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# Saturable absorption and thermal defocusing of light in dye solutions

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The nonlinear transmission (NT) of nanosecond laser radiation ($\lambda = 532$nm, $\lambda = 694.3$nm) by molecular solutions of organic dyes is investigated. It is found that at intensities $\approx 10^{25}$ cm$^{-2}$sec$^{-1}$ the NT of such systems is due to molecular absorption in a system of two or three singlet states, while at intensity higher than $10^{25}$ cm$^{-2}$sec$^{-1}$ the NT is determined by thermal defocusing. Saturation of the absorption as a result of two-step transitions was observed for molecules with three singlet states, as well as nonstationary thermal self-focusing in the nanosecond time interval.

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Resonant nonlinear absorption of intense light fluxes by complex-molecule solutions is due primarily to the appreciable changes of the populations of the combining states.[1] Many aspects of coherent and nonlinear optics are investigated by the nonlinear-absorption method by varying the frequency, duration, intensity, and coherence of the radiation acting on the investigated object.[2] A large number of nonlinear-absorption problems involves the use of the nonlinear absorption effect to generate and modulate laser emission,[3] to shape light pulses with specified parameters,[4,5] and for problems of dynamic holography.

A widely used method of studying nonlinear absorption is to measure the waveform of a quasimonochromatic radiation pulse and its energy (power) after passage through a nonlinear absorber. The information obtained in such experiments, particularly the transmission $T=f(I_0, \tau_p, R)$, where $I_0$ is the intensity at the input, and $\tau_p$ and $R$ are the pulse duration and the beam radius in the interaction region, is used to determine the physical picture of the interaction, the energy structure of the molecule, and others.

A number of earlier investigations[7-10] were made from approximately this viewpoint. In particular, an analysis[9,10] of the nonlinear molecular-absorption function $T=f(I_0)$ by the rate-equation method has predicted the existence, in a three-level system, of saturable absorption resulting from two-step transitions (the frequency of the applied radiation was at resonance with the two spin- and symmetry-allowed transitions). Experiment, however, did not yield this result. Furthermore, at high laser-pulse intensities (50–100 MW/cm$^2$) some workers observed a decrease of the nonlinear transmission. It was assumed that this result (the decrease of the nonlinear transmission with increasing pulse energy) was also due to redistribution of the populations of the combining levels[7,9] and to stimulated light scattering by thermal inhomogeneities of the medium.[11,12]

We present here the results of the first observation and investigation of the saturation effect due to two-step transitions in molecular solutions of organic dyes. The decrease of the light-scattering-induced nonlinear transmission at high incident-radiation energies is interpreted within the framework of the premises of nonstationary thermal self-focusing.

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## EXPERIMENTAL RESULTS

The nonlinear absorption was studied by measuring the energies and waveforms of the pulses entering and leaving the nonlinear absorbter. The pulsed quasi-monochromatic radiation sources were passive $Q$-switched ruby and neodymium lasers at their fundamental and second-harmonic frequencies. The lasers generated many transverse modes and a single longitudinal mode, the beams had relatively low spatial homogeneity, and the average pulse duration at half maximum was 25–35 nsec. The principal measurements were made at wavelengths 694.3 and 532 nm. The nonlinear absorber was contained in a plane-parallel cell 1–2 mm thick. IMO-2 calorimeters and high-speed photocells of the FK-2 type measured to energies and durations (waveforms) of the light pulses. A lens of 1 m focal length reduced the beam diameter in the interaction region to 0.5–1 mm. At the employed entry aperture of the calorimeter, an increase of the beam divergence to above 1° was taken to mean a decrease of its energy. In addition, the scattering screen was photographed to estimate the beam-defocusing angles.

