MODEL OF THE NONLINEAR ABSORPTION OF LIGHT

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The propagation of light in a polymer medium containing an admixture of different molecules with large photoabsorption cross section is considered theoretically. The absorptivity of the medium is assumed to depend strongly on the density of the internal energy. The solution yields two absorption regimes: intense, determined by the host medium, and weak, due solely to the impurity molecules.

1. The phenomena that result from the passage of resonantly absorbed monochromatic laser radiation in gaseous and liquid media have been well studied (bleaching waves [1], photochemical waves in gases [2]). The propagation and absorption of light in transparent polymer media have been considered less often. The successes of polymer chemistry, the great variety of possible structures and properties, and also the increasing number of studies of the migration of absorbed energy in an individual complex molecule and in a molecule implanted in a medium make it possible to predict and realize a number of effects resulting from the interaction of intense light beams with such substances.

In practical applications one has the problem of maintaining the intensity of a laser pulse that passes through a layer of matter in definite limits when there are arbitrary fluctuations in the radiation intensity on its entry into the medium. An interesting problem is the attentuation of an originally monochromatic light beam that propagates in a given direction. The part of the light flux that is diffusely re-emitted during the propagation process and also the radiation of the energy absorbed by the matter after the action of the light pulse has ceased are of no particular interest. We consider intensities and durations of the light flux that do not lead to optical breakdown in gases or mechanical destruction of a sample. Under such conditions it is of interest to pose and solve a model problem.

We assume that, beginning with the time $t = 0$, a plane-parallel monochromatic light flux of constant intensity is incident from the left on the surface of a material that fills the right-hand half-space. We consider a polymer material that is transparent at the initial time at the given frequency but contains an admixture of different molecules which have a large photon capture cross section. The transformation of the light energy absorbed by the impurity molecules is determined by the ratio of the probabilities of nonradiative processes and processes with the emission of a photon. Bearing in mind that for some organic compounds in an appropriate environment the probability of nonradiative relaxation of an excitation in the medium is large, we consider the case when this process is appreciably more probable than deactivation with radiation.

The energy of the photon absorbed by the impurity molecule is redistributed in the molecule-medium system and goes over into the internal degrees of freedom of the medium. The time of transition of the excitation to the medium is appreciably shorter than the time between two successive absorptions of photons by the molecule. As a result of the relaxation process, there is a rapid local heating of the medium near the impurity molecule. The absorptivity of polymer media depends strongly on the "temperature" and this process therefore raises the absorption in the considered region. As an example, we mention copolymers with groups of trans-3-thiabicyclo[3.3.0]octane or 2-aminopyrene, which have a steep drop in the absorption band in the region of 220 and 340 nm. We assume that adjustment to resonant n-photon absorption of light makes the main contribution to the temperature dependence of the absorption coefficient under these conditions. For copolymers with groups of trans-3-thiabicyclo[3.3.0]octane $n = 3$, while for the 2-aminopyrene $n = 2$ for a ruby laser photon. We consider also durations of the action of the light flux and

concentrations of impurity molecules at which overlapping of the expanding heated zones does not occur before the end of the pulse and each impurity molecule can be treated separately.

The excitations of the medium resulting from the n-photon absorption need not make a significant contribution to the further absorption of the original flux. We consider the two following possible channels for the suppression of the resulting excitations: direct fast deactivation with emission at new frequency and deactivation with emission after a possible fast escape of the excitation from the region in which it was formed. Because of the adjustment, the photoabsorption cross section of the photon of the new frequency is small and reabsorption in the considered layer of material can be ignored. We shall assume that these two processes succeed in reducing the density of excitations so much that the saturation effect does not occur for the considered pulse durations. The higher lying levels are assumed to have a structure such that the probability of occurrence of a higher excitation as a result of absorption of a photon of the original radiation is negligibly small. Under these conditions, the energy absorbed in the n-photon processes leaves the considered region and need not be considered further.

