The specific features of spontaneous and stimulated molecular radiation in high-power laser beams.

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ABSTRACT

Fluorescence characteristics of 2-(4-pyridyl)-5phenyloxazole (4PyPO) and trans-stilbene has been studied under high power XeCl laser excitation. Anomal fluorescence phenomenon has been found. Gain and losses were measured in 4PyPO active media in range of excitation rate from 10^{23} to 10^{26} phot/cm^2 s. Dinamics of losses in laser pulses in coumarine substituted was studied under XeCl laser pumping.

Keywords: power excitation, laser dyes, anomal superfluorescence, coefficient of gain, dinamics of losses.

1. INTRODUCTION

Successful application of tunable dye lasers requires higher output energy. To this end, high power exciplex and solid state lasers should be used. When the pumping power is increased the drop of laser efficiency, narrowing of wavelength tunability, changes in photostability and lifetime of active media as well as recoverable and unrecoverable alterations of optical parameters of solutions and optical elements are observed [1-3]. The aim of this paper is to find out reasons of these phenomena.

Lasing parameters of dyes are mainly determined by their radiative properties. Hence, study of luminescence in high power laser beams is of interest. This seems to be especially important since there are publications where possibility of change of Einstein coefficients for spontaneous emission in high-power laser beams is discussed. Moreover, influence of this change on laser parameters is considered [4].

2.RESULTS AND DISCUSSION

2.1. Fluorescence study.

In this paper, fluorescence characteristics of neutral aqueous and ethanol solutions of 4PyPO and ethanol solutions trans-stilbene were studied. Indeed, 4PyPO ethanol solution is efficient active medium at λ=398 nm with efficiency of 18 % under XeCl laser excitation [5]. Fluorescence quantum yield of 4PyPO in ethanol can reach 90% whereas trans-stilbene demonstrates only 5-8% due to efficient trans-zis-photoisomerization. However, though yield of fluorescence is rather low in trans-stilbene lasing in this dye is obtained at λ=351 nm and has high threshold (16 MW/cm^2) and low efficiency (4%).

Fluorescence was induced by XeCl laser at λ=308 nm with τ_{FWHM}=10 ns, E_{out}=30-40 mJ. Focusing of radiation enabled us to produce laser fields with power density of up to 10^{26} phot/cm^2 s. Radiation was focused by a cylindrical lens with F=250 mm on rectangle cell 0.2 mm thick and 1 cm wide through an aperture with dimensions of 0.14 cm×0.8 cm. Fluorescence was oserved in the direction perpendicular to pumping beam through an aperture of 0.1×0.1 cm located on the cell wall. On the opposite an aluminia mirror was mounted. It was preliminary aligned along the dye solution. This mirror could be screened. If it was necessary to perform fluorescence measurements in presence of resonator the screen was removed. In other cases, a 0.2 cm teflon sheet was introduced in the cell to avoid reflection from the opposite side. The excitation energy was measured by highly sensitive calorimeter KTP-2 coupled to nanovoltampermeter F-138 which was first calibrated using IMO-2N. Spectral and temporal characteristics were monitored by means of MDR-23 monochromator, photodetectors and S8-14 oscilloscope. Attenuation of radiation was carried out using neutral filters. Linearity of operation of registration system was tested during all sets experiments. The relative error of fluorescence and excitation intensity measurements was 10 %.

Fluorescence intensity versus excitation power density Φ is presented in Fig.1 in logarithmic scale. There is no saturation of fluorescence observed with Φ up to 10^{26} phot/cm^2 s in trans-stilbene and ethanol 4PyPO solution (curves 1 and 3). It is anomal results since population of excited S_1 state estimated basing on changes of transparency with Φ [7] is saturated at

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$\Phi \cong 10^{25}$ phot/cm ^{2} s [6] whereas fluorescence intensity is continuously increased. Such an excess of increase of fluorescence over increase in population of S_1 state observed in [4,8,10,11] with other dyes and excitation was called noncoherent superfluorescence [10]. In opinion of autors of [11], it is connected with increase of probability of spontaeous emission (Einstein coefficient A_{10}) under light power excitation. This phenomenon is caused by enhancement of vacuum field fluctuations in the case of non-degenerated four-wave mixing of spatially degenerated waves [12] under power excitation.

