VAPORIZATION OF CARBON IN AQUEOUS SUSPENSIONS UNDER PULSED LASER IRRADIATION

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Variations of optical transmittance of carbon black suspensions (CBS) irradiated by a powerful Q-switched neodymium laser have been studied. The experimentally observed kinetics and spectra of laser-induced absorption have been related to the evaporation of liquid around the particles and by the vaporization of particle material (carbon). Formation of fullerene C_{60} molecules in the carbon black suspension in water after laser irradiation has been revealed.

1. Introduction

Effects of heating up light-absorbing microobjects by pulsed laser irradiation become already appreciable at moderate radiation intensities. Elementary estimations testify that radiation emission of a neodymium Q-switched laser with intensity of about 20 MW/cm^2 can heat black (carbon) submicronic particles up to temperatures of an order of $10^3 - 10^4$ K. Under such conditions, incandescence (heat radiation emission) of laser-irradiated microobjects can be observed by even a naked eye. The overwhelming majority of experimental researches on laser-induced incandescence (LII) of microparticles is devoted to aerosol microparticles of soot (carbon), which are formed during burning [1, 2]. For instance, within the laser pulse time interval (of an order of 10^{-8} s), carbon microparticles suspended in air become heated up quickly up to a temperature of about 4000 K, which gives start to intense vaporization of carbon and brings about both substantial variations in the particle's energy balance and deceleration of the particle's temperature growth (since a significant part of energy is spent for the vaporization of the particle).

Incandescence of microparticles subjected to pulsed laser excitation is also observed in liquids and solids; e.g., in aqueous suspensions of carbon microparticles [3,4] and in borate glasses with light-absorbing microinclusions [5]. Unlike physical processes in aerodisperse carbon microparticles, those which occur when light-absorbing microparticles in the condensed media interact with pulsed laser radiation have been studied to a much lesser extent. For instance, the intense laser excitation in carbon suspensions and glasses is accompanied by a broadband glowing, the properties of which can be described, in the first approximation, by Planck's formula for an absolutely black body. Rapid heating of particles in carbon suspensions by laser irradiation gives rise to the formation of vapor-gas shells around them; this phenomenon is observed as the optical limiting and nonlinear scattering effects [6–10]. In work [11], experimental evidence was given for carbon vaporization processes, which result in a reduction of particle dimensions in suspensions caused by laser irradiation. In this paper, having for a goal to continue our studies, we have considered long-term physical and chemical changes that take place in aqueous suspensions of carbon microparticles after their irradiation with powerful pulsed laser radiation.

The model of interaction between carbon microparticles in aqueous suspensions and intense pulsed laser irradiation, which has been constructed as a result of previous studies [3, 10, 11], essentially predicts long-term consequences of laser irradiation for suspensions. For instance, principal physical mechanisms – evaporation of liquid around microparticles and vaporization of particle material – predetermine the emergence of vapor-gas formations (bubbles, shells) which can exist for rather a long time after the laser irradiation pulse terminated. In addition, vaporization of the particle material (carbon) lays the foundation for a number of extra potential opportunities for the long-term variations of optical characteristics of the suspension under investigation to appear. These variations can be governed by several factors. First, the vaporization-induced reduction of microparticle dimensions will give rise to respective modifications of their absorption and scattering cross-sections (according to the Mie theory), which must naturally affect the spectral and kinetic characteristics of the irradiated suspension. This aspect of the influence of laser irradiation on the suspension has been partially analyzed in previous studies, where the influence of irradiation on the glowing kinetics of the suspension has been examined [11]. Below, this analysis is continued from the viewpoint of the influence of irradiation on the scattering indicatrix and the spectral characteristics of suspensions.

Another important factor of the influence of laser irradiation on the optical characteristics of studied suspensions is an opportunity for some chemical and photochemical reactions to run during and after microparticle vaporization under the action of laser irradiation. Taking into account the available ideas of the mechanism and conditions of interaction between laser irradiation and suspensions (high local temperatures, high levels of light exposure, enhanced pressure, and so on), it is logical to assume that the products of particle material vaporization and surrounding liquid evaporation can enter into reactions during the action of a laser pulse and after its termination. The basis for such a conclusion is formed by the results of experiments which are analyzed below.

