Photonics of complex molecules under conditions of nonlinear absorption at high-power laser excitation. Part 2. Phototransformations of organic molecules

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Photostability of organic compounds with different emission and photochemical properties has been studied under conditions of nonlinear excitation as a function of the XeCl-laser emission parameters (intensity and degree of polarization) and the character (spontaneous or stimulated) of secondary emission of the studied compounds. Quantum yields of phototransformations are determined, the pulse-average population of the excited state is estimated from the transmittance measurements, and causes of the change in the efficiency of phototransformation are discussed.

Introduction

Highly emitting organic compounds are used as active media in tunable lasers and as fluorescent additions at laser sensing of aerosols in model objects and in the atmosphere. Under the effect of high-power pump radiation, such molecules experience transformations (bond dissociation, joining of substitutes, etc.). Therefore, to obtain adequate results, phototransformations in such molecules should be studied. Along with the decrease in the concentration of molecules in the irradiated volume, the phototransformations change the lasing properties of active media from such molecules, and the changes not always agree with the quantum yield of phototransformations.

In our earlier papers, we established the mechanisms of formation of photoproducts responsible for changes in lasing characteristics and found the relation between the quantum yield of these photoproducts and the lifetime of the lasing media.[1–5]

However, phototransformations are strongly affected by the parameters of the exciting radiation,[6] and the problem on establishing the relations between the characteristics of exciting radiation, character of the secondary emission, and photostability of organic molecules calls for a separate study.

In this paper, using compounds with different structure and different chemical properties, we demonstrate that the efficiency of phototransformations changes depending on the excitation conditions (intensity and polarization of the exciting radiation, the shape of the excited volume) and the type of the secondary emission (spontaneous emission, superluminescence).

Objects and methods of the study

As an object of the study, we took dicarboxylalkyl derivative of *n*-terphenyl (LOS-1) and dimethylamin derivative of pyridylphenyloxazole (4PyPON$(CH_3)_2$). This choice is caused by the fact that LOS-1 in ethanol fluoresces in the UV region (λ^{fl}_{max} = 375 nm) with the quantum yield of 0.96, XeCl laser excitation comes to the maximum of the long-wave absorption band, and the radiant efficiency of lasing under optimal excitation conditions reaches 45%. For 4PyPON$(CH_3)_2$, in the polar solvent (ethanol) formation of TICT (Twisted Intramolecular Charge Transfer) photoconformation is observed.[8] This photoconformation is characterized by anomalously large Stokes shift ($\Delta\nu_S$ = 9000 cm^{-1}) and low quantum yield of fluorescence (η = 0.3). At the same time, in nonpolar hexane this compound is an efficient fluorophore (η = 0.9, $\Delta\nu_S$ = 3500 cm^{-1}). In spite of the low quantum yield of fluorescence, 4PyPON$(CH_3)_2$ in polar solvents generates laser radiation in the band of anomalous fluorescence at XeCl pumping with the efficiency higher than in nonpolar solvents (up to 15% in ethanol and up to 20% in acetonitrile, and 7% in hexane[9]). We explain this by the property of TICT-photoconformation to strongly amplify radiation that exists only in the excited state, thus facilitating significantly formation of the population inversion.

As an excitation source, we used XeCl lasers with the following parameters: λ_{las} = 308 nm, τ_p = 15–22 ns, E_{las} = 40–100 mJ. The experimental setup is described schematically in the first part of this paper. Focusing radiation by use of two crossed cylindrical lenses allows the pumping power as high as 60 and 300 MW/cm^2 to be obtained in the variants *1* and *2*, respectively.

In the variant *1*, the pump radiation is focused within a 0.8×0.05 cm rectangular cell filled with a solution. In this case, there is a preferred direction of the excited volume normal relative to the pump direction. This corresponds to the conditions of the optimal lasing.