2. We consider the kinetics of the propagation and absorption of light in the medium on the basis of the balance equations

$$\partial u \,/\, \partial t + c\partial u \,/\, \partial x = -\sigma c N_1 u - b N_3 u^n, \quad \partial N_1 \,/\, \partial t = -\sigma c N_1 u + N_2 \,/\, \tau, \quad N_1 + N_2 = N \tag{2.1}$$

Here, u is the density of the photons of the radiation; N_1 and N_2 are the densities of the unexcited and excited impurity molecules; N is the total density of impurity molecules; N_3 is the density of the "heated" molecules of the medium capable of resonant n-photon absorption; σ is the cross section for the capture of a photon by an impurity molecule; c is the velocity of light in the medium; τ is the characteristic time of transfer of an excitation by an impurity molecule to the medium; and b is a constant that characterizes the process of n-quantum absorption of light by the medium.

We calculate N_3 approximately; it includes the molecules of the sections of the medium in which the density ρ of the internal energy is greater than a threshold value ρ_0, i.e., the sufficiently "hot" molecules.

If the matter has an isotropic distribution, these sections are spherical volumes with an impurity molecule at the center. If v is the velocity of propagation of an excitation in the medium, then at a time t after the absorption of a photon by an impurity molecule the energy ε of this photon has been dissipated in the volume of a sphere of radius $R = vt$. After a time $t \gg \tau$ the impurity molecule will have absorbed and transmitted to the medium $m = \sigma ctn$ photons. Taking m to be large, we shall assume it is equal to the nearest 0 integer. The radius of the sphere in which the energy of the i-th photon absorbed since $t = 0$ is distributed is

$$R_i = vt\,(m + 1 - i) \,/\, m, \quad 1 \leqslant i \leqslant m$$

and the corresponding energy density is

$$\rho_i = \varepsilon \,/\, V_i, \quad V_i = {}^4\!/_3 \pi R_i^3$$

The total energy density at a distance $r(R_{i+1} < r < R_i)$ from the impurity molecule is

$$\rho\,(r) = \sum_{j=1}^{i} \frac{\varepsilon}{V_j} \tag{2.2}$$

Light will be absorbed by the medium in the regions in which $\rho > \rho_0$ and $r < r_0$ (r_0 is the threshold radius). The main contribution to the absorption comes from the region with large values of r_0, and in (2.2) we can therefore go over from summation to integration:

$$\rho\,(r) = \frac{m\varepsilon}{vt} \int_{vt}^{r} \frac{dr}{4\pi r^3 \,/\, 3} = \frac{3m\varepsilon}{8\pi vt} \left(\frac{1}{r^2} - \frac{1}{(vt)^2} \right) \tag{2.3}$$

Since ρ_0 is appreciably higher than the initial energy density (originally there is no absorption) $r_0 \ll vt$, it follows from (2.3) that

$$r_0 = (3\varepsilon\sigma cu \,/\, 8\pi\rho_0 v)^{1/2} = (Au)^{1/2}$$

For the threshold volume V_0, we obtain

$$V_0 = {}^4/_3\pi \, (Au)^{3}$$

The density of the absorbing molecules of the medium is

$$N_3 = {}^4/_3 N\pi \, (Au)^{3} \, N_0 = (a/b) \, Nu^{3}$$

where N_0 is the density of the molecules of the medium. Here we have remembered that the contribution from each energy quantum ε transmitted to the medium by the impurity molecule is small after mixing and the absorbing volume around the molecules N_1 and N_2 is approximately the same. Equations (2.1) take the form

$$\partial u / \partial t + c\partial u / \partial x = -\sigma c N_1 u - aNu^{n+3/2}, \quad \partial N_1 / \partial t$$
$$= -\sigma c N_1 u + N_2 / \tau, \quad N_1 + N_2 = N \tag{2.4}$$

with the initial and boundary conditions

$$N_1(x, \ t = 0) = N, \quad u(x = 0, \ t) = w\theta(t)$$
$$\theta(t) = \begin{cases} 1 & \text{for} \quad t > 0 \\ 0 & \text{for} \quad t < 0 \end{cases}$$

where w is the density of the photons in the incident flux at its point of entry into the medium.

