

RADIATIVE PROPERTIES OF ORGANIC MOLECULES IN STRONG PHOTON FIELDS

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We have experimentally investigated the dependence of the luminescence intensity of ethanol solutions of 2-(4-pyridyl)-5-phenyloxazole on the intensity of the exciting radiation from an XeCl laser ($\lambda_{ex} = 308$ nm, $\tau_p = 10$ nsec, $E_{ex} = 10^{22}$ - 10^{26} photons/cm²·sec). We discuss the measurement technique and possible reasons for the change in radiative properties of the investigated solutions under the given conditions.

When using high-power pulsed lasers for excitation of solutions of organic molecules, intensities of the exciting radiation on the order of 10^{25} - 10^{27} photons/cm²·sec are created. Such photon fluxes create a high concentration of excited molecules during the excitation pulse, so the optical properties of the excited medium change both because of photophysical factors (transparency of the solutions at the excitation wavelength, absorption of light by excited molecules in different forms and states is observed) and because of a change in the thermo-optical properties of the solutions: formation of thermo-optical lenses, three-dimensional gratings [1], etc. All this leads to a decrease in the output energy of tunable lasers based on solutions of organic compounds with an increase in the excitation power [2-4]. The need to solve these problems, which were posed in the 1980s [5, 6], requires further investigation of the optical properties of molecules under the given conditions.

In a series of papers by V. P. Klochkov and coauthors, the results of which are generalized in [7], the possibility is indicated that a change occurs in the Einstein spontaneous emission coefficient for organic molecules A_{10} in strong photon fields with power density higher than 10^{23} photons/cm²·sec, formed by focused laser emission. This conclusion was drawn on the basis of the experimentally observed increase in luminescence intensity of dilute solutions of Rhodamine 6Zh, outstripping the growth of the population of the S_1 state, as a function of the excitation intensity.

In this paper, as the object of investigation we chose the 2-(4-pyridyl)-5-phenyloxazole (4PyPO) molecule, a characteristic feature of which is the decrease in the efficiency of conversion of the emission of excimer lasers with ethanol solutions of 4PyPO as the pumping power density increases [8]. Furthermore, owing to the increase in the proton-acceptor ability of the molecule on excitation in the S_1 state, formation of the 4PyPO photocation is possible, which fluoresces along with the neutral form in aqueous 4PyPO solutions [9]. In this paper, we present results only for the neutral form of 4PyPO in ethanol, but later we will investigate the dependence of the luminescence of the 4PyPO photocation on the excitation intensity.

As the excitation source we used an XeCl laser ($\lambda_{las} = 308$ nm, $\tau_p = 10$ nsec, E_{las} up to 60 mJ), the emission from which, focused by a cylindrical lens ($F = 250$ mm) into a horizontal 0.15×1 cm² strip, was directed onto a cuvet with dye K of thickness $l = 0.2$ cm and width $L = 1$ cm through diaphragm D_1 , the dimensions of which were varied: 0.15×0.8 cm² and 0.15×0.07 cm². The luminescence was registered in the perpendicular direction through diaphragm D_2 of dimensions 0.1×0.15 cm² with the help of an MDR-23 monochromator, an FÉU-79 photoelectron multiplier, and an S8-14 oscilloscope. (The oscilloscope was triggered by a signal from an FÉK-22.) In order to avoid multiple passes of the luminescence, a polyethylene insert of thickness 2 mm with a matte surface was set on the opposite face of the cuvet. In order to record the luminescence spectra, the signal from the FÉU-79 was sent to an N-306 x-y plotter. Since the FÉU-79 has high sensitivity but insufficient time resolution ≤ 15 nsec, in order to record the real shape of the pumping pulse and the luminescence we used an FÉK-22 with neutral light filter NS-1, completely filtering the scattered exciting radiation and passing 84% of the luminescence.

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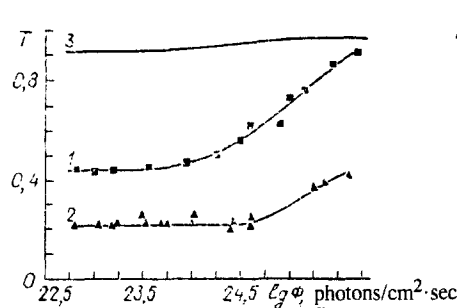


Fig. 1

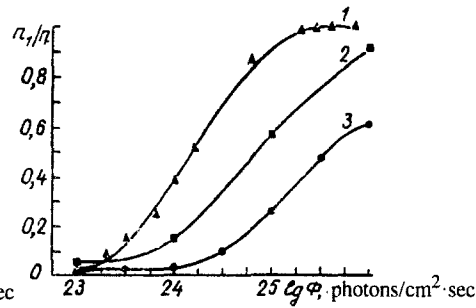


Fig. 2

Fig. 1. Transmission T vs. excitation intensity for ethanol solutions of 4PyPO: 1) $5 \cdot 10^{-6}$ moles/liter, $l = 2$ cm; 2) 10^{-4} moles/liter, $l = 0.2$ cm; 3) $5 \cdot 10^{-6}$ moles/liter, $l = 0.2$ cm.