The nonlinear absorbers were molecular solutions of polymethine dyes (PD) with indolenine end groups. The absorption spectra of these PD in ethanol saturated with atmospheric oxygen are shown in Fig. 1. Related to the long-wave absorption band of all the PD is the first allowed electron-vibrational transition $S_0 \to S_1$; the absorption bands in the 250–350 nm regions are connected with the $S_0 \to S_n$ molecular transitions.[13] This group of PD is characterized by a relatively low singlet-triplet conversion rate that depends on the structure of the molecules. The aggregate of the mentioned characteristics of the sources and of the investigated objects allows us to disregard triplet–triplet absorption at the excitation frequency. The energy spectrum of the investigated molecules can therefore be represented by three singlet vibronic states

$$S_0 \underset{\longleftarrow}{\overset{\longrightarrow}{\leftsquigarrow}} S_1 \overset{\longrightarrow}{\leftsquigarrow} S_n,$$

where the straight and wavy arrows denote respectively radiative and nonradiative transitions. In all three states, thermal equilibrium sets in rapidly compared with the excitation-pulse duration. It is assumed that the $S_1 \to S_n$ transition is not symmetry-forbidden in complex molecules, and that its probability depends on satisfaction of the condition $\hbar\omega = E_{S_n} - E_{S_1}$. At a given excitation wavelength (say $\lambda = 532$ nm) a change from the dye PD 518 to PD 539, PD 570, PD 608, or PD 654 is accompanied by a monotonic decrease of the $S_0 \to S_1$ absorption probability relative to the probability of $S_1 \to S_n$ absorption. A theoretical analysis of the nonlinear absorption in a three-level model of the molecule shows that such changes can influence decisively the form of the function $T = f(I_0, \tau_p, R)$.

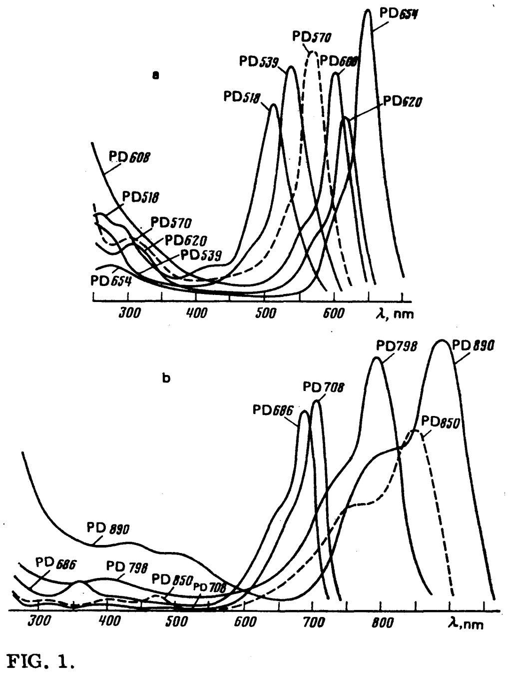

FIG. 1.

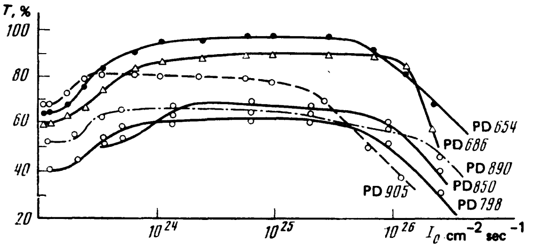

FIG. 2.

Experimental plots of $T = E_{\text{out}}/E_0$ at constant $\tau p$ and $R$ ($E_0$ and $E_{\text{out}}$ are the energies of the pulse as it enters and leaves the cell) are shown for $\lambda = 694.3$ nm in Fig. 2 (the curves are drawn through points that represent weighted averages of 5–8 measurements). All the presented plots, the 30-fold change of the cross sections for the $S_0 \to S_1$ transition notwithstanding, have the same character for all absorbers: an increase of the incident intensity causes bleaching, followed by a section in which the absorption is constant, and then by a section in which the bleaching decreases (darkening). The corresponding plots of the nonlinear absorption for excitation at $\lambda = 532$ nm are more complicated in character (Fig. 3). The solutions PD 518, PD 539, and PD 570 reveal the already known sequence: bleaching–saturation–darkening. For the remaining PD, which have a lower absorption probability for the $S_0 \to S_1$ transition,