The same effect was observed in [9,13,14] but it was explained in other ways. Also ocuring of collective processes in a media under power excitation in conditions of inverse population was predicted by Dicke in 1954[15] before laser effect demonstrated. It was stressed in [16-18] that this radiation is absoluting different from the stimulated radiation.

As it turns out from Fig.1, more rapid increase of fluorescence intensity with pumping rate is observed in ethanol solution of 4PyPO which is an efficient active medium. When stimulated radiation in 4PyPO was increased using resonator (curve 4, Fig.1) the increase in fluorescence intensity at pumping rate $\cong 10^{26}$ phot/cm^2 s was observed as compared with experiment without resonator (curve 3). When pumping rate or dye concentration is lower or the length of excited layer L is shorter the curves obtained with resonator and without it do not differ to pumping level of 6×10^{25} phot/cm^2 s. These curves are the same also in experiments with trans-stilbene.

The pulse shape derived from ethanol solution of 4PyPO (0.1 mMol/l) depends on pumping intensity. It is longer by 2-3 ns under "weak"pumping (10^{23} phot/ cm^2 s) and shorter by 3-4 ns under "high-power" pumping (5×10^{25} phot/cm^{2}s). There is no effect of resonator on this phenomenon. It should be meantioned here that curves 3 and 4 in Fig.1 are obtained taking into account pulse shortening since fluorescence intensity was estimated basing on area under pulse curve. Such a shortening was not observed with lower dye concentration (10^{-2}, 5×10^{-3} mMol/l) and with other solutions (4PyPO in water, trans-stilbene in ethanol).

Aqueous solution of 4PyPO shows saturation of fluorescence intensity (curves 2 and 6 in Fig.1), but photocathion structure formed in S_1 state and emitting at 470 nm demonstrates no saturation also (curve 5, Fig.1).

This is confirmed by fluorescence spectra under laser excitation presented in Fig.2,3. It was found that all solutions show blue shift of fluorescence band under high power excitation. This fact was noted also in [10] in experiments with R6G. Such a shift can be attributed to significant reduction of ground state population under conditions of intense excitation with transition from equilibrium existing under "weak" pulsed excitation to non-equilibrium. Fluorescence spectra of aqueous 4PyPO solution (see Fig.2) consist of two bands corresponding to the neutral and cathion structure with λ_{max} at 410 and 470 nm respectively. The absorption spectrum of this solution contains only the band of neutral molecule at 310 nm. Pulsed laser excitation leads to narrowing of the spectrum and increase of photocathion yield as compared with steady excitation (Spectrofluorimeter Hitachi-850). Relative fluorescence intensity of cathion structure is increased with pumping power demonstrating that recoverable photoconversion of 4PyPO with coupling of proton to nitrogen of pyridyn cycle becomes more efficient under high power pumping.

Fluorescence spectra of trans-stilbene were monitored taking into account that its phototransformation yield is very high (6×10^{-2}) and fluorescent photoproducts are formed. Steady fluorescence spectrum of stilbene solution after energy deposition of 2 J/cm^3 is shown in Fig. 3 (curve 4). Emission of photoproducts at λ>350 nm is evident. The discussion concerning the origin of these photoproducts are beyond the frames of this paper. Fluorescence spectrum of trans-stilbene under XeCl laser excitation was monitored in such a way that the total energy deposition was not hihger than 3 mJ/cm^3 under "weak" excitation and 300 mJ/cm^3 under high power pulsed excitation. As it comes out from Fig.3 the shapes of fluorescence spectrum obtained under high-power and steady excitation are actually the same, but there is the above mentioned shift to shorter wavelength. "Weak" excitation by XeCl laser results in increase of intensity at λ>350 nm compared with steady spectrum. This change can be connected with unrecoverable phototransformation since intensity in this region of spectrum is increased with irradiation dose (see curves 4, 5, in Fig.3). Similar regularity was noted in experiments with provitamin D where decrease of yield of phototransformation initiated by reaction cis-trans photoisomerization was reported under high power laser excitation [19].

Thus, investigation of fluorescent properties of organic molecules under high power excitation showed that noncoherent superfluorescence is manifested in experiments with wide circle of substances. Further investigations are necessary to obtain basic knowledge about this phenomenon and to use it in laser physics and photochemistry.

