INFLUENCE OF THE PHOTODESTRUCTION PRODUCTS ON THE PERFORMANCE CHARACTERISTICS OF DYE LASERS

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Photochemical stability of six aminocoumarines irradiated by emission of a Xe−Cl *laser is studied. Quantum yield of the photodestruction and absorption coefficients of the photodissociation products in the spectral regions of dye lasing and at the wavelengths of exciting radiation are determined. Investigation of a dinitrobicyclooctane (DNBCO) on the lifetime of dye lasers.*

Although dye lasers are now widely used and have many advantages the question on lifetime of dye lasing media is yet open because the latter undergo photochemical transformations under the irradiation by pumping radiation. Besides a decrease of an active medium concentration the lasing process is accompanied by formation of photodestruction products that absorb both the pumping radiation and the laser emission of a dye laser itself.

The effects of the above factors on the lifetime of a dye laser are studied for six compounds of close molecular structure (see Fig. 1).

Energy resource (ER) of a dye is defined as a total energy that can be pumped into 1 cm^3 during the time when the lasing efficiency becomes twice as low as the initial one. To provide a possibility of comparing individual photochemical strengths of different molecules we have determined quantum yields of a molecular dissociation (γ). This value is calculated as the ratio of a number of dissociated molecules to the total number of photons absorbed by solution. In turn, the number of dissociated molecules is determined from a decrease of the optical depth of a dye within the long−wave absorption band. For pumping dyes we have used a Xe−Cl eximer laser delivering radiation pulses at $\lambda = 308$ nm at a pulse repetition frequency 5 Hz that can provide from 15 to 20 MW/cm^2 power density of excitation.

Pumping of dyes has been performed in a transverse optical arrangement. A cavity of a dye laser is formed by a 100% reflecting mirror and a face of a rectangular cell with the area of 1 cm^2.

Some results of this study are given in the table. Here K^0_{308} is the absorption coefficient of the initial dye at the wavelength of pumping radiation, K^p_{308} is the absorption coefficient of the photodestruction products at the pumping radiation wavelength (after twofold decrease of the lasing efficiency), K^p_{308}/K^d_{308} is the fraction of the pump energy absorbed by photodestruction products after lasing (again after twofold decrease of the lasing efficiency), K^p_l is the absorption coefficient of the photodestruction products at the wavelength of a dye laser emission. The right column gives the relative number of molecules dissociated during the lasing process. All the dyes under study had the same initial concentration of $2\cdot10^{-3}$ mole/liter. This concentration is a limit determined by the capabilities of a Specord M−40 spectrophotometer used to record the absorption spectra.

TABLE I.

| Compound	K^0_{308}, cm^{-1}	K^p_{308}, cm^{-1}	K^p_{308}/K^d_{308}, %	K^p_l, cm^{-1}	P, J/cm^3	$\gamma\cdot10^3$	The number of dissociated molecules, %
K1	5.7	0.7	11	0.13	70	1.0	7
K1 + DNBCO	6.7	1	14	0.15	174	0.3	7
K1H	4.5	0.7	15	0.15	45	1.4	8
K1H + DNBCO	4.4	0.6	12	0.10	107	0.3	4.5
K120	8.4	1.3	15	0.14	42	2.0	12
K120 + DNBCO	8.4	0.7	8.3	0.19	55	1.2	8
K2	4.5	1.6	28	0.06	42	2.5	11
K2 + DNBCO	5.1	1.2	20.7	0.08	52	1.3	10
K102	4.3	1	23	0.10	62	1.7	14
K102 + DNBCO	4.1	1	21.5	0.10	160	0.5	11
LD490	3.5	1	25	0.15	37	2.9	14
LD490 + DNBCO	3.2	1.1	28	0.13	92	1.1	13
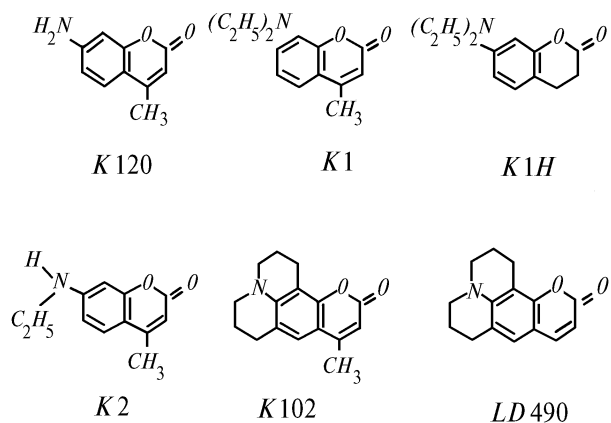
FIG. 1. Structure formulas of aminocoumarines under study.

First, it can be seen from the table that the fraction of molecules dissociated during the lasing process is not very high (5—15%). Normally, as the practice shows, such changes of a dye concentration does not result in any noticeable decrease of the lasing efficiency. It also follows from the table that the energy resource does not practically vary from compound to compound, maximum difference being between the resources of K1 and K2 compounds.

These two compounds can be used as an example for examining the influence of a destructive absorption of high at the wavelengths of pumping and dye laser radiation on the energy resource of the dye lasers. In the literature very often the emphasis is mostly laid on the absorption in the region of the dye laser emission. From our studies it follows that although the light absorption by photoproducts in the case of K2 dye, within the dye lasing range, is twice as low as that in the case of K1 dye its energy resource is also two times lower, and not *vice versa*. Moreover, it happens so that in the spectral region of pumping the fraction of destructive absorption, by the end of lasing process is 24—28% for the K2 dye while being 10—11% for the K1 dye.