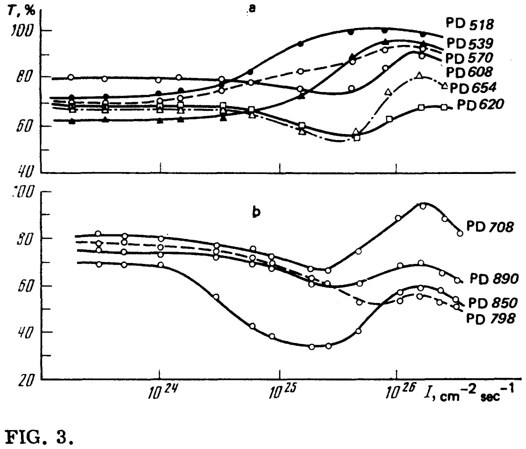

FIG. 3.

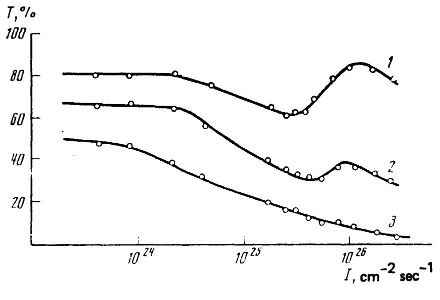

FIG. 4.

the transmission first decreases with increasing incident intensity, followed by a growth in the bleaching and again, in the maximum intensity region, by darkening.

Figure 4 shows the dependence of the nonlinear transmission of PD 686 at $\lambda = 532$ nm for three different initial transmissions: $T_0 = 80\%$ (curve 1), 67% (2), and 50% (3). The vanishing of the section of nonlinear bleaching with decrease of the initial transmission can be distinctly traced.

Figure 5 shows the evolution (from $a$ to $f$) of the $\lambda = 532$ nm incident-radiation divergence with increase of the pump-pulse energy, obtained for the nonlinear absorber PD 686; the results coincide with the region of decreased bleaching. The record of the radiation corresponding to the initial beam (central part not subjected to defocusing) shows that the pulse is shortened on account of the decrease of the power on the trailing edge. Oscillograms of the beam sections corresponding to the defocusing cone show that these sections contain the radiation power corresponding to the fall-off of the pulse. A shortening of the pulse duration at half maximum by a factor of two and three takes place in the same manner.

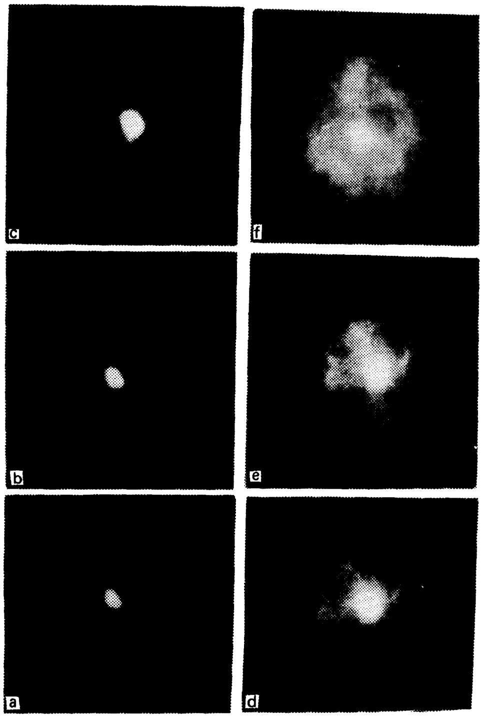

FIG. 5.

## ANALYSIS OF RESULTS

1. The experimental plots of the nonlinear absorption $T = f(I_0)$ can be related to two regions of the intensities acting on the investigated object. For intensities up to $10^{25}$ cm$^{-2}$ sec$^{-1}$ at the employed space-time parameters of the beam, the equilibrium thermodynamic state of the absorber does not change enough to act on the transmitted light. In this intensity region (at constant $\tau_p$ and $R$) the decisive influence on the beam parameter is exerted by the change of the populations of the impurity-molecule (PD) combining states. At light intensities higher than $10^{25}$ cm$^{-2}$ sec$^{-1}$ the thermodynamic parameters $T$, $P$, and $V$ of the solution begin to deviate from equilibrium, owing to absorption and heating. The transmitted radiation is subject to self-action due to the changes of the refractive index of the solvent and of the absorption coefficient of the impurity molecules. In the absence of heating, the permittivity of the solution is determined only by the solvent, in view of the very low density of the impurity ($c \leq 10^{-4}$ mole/liter).

