INVESTIGATION OF VIBRONIC ENERGY RELAXATION OF POLYMETHIN CYANINE DYES BY PICOSECOND SPECTROSCOPY

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The vibronic energy relaxation times of some polymethin cyanine dyes in dependence on temperature have been measured by using picosecond fluorescence spectroscopy. The results should be explained by means of the hypothesis of short-time conformation change during the relaxation process.

1. Introduction

In general, the values of the relaxation times of the radiationless transitions in dye molecules are known to be in the range of nanoseconds (see, for instance ref. [1]). In the last years, however, for a large number of dyes in fluid solutions the values of the times of depopulation of the singlet state S_1 have been found to be shorter than nanoseconds [2–14].

Such dyes can be used for mode-locking of picosecond pulse lasers and for pulse selection [15], provided that they do not decay after their excitation. Moreover, dyes with short vibronic relaxation times are important for the photochemical stabilization of molecular systems, especially, of plasts and man-made fibres.

Typical examples for dyes with short vibronic relaxation times are the polymethin dyes. The group of polymethin dyes used in our investigations is shown in fig. 1.

Already Hofer et al. [16] pointed out, that for polymethin dye molecules there is a connection between their structure and the radiationless decay rate of their first singlet state. From the fluorescence quantum yields measured they found an increasing fluorescence intensity and, consequently, a decreasing radiationless depopulation rate with increasing length of the polymethin chain within the homologous cyanine series

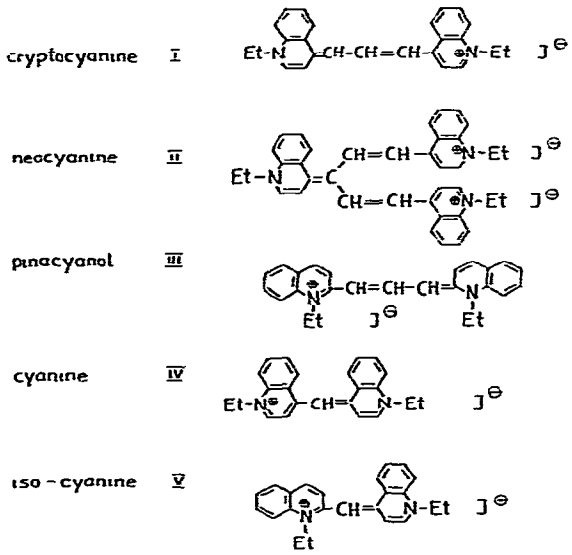

Fig. 1. Structural formulae of the polymethin cyanine dyes used.

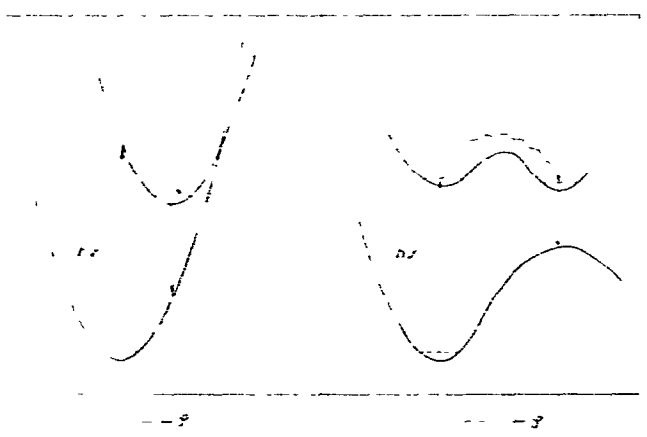

Fig. 2. The influence of displaced (a) and deformed (b) potential surfaces of the excited state on the energy gap.

used. This effect was explained by steric hindrance between the two end groups destroying the planar structure. This means, the equilibrium positions of one or more (torsional) normal modes of the molecule in its excited electronic state are displaced relative to the electronic ground state. According to fig. 2a such a displacement diminishes the S_1-S_0 energy gap.