In the variant *2*, the excited volume is a cylinder 0.12 cm in diameter, which is determined by the diaphragm, and 0.1 cm in height. The preferred direction is absent, and no lasing is observed for the studied compounds at the concentration selected. The error in determination of the radiation power density is 5–7%.

For LOS-1, the effect of the degree of polarization of the pump radiation on the efficiency of phototransformations was estimated. This is especially important for organic molecules, since laser radiation is often used for irradiation of biological objects. However, the effect of such properties of laser radiation as polarization and coherence is still a question to be addressed. To obtain linearly polarized XeCl laser radiation, the exit windows were set at the Brewster angle. In this case, the degree of polarization could be increased by an order of magnitude (from 0.09 to 0.9) with the polarization vector directed normally to the cavity axis. The degree of polarization of the exciting and secondary radiation was estimated from measurements carried out using a Glan prism: $P = (I_\uparrow - I_\rightarrow)/(I_\uparrow + I_\rightarrow)$, where $I_\uparrow$ and $I_\rightarrow$ are the intensities of radiation passed through the prism at its mutually perpendicular positions with respect to the polarization vector of the radiation analyzed. The error in determination of the degree of polarization was 3%.

The absolute quantum yields of irreversible phototransformations φ were determined from the changes in the absorption spectra of solutions. The spectra were recorded with a Specord M–40 spectrophotometer before and after irradiation using the technique described in Ref. 5; the error in this case did not exceed 10%. The advantage of this method is that the concentration of decomposed molecules is determined by spectroscopic methods without chemical separation of numerous photoproducts. Another peculiarity of this approach is that φ in this case determines the number of decomposed molecules per one absorbed photon. Therefore, it can be used both for single-photon excitation, which takes place in the case of low intensity, and for high-intensity excitation, in which case the processes of stepwise and two-photon excitation play a significant part. In addition to the absolute yield of phototransformations, we determined the relative yields of photoproducts absorption in different spectral regions, including the region where the compound under study shows lasing.

To determine the structure of the photoproducts, the stationary fluorescence spectra of these products were studied using a Hitachi–850 spectrofluorimeter, and spectral-fluorescent characteristics of the ion forms of the molecules[1,6,8,9] and the spectra of induced absorption were analyzed using a laser flash-photolysis setup.[5]

Along with the molecular photostability characterized by the quantum yields of phototransformations, the lifetime of the laser active medium from organic molecules or the lasing photostability is an important characteristic. It is measured as the total excitation energy absorbed by a unit volume until the initial efficiency of lasing decreases due to phototransformations down to a preset value: by 20% P_{80} or by 50% P_{50}. The lasing photostability in the experiment is usually measured in J/cm^3 with the error no higher than 10%. In the physical meaning, this parameter is opposite to the quantum yield of phototransformations, because it determines the number of exciting photons absorbed by every molecule causing degradation of the initial lasing efficiency down to a certain level. The total excitation energy is determined with the allowance for the transmission of exciting radiation by the solution studied that depends on the radiation power density.

The transmittance of the compounds studied was measured in a thin layer (l = 0.1 cm) as referred to the transmittance of the cell filled with the solvent (the error was 3%). Based on these measurements, the pulse-average population of the emitting state was estimated by the technique proposed in Ref. 11.

To determine the type of secondary radiation at laser excitation, its time and spectral characteristics were studied with a Real spectrometer that records the spectrum of radiation for a single pulse and a “technical vision” system consisting of MDR–23 monochromator, FEK–22 photodetector, S8–14 oscilloscope, and a TV camera, whose signal comes to a personal computer for the following processing. The energy characteristics are measured using both the photoelectric recording and with an IMO–2N and KTP–2 calorimeters equipped with an F–138 nanovoltmeter in which the linearity of the measured signal is controlled permanently.