On the basis of this assumption, the nonlinear absorption of the PD molecular solution can be described by using the rate equations. At a pulse duration $\tau_p \approx 30$ nsec, at a natural lifetime of the fluorescence of the employed molecules $\tau_e \approx 1$ nsec, at a negligibly small conversion into the metastable state, and at a rapid (compared with $\tau_p$) establishment of thermal equilibrium in the electron-vibrational states, the following balance equations are valid for the three-level model:

$$\begin{gathered}dN_2/dt = N_1\sigma_{12j}(\omega)I(\omega) - N_2[\sigma_{23}(\omega)I(\omega) \\ + \sigma_{2j1}(\omega)I(\omega) + k_{21}] + N_3[\sigma_{32}(\omega)I(\omega) + k_{32}], \\ dN_3/dt = N_2\sigma_{23}(\omega)I(\omega) - N_3[\sigma_{32}(\omega)I(\omega) + k_{32}]; \\ N_0 = \sum_{i=1}^{3} N_i.\end{gathered} \tag{1}$$

The stationary solution of the system (1) leads to the following expression for the nonlinear absorption coefficient:

$$\begin{gathered}\alpha_{12}(I(\omega)) = N_1(I(\omega))\sigma_{12}(\omega) - N_2(I(\omega))[\sigma_{21}(\omega) - \sigma_{23}(\omega)] \\ -N_3(I(\omega))\sigma_{32}(\omega) = \alpha_0(\omega)\frac{1 + b(\omega)I(\omega) - d(\omega)I^2(\omega)}{1 + a(\omega)I(\omega) + c(\omega)I^2(\omega)},\end{gathered} \tag{2}$$

where

$$\begin{gathered}a(\omega) = \frac{\sigma_{32}(\omega)k_{21} + \sigma_{21}(\omega)k_{32} + \sigma_{12}(\omega)k_{32}}{k_{21}k_{32}}, \\ b(\omega) = \frac{\sigma_{32}(\omega)k_{21} + \sigma_{23}(\omega)k_{32} - \sigma_{32}(\omega)k_{21}}{k_{21}k_{32}}, \\ c(\omega) = \frac{\sigma_{12}(\omega)\sigma_{23}(\omega) + \sigma_{12}(\omega)\sigma_{32}(\omega) + \sigma_{21}(\omega)\sigma_{32}(\omega)}{k_{21}k_{32}} \\ d(\omega) = \sigma_{21}(\omega)\sigma_{32}(\omega)/k_{21}k_{32},\end{gathered} \tag{2a}$$

$\sigma_{ij}$ are the absorption cross sections for transitions between states, $k_{ij}$ are the relaxation rates, $\alpha_0$ is the initial absorption coefficient in cm$^{-1}$; $\sigma_{ij}$ and $k_{ij}$ average out over all the equilibrium vibrational levels. The term $d(\omega)$ can be neglected since it is relatively small.

The absorption coefficient of an optically dense layer, which is obtained by integrating the equation

$$dI(\omega, z)/dz = -\alpha_{12}(I(\omega, z))I(\omega, z),$$

takes the form

$$\frac{T_0}{T(I(\omega, z))} = \left[\frac{1+b(\omega)T(I(\omega, z))I_0(\omega)}{1+b(\omega)I_0(\omega)}\right]^{\gamma}$$
$$\times\exp\left[\frac{c(\omega)}{b(\omega)}I_0(\omega)(T(I(\omega, z))-1)\right],$$
$$\gamma = \frac{a(\omega)}{b(\omega)} - \frac{c(\omega)}{b^2(\omega)} - 1, \quad T_i = \exp(-\alpha_i z),$$