Further, deformations of the potential surface in the excited state may give rise to an additional decrease of the energy gap (fig. 2b). Such transient conformational changes diminishing the S_1-S_0 energy gap lead to a strong increase of the corresponding relaxation rate parameter [17]. Since the effect of steric hindrance of the end groups should increase with decreasing length of the polymethin chains the dye molecules with the shortest chains can be expected to have the shortest vibronic relaxation times which is also confirmed by the experimental results of Derkatscheva et al. [3]. On the other hand in the case of very long polymethin chains Derkatscheva et al. [3] found the vibronic relaxation times to increase with increasing chain length. This result was explained by a decrease of the electronic energy gap S_1-S_0 with increasing chain length (red-shift of the absorption maxima).

Mourou et al. [18] explained the fast vibronic relaxation in polymethin cyanine dyes by rearrangements of dipoles arising from the solvent molecules. It is clear, that such rearrangements may also lower the energy gap in a way shown in fig. 2. The relaxation times due to both the intramolecular and the intermolecular conformational changes will be dependent on the viscosity of the solvent, and therefore from both models the observed influence of the viscosity of the solvent on the fluorescence lifetime of polymethin dyes [2,3] can be explained.

In the present work we will prove the above hypothesis of the connection between steric hindrance and relaxation time for several polymethin dyes with fluorescence lifetimes τ shorter than 100 ps at room temperature. Especially, we have measured the dependence of τ on temperature because for intramolecular conformational changes the existence of activation thresholds should be expected as is known, for instance, from the direct photoisomerization of stilbene [19,20].

2. Chemicals

The cyanine dyes investigated (fig. 1) were prepared as follows. Bis-(1-ethyl quinoline-4)-trimethin cyanine iodide I (cryptocyanine) [21]: 10 g of lepidine ethiodide, 11.0 g of ethyl orthoformate and 40 ml of dry pyridine were boiled under reflux. Cuprous brown crystals began to separate. After cooling the neocyanine ethiodide was removed and recrystallized from 1.5 ℓ of absolute ethanol. The yield of compound II was 1.3 g, m.p. 283–286°C.

The pyridine mother liquor was poured into boiling water, cooled and filtered in order to isolate the dye 1,1′-diethyl-4,4′-carbocyanine iodide. The obtained solid has a golden lustre and was recrystallized four times from absolute ethanol. After drying in vacuum at 100°C the yield of prisms of cryptocyanine with a green lustre was 2.5 g, m.p. 250–253°C.

Bis-(1-ethyl quinoline-2)-trimethin cyanine iodide III (pinacyanol) [22]: 5 g of quinaldine ethiodide, 5.5 ml of ethyl orthoformate and 20 ml of dry pyridine were boiled for 4 h under reflux. After cooling and separation of the green needles the solid dye III was recrystallized from alcohol. The yield was 3.2 g after drying in vacuum at 100°C, m.p. 287–290°C.

(1-ethyl-4-quinoline) (1-ethyl-4-quinoline)-methin cyanine iodide IV (cyanine) [23]: To a boiling solution of 2.5 g of lepidine ethiodide and 7.15 g of quinoline ethiodide in 30 ml of absolute ethanol was added under stirring to a solution of 0.58 g of sodium in 30 ml of absolute ethanol. After 20 min the mixture was cooled, the dye filtered off and washed several

times with alcohol and water. The yield was after recrystallization from methyl alcohol and drying 2.2 g of green crystals.

(1-ethyl-2-quinoline)(1-ethyl-4-quinoline)-methin cyanine iodide V (iso-cyanine): Procedure as above: 2.5 g of quinaldine ethiodide, 4.76 g of quinoline ethiodide, 100 ml of absolute ethanol, 0.23 g of sodium. The yield was after recrystallization from alcohol 0.9 g of compound V.

The dyes were solved (10^{-4} M solutions) in ethanol and dimethylsulfoxide (DMSO). Additionally, cryptocyanine was also solved in a solvent (polystyrol, 10^{-4} M solution), which is solid at room temperature. For the measurements we used a path length of 1 mm.