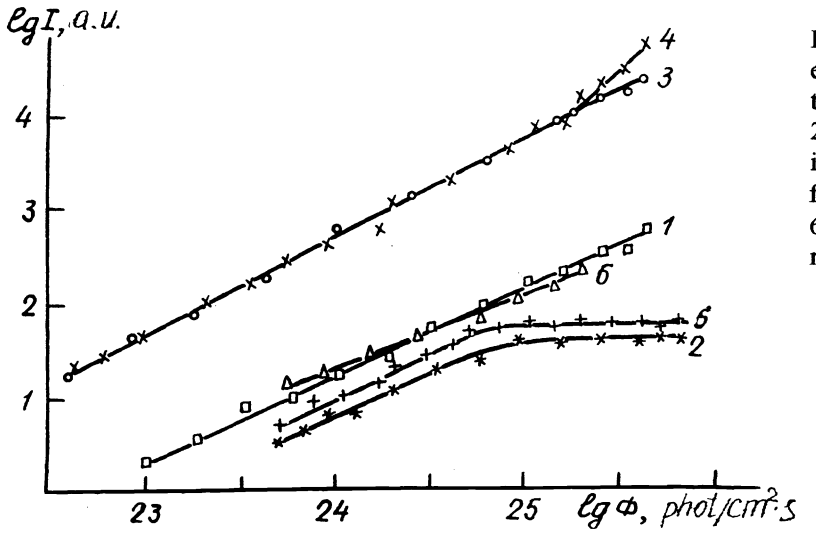


Fig.1 Fluorecence intensity versus exciting intensity in logarithmic scale for trans-stilbene - 1, 4PyPO in water - 2,5,6; 4PyPO in ethanol - 3,4. 1-4 - integral intensity within whole fluorescence band; 5 - λ_{rec}=400 nm; 6 - λ_{rec}=480 nm; 4 - excitation into resonator.

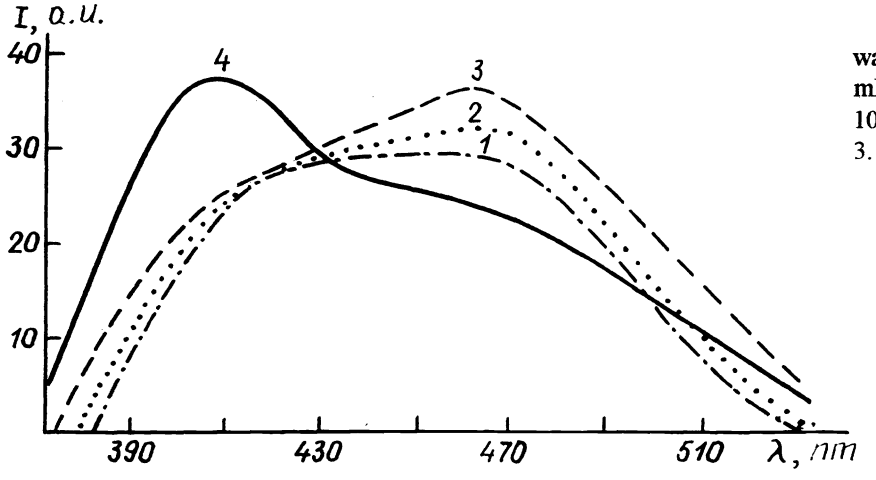


Fig.2. Fluorescence spectra of neutral water 4PyPO solution (C=5×10^{-3} mMol/l) under XeCl laser excitation: 10^{23} - 1, 8×10^{24} - 2, 5×10^{25} phot/cm^2 s - 3. Steady excitation (Hitachi-850) - 4.