Results

1. Phototransformations of LOS-1

Phototransformations of LOS-1 manifest themselves in the spectrum as a decrease in the intensity of the long-wave absorption band and formation of diffuse absorption in the short-wave (250 nm) and long-wave (360–450 nm) spectral regions.[10] The emission spectra of the irradiated solutions of LOS-1 show that, at excitation in the long-wave region of LOS-1 absorption, at least two photoproducts emit with spectral peaks at 430 nm and 470–480 nm. These characteristics coincide with the emission spectra of LOS-1 photocations obtained when studying acidulous solutions. This points to the structure of photoproducts, π-isoelectronic structure of photocations, i.e., the excited LOS-1 molecule interacts with the environment by the same centers as in formation of a photocation. The studies showed that the nature of photoproducts does not change, when the conditions of excitation and the character of secondary emission change, but the yields of phototransformations and their ratio change significantly. As the excitation intensity increases, the relative yield of the photoproduct emitting with the peak at 430 nm increases.

At excitation of the ethanol solution of LOS-1 (0.1 mmol/l) in the variant *1* (generation of laser radiation with $\lambda_{\text{las}}^{\max} = 372$ nm, $\Delta\lambda_{1/2} = 1$ nm, $\Delta\tau = 7$ ns, efficiency = 17%) the quantum yield of phototransformations is (3–4)$\cdot 10^{-4}$ at the excitation power density of 10–50 MW/cm^2.

At excitation in the variant *2* of the same solution, the lasing is absent. This is confirmed by spectral characteristics of radiation: at the power density $W < 50$ MW/cm^2 the emission spectra coincide with the fluorescence spectra ($\lambda_{max} = 375$ nm, $\Delta\lambda_{1/2} = 60$ nm), and the emission pulse practically follows the pump pulse shape.[7] As the excitation intensity increases, the emission spectrum narrows down to 40 nm at $W = 10$ MW/cm,^{2} and intensity fluctuations extending the pulse are observed in the pulse shape.[7,10] These fluctuations are indicative of the oscillating character of population of the emitting state in this mode. The quantum yield of LOS-1 phototransformations in this variant of excitation is shown in Fig. 1 (curve *6*). One can see from the figure that phototransformations in the absence of lasing in the variant *2* are more efficient as compared to the variant *1*, for which the data are given above. The quantum yield has the maximum value $\varphi = 10^{-3}$ at $W = 50$–60 MW/cm^2, and then it decreases, as the intensity further increases.

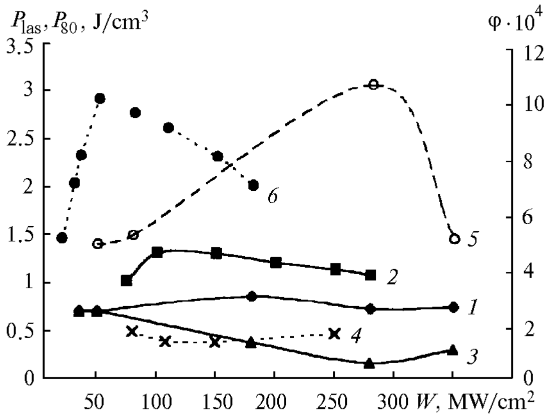

Fig. 1. Dependence of the quantum yield of phototransformations (curves *1*, *2*, *6*); relative yield of photoproducts absorbing laser radiation (curves *3*, *4*) and the LOS-1 (0.1 mmol/l) service life (curve *5*) on the power density of exciting radiation. The degree of polarization of the exciting radiation: $P = 0.9$ (curves *1*–*5*), $P = 0.09$ (curve *6*); lasing mode (curves *1*, *3*, *5*), superluminescence (*2*, *4*, *6*). The variant *2* of excitation.