3. Apparatus

The experimental technique used for the time resolved measurements is described in detail elsewhere [24]. Briefly, the dye molecules were excited by the second harmonic of a mode-locked Nd-glass laser (λ = 530 nm). In this way, the dye molecules were excited in the short-wavelength region of their S_0–S_1 absorption band, as is seen from fig. 3. The experiments

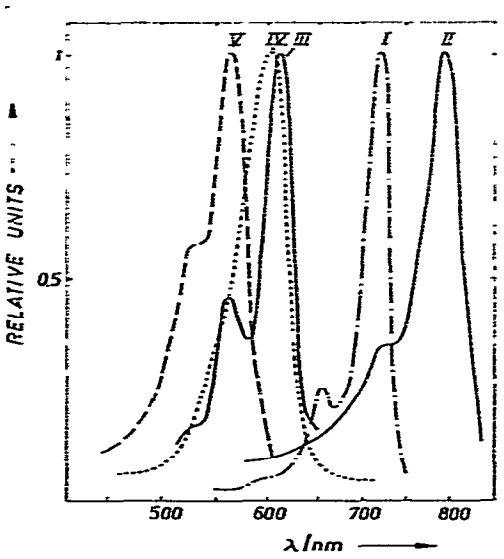

Fig. 3. Normalized absorption profiles of polymethin cyanine dyes solved in ethanol (10^{-4} M): cryptocyanine (I), neocyanine (II), pinacyanol (III), cyanine (IV), iso-cyanine (V).

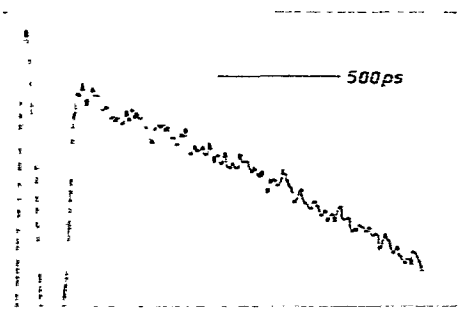

Fig. 4. Densitometer trace of a streak camera photo of the exciting pulse and the fluorescence light (cryptocyanine in ethanol, 10^{-4} M, T = −58°C).

were carried out with single pulses, their duration and energy density being about 10 ps and about 10^{15} photons cm^{-2}, respectively. The time behaviour of the fluorescence radiation was studied by a streak camera with a time resolution of about 35 ps. The directly scattered light was suppressed by glas filters. In addition to the fluorescence light an attenuated part of the exciting pulse was detected by the streak camera (fig. 4).

4. Results and discussion

The fluorescence lifetimes measured at room temperature are shown in table 1. For cyanine and iso-cyanine they are seen to be shorter than for those dye molecules with longer polymethin chains (pinacyanol and cryptocyanine). The fluorescence kinetics of the dye molecules with the shorter polymethin chains closely follows the pulse shape. Therefore, their fluorescence lifetimes should be less than 35 ps.

In a host matrix of polystyrol the value of the fluorescence lifetime of cryptocyanine was found to

Table 1
Fluorescence lifetimes of polymethin cyanine dyes in ethanol, DMSO, and polystyrol (10^{-4} M) at room temperature

	Ethanol	DMSO	Polystyrol
pinacyanol	(50 ± 9) ps	(70 ± 9) ps	
cryptocyanine	(80 ± 9) ps		(2.4 ± 0.2) ns
cyanine	35 ps	35 ps	
iso-cyanine	35 ps	35 ps	