2. Experimental Technique

In this work, suspensions of carbon microparticles were prepared by significantly diluting black gouache paint with water. According to the results of nephelometric measurements, the average radius of particles was approximately 0.1 μm. As to the particle concentration, it can be estimated from experimental data on light attenuation by the suspension and from the absorption and scattering cross-sections which are calculated in the framework of the Mie theory. In this work, typical values of particle concentration in the suspension were estimated as $10^{14} - 10^{15}$ m^{-3}, which corresponds to the optical transmittance (of about 0.7) of a dye cell 2 cm in thickness at a wavelength of 1.064 μm.

Suspensions were irradiated by a pulsed neodymium laser (the laser wavelength was 1064 nm, the pulse duration 15 ns, the pulse energy 15 mJ, and the power density of the order of 100 MW/cm^2). In the course of irradiation, the solution was constantly stirred. After irradiation, the suspension color changed visually from grey to light brown. The absorption spectra of suspensions were registered by a Specord two-beam spectrophotometer. To estimate the particle dimensions, we studied the angular dependence of the emission radiated by a helium-neon laser and scattered by the suspension.

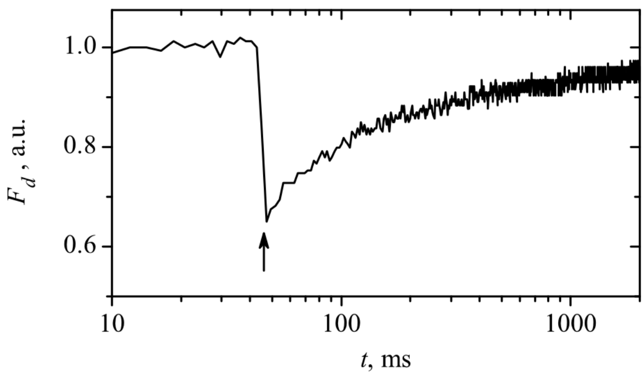

Fig. 1. Time dependence of the He–Ne laser emission intensity transmitted through a suspension layer with thickness $d = 2$ cm. The arrow denotes the moment of action of a powerful pulse from a neodymium laser

3. Results and Their Discussion

In the previous works [3, 4, 9–11] devoted to studying the interaction between powerful laser radiation and suspensions of carbon microparticles, all measurements were carried out under condition that the suspension concerned was pumped continuously through a dye cell in such a way that every laser pulse should interact with a "fresh portion" of suspension. Without such a pumping, changes in that volume of suspension, where a powerful laser beam passed through, could be detected even with a naked eye. Those changes remained appreciable during several tens of seconds after irradiation.

The experimental research of the optical transmittance variation kinetics after irradiation of the suspension with a single powerful laser pulse has been carried out. The transmittance was measured with the help of a continuous-wave helium-neon laser ($\lambda = 632.8$ nm). An example of the optical transmission oscillogram is depicted in Fig. 1. The time moment of suspension irradiation with a powerful laser pulse is designated by an arrow. The figure makes clear that the laser-induced reduction of the suspension transmittance relaxed slowly (for tens of seconds), so that the complete restoration of transmittance after irradiation within the given time interval was not observed.

Thus, our experiments testify that there are long-term variations of optical characteristics of the suspension after its irradiation with light. One of the possible explanations of the observed transmittance variations is the emergence of long-living bubbles in the irradiated suspension, while its prolonged relaxation (Fig. 1) could be explained as an effect produced by those bubbles that leave the beam owing to diffusion and