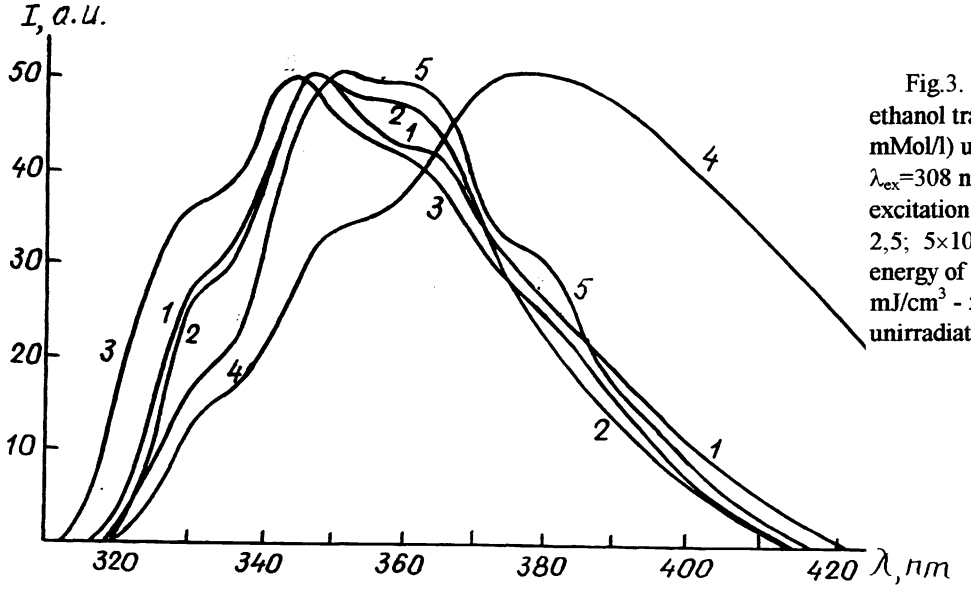


Fig.3. Fluorescence spectra of ethanol trans-stilbene solution (C=5×10^{-2} mMol/l) under steady (Hitachi-850, λ_{ex}=308 nm) - 1,4 and XeCl - 2,3,5 - excitation. Power of excitation: 5×10^{23} - 2,5; 5×10^{25}phot/cm^2 s - 3. Pumped energy of irradiation: 3mJ/cm^3 -2, 30 mJ/cm^3 - 5, 300 mJ/cm^3 -3, 2 J/cm^3 - 4, unirradiated solution - 1.

2.2. Determination of gain.

To find correlation of changes in emission properties and lasing the gain of ethanol 4PyPO solution was studied at the same parameters of XeCl laser excitation. The gain was measured using method of calibrated losses [20] that are introduced in resonator with reflection of the mirrors:R_1=1 and R_2=0.07; 0.2; 0.38; 0.83 to reach threshold conditions. The gain or coefficient of negative absorption in threshold condition can be written as $-K_{ampl}=K_l+K_{rad}$. Here K_l is coefficient of intracavity losses connected with scattering of pumping and laser radiation , "harmful" reabsorption from the ground state etc., K_{rad} is coefficient of usful losses for radiation. These losses can be described by the following equation taking into account calibrated losses: $K_{rad}=1/2L\times\ln 1/R_1\ R_2\ T^2$. Here T is transmitance of the filter in the cavity leads to threshold conditions at the certain pumping rate, L is active length. The value of sum $-(K_{ampl}+K_l)=K_{rad}$ was measured in our experiments with accuracy of 15% versus pumping power density and presented in Fig.4. Fig.4 shows that at low pumping rate ($\cong 10^{23}$ phot/cm^2 s) nearly linear increase of this value is evident due to increase of inversion with excitation power. The saturation is observed at 10^{24}phot/cm^2 s and the value of $\cong$3.8 cm^{-1} is achived at 10^{25}-10^{26} phot/cm^2 s. The sum is not affected by R_2 within experimental error.

To evaluete the effect of K_l on $K_{ampl}(W_{pump})$ we estimated K_l using method based on measurement of quantum laser efficiency η as a function of mirror transparency [21] (see Fig.5). Accordingly to this method [21] K_l is determined as inclination of the line plotted in coordinate axis $1/\eta$ and $1/K_r$ and crossing the ordinate axis in point y=C. Here K_r are losses for radiation without calibrated losses T. Then, $K_l=tg\alpha/C$ (see Fig.6). These lines are plotted at different excitation rates. This method can be used if the function $1/\eta(1/K_r)$ is linear. Physical processes which are responsible for this mathematical conditions are analyzed in [21]. In our case, linear function is observed at W$\geq 10^{24}$ phot/cm^{2}s. Estimated value of K_l is changed from 0.18 to 0.42 cm^{-1} when pumping rate is changed from10^{24} to 6×10^{25} phot/cm^{2}s. This is within experimental error of -$(K_{ampl}+K_l)$ measurements and K_l does not affect K_{ampl}(W) at high power excitation. It should be noted that similar increase of losses was obtain in experiments with R6G [21] under longitudinal pumping when pumping rate was increased. Reduction of laser efficiency with increase of pumping rate (Fig.5) can be caused as by change of ratio of photophysical processes in active media and by change of intracavity losses.

