Influence of photodisintegration on the lasing efficiency in dyes

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Received February 2, 2000

The dependence of lasing efficiency on the pump density and excitation wavelength, as well as the pulse duration was estimated theoretically for the standard POPOP ethanol solution. Close agreement between the theoretical and experimental data was obtained.

The use of high-power solid-state and gas lasers as pump sources for dye lasers leads to a significant decrease in lasing efficiency. It was found that the lasing efficiency in these lasers depends on the pump radiation wavelength, and the highest value is achieved at the long-wave wing of the absorption spectrum.[1–3]

Similar behavior of the lasing efficiency was observed at different pump intensity.[4] It was assumed that this behavior is connected with the reabsorption of the pump radiation in the system of excited singlet and triplet levels. However, the theoretical analysis showed that the observed dependence takes place even ignoring the induced reabsorption.[5,6] This can be caused by several reasons. One of the most important reasons is photodisintegration of molecules. Therefore, in this paper we study the influence of photodisintegration by the method of mathematical simulation using as an example 1,4-di[2-(5-phenyloxazolil)]benzene (POPOP) in ethanol. The main principles of the model were described in Ref. 5. It was assumed that at high-power pumping the excited states of a dye deactivate with a high quantum yield, and this deactivation is accompanied by the formation of an reversible photoproduct.[7]

First of all, let us consider the influence of photodisintegration on lasing characteristics in the approximation of a thin layer. The calculations were made for the case of non-absorbing disintegrated molecules at continuous pumping.

If the disintegration of active particles occurs, the equation has the following form (designations correspond to those in Ref. 5):

$$\frac{dn_3}{dt} = -n_3 [p_{31} + I_p (\sigma_{31}^p + \sigma_{35}^p) + I_g (\sigma_{31}^g + \sigma_{35}^g)] + n_1 (I_p \sigma_{13}^p + I_g \sigma_{13}^g) + n_d p_r. \quad (1)$$

Assuming $I_g \sigma_{13}^g \ll I_p \sigma_{13}^p$ and neglecting the influence of triplet levels ($n = n_1 + n_2 + n_d$), we have

$$\frac{dn_3}{dt} = -n_3 [p_{31} + I_p (\sigma_{31}^p + \sigma_{13}^p + \sigma_{35}^p) + I_g (\sigma_{31}^g + \sigma_{35}^g)] + n_d (p_r - I_p \sigma_{13}^p) + nI_p \sigma_{13}^p. \quad (2)$$

This equation together with the equation for the concentration of disintegrated particles

$$\frac{dn_d}{dt} = n_3 (I_p \sigma_{35}^p + I_g \sigma_{35}^g) \gamma - n_d p_r, \quad (3)$$

as well as the condition of a quasi-stationary state

$$k_r \equiv \frac{1}{2L} \ln \frac{1}{r_1 r_2} = n_3 (\sigma_{31}^g - \sigma_{35}^g), \quad (4)$$

where L, r_1, and r_2 are the characteristics of a laser cavity, form the complete set of equations describing the behavior of the system.

From Eqs. (2)–(4) we have that $I_g(t)$ and $n_d(t)$, are expressed as follows:

$$I_g(t) = c_1 c_4 / c_3 [\exp(c_3 t) - 1] + c_2; \quad (5)$$

$$n_d(t) = c_4 / c_3 [\exp(c_3 t) - 1], \quad (6)$$

where

$$c_1 = \frac{p_r - I_p \sigma_{13}^p}{(\sigma_{31}^g + \sigma_{35}^g)},$$

$$c_2 = \frac{nI_p \sigma_{13}^p - n_3 (p_{31} + I_p [\sigma_{31}^p + \sigma_{35}^p + \sigma_{13}^p])}{n_3 (\sigma_{31}^g + \sigma_{35}^g)},$$

$$c_3 = n_3 \sigma_{35}^g c_1 \gamma - p_r, \quad c_4 = n_3 (I_p \sigma_{35}^p + \gamma c_2 \sigma_{35}^g).$$

In Eqs. (5) and (6) it is taken that $n_d(0) = 0$. The time of lasing termination can be found from the condition $I_g(t_k) = 0$, what gives

$$t_k = \frac{1}{c_3} \ln \left(1 - \frac{c_2 c_3}{c_1 c_4}\right). \quad (7)$$

In the pulsed mode, the differential efficiency can be estimated as

$$\varepsilon = \frac{\lambda_p}{\lambda_g} \frac{\Theta}{I_p^0 \lambda_p} \frac{c_2}{c_3} \left[\left(1 - \frac{c_1 c_4}{c_2 c_3}\right) \ln \left(1 - \frac{c_2 c_3}{c_1 c_4}\right)\right],$$

where

$$\Theta = \frac{k_r \exp(k_r L) (r_2 (1 - r_1) \exp(k_r L) + 1 - r_2)}{[\exp(k_r L) - 1] [r_2 \exp(k_r L) + 1]}. \quad (8)$$