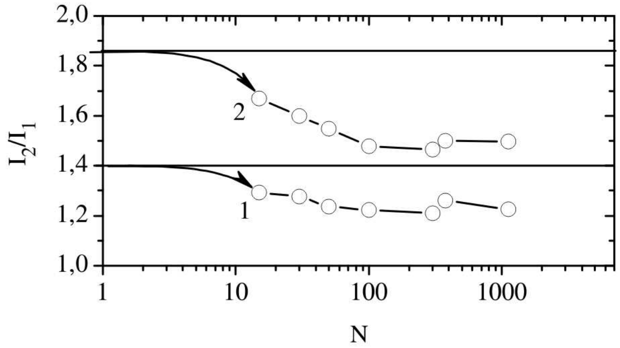

Fig. 2. Intensity ratio I_2/I_1 for light scattered at the angles $\pi/2\pm\alpha$ for $\alpha = 10$ (*1*) and 20 (*2*) as a function of the number of laser irradiation pulses N

convection. A slow disappearance of bubbles owing to the dissolution of their content cannot be excluded as well.

The following series of experiments were aimed at studying those remote consequences of suspension laser irradiation, which manifest themselves after forced stirring of the irradiated suspension. The researches were carried out as follows. The suspension was irradiated with a series of powerful laser pulses. During the time interval of irradiation (and after it), the suspension was stirred forcibly, which allowed us to prevent sedimentation and to create such conditions for irradiation that made the simulation of the process of dose absorption to a certain value possible. In 10–20 min after irradiation, the spectra of attenuation and intensity of scattered light were measured. Afterwards, irradiation of the suspension was continued.

In the course of absorbing the laser irradiation dose, the variations of the asymmetry of a light-scattering indicatrix were studied. For this purpose, a small portion of irradiated suspension was additionally diluted with distilled water; the thus obtained diluted suspension was illuminated by the beam of a helium-neon laser; and the ratio between the intensities of light scattered at the angles $\pi/2 \pm \alpha$ was measured. Making use of the Mie scattering theory [12], such measurements allow the average dimensions of light-scattering particles to be evaluated.

The results of corresponding studies are exhibited in Fig. 2 for $\alpha = 20$ and $10°$. The suspension volume subjected to irradiation was $V_0 = 2$ cm^3. The figure demonstrates that an appreciable reduction of the ratio between light intensities I_2/I_1 is observed in the range of low exposure doses (up to 100 pulses). This means that the scattering indicatrix becomes less prolonged forward as the exposure dose increases, which testifies that the average dimensions of suspension microparticles becomes smaller owing to their vaporization under the action of laser irradiation.

Let us take advantage of the results presented in Fig. 2 and try to estimate the variation of the particle dimensions under the action of laser irradiation. The suspension volume irradiated by a laser pulse is equal to $V = Sd$, where S is the area of the laser beam transverse cross-section and d is the cell thickness. In the first approximation, we neglect the laser beam attenuation along its path. Let the particle concentration in suspension be designated as N. Assume that the suspension consists of monodisperse spherical carbon particles of radius R_0. The probability for a particle to be irradiated k times after m laser pulses is given by the binomial distribution $P_k = C_m^k (V/V_0)^k (1 - V/V_0)^{m-k}$. Let the radius of a particle irradiated with a single laser pulse become smaller by ΔR_0. Then the average radius $\overline{R}_m$ of particles in suspension after m irradiation pulses equals $\overline{R}_m = \sum_{k=0}^{m} (R_0 - k\Delta R_0)P_k$.

The results of calculation showed that the variation of the ratio I_2/I_1 from 1.85 to 1.47, which was observed experimentally after 100 irradiation pulses, corresponded to the reduction of the average particle dimensions from 100 to 80 nm, which enabled us to estimate $\Delta R_0 =$ 14 nm. Therefore, every act of interaction between a single 15-ns laser pulse with the power density of about 100 MW/cm^2 and a particle of the radius $R_0 = 0.1$ μm brought about the decrease of the particle radius by $\Delta R_0 = 0.014$ μm.

Under excitation by a 15-ns laser pulse, the suspension glowing is realized through emission of an asymmetric light pulse with the leading and trailing edge durations of about 5 and 20 ns, respectively, with the pulse width at the 0.5-level being close to 25 ns. The reduction of particle dimensions owing to the laser irradiation results in that the pulse of incandescence from suspension becomes shorter. Therefore, the higher is the intensity of a laser, the smaller becomes the particle at the time moment of laser pulse termination, the quicker is the thermal relaxation, and the shorter is the trailing edge of the suspension glowing pulse.

