

# Direct observation of picosecond relaxation of high-lying electronic states of certain dye molecules in solution

A. M. Freĭberg and K. É. Timpmann

*Institute of Physics, Academy of Sciences of the Estonian SSR*

(Submitted 2 January 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 5, 209–212 (5 March 1983)

The picosecond decay times of the fluorescence from the second excited electronic state have been measured directly for certain polymethine dyes in solution. The decay times depend on the excitation conditions.

PACS numbers: 31.70.Hq, 33.50.Dq

A detailed study of the mechanisms and channels for energy relaxation at the molecular level, including electronic states lying above the first excited, singlet state, is of interest for many research and applied problems in physics, chemistry, and biology. Despite many attempts, however, no reliable direct data have so far been obtained on the relaxation times of the high-lying singlet electronic states of polyatomic molecules in a condensed medium, with the possible sole exception of molecules of the azulence type (see Ref. 1, for example). We have had to be content with order-of-magnitude estimates extracted from indirect measurements. The primary difficulty is the high efficiency of the radiationless transitions of highly excited levels, which causes a low quantum yield and picosecond or subpicosecond level decay times, which complicate experimental study.

We report here the first direct measurements of picosecond-range decay times of the fluorescence from the second excited singlet level of complex molecules in solution. The particular systems are some polymethine dyes (DCI, DDI, PK-682, PK-750, and

TABLE I.

		DCI	DDI	PK 682	PK 745	DOTCI	
R	R	70	11	360	720	~ 1600	
	B	8	3	9	8	4	
B	R			360	1120	60	1
		Not observed	Not observed			620	
	B	110 ~ 2800	0,3 350	90 560	3 2	~1800	≤ 3 10

Note. The error for the data in the first row is  $\pm 10\%$ , that for the second row is  $\pm 30\%$ , and that for the other rows is  $\pm 15\%$ .

DOTCI)<sup>1)</sup> which are important in laser technology and photochemistry, in "especially pure" ethanol solutions at room temperature (concentrations  $\sim 10^{-4}$  M).

The sample, in cells, were excited by 3-ps focused pulses from a quasi-cw Spectra Physics synchronously pumped laser using the dye oxazine 1 (pulse repetition frequency of 82 MHz). Two excitation methods were used: (1) excitation by the fundamental harmonic in the  $S_0 \rightarrow S_1$  absorption band of the dyes in the region  $\lambda_r = 680\text{--}750$  nm ("red" excitation) and (2) the second harmonic at  $\lambda_b = \lambda_r/2$ , in a higher-lying and weaker absorption band,  $S_0 \rightarrow S_2$  ("blue" excitation). The average excitation power density at the sample was  $\leq 10$  kW/cm<sup>2</sup> for the fundamental harmonic and  $\sim 10$  W/cm<sup>2</sup> for the second harmonic. The spontaneous emission from the sample in a 90° excitation and observation arrangement was detected by the reflection method with a UMI-93M or PV-001 A/PMK-1 time-resolving electron-optical image convertor, whose sweep was synchronized with the exciting pulses. The spectral regions of interest were singled out through the use of filters. A polarizer was installed in front of the slit of the image convertor at an angle of 54.7° from the polarization of the exciting pulse to prevent distortion of the decay curves by rotational-diffusion processes.<sup>2</sup> The experimental procedure is described in more detail in Ref. 3.

For excitation of both types, the emission spectrum of the dyes is shifted in the Stokes direction and consists primarily of two relatively broad bands in the blue and red parts of the spectrum.<sup>2)</sup> It should be noted, however, that the details of the corresponding spectra with the different types of excitation are not exactly the same. This is particularly true of the DCI and DDI solutions, for which the red emission could not be detected in the case of blue excitation, as in Ref. 4. All the measurements of the decay time  $\tau$ , in picoseconds and corresponding to the  $1/e$  level, are listed in Table I. For a complete picture, we measured the decay of the emission in both the blue and red regions (with respect to the  $S_1$  states). In the first two columns of the table, *R* and *B* specify the type of excitation and the region in which the emission is measured. In the case of a two-exponential decay law, two values of  $\tau$  are shown, along with the ratio of the initial amplitudes of the shorter and longer components.

