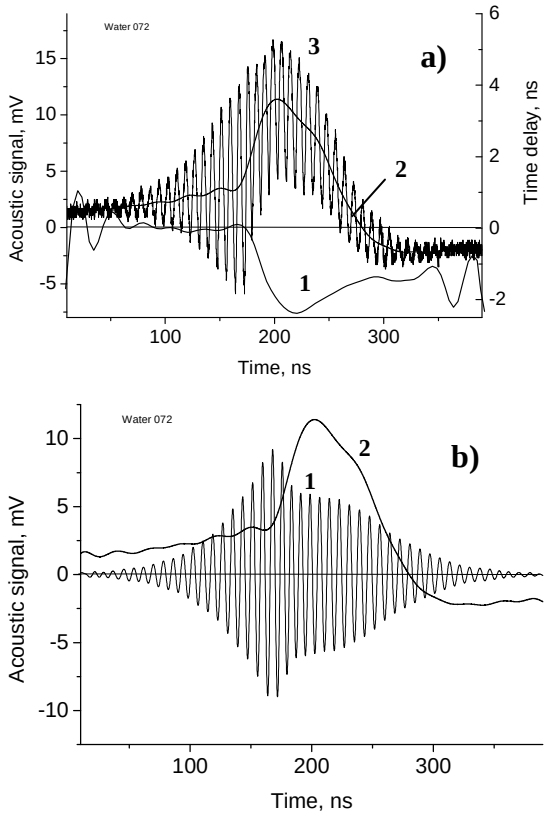

Figure 8: Pressure response to modulated laser pulse and delay time behavior (water) a: curve 1 – time delay, 2 - slow pressure component, 3 – total pressure signal; b: 1 – modulated pressure component, 2 – slow pressure component

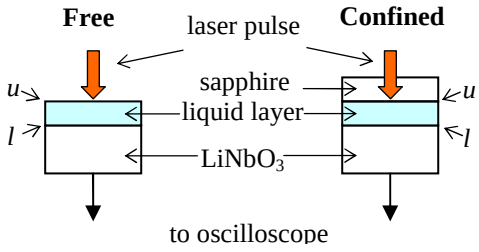

Figure 9: Scheme of the experimental setup

In the case of constrained irradiated liquid surface covered with transparent plate (sapphire, thickness 8 mm) PA signal changes its form in comparison with free surface case. One of these changes manifests itself during its reflection at the lower (*l*) and upper (*u*) boundaries of liquid layer (Fig. 9).

For the free surface case PA signal after reflection at *l* and *u* boundaries changes its sign while in the constrained case reflected PA signal retains the same polarity. This behavior of PA signal is illustrated by Fig. 10 which shows multiple reflections of PA signals in the case of free (*a*) and confined (*b*) surface. Liquid layer thickness at (a) is 0.6 mm (0.8 us reflection delay between the first maximum and the first minimum which are due to vaporization process) and at (b) thickness is 1.1 mm (1.6 us reflection delay between the first and the second maximum which also correspond to the vaporization process.

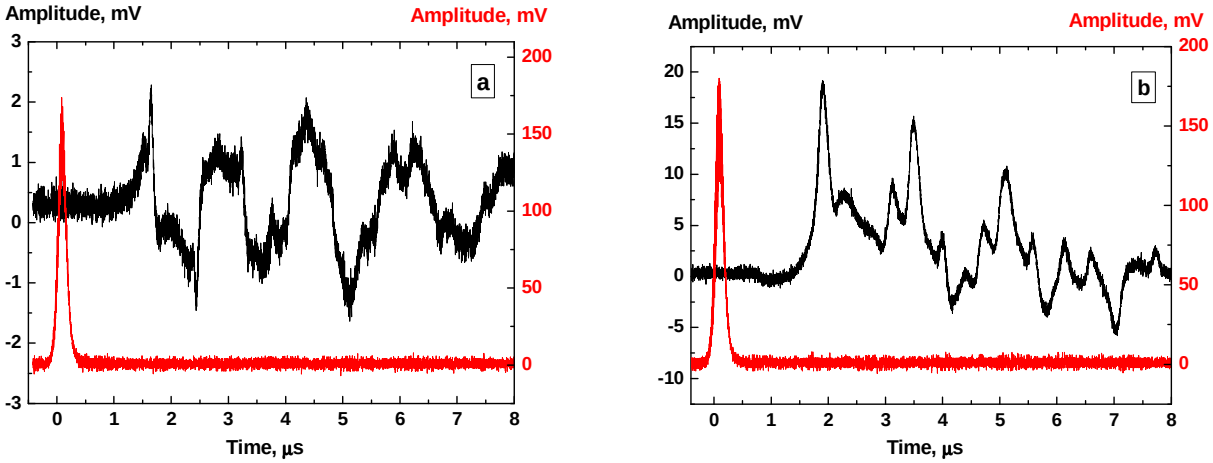

Figure 10: Pressure signals with multiple reflections in the case of free (a) and confined (b) surface

