PHOTOSTABILITY OF ACTIVE LASER MEDIA BASED ON 2-(4-PYRIDYL)-5-PHENYLOXAZOLE

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Results of investigation into the laser generation characteristics of active media based on 2-(4-pyridyl)-5-phenyloxazole solution with intense laser excitation attendant to variations of pumping power density and pulse repetition frequency are presented. Reasons for a change of the laser lifetime and conditions for optimization of active media against this parameter are discussed.

One of the principal problems of the advent of dye lasers is to maintain their lasing efficiency for a long time. The decrease of the laser radiation energy is caused by the increase of the pumping and generation energy absorption by stable photoproducts. Investigations into a mechanism of forming such photoproducts allow one to develop the methods for their inhibition as well as to increase the laser lifetime. However, there is an inverse problem, namely, elucidation of effects of laser generation dynamics on the rate of photochemical processes. Optimal modes of lasing chosen on this basis increase the dye laser lifetime.

This paper presents the results of investigation into the laser generation characteristics of ethanol solution of 2-(4-pyridyl)-5-phenyloxazole (4PyPO), $C = 5 \cdot 10^{-4}$ mol/l, versus the excitation conditions – frequency f and exciting pulse power density W. A resonator formed by a nontransparent mirror with $R = 0.9$ and a cell end ($R = 0.04$) was used. Its parameters remained unchanged during the experiment. The Specord M–40 and Hitachi–850 spectrophotometers were used to record the spectral changes caused by the irradiation of the dye by an exciplex XeCl* laser with the parameters $\lambda_{gen} = 308$ nm, $E_{gen} \le 40$ mJ/pulse, and $\tau_p = 10$ ns. The molecular photostability of a specimen characterized by the quantum yield of photoconversion φ and relative quantum yields of photoproducts absorbing in the regions of generation (P_g) and pumping (P_p) were determined from changes in the absorption spectra of solutions before and after irradiation using the technique described in Ref. 1.

Because the relative quantum yields of photoproducts were determined to within the constant inversely proportional to the extinction coefficient of a specific photoproduct, quantitative comparison versus the excitation conditions and concentration was rightful only for the given photoproduct. It was impossible to compare the P_g and P_p values. The lifetime was determined from the decrease of the lasing efficiency. It was measured as the total energy fed in a unit volume of lasing solution whose lasing efficiency decreased by 20%, i.e., at a level of P_{80}. In addition, the dependence of the initial efficiency on the excitation power density, ranging from the threshold values to 50 MW/cm^2, was measured when the radiation was focused with the same cylindrical lens with $F = 125$ mm. The pumping energy was varied by insertion of a neutral light filter from a set. Two measuring regimes were realized: a single-pulse regime with a pulse duty factor of ≥ 1 min and a periodic-pulse regime with a pulse repetition frequency of 2 Hz.

Figures 1 and 2 show the obtained results. The initial efficiency is seen to have the maximum in the region 20–30 MW/cm^2 versus the pumping intensity. The sharpest increase of the efficiency is observed near the lasing threshold due to the increase of the population inversion and the slow decrease of the efficiency versus pumping (curve *1* in Fig. 1) is observed when the exciting pulse power density W exceeds 25 MW/cm^2. The maximum lifetime is observed near 30 MW/cm^2. The lifetime is seen to decrease toward higher and lower pre-threshold pumping powers (see curves *2* and *3* in Fig. 1).

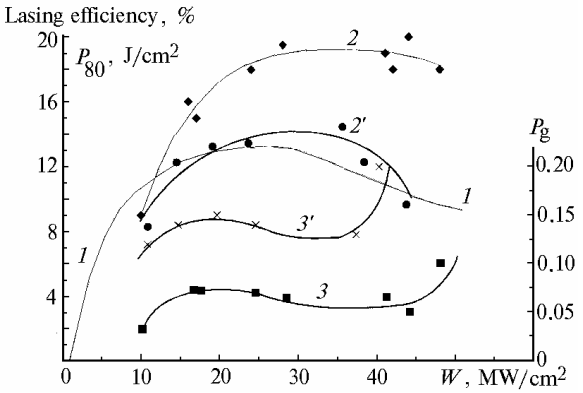

FIG. 1. Dependence of the initial efficiency (1), lifetime at a level of P_{80} (2, 2′), and relative Cuantum yield of the photoproduct P_g (3, 3′) on the pumping power in the single-pulse regime (2, 3) and the periodic-pulse regime at $f = 2$ Hz (2′, 3′).