where $I_0(\omega)$ is the intensity at the entry into the absorber. Plots of $T[I(\omega, z)]$ calculated from Eq. (3) are shown in Fig. 6. The constants used in the calculation, $T_0 = 50\%$, $a(\omega) = 10^{-26}$, $b(\omega) = 2 \times 10^{-26}$, and $c(\omega) = 10^{-53}$, were obtained by substituting in (2a) typical spectroscopic parameters of the molecules. The obtained form of plot 1 in Fig. 6 is possible under the condition $b(\omega) > a(\omega)$, meaning that the $S_1 \to S_n$ transition has a higher probability than $S_0 \to S_1$. Satisfaction of this condition leads initially to an increase of the absorption coefficient over the initial value $\alpha_0(\omega)z$. When the intensity reaches $10^{24}$ cm$^{-2}$ sec$^{-1}$ an important role is assumed in such a system by two-step transitions determined by the product of the probabilities for each of the transitions $S_0 \to S_1$ and $S_1 \to S_n$ separately. Finally, at intensities $10^{28}$ cm$^{-2}$ sec$^{-1}$ complete bleaching sets in such a three-level system; under the experimental conditions, nonlinearities of different nature assume an important role already at intensities $10^{25}$–$10^{27}$ cm$^{-2}$ sec$^{-1}$, and hinder the bleaching.

Compared with curve 1, the calculated plots 2 and 3 of Fig. 6 correspond to a two- and threefold decrease of the cross section $\sigma_{23}(\omega)$; the plot 4 of the same figure corresponds to an increase of $\sigma_{23}(\omega)$. The qualitative agreement between the experimental results and those predicted by our model is good. Thus, the curves of Fig. 2 correspond to the case $b(\omega) < a(\omega)$, since $\sigma_{23}(\omega) < \sigma_{12}(\omega)$ for all the employed PD with $\lambda = 964.3$ nm. (The corresponding theoretical curves are not shown in Fig. 6; they can be found, e.g., in Ref. 10).

The plots of $T = f(I_0)$ for the group of absorbers based on PD excited at $\lambda = 532$ nm illustrate clearly the transition from bleaching $[a(\omega) > b(\omega)]$ to darkening $[b(\omega) > a(\omega)]$.

In the model employed, the saturation due to two-step transitions does not depend on the layer optical thickness; the effect disappears in experiment (Fig. 4), apparently owing to stationary self-defocusing of thermal origin.

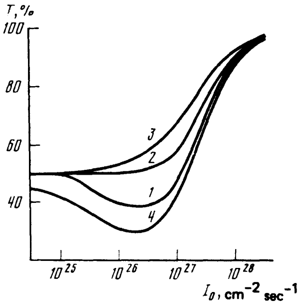

FIG. 6.

2. Although self-defocusing of beams has been known for a relatively long time,[14] its importance for nanosecond pulsed radiation was apparently not stressed heretofore. Yet the presence of this effect in a large number of processes connected with the use of molecular solutions of organic compounds (generation and modulation of light) makes it important to understand the conditions under which it occurs. The thermodynamic parameters of the solution $(P, T, V)$ when up to 1 $\mu$W of radiation is absorbed do not deviate from their equilibrium values because of the small effective power and the ineffective outward dissipation of the heat.

When the intensity is raised to ≈1 W/cm$^2$ and the irradiation is continuous, the solution is isobarically heated in the region of interaction of the absorbing centers with the laser beam. Deviation from equilibrium at an arbitrary point of the volume occurs when the necessary amount of energy is absorbed within a time $(t_p)$ that is short compared with the temperature-relaxation time: $tT \approx \pi R^2/\chi$ (where $R$ is the radius of the laser beam and $\chi$ (cm$^2$/sec) is the thermal diffusivity), but long compared with the excess-pressure relaxation time $t_s = 2R/v_s$ (where $v_s$ is the speed of sound in the medium). For example, at typical values $R = 1$ mm, $\chi = 10^{-3}$ cm$^2$/sec, and $v_s = 1.5 \times 10^5$ cm/sec the temperature relaxation time is $t_T \approx 10$ sec and $t_s \approx 1$ $\mu$sec. The excess over the equilibrium temperature is given in this case by