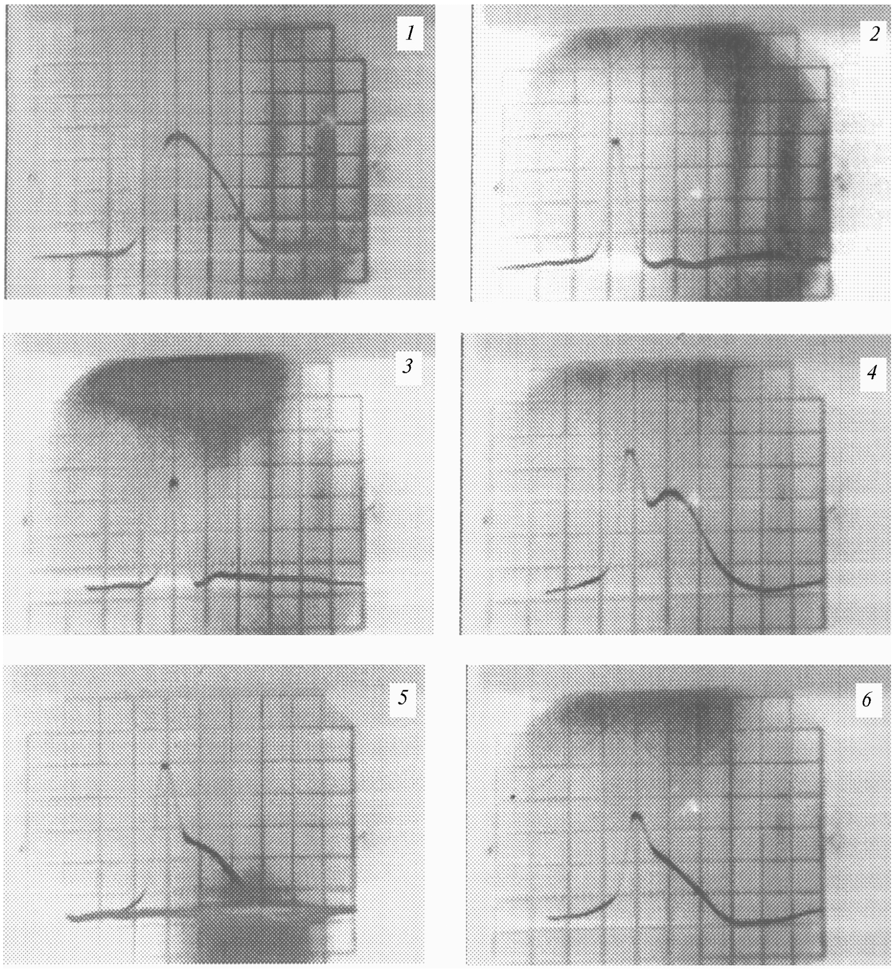

Fig. 2. Pump (curve *1*), LOS-1 lasing (*2*, *3*), and LOS-1 superluminescence (*4*–*6*) pulses. The power density of the exciting radiation with $P = 0.9$ is 350 (*2*, *4*), 170 (*5*), and 85 MW/cm^2 (*3*, *6*). Scanning: 10 ns/point; amplification: 2 V/point (*1*–*3*) and 0.1 V/point (*4*–*6*).

Excitation of the same solution by a linearly polarized XeCl laser radiation significantly decreases the quantum yield of phototransformations (from 10^{-3} to $4 \cdot 10^{-4}$) both under conditions of single-pass amplification (superluminescence) and under the lasing conditions (cf. curves *1*, *2*, and *6* in Fig. 1). The spectral and time characteristics of the pulse are qualitatively close to the characteristics of superluminescence obtained at excitation by unpolarized radiation: narrowing of the emission spectrum down to 35 nm at superluminescence and to 1 nm under lasing conditions, as well as the increase of the pulse halfwidth from 7 ns under the conditions of lasing to 25 ns at superluminescence due to intensity oscillations (Fig. 2). It should be noted that the laser emission from LOS-1 at a transverse pumping is highly polarized, whereas at longitudinal pumping the degree of polarization is much lower, and it is almost independent of the degree of polarization of the pump radiation (Table 1). The degree of polarization of superluminescence recorded in the transverse direction (emission in the absence of a cavity) is rather low ($P \cong 0.2$–0.3) and tends to increase as the excitation intensity increases.

