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Photovoltaic effect in water induced by a 2.92-μm $Cr^{3+}:Yb^{3+}:Ho^{3+}$: YSGG laser

N.N. Il'ichev, L.A. Kulevsky, P.P. Pashinin

***Abstract*. The appearance of the potential difference is observed on electrodes placed in a cell with water irradiated by a *Q*-switched 2.92-μm $Cr^{3+}:Yb^{3+}:Ho^{3+}$:YSGG laser.**

Keywords: *photovoltaic effect, bias current, interaction of laser radiation with water*.

Water in the liquid state has the extremely high absorption coefficient (1.3×10^4 cm^{-1}) at a wavelength of 2.9 μm [1]. A *Q*-switched holmium or erbium laser emitting at this wavelength provides a high rate and amount of the energy deposition to the unit volume, achieving 10 kJ cm^{-3}, which exceeds the energy deposition required to evaporate the liquid completely almost by four times. Under such conditions, water undergoes transition to the supercritical aggregate state, when its temperature and pressure achieve a few thousands of degrees and a few thousands of atmospheres, according to estimates [2–4]. Such a state of water can be achieved neither in experiments on the generation of shock waves nor upon quasi-static compression or heating. A high specific rate of energy deposition can be achieved, for example, by using a 1.06-μm neodymium laser. However, in this case, the optical breakdown of water resulting in a plasma formation inevitably occurs, and the aggregate state of water strongly changes.

Note that high-power IR radiation of a $Cr^{3+}:Yb^{3+}:Ho^{3+}$:YSGG laser at 2.92 μm is strongly absorbed in water. The emission wavelength of this laser coincides with the wavelengths of strong absorption bands of a broad class of hydroxyl-containing liquids (one-, two-, and three-atomic alcohols and carbonic acids). The absorption coefficient of these liquids is lower than that of water, however, it provides the high rate and amount of energy deposition to the unit volume of these liquids, which allows one to transfer them to the nonstationary critical state.

All the above-mentioned liquids exhibit a number of nonlinear optical effects upon exposure to a high-power laser radiation at a wavelength close to the resonance absorption line at ~3 μm. In particular, upon exposure of alcohols and water to high-power IR radiation, the absorption of this radiation in these liquids decreases. The refractive index n of water in the visible region also considerably decreases from 1.33 to 1.1 [3, 5, 6]. The latter effect is still not fully explained. The search for new nonstationary absorption bands at ~0.7 μm was performed [7]. The presence of these bands could explain such a change in the refractive index; however, to answer finally to the question about the possible contribution of nonstationary absorption bands, it is necessary to improve the accuracy of measurements.

It is known that water and aqueous solutions in the supercritical state have particular physicochemical properties, in particular, they can dissolve substances which are insoluble under normal conditions [8]. For example, the dissolving of sapphire in water in the supercritical state was observed in [9], which can be treated as one of the mechanisms of laser ablation. In [4], the dissolving of graphite on the surface of ultradispersion diamond was studied upon irradiation of the diamond suspension by a high-power holmium laser. Interest in such processes considerably increased recently in connection with the problem of utilisation of radioactive waste.

The transition of a liquid to the supercritical state induced by laser radiation is nonstationary. Temperature and pressure in the irradiation region remain high only for a short time, which is determined by the laser pulse duration and geometry of the experiment. Direct measurements in this region are complicated due to the difficulties involved in determining temperature and pressure with high spatial and temporal resolutions. However, for substances studied here by using a 2.92-μm laser, the conditions can be quite easily realised at which the pressure pulse amplitude achieves a few kilobars and temperature exceeds the critical temperature.

All the above said suggest that the use of ~3-μm lasers allows one to obtain the supercritical parameters of hydroxyl-containing substances, in particular, water at room temperature of a vessel. The estimates of temperature and pressure produced in liquids irradiated by 100–150-ns, 2.9-μm, 10-mJ pulses (the Gaussian beam radius is $w \sim 0.1$ cm) give the values 1500 K and 5×10^8 Pa (5 kbar), respectively [4]. Although these estimates are rather rough and neglect the possibility of the phase transition in a material, they show that extreme conditions can be in principle achieved in the heated region.

The exposure of a substance to laser radiation can also induce various electric effects. In this paper, we observed the photovoltaic effect in water irradiated by a high-power 2.9-μm holmium laser.

N.N. Il'ichev, L.A. Kulevsky, P.P. Pashinin A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia; e-mail: ilichev@kapella.gpi.ru

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The scheme of this experiment is shown in Fig. 1. Water in a cell was irradiated either through a free surface or a quartz plate lying on the water surface. The cylindrical cell of diameter 6 mm and height 15 mm was placed in a paraffin block of size $100 \times 150 \times 50$ mm. An electric signal was taken from ring electrodes located at the cell ends. The cell capacitance, measured with a high-frequency E7-9 inductance and capacitance meter, varied from 5 to 8 pF depending on the height of a water column. The electric signal was fed from electrodes through a cable to an oscilloscope. The total capacitance of the cable and the input capacitance of the oscilloscope was ~ 100 pF.

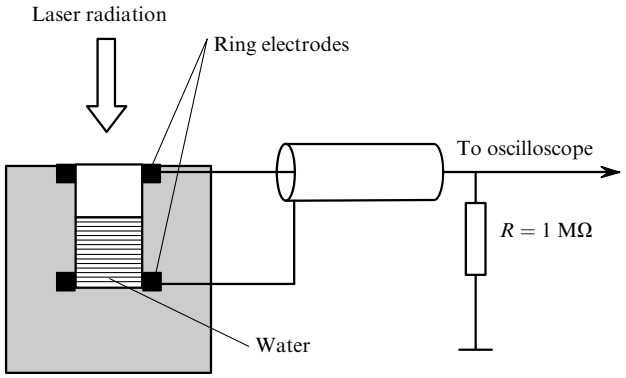

Figure 1. Scheme of the experiment.