The estimation obtained above for the variation of the particle radius allowed us to evaluate the relative reduction of the length of the incandescence pulse. For this purpose, we used the model proposed in work [11]. The model makes allowance for three principal mechanisms of consuming the energy of a heated particle: heat exchange with the particle's environment, evaporation of water around the microparticle, and vaporization of carbon. The estimation obtained above for ΔR_0 allows us to impose restrictions upon one of the variation parameters of the model and to calculate the pulse duration for the microparticle incandescence. Our calculations demonstrated that the variation of particle dimensions by 20% stimulates the variation of the incandescence pulse duration by 10%. Such an estimation completely satisfies the results of the following experiments. In particular, oscillograms of suspension incandescence pulses in the visible spectral range were registered after the suspension had been excited with a sequence of two pulses of laser radiation emission separated in time by about 200 ms. The interval between laser pulses was selected within the time interval of induced attenuation (Fig. 1) in order that the second laser pulse should interact with the same particles that were irradiated by the first pulse. The experiments showed that the second pulse of incandescence was by 8–12% shorter than the first one.

It is of interest to study possible variations of suspension spectral characteristics after laser irradiation. In Fig. 3, the differential extinction spectra of the suspension of carbon microparticles are depicted for various doses of irradiation by a neodymium laser. The spectra presented are the difference between the optical densities of irradiated and non-irradiated suspensions, provided the 1-cm thickness of the dye cell. It is clear from Fig. 3,*a* that the increase of exposure dose up to 1000 laser pulses is accompanied by an increase of extinction in the suspension in the UV range. At doses higher than 1000 laser pulses, the extinction growth in the UV range terminates, and two distinctly pronounced bands of induced absorption near wavelengths of 218 and 264 nm, as well as a weak band at 340–350 nm, are formed in differential spectra. Additionally, in the red section of the spectrum, some bleaching which gradually expands on the whole visible spectral range as the dose increases is observed. Qualitatively, a similar behavior is also observed if the suspension is irradiated by the focused laser irradiation with an intensity of about 500 MW/cm^2 (Fig. 3,*b*).

The observable behavior of the differential extinction spectra (Fig. 3) testifies to an essential transformation of the suspension concerned in the course of laser irradiation. In particular, the observable bleaching in the visible range of the spectrum can be explained by a reduction of particle dimensions in the suspension owing to the particle vaporization under the action of laser irradiation.

Concerning the nature of the induced-absorption bands at 218 and 264 nm (Fig. 3), it seems expedient to propose the following consideration. Experiments testify

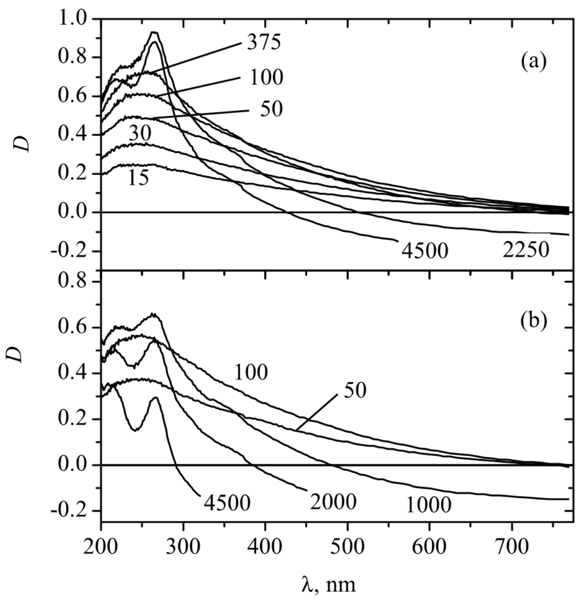

Fig. 3. Spectra of induced absorption in the aqueous suspension of carbon microparticles after their infra-red irradiation by a neodymium laser. Numbers near curves correspond to the numbers of laser irradiation pulses. The laser intensity is 100 (*a*) and 500 MW/cm^2 (*b*)

that those absorption bands practically do not change after the irradiated suspension is let settle for a week, as well as after centrifuging it for 10 min at 6600g. It should be noted that, if a non-irradiated suspension is subjected to the same centrifugation, its absorption spectrum in the UV range practically coincides with the absorption spectrum of solvent (water). Therefore, it is logical to assume that the absorption bands at 218 and 264 nm correspond to water-soluble products of laser ablation of carbon microparticles.