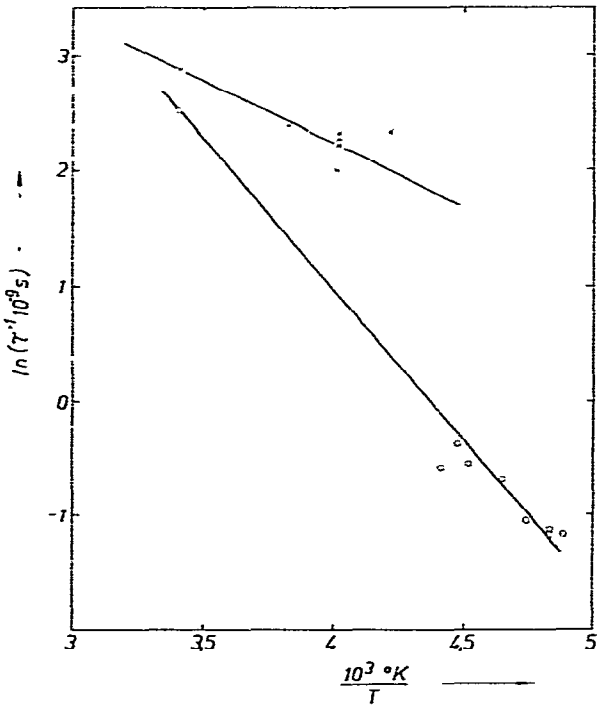

Fig. 5. Fluorescence life times τ in dependence on the temperature (10^{-4} M solutions in ethanol): ○ cryptocyanine, × pinacyanol.

be 2.4 ns. On the other hand, the fluorescence lifetime of cryptocyanine in ethanol shows a strong dependence on temperature (fig. 5). From $\tau = 80$ ps at room temperature the value of τ increases up to 3.2 ns at −66°C. Note, that −66°C ethanol still is a liquid. A similar but weaker dependence on temperature was measured for pinacynol (fig. 5). As mentioned, at room temperature the fluorescence lifetime of cyanine both in ethanol and in DMSO is shorter than the limit of resolution of our detecting system. At −54°C, however, in both solvents we observed a fluorescence lifetime $\tau \approx 100$ ps. This shows that the freezing point of the solvent (for DMSO 8°C) does not dramatically change the relaxation behaviour.

The values of the fluorescence lifetime of cyanine and iso-cyanine and their comparison with those of pinacynol and cryptocyanine can be considered as a proof of the hypothesis that steric hindrance of the end groups in the S_1 state leads to conformational changes (torsions of the planar structure) giving rise to a diminution of the fluorescence lifetimes. Strong steric hindrance should be expected for molecules with very short polymethin chains and for those with a structure similar to that of neocyanine. This could be an argument for explaining the fact that we did not observe fluorescence radiation of neocyanine.

As mentioned in section 1, Mourou et al. [18] suggested an intermolecular dipole–dipole interaction giving rise to the short relaxation times of the polymethin dyes. In this case the relaxation times under consideration should be strongly dependent on the polarity of the solvent used. We did not succeed in measuring the dependence of the relaxation times on the polarity of the solvent because of the insufficient solubility of the dyes used in nonpolar solvents. However, a serious objection to the mechanism suggested in ref. [18] can be made by analyzing the dependence on temperature of the relaxation times as measured, for example, for cryptocyanine (fig. 5). In the range of temperature under consideration the viscosity of the solvent ethanol is changed unessentially but the value of the fluorescence lifetime increases from $\tau =$ 80 ps at room temperature to $\tau = 3.2$ ns at −65°C, which exceeds the corresponding value for cryptocyanine in polystyrol at room temperature. By assuming an intramolecular conformational change which is based on a potential surface as shown in fig. 2b the experimental result can be understood. In a similar way as in the Orlandi–Siebrand model [25] of the photoisomerization of stilbene the dependence on temperature of the fluorescence lifetime of the polymethin dyes under consideration can be explained by the existence of a potential barrier for the conformational change. From fig. 5 an Arrhenius law for the dependence on temperature of the decay rates $k = \tau^{-1} = A \exp(-E_A/k_B T)$ can be derived with the fitting parameters $A = 10^{14}\ s^{-1}$, $E_A \approx 1850\ cm^{-1}$ for cryptocyanine and $A = 8 \times 10^{11}\ s^{-1}$, $E_A \approx 526\ cm^{-1}$ for pinacyanol.

Finally we note that the value of the decay rate of pinacyanol in DMSO measured by us ($k^{-1} = 70$ ps) is different from the value given in ref. [2]. The reason for this could be the different anions of the pinacyanol in our experiments (I^-) and in ref. [2] (Cl^-), which leads to different potential curves with respect to the conformational change.

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