The laser operated in the Q-switching regime at the fundamental TEM_{00} mode. The laser pulse duration was 150 ns, its energy was ~ 10 mJ, and the Gaussian beam radius was $w = 0.1$ cm. When the cell with water was irradiated by a giant pulse, an electric signal was observed on the oscilloscope screen.

Figure 2 shows the electric pulse shape observed upon irradiation through a free surface of water. The greater part of the signal had the negative polarity and amplitude at the maximum amounting to 10 mV. The delay of the signal maximum with respect to the electric pulse onset was 50 μs and the total signal duration was 150–200 μs. Note that the cable capacitance together with the input capacitance of the oscilloscope exceeded the capacitance of the cell with water approximately by a factor of 20. This suggests that a signal from the cell without connected parallel capacitance of the cable will be greater by the same factor.

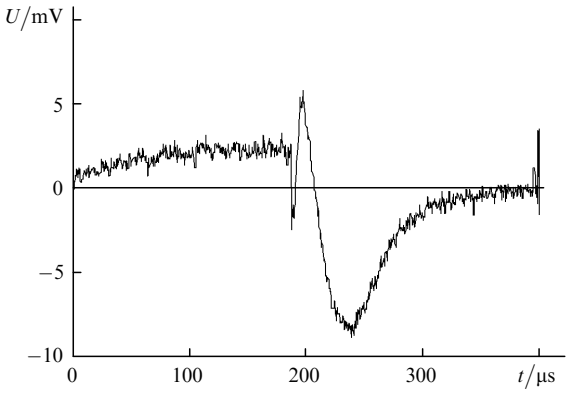

Figure 2. Electric pulse shape U observed upon irradiation of a free water surface by a high-power laser pulse.

Because the laser pulse energy had a certain instability, the electric-signal amplitude also varied from pulse to pulse; however, the signal shape and duration were similar.

Figure 3 shows the electric signal shape observed upon irradiation of water through a quartz plate. This signal differs from that observed upon irradiation through a free water surface (Fig. 2) and its reproducibility from pulse to pulse is worse that in the case of irradiation through a free surface. It is possible that upon irradiation through the quartz plate, water boils up in microbubbles in the plate-water interface, resulting in the appearance of discrete spikes on a comparatively smooth envelope of the signal.

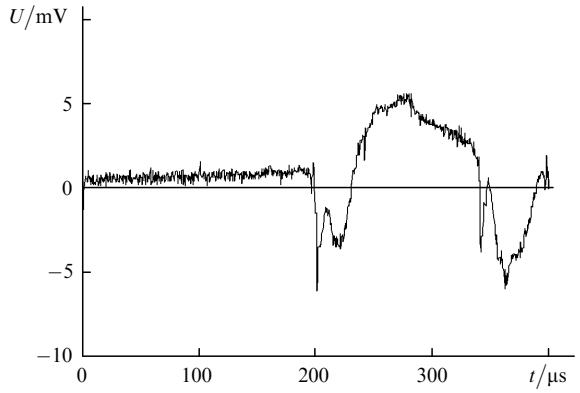

Figure 3. Electric pulse shape U observed upon irradiation of water through a quartz plate by a high-power laser pulse.

To interpret the effect observed in our experiments, it is necessary to take into account that water exposed to the 2.9-μm laser radiation experiences a drastic overheating for a short time because of the high absorption coefficient $\alpha = 1.3 \times 10^4$ cm^{-1}.

Note that the photovoltaic effect is not observed upon irradiation of heavy water or ethanol probably because the absorption coefficient in the valence band of these liquids at 2.9 μm is lower. No electric signal was observed upon irradiation of water by a pulse from a free-running laser probably because the energy deposition rate was insufficient.

For the 100-ns, 10-mJ laser pulse and the laser beam radius ~ 0.1 cm, we obtain the energy deposition to the unit volume of water $W/V = W/[(1/\alpha)(\pi w^2/2)] = 8 \times 10^3$ J cm^{-3}.

The observed effect can be explained taking into account the fact that the increase in temperature leads to the shift of the equilibrium constant of water dissociation to the side of increasing concentrations of H^+ and OH^- ions located in a thin liquid layer, giving rise to a considerable gradient of their concentration. The H^+ and OH^- ions, having different diffusion coefficients, begin to separate in space by producing an electric field, which will prevent the separation of charges of opposite signs. During diffusion, the electric field strength E will first increase in time due to the charge separation, achieving a value E_{cr}, at which the charge separation ceases, and then it will decrease.

The electric field will decrease due to two factors at least: the decrease in the concentration gradients for each of the ions (H^+ and OH^-) and cooling of water with time and,

hence, the decrease in the degree of dissociation of water into H^+ and OH^- ions.

These processes give rise to the bias (diffusion) current, which is observed in an electric circuit. Unfortunately, this interpretation suffers from some disadvantages because diffusion charge separation is usually considered in the case of a homogeneous distribution of temperature. In our case, the temperature distribution is strongly inhomogeneous. In addition, we neglected a number of effects observed in the presence of the temperature gradient, for example, thermal diffusion. Therefore, we consider our interpretation as only preliminary.

The observation of the photovoltaic effect in water exposed to a high-power three-micron laser radiation, along with its self-contained interest requiring further studies, can give new information on the aggregate state of water and other hydroxyl-containing strongly absorbing liquids.

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