It should be noted that these conclusions are in full agreement with the results of "computer" experiments [7].

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INTENSE FLUORESCENCE FROM THE SECOND EXCITED STATE OF MOLECULAR SOLUTIONS OF ORGANIC DYES

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According to a number of reports [1, 2], the fluorescence of molecules in solutions, which is connected with transitions from higher excited states, is very weak, owing to the rapid nonradiative energy degradation, and for its registration it is necessary to have sensitive apparatus or powerful excitation sources [3, 4]. We have observed intense short-wave emission of a number of solutions of cyanine dyes, which can be interpreted as radiation from the second excited electronic state ($S_2 \rightarrow S_0$).

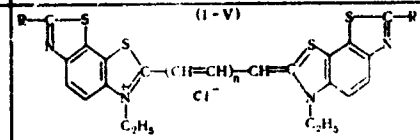
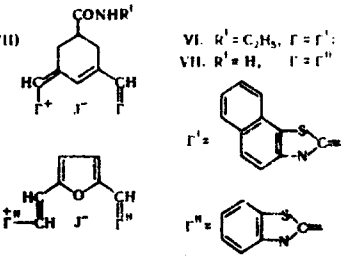
The investigated solutions (dyes I - IV, see the table) have the following spectral characteristics: 1) the first electronic transition ($\lambda \sim 600$ - 900 nm, possible symmetry $^1A_1$ - $^1B_1$) is characterized by a large oscillator strength (~ 1), the quantum yield of the fluorescent $S_1 \rightarrow S_0$ is sufficiently high for effective generation when excited by a Q-switched ruby laser [5]; 2) the absorption at the maximum of the second electronic transition ($\lambda \sim 300$ - 400 nm) is weaker by a factor of 3 - 6 than at the maximum of the first, and this transition can be characterized as fully-symmetrical $^1A_1$ - $^1A_1$; its intensity is determined by the extent of the molecule along the symmetry axis.

The dye solutions were excited with the second harmonic (SH) of a 5-MW ruby laser and with a mercury lamp DRSh-250 (λ = 313, 366, 405 nm). The resultant fluorescence is characterized by the following regularities: when dye II is excited, two bands are observed in the fluorescence spectrum, the usual long-wave one, and a short-wave one having a large Stokes shift and a structureless contour. The short-wave fluorescence of dye II exceeds by more than one order of magnitude the fluorescence intensity of azulene from the second excited electronic state [1].

The figure shows the absorption (a) and fluorescence (b) spectra of a solution of dye II in absolute alcohol at T = 300°K (the solvent produced no glow whatever under these conditions).

Dye III, characterized by a larger energy gap between S_1 and S_2 than dye II, radiates only in the short-wave region when excited in the second singlet state (SH or λ = 366 nm). Dye IV, which has the largest conjugation chain and

Table of Dyes

№	Structure formulas	Maximum absorption, nm		Energy gap betw.	Maximum fluorescence, nm	
		S_1	S_2	S_1 & S_2	S_1	S_2
I	 (I - V)	600	350	250	630	–
II		695	380	315	720	490
III		800	385	415	840	500
IV	I. n = 1, R = C_6H_5; III. n = 3, R = C_6H_5; II. n = 2, R = C_6H_5; IV. n = 4, R = C_6H_5.	920	420	500	970	–
V	V. n = 3, R = C_4H_3S.	810	410	400	840	500
VI	 (VI-VII) VI. R' = C_2H_5, Γ = Γ'; VII. R' = H, Γ = Γ''	680	360	320	710	470
VII		650	330	320	678	470
VIII	(VIII)	720	360	370	745	440

Note: Solvent - absolute alcohol.