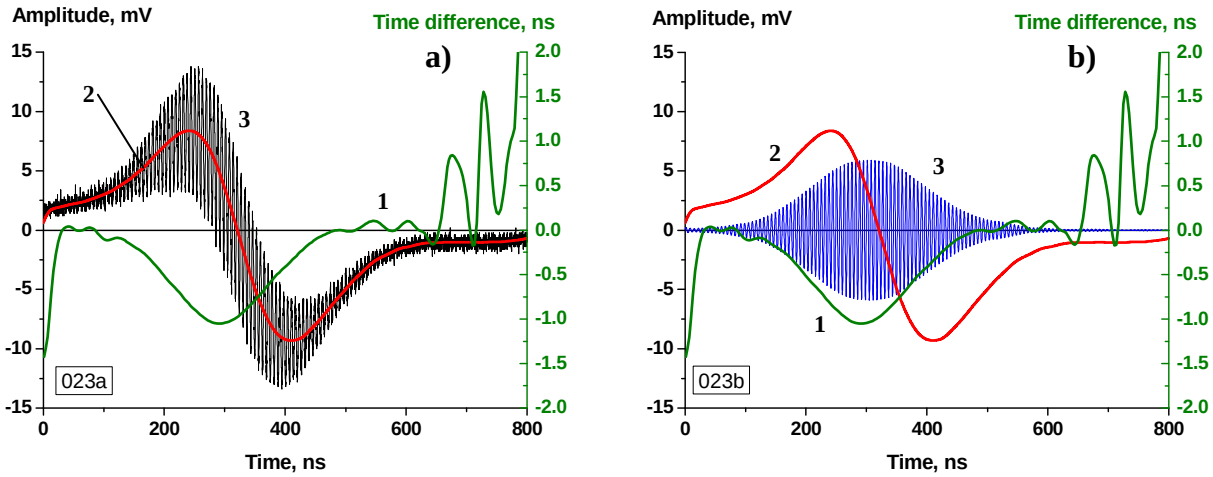

Figure 11: Pressure response to modulated laser pulse and delay time behavior (water, confined surface) a: curve 1 – time delay, 2 - slow pressure component, 3 – total pressure signal; b: 1 - time delay, 2 – slow pressure component, 3 – modulated pressure component

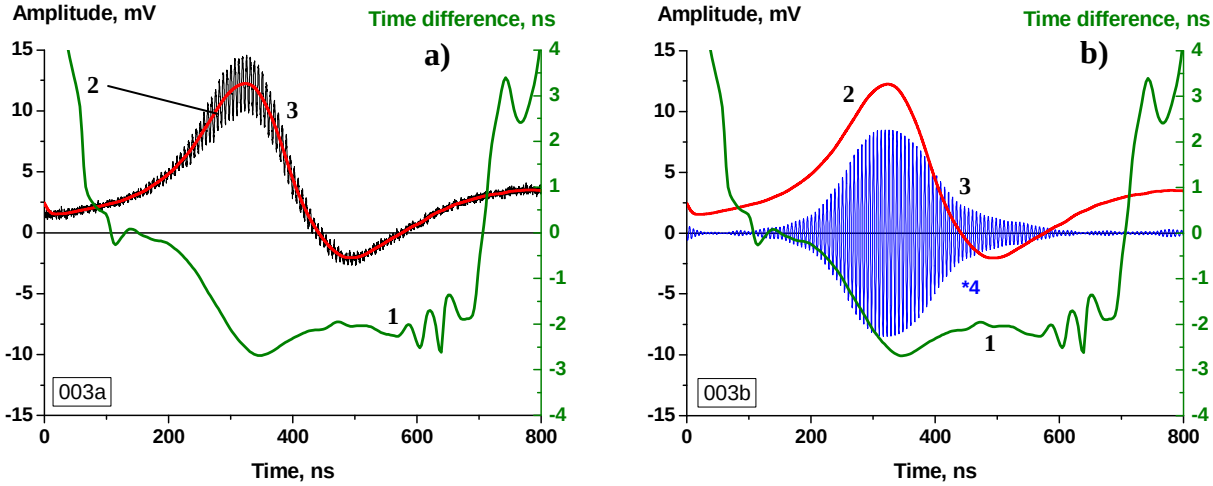

Figure 12: Pressure response to modulated laser pulse and delay time behavior (water, confined surface) a: curve 1 – time delay, 2 - slow pressure component, 3 – total pressure signal; b: 1 - time delay, 2 – slow pressure component, 3 – modulated pressure component (multiplied by factor 4)