0235-6880/00/03 275-04 $02.00

Figure 1 plots t_k for different wavelengths of the pump radiation at the varying power density of the pump radiation. As is seen from Fig. 1, for most wavelengths there exist two intervals, within which the lasing is possible only in the pulsed mode. For example, for $\lambda = 360$ nm at these parameters the lasing is possible already at the pump intensity $I_p = 0.5$ MW/cm^2. As the pump intensity further increases, the lasing duration increases sharply, and the stationary lasing is possible at the pump intensity from 0.55 to 3.50 MW/cm^2. At $I_p > 3.50$ MW/cm^2 only pulsed lasing is possible, and its duration decreases as I_p increases. Comparing the intervals of intensities, at which the duration of lasing would be more than, for example, 5 ns, we can see that the interval for $\lambda = 380$ nm is the longest one.

Let us consider the case of pulsed pumping (duration of 20 ns), when the disintegrated molecules absorb the photons of pump and lasing emission, and reversible and irreversible photoproducts are formed in the process of absorption. To write the nonstationary equations for population of energy levels and light fluxes, we made use of the scheme described in Ref. 7 (such a process of lasing is observed in the polar solutions of organic compounds):

$$\begin{array}{ccccc} & & T & & \\ & & \uparrow & & \\ S_0 & \Rightarrow & S_1 & \rightarrow & (p^+ \cdots e^-) \overset{\gamma}{\rightsquigarrow} \text{OPhP} \\ \uparrow & & & & \\ \underset{1-\gamma}{\leftsquigarrow} & & & & \end{array}, \qquad (9)$$

$$\frac{dn_3}{dt} = -n_3 [p_{31} + p_{32} + I_p (\sigma^p_{31} + \sigma^p_{13} + \sigma^p_{3n}) + (I^+ + I^-) (\sigma^g_{31} + \sigma^g_{13} + \sigma^g_{3n})] + (n - n_2 - n_d) \times [I_p \sigma^p_{13} + (I^+ + I^-) \sigma^g_{13}] + n_d p_r; \qquad (10)$$

$$\frac{dn_2}{dt} = -n_2 p_{21} + n_3 p_{32}; \qquad (11)$$

$$\frac{dn_d}{dt} = -n_d p_r + n_3 [I_p \sigma^p_{3n} + (I^+ + I^-) \sigma^g_{3n}] \gamma; \qquad (12)$$

$$\pm \frac{dI^{\pm}(z, x, t)}{dx} = I^{\pm}(z, x, t) [n_3 \{\sigma^g_{31} + \sigma^g_{13} - \sigma^g_{3n}\} + n_2 \{\sigma^g_{13} - \sigma^g_{2n}\} + n_d \{\sigma^g_{13} - \sigma^g_d\} - n\sigma^g_{13}] + p_{31} n_3 E(\lambda_g) g^{\pm}(x) \Delta\lambda_g; \qquad (13)$$

$$\frac{dI_p(z, x, t)}{dz} = I_p(z, x, t) [n_3 \{\sigma^p_{31} + \sigma^p_{13} - \sigma^p_{3n}\} + n_2 \{\sigma^p_{13} - \sigma^p_{2n}\} + n_d \{\sigma^p_{13} - \sigma^p_d\} - n\sigma^p_{13}], \qquad (14)$$

where

$$\pm \frac{dI^{\pm}(z, x, t)}{dx} = \left(\frac{\partial}{\partial x} \pm \frac{1}{\vartheta} \frac{\partial}{\partial t}\right) I^{\pm}(z, x, t); \qquad (15)$$

$$\frac{dI_p(z, x, t)}{dz} = \left(\frac{\partial}{\partial z} \pm \frac{1}{\vartheta} \frac{\partial}{\partial t}\right) I_p(z, x, t) \qquad (16)$$

(ϑ is the speed of light in the laser medium; it depends on the kind of a solvent).