Table 1. Degree of polarization of the laser emission from LOS-1 at the degree of polarization of the exciting radiation of 0.9 (*P*) and 0.09 (*P) depending on the pump power density**

W, $\frac{\text{MW}}{\text{cm}^2}$	P, transverse excitation	P, longitudinal excitation	P^*, transverse excitation	P^*, longitudinal excitation
8	0.85	0.1		
15	0.92	0.35		
20			0.79	0.36
30	0.9	0.15		
40			0.89	0.21
60	0.85	0.14		
80			0.82	0.15

The LOS-1 lasing photostability correlates with the outcome of the photoproduct absorbing lasing radiation (curves *3* and *5* in Fig. 1), as in the case with unpolarized pumping.

2. Photostability of 4PyPON(CH_3)$_2$

Phototransformations of 4PyPON(CH_3)$_2$ were observed as well. Those were judged on from the changes in its absorption and fluorescence spectra. Formation of a photoproduct absorbing lasing radiation is connected with the interaction between most reactive centers – nitrogen atoms of substituted amides and pyridine cycle.[9] Figure 3 shows the quantum yields of phototransformations of 4PyPON(CH_3)$_2$ (0.5 mmol/l) in ethanol as a function of the power density of the pumping XeCl laser radiation (the degree of polarization of the pump radiation is low: $P = 0.09$). It follows from this figure that under lasing conditions in the variant *1* at $W = 5$–40 MW/cm^2 the quantum yield of phototransformations is $(1$–$2) \cdot 10^{-3}$. Phototransformations of 4PyPON(CH_3)$_2$ in hexane and acetonitrile in this variant are even more efficient: $\varphi = 4 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$, respectively. In the variant *2*, in which lasing is absent, the quantum yield of phototransformations of 4PyPON(CH_3)$_2$ in ethanol decreases by 4–5 times, as the intensity of pump radiation increases up to 100–200 MW/cm^2 (Fig. 3).

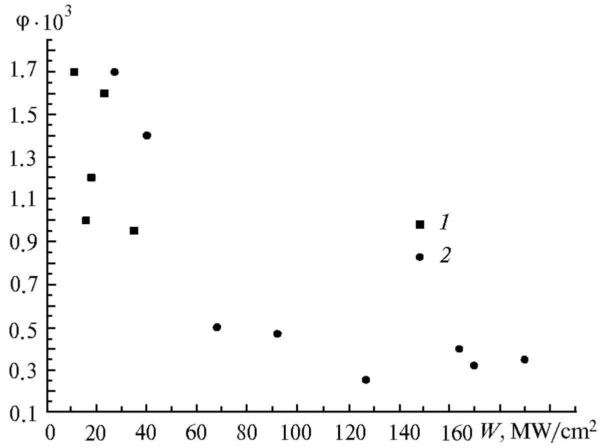

Fig. 3. Quantum yield of phototransformations of 4PyPON(CH_3)$_2$ in ethanol: variants *1* and *2*.

