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DESTRUCTION OF TRANSPARENT DIELECTRICS BY LASER RADIATION

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It has by now been well established experimentally that the phenomenon of destruction of transparent dielectrics by laser pulses of duration $\tau \sim 5 \times 10^{-8}$ sec has a clearly pronounced threshold character with respect to the radiation intensity I . This effect can be explained with a minimum of contradictions by using the mechanism of electric breakdown in the optical field of the laser beam [1]. However, the final stage of optical destruction of transparent dielectrics is connected with local release of a sufficiently large amount of heat. From this point of view, it is interesting to consider one more destruction mechanism, or more accurately its initial stage, connected with the occurrence of electronic excitations as a result of the absorption of laser light by the matter, and the subsequent conversion of the excitations into heat. Insofar as the authors know, the role of bound electron-excited states has never been considered in the theory of optical destruction.

We shall assume that the laser light is absorbed by certain impurity centers [2], although the analysis presented below remains valid, in principle, also if the electron states of the dielectric itself are excited as a result of multiphoton absorption [1]¹). The electron excitation produced on some center can vanish either by radiation or in nonradiative fashion with rate constants ν_R and ν respectively. Here $\nu_R = \nu_{RS} + \sigma I/\epsilon$, where ν_{RS} is the probability of spontaneous radiation of a photon with energy ϵ ; σ is the absorption cross section of this photon; I is the power flux density of the laser radiation, in units of energy/cm²sec. Usually ν_R depends little on the temperature T , whereas ν has a strong dependence on it [3]. Near a certain temperature T_0 we can represent the experimental dependence of the constant ν on T in the form [3]

$$\nu(T) = B \exp(CT), \quad (1)$$

where B and C are constants. We note that the concept of local temperature used below and in formula (1), is meaningful when the inequality $\nu \leq 1/\tau_{vib}$ is satisfied, where $\tau_{vib} \sim 10^{-11} - 10^{-12}$ sec is the characteristic relaxation time of the vibrational energy in the solid phase.

¹) Usually the energy of the laser photon is much lower than the energy of the electron-excited state of transparent dielectrics. Therefore the occurrence of electron excitations can take place here only as a result of the multiphoton process, which is the most probable in the case of self-focusing [1].

Owing to the nonradiative electron transitions in the impurity centers, with probability $\nu(\nu + \nu'_R)$, the latter constitute, as it were, the sources of heat. Here $\nu'_R = \nu_R + \sigma I/\epsilon$. We consider for simplicity the case of sufficiently low concentration of impurity centers, at which the local temperature of the chosen center depends little on the presence of other centers. Assume that at the initial instant of time $t = 0$ the temperature of some center is $T_0 = T(t = 0, r = a)$, where a is the radius of the center and $r = |\vec{r}|$; the impurity center is located at the point $\vec{r} = 0$. Let us examine the qualitative time behavior of the temperature increment $\delta T(t, r)$, where $0 \leq t < \tau$. As noted above, we are dealing here with the initial stage of destruction, i.e., we consider times t preceding the direct start of the destruction of the medium.

Assuming that $T = T_0 + \delta T$, where $T_0 \gg \delta T$, and putting in formula (1) $C \cdot \delta T \ll 1$, we obtain $\nu(T(t)) \approx \nu(T_0)(1 + C \cdot \delta T)$. Taking this into account, we determine δT from the equation

$$\frac{\partial \delta T}{\partial t} = \kappa \Delta \delta T + (\alpha + \beta \delta T) f(r) \quad (0 \leq t < \tau) \quad (2)$$

Here $\kappa = \lambda/c\rho$, where λ is the thermal conductivity coefficient, c the specific heat, and ρ the density of the medium;

$$\alpha = \frac{I\sigma}{c_c \rho_c} \frac{\nu(T_0)}{\frac{4}{3}\pi a^3 \nu(T_0) + \nu'_R},$$

where the subscript "c" refers to the center; $\beta = a\nu'_R C/(\nu(T_0) + \nu'_R)$; $f(r) = 1$ if $r \leq a$ and $f(r) = 0$ if $r > a$. From (2) we have

$$\delta T(r = a, t) = \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} dp e^{pt} \times \frac{\alpha [1 - e^{-a\sqrt{p/\kappa}}(1 + a\sqrt{p/\kappa})]}{p\{p - \beta[1 - e^{-a\sqrt{p/\kappa}}(1 + a\sqrt{p/\kappa})]\}} \quad (0 \leq t < \tau) \quad (3)$$