2.3. Investigation of losses dinamics.

To find differences in losses dinamics during laser pulse we studied active media in different solvent with different thermooptical properties: in ethanol and water. Unfortunately, aqueous solutions of 4PyPO do not provide laser emission in neutral water. However, taking into account that function η(W) presented in Fig. 5 is qualitatively similar for oxazole and coumarine derivatives we studied aqueous and ethanl solutions of coumarine 175 (K175) and ethanol solutions of coumarine 2 (K2) whose structure is close to K175. Attenuation of probing signal from R6G at λ=590 nm which was passed across generating zone of K175 or K2 was measured in these experiments. Diagram of experimental setup is showing in Fig.7. Dyes were excited by XeCl laser with τ_{FWHM}=30 ns and end-to-end duration 60 ns.

Fig.8 presents oscillograms of K175 laser pulse and probing pulse passed through unexcited and generating medium. It is seen that probing beam passed through generating zone of K175 and K2 is attenuated. Both amplitude and temporal parameter of this attenuation are dependent on solvent and pumping power density. In assumption that occuring and decay of losses inducing attenuation of probing beam at 590 nm change according exponential law the function $\ln(\lg I_0/I)$ of t(ns) should be linear. The inclination of this line allows to estimate rise and decay time of losses. Date presented in Fig.9 show that this assumption is true under our experimental conditions. In ethanol solutions of K175 and K2 the losses are increased during the pulse. Aqueous solutions of K175 demonstrate deviation from linear function , hence, the origin of losses is changed. However, linearization of this function gives decay time of losses τ_d=25-30 ns

Such behavior of losses at 590 nm in generating medium of coumarine derivates can be connected with induced triplet absorption. However, no T-T absorption is observed in this region of spectrum without sensibilization in compounds of the same type[22]. On the other hand , these losses can be independent on wavelength and be related to thermooptikal distorsions in solution formed during laser pulse due to Stokes heat deposition. The decay of thermooptical inhomogenaties should be faster in water then in ethanol [23]. Hence , according to Fig.9 the losses occuring in generating zone of coumarine derivates are reasonably to be attributed to thermooptical distorsions (fast component of change refraction index[23]) which are responcible for reduction of laser efficiency under high power excitation.

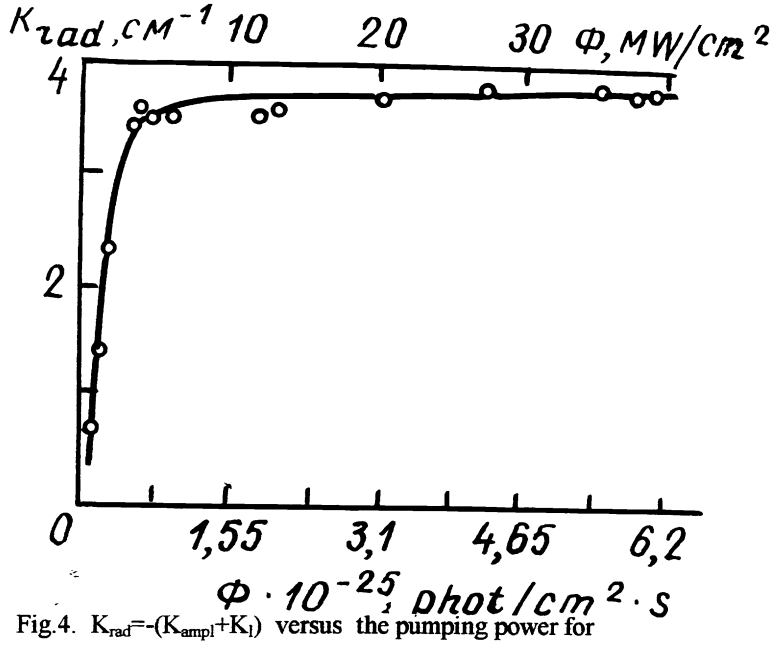


Fig.4. $K_{rad}=-(K_{ampl}+K_l)$ versus the pumping power for ethanol 4PyPO solution.