In order to reveal the influence of destructive absorption of pumping radiation on the efficiency of dye generation we have conducted special experiment. We have added (portion by portion) a 2.5—diphenyloxazol to a solution of the K102 dye, the former being transparent in the region of K102 dye lasing while strongly absorbing the pumping radiation. It is natural that generation efficiency of a dye is inversely proportional to the fraction of destructive absorption of pumping radiation (see Fig. 2).
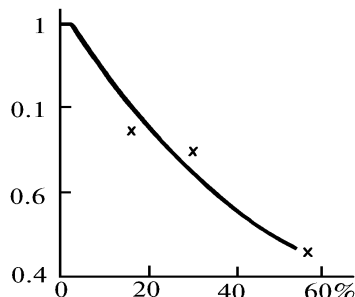

FIG. 2. The efficiency of a K102 dye lasing as a function of a fraction of the destructive absorption of pumping radiation.

Thus it is clearly seen from this figure that the destructive absorption of pumping radiation by the

photodestruction products should be necessarily taken into account. Moreover, in dye lasers with a transverse optical arrangement of pumping and small lasing zone (l), as in our case, the destructive absorption of pumping radiation is the main cause of the lasing efficiency fall off.

At the same time in different cases (e.g., large l and essential absorption by photodestruction products at the dye lasing wavelengths) one should have information about accumulation of photodestruction products absorbing in the region of dye—laser generation. To study this process we have irradiated the dyes under study by a Xe—Cl laser radiation for a long time in the generation mode. The dependences of the absorption coefficient at the lasing wavelengths λ_l, i.e., at 440 nm for K120, 460 nm for K1, 446 nm for K2, 468 nm for K1H, 470 nm for K102, and 485 nm for LD490, on the total energy of irradiation are shown in Fig. 3. The concentration of the dye was $2 \cdot 10^{-3}$ mole/liter.
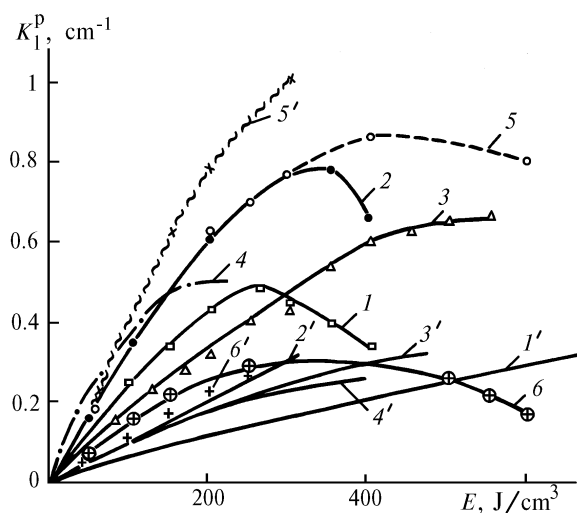

FIG. 3. Absorption by photodestructive products in the regions of lasing of K102 (curve 1), LD490 (curve 2), K1 (curve 3), K1H (curve 4), K120 (curve 5), and K2 (curve 6). Curves 1'—6' represent the data obtained for the corresponding dyes with $5 \cdot 10^{-2}$ mole/liter DNBCO added into the dye solution.

The maximum increase of absorption at the lasing wavelengths is observed for K120 and LD490 dyes. In the figure all the curves have maxima. This is indicative of the fact that the photodestruction products themselves undergo light—induced transformations producing thus new photodestruction products.

The problem in seeking inhibitors is still an urgent one. Deoxygenation of solutions could be effective for many aminocoumarines.[1,2] However, the use of this method in practice is too problematic. For some aminocoumarines an addition of dinitrobicyclooctane (DNBCO)[1,3] makes the best inhibiting effect.

In this study we have investigated the inhibiting effect of DNBCO in all the above—mentioned dyes under the same experimental conditions. Some results of these experiments are presented in the table and in Fig. 3. A noticeable two— and threefold, enhancement of the energy resource is observed for K1, K1H, LD490, and K102 dyes, whereas in K120 and K2 the effect produced by DNBCO is very weak. Incidentally there is a good correlation between the decrease of γ values in the presence of DNBCO and the increase of the energy resource of a dye laser. The latter fact indicates

that DNBCO prevents photon—induced transformations of an isolated molecule of a dye.

Data presented in Fig. 3 clearly demonstrate an increase of the absorption coefficient of the photodestruction products at the wavelengths of dye laser emission in the presence of DNBCO. As a matter of fact, for most compounds under study there is observed a decreased accumulation of the photodestruction products in the presence of DNBCO as compared to pure compounds, with the exception of K120 and K2 dyes. In the case of K2 we observe the situation that both curves are practically coincident, while in the case of K120 dye one can see a more rapid increase of K_l^p in the presence of DNBCO compared to the curve obtained without DNBCO. Since in these two cases there is no increase in γ in the presence of DNBCO, or even small decrease can occur, this situation is obviously indicative of redistribution of the photon—induced transformations over decay channels towards increase of photodestruction

products that absorb at the dye—laser emission wavelengths. It can also occur so that the presence of DNBCO prevents the dissociation of both the photodestruction products and the initial molecules as well.

Thus, the influence of DNBCO on the energy resource of dye lasers is not universal, in the case of aminocoumarines. A very weak effect observed in the case of K2 and K120 dyes should be additionally studied in more detail.

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