A good many publications devoted to studying the processes of laser vaporization of solid targets can be found in the literature. Despite that the first experiments on laser ablation are dated by the 1960s, the complete comprehension of the examined processes of interaction between powerful laser irradiation and substance is still lacking. An important place in experiments on laser ablation is occupied by carbon targets: first, owing to their simple element composition and, second, owing to the prospects of possible practical applications (growing of films with unique properties, synthesis of molecules, clusters, nanotubes, nanoparticles, and so on). The overwhelming portion of researches in laser ablation domain is carried out in vacuum or a controllable gas atmosphere.

Among products which are formed at laser vaporization of carbon targets, an important place is occupied by fullerene molecules (C_{60}, C_{70}, and so on) [13–15]. In two last decades, these molecules, owing to their specific properties, continue to attract considerable attention of many researchers. Of three allotropic modifications of carbon, which are known nowadays, only fullerenes demonstrate the appreciable solubility in organic solvents [16, 17]. This circumstance is used in modern methods of producing fullerenes for their separation from soot.

Owing to low solubility of fullerenes in water, the aqueous solutions of fullerenes have been studied poorly. In work [18], an original ultrasound-based technology for fabricating the aqueous solutions of fullerenes was applied, and the absorption spectrum of fullerene-60 in water was obtained. In particular, three wide bands located at about 220, 265, and 345 nm were observed in the ultra-violet section of the absorption spectrum of the aqueous solution of fullerene-60. Similar absorption bands (with a small spectral shift) were also observed in solutions of fullerenes in other solvents and in fullerene layers sputtered onto transparent substrates [17, 18]. The above-mentioned bands at about 220, 265, and 345 nm in the absorption spectrum of the fullerene aqueous solution [18] were in good agreement with the spectra of induced absorption in irradiated suspensions, which are depicted in Fig. 3. Such a coordination gives grounds to assume that laser irradiation of the aqueous suspension of carbon microparticles results in the formation of a solution of fullerene molecules in water. It is worth noting that this conclusion is based only on the similarity of UV absorption spectra. Attempts to register the characteristic spectral lines of fullerene molecules in the IR absorption spectra of the solid residue of irradiated suspension and in Raman spectra failed, probably owing to a low concentration of the solution obtained.

4. Conclusions

The results obtained in this work evidence for the presence of carbon vaporization processes accompanying the irradiation of aqueous suspensions of carbon microparticles with powerful laser pulses. Owing to vaporization, microparticles in the suspension diminish their dimensions, which is confirmed by the results of studying the kinetics of suspension glowing at intensive laser excitation, as well as by nephelometric measurements. In addition, laser irradiation of carbon microparticles in an aqueous medium may probably be accompanied by the formation of fullerene-60 in the form of aqueous solution.

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ВИПАРОВУВАННЯ ВУГЛЕЦЮ У ВОДНИХ СУСПЕНЗІЯХ ПРИ ІМПУЛЬСНОМУ ЛАЗЕРНОМУ ОПРОМІНЕННІ

С.Є. Зеленський, О.С. Колесник, О.В. Копишинський

Р е з ю м е

Досліджено зміни оптичного пропускання водних суспензій вуглецевих мікрочастинок після опромінення потужним випромінюванням неодимового лазера з модульованою добротністю. Спостережувані на експерименті кінетика та спектри наведеного поглинання зумовлені випаровуванням оточуючої рідини навколо мікрочастинок і випаровуванням матеріалу частинок (вуглецю). Виявлено утворення молекул фулерену C_{60} у водному розчині після лазерного опромінення вуглецевої суспензії.