The correlation between the lifetime change and the relative yield of the photoproduct P_g versus the power density should be emphasized: the higher is P_g, the shorter is the lifetime, even though the

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photoconversion quantum yield φ changes only very slightly in the single-pulse regime (curve *2* in Fig. 2) and monotonically decreases with the increase of pumping in the periodic-pulse regime (curve *2′* in Fig. 2). The same correlation is observed in going from the single-pulse regime to the periodic-pulse one, namely: the quantum yield of photoconversion φ and photoproduct yields P_g and P_p are higher whereas the lifetime is shorter for the periodic-pulse regime in comparison with the single-pulse regime throughout the investigated pumping range. The decrease of the quantum yields φ and P_p (according to Refs. 2 and 3, P_p is produced by photodissociation of the oxazole ring) with the increase of pumping may be attributed to the increase of the role of a competitive channel producing the photoproduct P_g. Its yield increases in the range of intense pumping thereby increasing the energy losses into the resonator and resulting in the decrease of the lifetime.

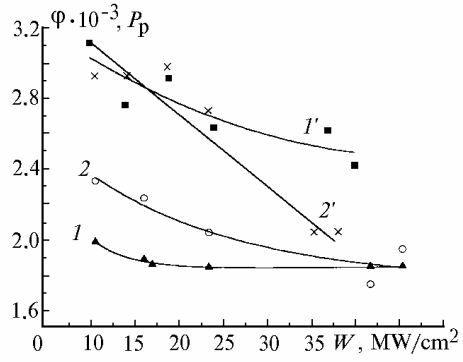

FIG. 2. Dependence of the Quantum yield of photoconversions φ *(1, 1′) and the relative Quantum yield of photoproduct* P_p *on the pumping power in the single-pulse regime (1, 2) and the periodic-pulse regime at* f = 2 Hz *(1′, 2′).*

In our previous paper,[4] the structure P_g is assumed to be caused by the photooligomerization of dye and solvent radicals formed by ring dissociation as well as by the excited 4PyPO molecules that exhibit clearly defined proton acceptor properties (the photocation type is assumed). The emission of the irradiated 4PyPO solution excited to the absorption band P_g in the region of the cation form of 4PyPO (Fig. 3) proves the above-mentioned assumption. The increase of P_g with the increase of pumping corresponds to the decrease of φ and P_p, because the photocation yield increases at intense pumping.

Our investigations of the 4PyPO fluorescence properties in intense light fields with pumping ≤ 15 MW/cm² for which the efficiency sharply decreased showed that the lifetime change did not correlate with the change of P_g: both P_{80} and P_g decrease. Such behavior of these parameters can be caused by a considerable decrease in the generation efficiency due to the decrease of inversion in the above-mentioned range of pumping. This causes the increase of the number of passes through the resonator, i.e., in the increase of losses at smaller P_g and in the decrease of the lifetime.

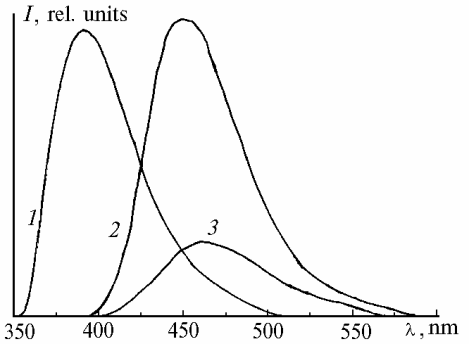

FIG. 3. Fluorescence spectra: neutral form (1) (λ_{exc} = 308 μm) *and cation form (2) of the nonirradiated solution of* 4PyPO (λ_{exc} = 400 μm) *and irradiated* (17 J/cm³) *ethanol solution of* 4PyPO *(3)* (λ_{exc} = 400 μm).

The increase of P_g in the periodic-pulse regime with a pulse repetition frequency of 2 Hz supposes the formation of P_g due to photooligomerization of intermediate radicals and particles with lifetimes of several hundreds of milliseconds. The relaxation of such particles for several hundreds of milliseconds to a nonreactive state decreases the oligomer production in the single-pulse regime. Note that the long-lived (> 2 μs) reversible photoproducts of 4PyPO were identified in Ref. 1, but it was impossible to determine their true lifetimes because of limited temporal resolution of the setup (duration of a sounding spark was 1 μs).

Thus, the generation of 4PyPO is accompanied by the formation of at least two photoproducts: the short-wave product P_p, which determines the degree of photoconversion of 4PyPO through the pre-dissociation mechanism of the oxazole ring in the excited state, and the long-wave product P_g resulted from the photooligomerization of the intermediate long-lived particles. The product P_g is responsible for the generation photostability. The lifetime is shown to correlate with the yield P_g in the region of stable generation of 4PyPO. Thus, its increase calls for the inhibition of this photodestruction channel. The choice of the pumping power density is shown to increase the lifetime of the 4PyPO-based active laser medium.

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