In Eqs. (10)–(13), p_{31} and p_{32} are the probabilities of spontaneous transitions from the level S_1 to the ground state S_0 and the triplet state T_1, respectively; p_{21} is the probability of transition from the state T_1 to the ground state; γ and p_r are the conditional probabilities of the photodisintegration of the state S_1 at absorption and of spontaneous inverse process, respectively; σ^p_{31}, σ^p_{13}, σ^g_{31}, and σ^g_{13} are the cross sections of stimulated emission and absorption at the pump frequency p and at the lasing frequency g, respectively; σ^p_{2n}, σ^p_{3n}, σ^g_{2n}, and σ^g_{3n} are the cross sections of absorption in the triplet state and the cross sections of induced singlet-singlet absorption at the pump p and lasing g frequency, respectively; σ^p_d and σ^g_d are the absorption cross sections of the particles in the disintegrated state; I_p, I^+, and I^- are the photon flux densities at the pump frequency and at the lasing frequency; n is the concentration of particles of the active substance, and n_3, n_2, and n_d are the populations of the levels S_1 and T_1 and the concentration of molecules experienced reversible photodisintegration, respectively; $\Delta\lambda_g$ is the laser line halfwidth.

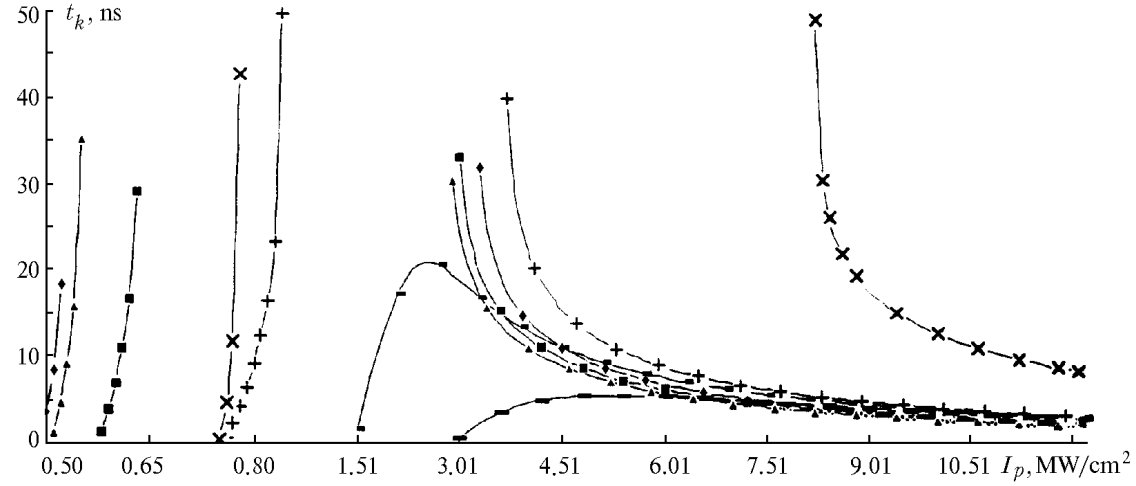

Fig. 1. Duration t_k of the quasistationary lasing of POPOP solution in ethanol vs. pump power for different pump wavelength at $L = 0.2$ cm, $r_1 = r_2 = 0.8$, $n = 5 \cdot 10^{16}$ cm^{-3}: 350 (— —), 360 (—♦—), 365 (—▲—), 375 (— + —), 380 (—×—), 385 (—■—), and 390 nm (—■—).

The function $E(\lambda)$ is normalized according to the condition $\int E(\lambda)\,d\lambda = \phi_f$, where ϕ_f is the quantum yield of the fluorescence.

The geometrical factor $g^{\pm}(x)$ introduced for taking the lasing anisotropy into account was estimated by the equation[8]:

$$g^{+}(x) = 0.5\,\{1 - (L - x)/\sqrt{(L - x)^2 + \varepsilon^2}\},$$
$$g^{-}(x) = 0.5\,\{1 - x/\sqrt{x^2 + \varepsilon^2}\}, \qquad (17)$$

where L is the length of the active area; ε is the radius of the laser beam at the exit from the active medium.

The boundary conditions for the set of equations (10)–(14) were as follows:

$$I_p(0, x, t) = I_p^0\,\alpha t \exp(-\beta t^2),\ 0 \le x \le L,\ 0 \le t \le t_0; \qquad (18)$$
$$I^{+}(z, 0, t) = r_1\, I^{-}(z, 0, t - 2d/v); \qquad (19)$$
$$I^{-}(z, L, t) = r_2\, I^{-}(z, L, t - 2d/v), \qquad (20)$$

where t_0 is the pump duration; r_1 and r_2 are the reflection coefficients of mirrors; d is the distance from each mirror to the nearest edge of the active medium (the symmetric case was considered); I_p^0 is the maximum instantaneous power density of the pump radiation. The shape of the pump pulse was approximated as $I_p(t) = I_0\,\alpha t \times \exp(-\beta t^2)$, where $\alpha = 0.32354\ ns^{-1}$. The calculations were made for the POPOP in ethanol.