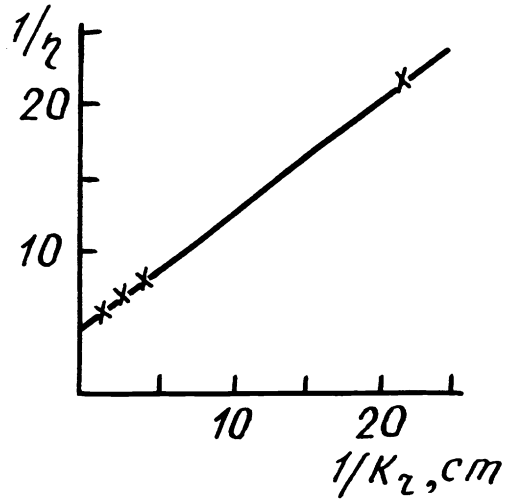


Fig.6. Laser quantum efficiency η versus K_r in inverted scale under 10 MW/cm^2 =1,55×10^{25} phot/cm^2 s pumping power.

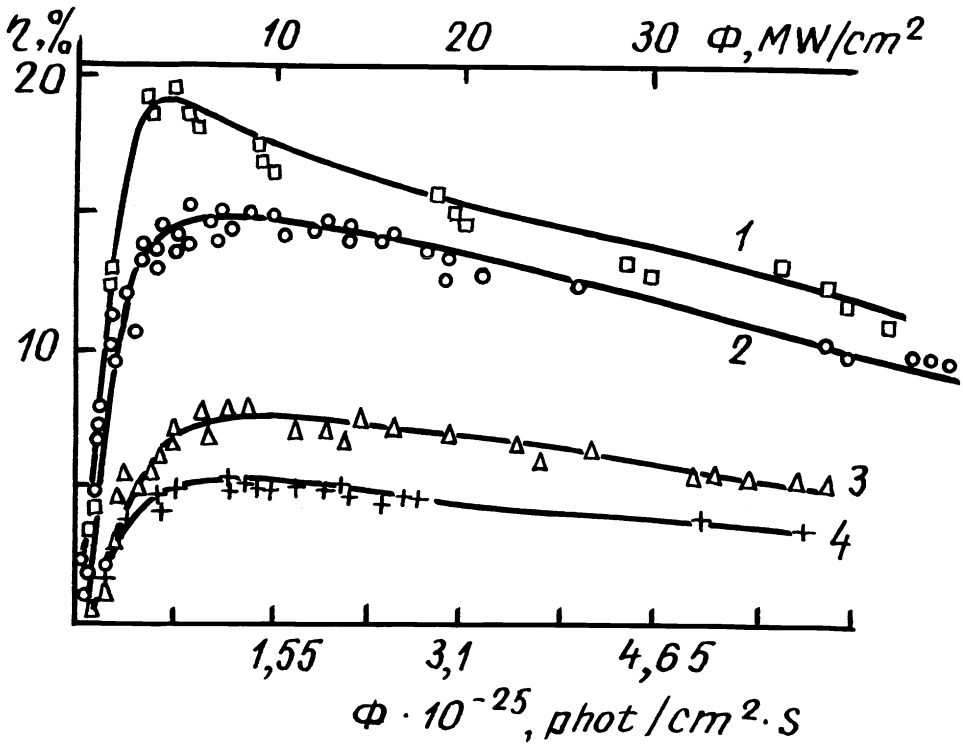


Fig.5. Laser quantum efficiency of ethanol 4PyPO solution versus the pumping power by different reflection of output mirror: R_2= 0,07 - 1; 0,2-2; 0,38 - 3; 0,83 - 4.

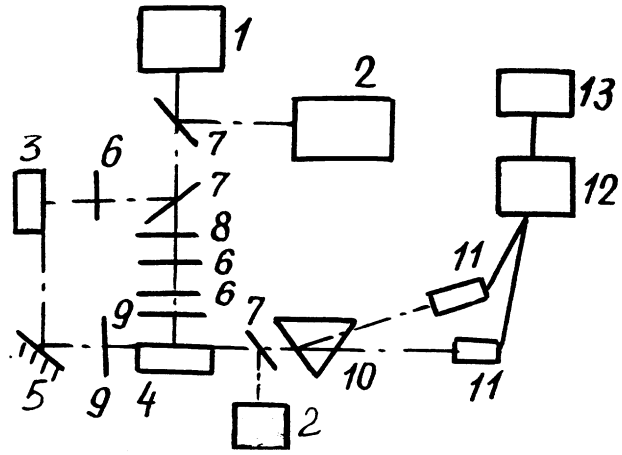


Fig.7. Schematic diagram of experimental setup for investigation of losses dinamics. 1-XeCl laser, 2-powermeter, 3-R6G cell, 4-coumarin cell, 5-mirror, 6-cylindrical lenses, 7-divided plates, 8-attenuators of pump, 9-shutters, 10- dispersional prism, 11-wave-guides, 12-photodetector, 13-oscillograph.