$$\delta T(r) = \alpha_0(\omega)I(\omega, r)t_p/\rho c_p E,$$

where $\alpha_0(\omega)$ is the linear coefficient of absorption, $I(\omega, r)$ is the light intensity at the considered point $r$; $\rho$ and $c_p$ are the specific density and specific heat for the isobaric process, and $E = 4.19$ J/cal. For typical liquid parameters $\rho = 1$ g/cm$^3$, $c_p = 0.5$ cal/g-deg, $I(\omega, r) = 1$ W/cm$^2$, $t_p = 1$ sec, and $\alpha(\omega) = 10$ cm$^{-1}$ we have $\delta T(r) \approx 2^\circ$ C.

Stationary action of such a beam on an absorbing solution leads to establishment of a stationary temperature gradient. Owing to thermal diffusion, the temperature gradient leads to a density gradient. In an isotropic medium, the connection between the specific density and the refractive index is determined by the known formula for the specific refraction.

If $\rho$ and $T$ are chosen as the independent thermodynamic parameters, the change of the permittivity is given by

$$\delta\varepsilon(T, \rho) = \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \delta\rho + \left(\frac{\partial\varepsilon}{\partial T}\right)_\rho \delta T. \tag{4}$$

In isobaric heating

$$\delta\rho = (\partial\rho/\partial T)_p \delta T. \tag{5}$$

The second term in (4) is small compared with the first, and can usually be neglected.[14] Thus, the temperature-gradient-induced change of the specific density manifests itself in a change of the refractive index. For liquids we have in the main $\delta\varepsilon(\rho) < 0$; therefore the self-action of the beams manifests itself in defocusing of the transmitted radiation.

Since the stimulated processes are characterized by a nonlinear connection with the intensity, the defocusing of the incident radiation can influence significantly the quantitative characteristics such as efficiency, beam divergence, and lasing duration of dye-solution lases, as well as the nonlinear change of the absorption coefficient and the duration of the generated pulse in passive-$Q$-switched lasers based on such systems.

A lowering of the excitation threshold of stimulated Raman scattering by the self-focusing of the pump was observed in the very first studies of this process.[15] The influence of self-defocusing on the nonlinear absorption and generation of light by dye solutions in the nanosecond range has hardly been studied. The difficulties of investigating self-defocusing under the mentioned conditions are due to the presence of a number of competing processes, such as stimulated thermal scattering,[16,17] scattering by halos produced around plasma formations (when the intensity is sufficient to break down the liquid[18]), which are commensurate with respect to their effect on the transmitted power. In addition, at interaction durations much shorter than the temperature relaxation time $t_T$, it is legitimate in principle to raise the question of the possibility of interpreting the experimentally observed increased angular divergence of the transmitted beam as a result of nonstationary defocusing. One must bear in mind, however, that $\delta\rho$ (and correspondingly $\delta\varepsilon$) can be changed by a mechanism other than slow thermal diffusion. The heating of the medium upon absorption of nanosecond light pulses with energy density $\approx 1$ J/cm$^2$ (in an adiabatic process) is accompanied by the onset of a pressure jump[14] exceeding the equilibrium value by an amount

$$\Delta P(t,r)=\Gamma\alpha(\omega)\int_0^{\tau_p} I(\omega)\,dt, \tag{6}$$

where $\Gamma=(\rho T)^{-1}(\partial P/\partial S)_\rho$ is the Grüneisen coefficient for liquids and solids, $S$ is the entropy, and $\alpha(\omega)$ and $I(\omega)$ are the nonlinear coefficient of absorption and the intensity, averaged over the ordinate $z$ (it is assumed that the quantum yield of the dye is very small and the lifetime $\tau_e \leqslant 1$ nsec). At typical parameters of the dye solutions used as passive $Q$-switches, $\alpha(\omega)\approx 1$ cm$^{-1}$, $I(\omega)=20$ MW/cm$^2$, $\Gamma=2$ and $\tau_p=30\times 10^{-9}$ sec, the excess pressure is $\Delta P$ 14 bar. The resultant pressure drop propagates at the speed of sound from the heating region in the form of a packet of traveling waves (spherical, plane, or cylindrical, depending on the spatial distribution of the absorbed energy). The quasi-equilibrium pressure and the distribution of the density $\rho$ in the heated region are established in this case with a relaxation time $t_s$.