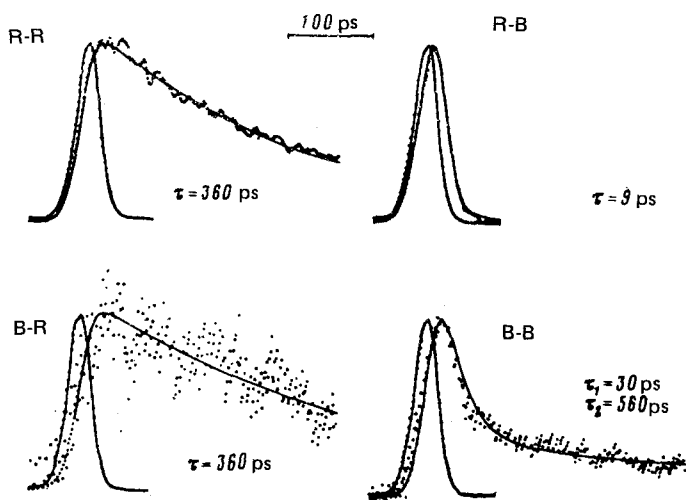


FIG. 1. Fluorescence decay curves of the dye PK-682 when excited at the wavelengths  $\lambda_r = 690$  nm and  $\lambda_b = 345$  nm. The shape of the exciting pulse measured by the detection system, the time scale, and the excitation and detection conditions are indicated. The solid curves are one- or two-exponential approximations of the experimental curve, constructed by least squares.

Despite some variations, the experimental results reveal some regular behavior: (1) In the case of the red excitation, the time  $\tau$  for the blue fluorescence is shorter than 10 ps and much shorter than  $\tau$  for the red fluorescence. (2) In the case of the blue excitation, nearly all the fluorescence decay curve are two-component curves, and the  $\tau$  components are not the same as the  $\tau$  of the emission during red excitation. (3) In agreement with Refs. 5 and 6,  $\tau$  for the  $S_1$  state generally increases with increasing length of the polymethine chain of the molecule. The first two of these results can be seen well in Fig. 1.

The observed behavior of  $\tau$ , combined with data from purely spectroscopic measurements carried out in parallel (to be reported separately) and the properties of the polymethine dyes found previously (see Ref. 7, for example), allows us to confidently assert that the states to which these systems are excited by the blue and red excitation are very different. The difference may result from an inhomogeneity of the composition of the system (the existence of several forms or fragments of dyes with similar spectra in the solution) and/or a change in the structure of the molecule upon the phototransition, which gives rise to a nontrivial shape of the potential hypersurfaces of the actual states. Although an unambiguous interpretation is not possible at this stage of the research, there is reason to believe that the short-lived blue emission observed during red excitation is a fluorescence of the dyes from the  $S_2$  state to the ground state, because of the low sensitivity of the two-step excitation to slight impurities. With regard to the energy relaxation of electronic excitations in dye molecules with a short polymethine chain, it is known that for the  $S_1$  state this relaxation generally proceeds without the involvement of the triplet state.<sup>5</sup> It is apparently not permissible to ignore the role of interconversion transitions in the case of the  $S_2$  state (and higher-lying

singlet states), although a more solid conclusion can be reached on the basis of data on the positions of the triplet levels in the given molecule.

Interestingly, the conversion times of the high-lying states are quite short in comparison with the expected vibrational-relaxation times. It may be suggested in this connection that in certain cases nearly all the observed secondary emission is hot-carrier luminescence.<sup>8</sup>

In summary, these results show that the kinetic characteristics of highly excited electronic states of molecules in the picosecond time range can be studied completely successfully at the present level of experimental sophistication. The characteristic times and decay curves for the  $S_2$  state have been determined for some specific cases: the molecules of certain polymethine dyes.

We wish to thank K. K. Rebane for interest and for a useful discussion of the results, Yu. K. Mets and S. F. Savikhin for participation in the experiments, and M. V. Melishchuk for graciously furnishing the PK-682 and PK-745 dyes.

<sup>1</sup>For simplicity, we are using the abbreviations customarily used in the literature on laser dyes; for example, DCI is 1, 1-diethyl-4, 4-carbocyanin iodide (cryptocyanin).

<sup>2</sup>Excitation in the  $S_2$  state during illumination with red light results from two photons and involves the intermediate state  $S_1$ .

<sup>1</sup>T. C. Felder, K. J. Choi, and M. R. Topp, Chem. Phys. **64**, 175 (1982).

<sup>2</sup>T. Tao, Biopolymers **8**, 609 (1969).

<sup>3</sup>A. O. Aniyalg, P. M. Saari, T. B. Tamm, K. É. Timpmann, and A. M. Freilberg, Kvant. Elektron. (Moscow) **9**, 2449 (1982) [Sov. J. Quantum Electron. **12**, 1597 (1982)].

<sup>4</sup>R. Köig, D. Leupold, B. Voigt, and S. Dähne, J. Luminescence **9**, 113 (1974).

<sup>5</sup>C. J. Tredwell and C. W. Keary, Chem. Phys. **43**, 307 (1979).

<sup>6</sup>R. Kaarli and A. Rebane, Izv. Akad. Nauk ESSR, Fiz. Matem. **30**, 287 (1981).

<sup>7</sup>O. V. Przhonskaya and E. A. Tikhonov, Izv. Akad. Nauk SSSR, Ser. Fiz. **39**, 2275 (1975).

<sup>8</sup>K. Rebane and P. Saari, J. Luminescence **16**, 223 (1978).

Translated by Dave Parsons

Edited by S. J. Amoretty