It follows from (3) that in the case $\eta = a\sqrt{\beta/\kappa} \ll 1$ the heat has time to be drawn from the center. At low values of the time, i.e., when $bt \ll 1$, where $b \sim \kappa/a^2$, we have $\delta T(r = a, t) \approx \alpha t$, and at large t , i.e., when $bt \gg 1$, we have $\delta T(r = a, t) \approx \alpha/b$. In the case $\eta \gg 1$, on the other hand, there is no time for the heat to be drawn away from the impurity center. Here $\delta T(r = a, t) = (\alpha/\beta)[e^{\beta t} - 1]$ or $\delta T(r = a, t) \sim e^{\beta t}$ if $\beta t \gg 1$. Physically this character of the dependence of δT on the time corresponds to a thermal explosion, which can be connected with the start of the destruction of the medium.

It is clear from the foregoing that the condition for the occurrence of a thermal explosion corresponds to $\eta \sim 1$. The intensity of the laser radiation I_{thr} , at which the optical destruction takes place, is therefore

$$I_{thr} = \frac{\pi a \lambda}{\sigma} \frac{(\nu(T_0) + \nu'_R)^2}{\nu(T_0)\nu'_R} \frac{1}{C} \frac{c \rho}{c_c \rho_c}.$$

Let us estimate the value of I_{thr} corresponding to the destruction of samples of fused quartz by radiation pulses from a neodymium laser with photon energy

$\epsilon \approx 1.12$ eV. Assuming $a \approx 3 \times 10^{-8}$ cm, $\sigma \approx 3 \times 10^{-19}$ cm², $\nu(T_0) \approx \nu'_R$, $1/C \approx 300^\circ\text{K}$ [3], and $c\rho \sim c_c\rho_c$, and recognizing that for fused quartz $\lambda \sim 10^{-3}$ cal-cm⁻¹sec⁻¹deg⁻¹, we obtain $I_{\text{thr}} \sim 10^{11}$ W/cm². This agrees with the experimental data [1]. We note that here $\nu'_R \approx 2\sigma I_{\text{thr}}/\epsilon \sim 10^{11}$ sec⁻¹, and consequently the value $\nu(T_0) \approx \nu'_R \sim 10^{11}$ sec⁻¹ is perfectly reasonable. We call attention to the fact that I_{thr} does not depend on the concentration of the impurity centers.

Thus, the proposed model of the initial stage of the process of optical destruction of transparent dielectrics explains the threshold character of this phenomenon on the basis of the occurrence of a thermal explosion.

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USE OF LASERS FOR SELECTIVE BREAKING OF CHEMICAL BONDS

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We propose the use of two-step excitation for selective breaking of previously chosen chemical bonds of molecules.

The development of powerful cw lasers in the infrared band uncovers a possibility of controlled action on molecular processes, such as initiation and acceleration of chemical reactions, selective excitation and breaking of chemical bonds. These questions have already been the subject of a number of papers [1 - 6].

A serious obstacle to the solution of the problem of selective breaking of bonds with the aid of laser radiation is the anharmonicity of the molecule vibrations. For most molecules, the processes of vibrational-translational relaxation at the lower levels are much slower than exchange of quanta within the limits of one mode of vibration. This makes it possible to excite individual modes by resonant absorption of radiation from a lower level. However, owing to the harmonicity, vibrational-translational relaxation begins to predominate at higher levels, but still far from the dissociation limit [7, 8]. So long as the heating of the gas upon absorption of the radiation does not lead to a diffuse propagation of the excitation over these levels, the dissociation of the molecules will have a very low probability. In the case of polyatomic molecules, predissociation, not accompanied by heating of the gas, is possible as was observed experimentally in [1]. In both cases, the same bond is broken.

For selective breaking of bonds chosen beforehand, one can use the two-step photoexcitation proposed in this paper. To this end the molecules, resonantly absorbing the radiation from a laser in the infrared band, are simultaneously irradiated with light from another laser in the visible or in the near ultraviolet. The wavelength of the second laser is chosen such as to permit photodissociation from those energy levels of the electronic ground state, which