The ratio of the negative pressure due to heating to the positive pressure due to electrostriction was theoretically investigated by Raĭzer.[14] According to him, if $\tau_p < t_T$ and $\tau_p < t_s$ the pressure due to light absorption exceeds that of electrostriction after a time interval $\Delta t$:

$$\Delta t=\rho(\partial\varepsilon/\partial\rho)_T/2\Gamma\alpha(\omega)v; \tag{7}$$

for typical parameters of the liquids $\rho(\partial\varepsilon/\partial\rho)_T\approx 1$, $\Gamma=2$, and $v=2\times 10^{10}$ cm/sec we have $\Delta t=0.05$ nsec already at $\alpha(\omega)=0.1$ cm$^{-1}$. In dye solutions used for lasing and $Q$-switching, the absorption as a rule exceeds 1 cm$^{-1}$.

Experimental evidence of the significance of impact heating for the generation of sound waves upon absorption of nanosecond pulses is provided by Refs. 19–21.

On the basis of linearized hydrodynamic equations, neglecting the longitudinal (along the beam) motion of the liquid (nonlinear filter in the bleached state), Raĭzer[14] obtained a solution for the radial (across the beam) changes of the density in three characteristic time intervals: $t<t_s$, $t>t_s$, and $t=t_s$. Of importance for the analysis of the defocusing of nanosecond light pulses is the result for $t<t_s$:

$$\delta p\left(\frac{r}{R}\right)=\frac{\psi}{6}\,\frac{\Gamma\alpha(\omega)I(\omega)\tau_p{}^3}{R^2}\left(1-\frac{3\Delta t}{\tau_p}\right)=\frac{\psi}{6}\,\frac{\Delta P(t,r)}{v_s{}^2}\times\left(\frac{\tau_p}{t_s}\right)^2\left(1-\frac{3\Delta t}{\tau_p}\right), \tag{8}$$

where

$$\psi=-\left(\frac{\pi}{2}\right)^2\left[\cos\left(\frac{\pi r}{2R}\right)+\sin\left(\frac{\pi r}{2R}\right)\Big/\frac{\pi r}{2R}\right]$$

if the radial beam distribution is simulated by the function $\cos(\pi r/2R)$, where $r$ is the radial coordinate. Substituting (8) in (4) we obtain the permittivity change $\delta\varepsilon$ that determines the defocusing angle.

The deflection angle was determined by Raĭzer[14] in the geometric-optics approximation: the redistribution of the density under the influence of a beam with a given profile was first obtained, after which its deflection in the produced lens was considered. Integration of the refraction equation

$$\frac{d\theta}{dz}=2\varepsilon\frac{d\varepsilon}{dr}$$

yielded for the deflection angle $\theta$

$$\theta_d\approx(|\delta\varepsilon|/\varepsilon)^{1/2} \tag{9}$$

at $r=R/2$ ($\theta_d$ is a finite deflection angle).

We present a numerical estimate of the deflection angle in accord with formulas (9), (8), and (4). Using the same quantities as in the determination of $\Delta P(t,r)$, as well as $\rho\partial\varepsilon/\partial\rho\approx 1$, we obtain $\delta\rho=-10^{-6}$ g/cm$^3$, and accordingly $\delta\varepsilon=-10^{-6}$. The defocusing angle is negligible in this case, $\theta_d\approx 10^{-3}$, in contradiction to the experiment (Fig. 5).