Fig. 2. Relative population of the S_1 state of 4PyPO vs. excitation intensity. 1) Calculated from (1); 2, 3) calculated from (2); 2) $5 \cdot 10^{-6}$ moles/liter; 3) 10^{-4} moles/liter.

science in the 400 nm region. The pumping radiation was monitored with the help of an IMO-2N and was attenuated by up to a factor of $\cong 2000$ by a set of calibrated metallic grids. During all the experiments, we constantly monitored the linearity of the characteristics of the registration systems.

The average population of the excited S_1 state over the pulse was estimated first of all from the formula given in [7] for a P-shaped pulse:

$$n_1/n = \sigma_{01}\Phi/\Delta t(r_1 - r_2) \{1/r_1[\exp(r_1\Delta t) - 1] - 1/r_2[\exp(r_2\Delta t) - 1]\}, \quad (1)$$

where

$$r_{1,2} = -1/2\tau \{1 + (\sigma_{01} + \sigma_{10})\Phi\tau \pm \sqrt{[1 + (\sigma_{01} + \sigma_{10})\Phi\tau]^2 + 4\sigma_{01}\Phi\tau[\tau(A+d) - 1]}\}$$

n is the concentration of the molecules in solution; τ is the lifetime of the excited state = 2.5 nsec; A and d are radiative and nonradiative constants ($4 \cdot 10^8$ and $8 \cdot 10^6$ sec $^{-1}$, respectively); σ_{01} and σ_{10} are the effective absorption and stimulated emission cross sections at the excitation frequency ($7.3 \cdot 10^{-17}$ cm 2 and 0, respectively); $\Delta t = 10$ nsec is the duration of the exciting pulse; Φ is the excitation intensity.

On the other hand, the population was estimated from measurement of the transmission of the exciting radiation by the investigated solution as a function of its intensity according to the formula proposed in [7]:

$$n_1/n = (\lg T_\Phi/T_0) / [(\sigma_{1n}/\sigma_{01} - \sigma_{10}/\sigma_{01} - 1) \lg T_0]. \quad (2)$$

Here the transmission of the solution $T = I/I_0$, where I and I_0 are the intensities of the exciting light passing through the cuvet and incident on the cuvet, respectively. For low intensities of the exciting light $\Phi \leq 10^{22}$ photons/cm 2 ·sec, $T = T_0$ and coincides with the transmission measured on a Specord spectrophotometer; T_Φ is the transmission by the solution of exciting light with power density Φ ; σ_{1n} is the effective $S_1 - S_n$ absorption cross-section at the frequency of the exciting light. (According to quantum chemical calculations, this absorption is 2-3 orders of magnitude less than for $S_0 - S_1$ absorption.) Formula (2) is obtained by simultaneous solution of the equations for transmission under conditions of low and high photon fluxes:

$$\begin{aligned} \lg T_0 &= -\sigma_{01} \cdot n \cdot l, \\ \lg T_\Phi &= -\sigma_{01} \cdot n_0 \cdot l - \sigma_{1n} \cdot n_1 \cdot l + \sigma_{10} \cdot n_1 \cdot l. \end{aligned} \quad (3)$$

The intensity of the transmitted light was measured using a high-sensitivity KTP-2 calorimetry attachment connected to an F-138 nanovoltmeter, which were precalibrated using an IMO-2N. The absence of a luminescence signal in the KTP-2 was constantly monitored.

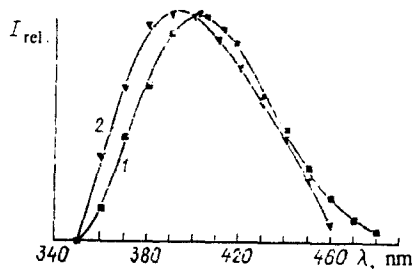


Fig. 3

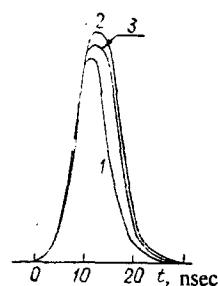


Fig. 4

Fig. 3. Luminescence spectra of ethanol solutions of 4PyPO with concentration 10^{-5} moles/liter. Excitation intensity: 1) $< 10^{22}$ photons/cm 2 ·sec; 2) 10^{26} photons/cm 2 ·sec.