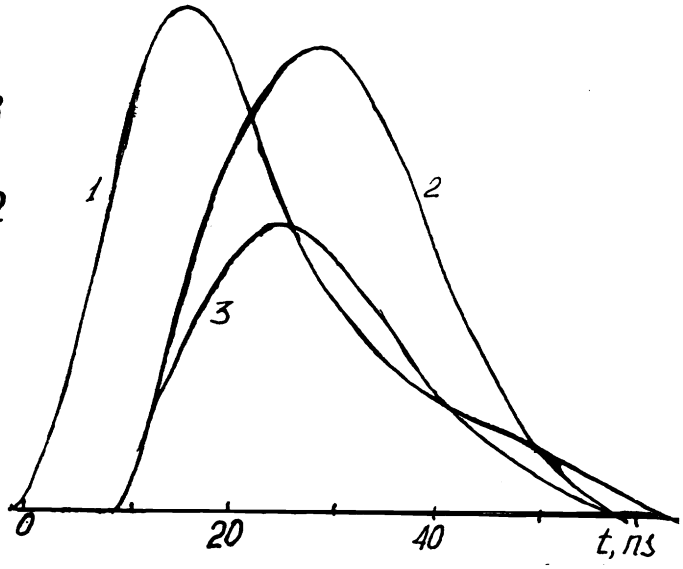


Fig.8. Oscillograms of K175 in ethanol laser pulse - 1, R6G pulse, passed through unexcited K175 solution - 2, through lasing volume - 3. Pumping power =35 MW/cm^2, efficiency of K175=9%.

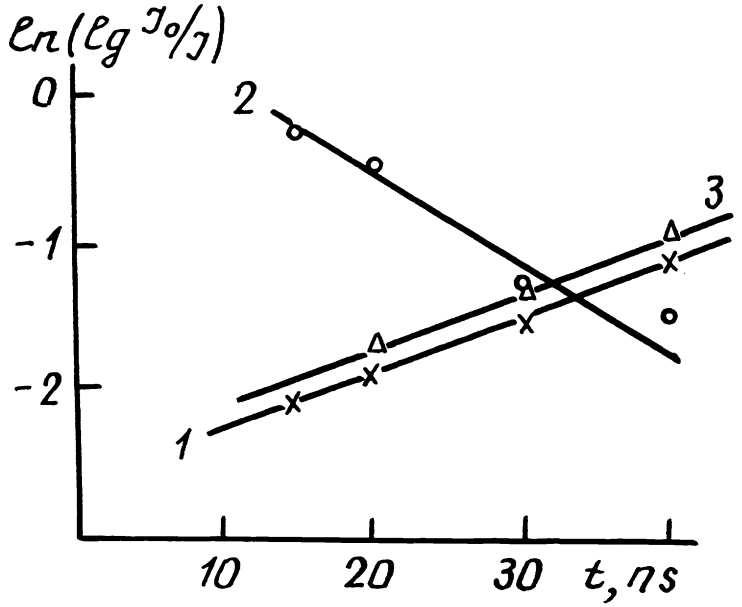


Fig.9. Modification of the optical density =lgI_0/I on λ=590 nm in logarithmic scale during K175 laser pulse in ethanol - 1, in water - 2, during K2 in ethanol laser pulse - 3. Pumping power =35 MW/cm^2= 5,4×10^{25} phot/cm^2 s.

3. CONCLUSIONS

The results of our work demonstrate that the phenomenon of anomal superfluorescence is observed in 4PyPO and trans-stilbene active media pumping by XeCl laser at excitation rate 10^{24}-10^{26} phot/cm^{2}s. Its specific feature is absence of saturation with increase of pumping power. Reduction of laser efficiency obtained under these condition of excitation is rather connected with higher losses due to thermooptical distorsions in solutions under high power pulsed excitation and least of all with change of gain in the medium.

4.ACKNOWLEDGEMENTS

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