For the passive-$Q$-switch lasers used in the experiment, the leading front of the single pulse is increased to approximately the duration of the free-lasing flash (to 1 $\mu$sec). The power of such a "pedestal," however, is smaller by 2–4 orders than the peak power of the pulse.[22] Taking into account the cubic dependence of $\delta\rho$ on the pulse duration, we consider an equivalent problem in which an intense pulse probes a perturbation (negative lens) produced by a relatively long pedestal but of low power. Then, using Eq. (8) with $\tau_p=10^3$ nsec, $I_0=0.1$ MW/cm$^2$, and $\alpha_0(\omega)=10$ cm$^{-1}$ (the initial value of the absorption coefficient is assumed, since there is no saturation at low intensities), and the other parameters unchanged, we obtain $\delta\rho=-(10^{-3}-10^{-2})$ g/cm$^2$. Correspondingly, $\delta\varepsilon=-(10^{-3}-10^{-2})$ and $\theta_d=10^{-2}-$

$10^{-1}$ rad. These values are already close for the experimentally obtained defocusing angles (Fig. 5).

The foregoing data correlate with the results of Ref. 23 where experiments on nonstationary defocusing of the emission of a xenon laser with pulse duration 2–5 $\mu$sec and energy up to $10^{-3}$ J yielded a defocusing angle $\approx 20°$ in an alcohol solution of fuchsin with $\alpha_0(\omega) = 20$ cm$^{-1}$. Just as in our case, the defocusing took place mainly in the trailing edge of the pulse.

## CONCLUSION

We have described the results of an investigation of a new effect in optics, namely nonlinear absorption of saturation of the second vibronic state of dye molecules, a state produced when two-step transitions take place in the system in a quasimonochromatic radiation field. Since the probability of such transitions is proportional to the square of the effective intensity, the bleaching effect due to the two-step transitions becomes predominant at any initial $T = f(I_0, \omega)$ dependence. Observation of this effect at a selected frequency depends primarily on the relation between the frequency of the incident light and the frequencies and probabilities of the two successive transitions $S_0 \to S_1$ and $S_1 \to S_n$.

If, at a given incident-radiation frequency, the probability of the $S_0 \to S_1$ transition is higher than that of $S_1 \to S_n$, then the saturation of the absorption (bleaching) can proceed in two steps. For a cryptocyanine solution excited by a ruby-laser single pulse of 8 nsec duration, a similar $T = f(I_0)$ dependence is given in Schäfer's review.[3] When the $S_1 \to S_n$ absorption probability exceeds the probability of the $S_0 \to S_1$ transition, the initial decrease of the transmission gives way to an opposite effect, namely bleaching as a result of cascaded two-step transitions. However, the longer the exciting pulse, the larger, at the same intensity, the heating and the optical inhomogeneity of the medium. Other conditions being equal, the heating is larger in absorbers described by three energy states.

The reasoning presented in this paper for the defocusing is based on the experimentally observed deflection ($\leq 30°$) of the beam from the paraxial direction. The scattering indicatrix has a maximum in the direction of the initial beam; the power due to the Fresnel reflection from the exit face of the cell travels in the opposite direction. What is mainly defocused is the radiation on the trailing part of the train. When shorter pulses are used, the defocusing intensity threshold rises considerably. For radiation pulses of 18–22 nsec duration, many of the absorbers where 100% bleached in a wide range of intensities. The same absorbers lost their optical transparency when excited by 25–35 nsec pulses at intensities $\gtrsim 10^{25}$ cm$^{-2}$ sec$^{-1}$.

It is concluded in the analysis that the large-angle deflection of the incident light is due to nonstationary thermal defocusing. The use of Raĭzer's theoretical formulas[14] gives defocusing angles close to those in experiment, if account is taken of the presence of a long "pedestal" in the single-pulse radiation of nanosecond duration.[22]

A comparison of the obtained and known facts does not make it possible to describe the scattering in terms of SMBS or STS-2.[16,24] These types of scattering should develop primarily in a direction antiparallel to the pump, owing to the possibility of amplifying the scattered-radiation components in the active medium. Attempts to record any noticeable influence on the residual absorption of the STS-2 grating for two settings of the cell—at the Brewster angle and normal to the incident beam—yielded no results. It is most probable that the STS-2 took place under the conditions of the described experiments as a secondary process. Its role in nonlinear absorption and generation of light by dye solutions must be clarified in the future.

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