3. With allowance for the initial conditions for N_1, we obtain from (2.4)

$$N_1 = N\left[1 + \int_0^t \exp\left\{\int_0^{t_1}[1 + \sigma c\tau u(t_2, x)]\,\tau^{-1}\,dt^2\right\}\frac{dt_1}{\tau}\right]\exp\left\{-\int_0^t[1 + \sigma c\tau u(t_2, x)]\,\tau^{-1}\,dt_2\right\} \tag{3.1}$$

In accordance with the adopted assumptions $\sigma c\tau u \ll 1$, and $N_1 \approx N$ follows from (3.1). The first of Eqs. (2.4) takes the form

$$\partial u / \partial t + c\partial u / \partial x = -\sigma c N u - aNu^{n+3/2} \tag{3.2}$$

Going over to the variables $x_1 = x$, $t_1 = t - x/c$, and making transformations, we obtain

$$\frac{c}{n + 1/2}\frac{\partial u^{n+1/2}}{\partial x_1} = -\sigma c N u^{n+1/2} - Nau^{2n+1}$$

This relation can be integrated:

$$u = \left[\frac{\sigma c}{a}\{B\exp[\sigma N(n + 1/2)x] - 1\}^{-1}\right]^{1/(n+1/2)} \quad B = \frac{\theta(t - x/c)\,w^{n+1/2} + \sigma c/a}{\theta(t - x/c)\,w^{n+1/2}} \tag{3.3}$$

where the boundary conditions have been used.

For sufficiently large t, B = const and the coordinate dependence of the density of quanta is determined by (3.3). Let us consider a case of practical interest: $\sigma c/a \ll w^{n+1/2}$. Under these conditions the intensity decreases for small x as

$$u = w\left[\frac{\sigma c}{aw^{n+1/2}}\frac{1}{N\sigma(n + 1/2)x'}\right]^{1/(n+1/2)} = w\left(\frac{\Delta'}{x'}\right)^{1/(n+1/2)}$$
$$x' = x + \Delta', \quad \Delta' = c[Naw^{n+1/2}(n + 1/2)]^{-1}$$

For large x, (3.3) yields

$$u \approx (\sigma c / a)^{1/(n+1/2)} \exp(-x / \Delta)$$

where $\Delta = 1/N\sigma$. It can be seen from the relation

$$\Delta' / \Delta = \sigma c\,[aw^{n+1/2}(n + 1/2)]^{-1} \ll 1$$

that in the considered case the fall-off of the intensity at the coordinate origin is more rapid than in the remaining part of the material.

4. The region of a light flux whose intensity on entry into the medium is sufficiently high breaks up

into two zones. In the first, which is comparatively thin (characteristic distance $-\Delta'$), there is intense absorption of light by the host medium. The major part of the light flux is absorbed here. The second region is much thicker (characteristic distance Δ). In it the absorption of light is determined by the impurity molecules and is much weaker than in the first zone. If the intensity of the incident flux is increased, the relative thickness of the first zone decreases. The photon density at a fixed x in the second zone depends weakly on the intensity of the incident flux [see (3.3)]. If the intensity of light is increased, it remains almost constant.

The transition between the two absorption regimes is abrupt. This can be seen from (3.2). To the former there corresponds a term linear in the density, to the latter, a term containing the photon density to the power $n + 3/2$. The abruptness of the transition from one absorption regime to the other is due to the large difference between these powers. The corresponding coefficients in (3.2) are determined by the physical properties of the medium and the impurity molecules and lie within ranges of practical interest for a number of substances.

LITERATURE CITED

1. V. M. Ovchinnikov and V. E. Khartsiev, "Bleaching waves in two-level systems," Zh. Éksp. Teor. Fiz., 49, No. 1, 315 (1965).
2. A. N. Oraevskii, V. P. Pimenov, and V. A. Shcheglov, "Photochemical waves in gases," Zh. Éksp. Teor. Fiz., 62, No. 1, 89 (1972).