Discussion

We believe that the change in the efficiency of phototransformations of the studied compounds under varying excitation conditions and unchanged final photoproducts is connected with the dependence of pulse-average population of the excited state, wherefrom the phototransformations start, on the excitation and lasing conditions. The population of the excited state S_1 was estimated by the method proposed in Ref. 11. This method is based on measurements of a solution transmittance for pump radiation at different radiation intensity (Fig. 4). Linear absorption of the low-intensity pump radiation ($W \ll 1$ MW/cm^2) by the studied solutions can be measured by a spectrophotometer ($T_0 = 0.28$ for LOS-1 and 0.45 for 4PyPON(CH_3)$_2$). Unlike linear absorption, the transmittance at $\lambda = 308$ nm at laser excitation increases for the LOS-1 solution and decreases for the 4PyPON(CH_3)$_2$ solution. The nonlinear character of variation of the absorption coefficient at the increasing intensity of pump radiation is connected with the change in population of different states during the pump pulse due to the transition of a marked fraction of molecules from the ground state to the excited one. The difference in the behavior of the LOS-1 and 4PyPON(CH_3)$_2$ transmittance on the pump power density is connected with different ratios of the effective cross sections of the absorption from S_0 (σ_{01}) and S_1 (σ_{1n}) states. For LOS-1 $\sigma_{01}^{308} > \sigma_{1n}^{308}$, i.e., the absorption at $\lambda = 308$ nm decreases as n_0 decreases (see Fig. 4).

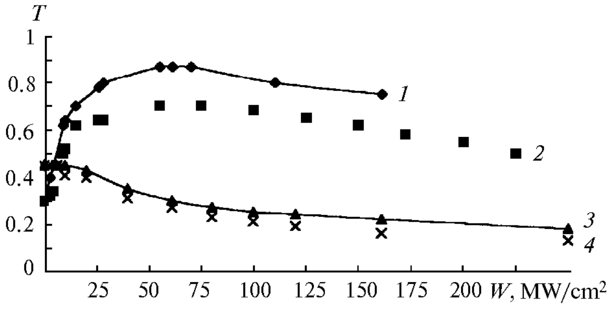

Fig. 4. Transmittance of the LOS-1 (*1* and *2*) and 4PyPON(CH$_3$)$_2$ (*3* and *4*) solutions for the pump radiation as a function of the pump power density at the degree of polarization: $P = 0.9$ (*2*), $P = 0.09$ (*1*, *3*, and *4*); solutions in ethanol (*1–3*) and hexane (*4*); variant *2*.

The estimate of the pulse-average population of the excited state S_1 under the condition that $\sigma_{1n}/\sigma_{01} = 0.1$ shows that, neglecting forced processes, the S_1 population reaches roughly 0.9 n at $W = 60$ MW/cm^2 (Ref. 7). The account of the forced processes significantly decreases the S_1 population. This is just the cause of the decrease in the quantum yield of phototransformations under lasing conditions as compared to that under conditions of spontaneous emission. If every excited molecule takes part in the stimulated emission, i.e., $\sigma_{10}/\sigma_{01} = 3.4$, as follows from the spectroscopic data[7,12] (here σ_{10} is the effective cross section of the stimulated emission), then the population decreases from 0.9 to 0.2 n. Under actual experimental conditions, the decrease of the pulse-average population of the excited state follows from the decrease in the clearing-up of the active solution as compared to the inactive one, as shown in Ref. 10, what agrees with the results presented in Ref. 13 for polyphenyls. In Ref. 13, the decrease of the clearing-up was connected with the shorter lifetime due to forced processes. The analysis of the results presented in Figs. 2 and 5 shows that the decrease in the transmittance of the inactive LOS-1 solution, as the pump power density increases above 60 MW/cm^2, is connected with the decrease in the S_1 population under these conditions.

The decrease in the S_1 population is caused by the increasing role of forced processes in LOS-1 emission at high-power pumping. This is supported by spectral and temporal characteristics of radiation: the decrease of the spectrum halfwidth from 60 to 30 nm and relaxation oscillations of the intensity in a pulse that reflect oscillations of the population at formation of superluminescence. The oscillations are especially pronounced in the case of superluminescence formation under the exposure to polarized pump radiation (Fig. 2). Under the exposure to unpolarized pump radiation, the second maximum in the superluminescence pulse manifests itself as the pulse elongation due to an additional "arm."[7,10] These results allow us to state that the LOS-1 phototransformations decreasing with the decrease in the population of the emitting state come from the S_1 excited state, and the change in the photostability characteristics depending on the excitation conditions and the character of emission is connected with the change in the pulse-average population of the state responsible for phototransformations.