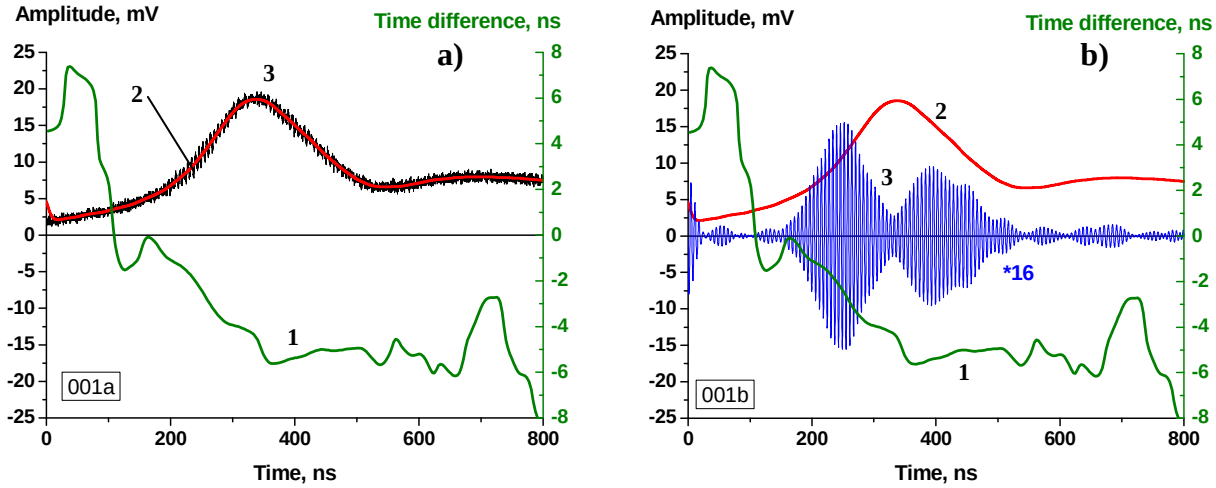

Figure 13: Pressure response to modulated laser pulse and delay time behavior (water, confined surface) a: curve 1 – time delay, 2 - slow pressure component, 3 – total pressure signal; b: 1 - time delay, 2 – slow pressure component, 3 – modulated pressure component (multiplied by factor 16)

It should be noted that the amplitude and width of PA signals in the confined case exceed those in the free surface case at the same absorbed laser intensity.

Despite the surface confinement at low intensity (Fig. 11) the form of PA signal resembles that in free surface case. This somewhat unexpected behavior may be probably due to thin cavity formation between the transparent plate and upper liquid surface (*u)* though vaporization signal is only slightly pronounced in Fig. 11 (curve 1). Such a PA signal behavior can be explained by the peculiarities of vaporization process in the confined case.

The cavity formation is in agreement with downward displacement of liquid surface which is present in all Fig. 10-13. However, the vaporization effect on PA modulation amplitude is clearly visible only at larger laser intensity (Fig. 13) when the vaporization mechanism dominates in PA signal as it is seen also in Fig. 3. From Fig. 11-13 it is also seen that modulation amplitude of PA signal decreases with laser intensity increase.

Concluding remarks

Experimental results presented here demonstrate new possibilities in studying laser ablation provided by using laser pulses with periodically modulated intensity and registration of PA signals generated in irradiated matter. The new information can be inferred from amplitude and phase behavior of modulated part of PA signal while the smooth part of PA signal describes the mean pressure behavior. Simultaneous measurements of irradiated surface displacement and pressure behavior is one of the advantages of this method.

It should be added in conclusion that in PA signal investigations during laser ablation of absorbing liquid with free surface short (subnanosecond) pressure pulses were observed which can be attributed to explosive boiling [4]. This effect takes place at higher laser intensities not considered here. The explosive boiling can be observed only in the case when the pressure in the irradiated zone is lower then the critical pressure P_c and this fact can be used to determine the P_c value.

The work was partially supported by RFBR grant № 12-02-00641-a.

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