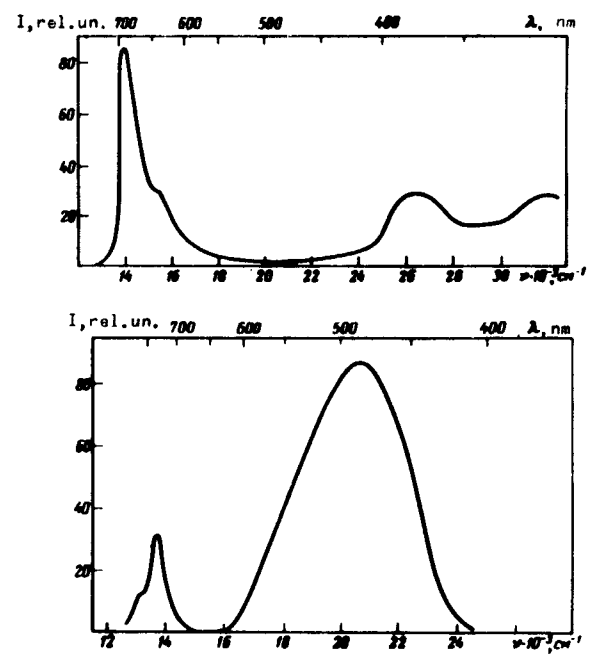
the smallest quantum yield, showed no glow from S_1 and S_2 at the given experimental sensitivity. Radiation from the solution of dye I, which has the smallest energy gap between S_1 and S_2 and the maximum overlap of the electron-vibrational states, is observed only in the long-wave region.

The spectral characteristics (1) and (2) listed above are possessed also by dyes V - VIII (see the table), which differ in the structure of the end groups and in the presence of different nuclei in the polymethane chain. Excitation of dye molecules VI, VII, and VIII in states S_2 leads to the appearance of two fluorescence bands, and excitation of dye V, which is an analog of dye III, leads to only one short-wave band.

Several additional experiments were performed to confirm that the observed short-wave glow is fluorescence due to transitions from the second excited state of the organic-dye molecules in the solution, and is not connected with photochemical decomposition of the dyes or with the presence of impurities in the dyes.

Stationary excitation of the dye solutions with light having λ = 366 nm produced no enhancement of the intensity of the short-wave fluorescence or changes in the absorption spectra.

The intensity of the short-wave fluorescence is sufficiently large already at dye concentrations $\sim 10^{-6}$ m/l in the



Absorption (a) and fluorescence (b) spectra of a solution of dye II in absolute alcohol at T = 300°K.

solution. The use of such low concentrations excludes the possibility of glow of the proposed impurities, since their concentration in the solutions (analytically pure dyes were used) would be of the order of 10^{-8} - 10^{-9} m/l.

When dye II was simultaneously excited by ruby-laser radiation and its second harmonic, a lowering of the intensity of the short-wave fluorescence was observed. This indicates that the long- and short-wave fluorescence bands belong to the same molecule.

In two-step excitation by a single-pulse ruby laser (power ∿50 MW) of the same dye made it possible to observe simultaneously generation on the $S_1 \rightarrow S_0$ transition and short-wave fluorescence. It was established that the dependence of the intensity of the short-wave fluorescence on the pump intensity is linear. Such a dependence will be observed in the case when the generation from the S_1 is stationary, and the short-wave fluorescence is connected with $S_2 \rightarrow S_0$ transitions in the same molecule. In the case of impurity fluorescence, the excitation would have a two-photon character and the corresponding dependence would be quadratic.

The weak coupling between the first and second excited states can be probably attributed to the predominant localization of the excitation on the polymethine chain and on the heterocyclic nuclei of the molecules for the second.

In conclusion we note that the investigated dyes can be used to obtain generation on the $S_2 \rightarrow S_0$ transition.

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TEMPERATURE PULSATIONS AND MULTIFREQUENCY GENERATION OF $YAlO_3:Nd^{3+}$

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1. The spectral composition and polarization of stimulated emission (SE) of lasers based on anisotropic activated crystals are determined by the polarization of the radiation of the ensemble of elementary radiators of the impurity atoms, by the crystal-optical properties of the base matrix, and by the temperature. This is the basis of several highly effective and widely used temperature methods of SE spectroscopy, which make it possible to extract extensive information on the electron-phonon interaction and on the processes occurring in the excited state on the generation conditions, and can also yield most accurate information on the position of the energy levels of the activator ions.