Fig. 4. Oscillograph traces of excitation (1) and luminescence (2, 3) pulses for excitation intensities: 2) $< 10^{22}$ photons/cm 2 ·sec; 3) 10^{26} photons/cm 2 ·sec.

Since the initial transmission of the 4PyPO solution at a concentration of $5 \cdot 10^{-6}$ moles/liter for cuvet thickness $l = 0.2$ cm is 92% while the error in measurement of T according to the described procedure is equal to 7%, the change in the transmission as the intensity increases for this concentration was measured for a cuvet of thickness 2 cm: in this case, $T_0 = 45\%$. The measured curve is shown in Fig. 1, from which it follows that starting from a density on the order of 10^{23} photons/cm 2 ·sec, the transmission of a solution of this concentration increases as a result of a decrease in the concentration of molecules in the S_0 state, while for $\Phi = 3 \cdot 10^{25}$ photons/cm 2 ·sec the solution is practically completely "transparent." Considering that $\lg T$ is proportional to l (3), the transmission is rescaled to $l = 0.2$ cm (Curve 3 in Fig. 1). From this curve according to formula (2), we estimated the dependence of n_1/n on $\lg \Phi$ (Fig. 2). On the same figure, we give the dependence of n_1/n on $\lg \Phi$ for a 4PyPO concentration of 10^{-4} moles/liter, estimated from Curve 2 in Fig. 1 (in this case, the transmission was measured for $l = 0.2$ cm, $T_0 = 0.21$). Curve 1 represents the population estimated according to formula (1). As we see from Fig. 2, the populations estimated from formulas (1) and (2) are close only for low intensities of excitation and are substantially different as Φ increases, although the S-shape of the curve is retained in all cases.

In Fig. 3, we present the luminescence spectra of the investigated 4PyPO solutions. We see that with an increase in the excitation power density, the luminescence band undergoes a slight shift toward shorter wavelengths, analogous to what was observed in [7] for Rhodamine 6Zh. Such a slight change in the shape of the luminescence band may be connected, as is explained in [7], with redistribution of the intensity of the vibronic maxima as a result of a change in the dipole moment of the transition for strong excitation. Possibly the reason for such an intensity redistribution may also be connected with a decrease in the concentration of unexcited molecules on strong excitation, which may disrupt the thermal equilibrium in the ground state.

As far as the shape of the luminescence pulse is concerned, with accuracy up to the thickness of the oscilloscope beam it does not depend on the excitation intensity for concentrations of $5 \cdot 10^{-6}$ and 10^{-5} moles/liter. The luminescence pulse is lengthened by 2.5 nsec compared with the pumping pulse (Fig. 4), which is due to the lifetime of the investigated emission.

The dependence of the luminescence intensity on the excitation intensity for a concentration of $5 \cdot 10^{-6}$ moles/liter = $3 \cdot 10^{15}$ cm $^{-3}$ qualitatively reproduces the dependence obtained in [10] for R6Zh solutions. That is, neglecting the population of the S_1 state, the dependence of the luminescence intensity on the power density of the exciting flux first undergoes abrupt growth, probably as a result of the growth in the population of the excited state, and then approaches saturation, when the population of the S_1 state is practically constant.

If the luminescence intensity is divided by the population of the S_1 state, then in log—log coordinates (as is done in [7]) this dependence takes on the form given in Fig. 5. J_0 and J correspond to the ratio of the luminescence intensity to the population of the S_1 state for low intensities of the exciting light ($\Phi = 10^{22}$ photons/cm 2 ·sec), $J_0 = I_0/(n_1)_0$ and high intensities of the exciting light ($\Phi > 10^{22}$ photons/cm 2 ·sec), $J = I/n_1$. From Fig. 5 it follows that the threshold value of Φ^* , after which the luminescence intensity increases faster than the population of the luminescent level, depends considerably on the value of the population. $\Phi^* \cong 10^{23}$ photons/cm 2 ·sec, independently of the concentration, when using formula (1) for estimating the population (Fig. 5a); and when using formula (2), Φ^* is an order of magnitude higher for a concentration of $5 \cdot 10^{-6}$ moles/liter