The decrease of LOS-1 phototransformations when pumped by polarized radiation ($P_{308} = 0.9$) is also connected with the decrease in the population of the excited state, since the clearing-up in this case decreases significantly with the increasing pump power density: the transmittance at 60 MW/cm^2 decreased from 0.9 to 0.7 (Fig. 4). All other parameters being unchanged, this decreased the relative population from 0.9 to 0.8. It should be noted that the lasing efficiency of the LOS-1 solution at the polarized pumping decreased as compared to the unpolarized pumping (down to 14% vs. 32%). The cause of the decrease in the clearing-up and the population of the S_1 state, as well as the lasing efficiency at polarized excitation is to be found in the future.

The increase in the 4PyPON(CH$_3$)$_2$ absorption during the pump pulse with the increase of its intensity (Fig. 4) indicates that $\sigma_{1n} > \sigma_{01}$. At medium pump power density usually used for pumping laser dyes ($\cong 20$ MW/cm^2), the transmittance is nearly linear, i.e., the population of the excited state responsible for reabsorption of the pump radiation is low. Although the emitting states of 4PyPON(CH$_3$)$_2$ in ethanol and hexane are significantly different ($\lambda_{\max}^{\rm fl} = 560$ and 415 nm, respectively[8,9]), the transmittance curves for them are qualitatively similar; only as the pump power density increases above 80 MW/cm^2, the difference in the transmittance of the solutions having the same linear transmittance at $\lambda = 308$ nm goes beyond the limits of the error (3%): the ethanol solution darkens less efficiently as compared to the hexane solution (see Fig. 4). This may mean that the pump radiation is mostly absorbed from the non-equilibrium state, whose pulse-average population depends on the pump intensity.

Table 2. Estimate of the pulse-average population of the 4PyPON(CH$_3$)$_2$ emitting state

W, MW/cm^2	Φ, phot/(cm^2 s)	n_1/n, (in ethanol)	n_1/n, (in hexane)
20	$3.1 \cdot 10^{25}$	0.02	0.03
30	$4.65 \cdot 10^{25}$	0.04	0.045
60	$9.3 \cdot 10^{25}$	0.13	0.12
100	$1.55 \cdot 10^{26}$	0.17	0.15
200	$3.1 \cdot 10^{26}$	0.24	0.21

The estimate of relative population of the 4PyPON(CH$_3$)$_2$ emitting state by the method proposed in Ref. 11 at $\sigma_{1n}/\sigma_{01} = 10$ shows that as the pump intensity increases, the population increases for both hexane and ethanol solutions (Table 2). The decrease in the efficiency of 4PyPON(CH$_3$)$_2$ phototransformations with the increase of pump intensity (see Fig. 3) suggests that phototransformations occur from some intermediate state, rather than the emitting state itself, or at interaction of intermediate photoproducts with the

$4PyPON(CH_3)_2$ molecule in the ground state. For more specific determination of these states, long-lived absorption and emission of $4PyPON(CH_3)_2$ should be studied with a higher time resolution.

Conclusion

The results presented in this paper show that as the high-power laser radiation interacts with complex organic molecules, they experience phototransformations depending on the structure of molecules and the solvent, as well as the pumping parameters and the character of secondary emission. The characteristics of photostability are determined by the population of the photoreactive state during the pump pulse. Phototransformations slow down under conditions of lasing as compared to spontaneous emission, if they come from the fluorescing state taking part in the formation of superluminescence decreasing the pulse-average population of this state. In the case that some intermediate excited state, which the molecule takes due to relaxation or reabsorption of high-power radiation, is responsible for phototransformations, no slowing-down of the phototransformations under lasing conditions can be observed. The study of the transmittance for the pump radiation bears important information for the development of the model of photoprocesses in a particular case.

Acknowledgments

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