Figure 2 shows the lasing efficiency for the transverse pumping of the solution ($n = 1.0 \cdot 10^{+17}\ cm^{-3}$) at different pump power density and reflection coefficients of the output mirrors of the cavity. The main spectroscopic parameters were taken from Ref. 9, and the estimates from Ref. 7 were additionally used for the parameters of photodisintegration. Thus, for example, it was assumed that $\gamma = 0.3$, $\sigma_d^p = 0.7 \cdot 10^{-16}\ cm^2$, $p_r = 0.1 \cdot 10^9\ s^{-1}$. The calculations were made for the cavity with $L = 0.3$ cm and $d = 1$ cm. The reflection coefficients of the output mirrors were taken to be equal to 0.7, 0.8, and 0.9 (they correspond to the curves *1–3* in Fig. 2). At their further increase, some growth of the efficiency was observed, and at $r \approx 0.95$ it decreases sharply. It was shown that the lasing efficiency is maximum at the intensity ~ 5–10 MW/cm^2, and then it decreases. Quite similar dependence was found experimentally by Sergeev et al.[4]

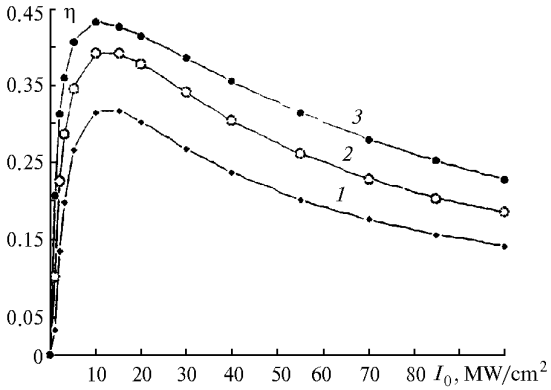

Fig. 2. Lasing efficiency η of POPOP in ethanol vs. pump intensity at different reflection coefficients r.

Within the framework of the considered model, the effect of saturation[4] is explained by the presence of singlet-singlet absorption and reversible photodisintegration of molecules of the active substance. Actually, it is seen from the above equations that absorption of a pump photon by the molecule being in the state S_1 leads either to relaxation into the state S_0 (in this case two pump energy quanta are lost) or to formation of OPhP. The latter, in its turn, also leads to additional losses and, especially at highly intense pumping, to the total decrease of the concentration of active molecules.

The study of the dependence of lasing efficiency on the pump wavelength is difficult because of the absence of reliable data on γ and σ_d^p. However, it is interesting to reveal how the possibility of active particle departure itself affects this dependence. Table 1 gives the values of the lasing efficiency for the same solution at longitudinal excitation (the influence of the absorption by disintegrated particles was neglected and $\gamma = 0.3$ was additionally assumed for all the wavelengths).

Table 1. Calculated lasing efficiency of POPOP in ethanol at longitudinal pumping taking into account induced singlet-singlet absorption (1) and neglecting it (2). $L = 0.43$ cm, $n = 1.0 \cdot 10^{17}\ cm^{-3}$

	$r_1 = r_2 = 0.9$								$r_1 = r_2 = 0.7$							
λ_p,	5 MW/cm^2		10 MW/cm^2		30 MW/cm^2		50 MW/cm^2		5 MW/cm^2		10 MW/cm^2		30 MW/cm^2		50 MW/cm^2	
nm	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
360	0.37	0.49	0.44	0.56	0.48	0.61	0.48	0.62	0.16	0.31	0.29	0.46	0.39	0.59	0.33	0.62
365	0.38	0.50	0.44	0.57	0.48	0.62	0.48	0.63	0.16	0.32	0.29	0.47	0.39	0.60	0.29	0.62
370	0.39	0.50	0.45	0.57	0.49	0.62	0.48	0.63	0.18	0.32	0.32	0.48	0.41	0.60	0.35	0.63
375	0.39	0.51	0.46	0.58	0.49	0.63	0.48	0.64	0.19	0.33	0.32	0.48	0.41	0.61	0.34	0.64
380	0.41	0.52	0.48	0.58	0.51	0.63	0.50	0.64	0.22	0.33	0.36	0.49	0.46	0.62	0.44	0.65
385	0.38	0.49	0.45	0.56	0.47	0.61	0.45	0.62	0.17	0.29	0.30	0.45	0.36	0.57	0.28	0.60
390	0.33	0.43	0.39	0.49	0.42	0.54	0.39	0.56	0.10	0.20	0.22	0.34	0.27	0.46	0.23	0.49

It is seen from the Table that for all the considered parameters the maximum lasing efficiency is achieved at the long-wave wing of the absorption spectrum. These data are in qualitative agreement with the experiment.

Thus, the photodisintegration of active molecules in lasers of organic compounds' solutions produces a significant effect on the dependence of lasing efficiency on the pump wavelength and intensity.

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