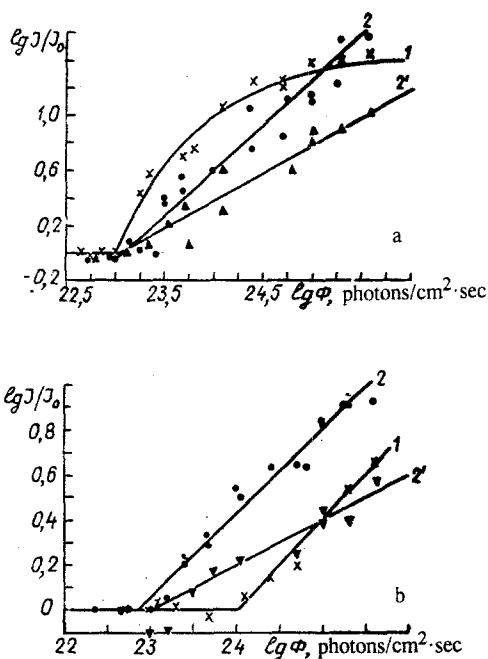


Fig. 5. Relative logarithm of J , equal to the ratio of the fluorescence intensity to the population of the fluorescent S_1 state, vs. the logarithm of the intensity of the exciting light. Concentration of 4PyPO: $5 \cdot 10^{-6}$ (1) and 10^{-4} moles/liter (2, 2'), $L = 0.8$ (2) and 0.07 cm (2'). n_1 is estimated from (1) for (a), and from (2) for (b). The experimental error is $\pm 10\%$ in determination of J and $\pm 2\%$ in measurement of Φ .

than for 10^{-4} moles/liter (Fig. 5b). It is characteristic that in both cases, for a concentration of 10^{-4} moles/liter, the rate of growth in $\lg J$ decreases with a decrease in the length of the excited (and emitting) zone L from 0.8 to 0.07 cm (compare curves 2 and 2' in Fig. 5).

The experimental data obtained for 4PyPO qualitatively agree with the experimental data from [7] for R6Zh. But we feel that the reason for the observed increase in luminescence on intensive pumping, connected by those authors with an increase in the rate of spontaneous emission of the molecules in strong photon fields, is not obvious, since they did not consider the following possible phenomena also leading to an increase in luminescence. As follows from [11, 12], it is practically impossible to differentiate between photons of spontaneous and stimulated emission flying off in the same direction. Since the amplification is proportional to the length of the excited zone L , it is logical to assume that the difference between the slopes of the curves in Fig. 5 arises due to the fact that in the case of large $L = 0.8$ cm, amplification of stimulated emission in a single pass is higher than for $L = 0.07$ cm. The fact that for these excitation intensities the probability of stimulated emission may be no less than the probability of spontaneous emission is implied by the following estimates [12]:

$$I_{\text{rad}} = h\nu_{10}n(A_{10} + B_{10}u_{\text{rad}}). \quad (4)$$

Here $B_{10}u_{\text{rad}}$ is the probability of stimulated emission, u_{rad} is the density of the luminescence which is the stimulating emission. For 4PyPO at the maximum of the luminescence band, $B_{10} = 3.2 \cdot 10^6 \text{ cm}^3/\text{erg} \cdot \text{sec} = 1.45 \cdot 10^{-5} \text{ cm}^3/\text{photons} \cdot \text{sec}$. In the case when the second term in (4) is comparable in magnitude with the first term, $u_{\text{rad}} = 2.8 \cdot 10^{13} \text{ photons/cm}^3$. For a luminescent quantum yield of 0.98 , this density is achieved for a concentration of excited molecules which is created by a number of absorbed photons per unit volume in the time over which the fluorescence photon does not leave the limits of the excited zone:

$$N_{\Phi} = n_0 \cdot \sigma_{01} \cdot \Phi t,$$

where n_0 is the concentration of molecules; σ_{01} is the effective absorption cross section at the pumping frequency; Φ is the excitation intensity (photons/cm²·sec); τ is the time over which the photon flies through the excited zone in the direction of registration, equal to $3 \cdot 10^{-11}$ sec ($0.8 \text{ cm}/3 \cdot 10^{10}/\text{sec}$).

Then for a concentration of $5 \cdot 10^{-6}$ moles/liter, $\Phi = [2.8 \cdot 10^{13} \text{ photons/cm}^3]/[(3 \cdot 10^{15} \text{ cm}^{-3}) (7.3 \cdot 10^{-17} \text{ cm}^2) (3 \cdot 10^{-11} \text{ sec})] = 4 \cdot 10^{24} \text{ photons/cm}^2 \cdot \text{sec}$, while for 10^{-4} moles/liter, $\Phi = 2 \cdot 10^{23} \text{ photons/cm}^2 \cdot \text{sec}$, in order for the probability of stimulated emission to be competitive with the probability of spontaneous emission.

Hence, the anomalous increase in the emission intensity as Φ increases may be connected not only with a change in A_{10} , but also with an increase in the fraction of stimulated emission, which for lower pumping rates is negligibly small compared with spontaneous emission.

Correct estimation of the population of the S_1 state becomes especially important. In particular, the difference between the curves in Fig. 2, estimated from different approaches according to (1) and (2), may be connected (for example) with invalid application of Bouguer's law in integral form for intensive excitation, as is indicated in [11]. The effect of the above-indicated factors on the increase in luminescence of organic compounds in strong photon fields will be discussed in the next paper.

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