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Primary Photoprocesses in Colorant Molecules

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A survey is made of primary photoprocesses in dye molecules in solution—photophysical processes in excited singlet and triplet states (absorption from an excited level, vibrational and rotational relaxation, lifetimes, quantum efficiencies of fluorescence, intersystem and internal conversions, deactivation and quenching of the triplet state, etc.) and primary photochemical reactions (*cis-trans*-isomerisation, electron transfer, etc.). A list of 309 references is included.

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I. INTRODUCTION

Organic colorants are widely employed in various fields of science and technology—in the textile industry, colour and black-and-white photography, printing, etc.—absorbing light radiation efficiently and then transforming the resulting electronic excitation into various other forms of energy. Investigation of the interaction of intense light pulses with dye solutions led to the production of optical quantum generators having a tuned generation frequency (dye lasers). As traps for electronic excitation energy colorants can be used for the photostabilisation of polymeric materials. Finally, considerable interest has been aroused by study of the photosemiconductor properties of colorants with the aim of "sensitising" electrographic layers.

The development of experimental technique produced a substantial expansion of research on photoprocesses in colorant molecules. Laser sources enabled light pulses to be obtained of high intensity (~10^{13} W cm^{-2}) and short duration (10^{-9}–10^{-12} s). The use of such pulses to excite molecules made it possible to investigate primary photoprocesses lasting as little as 10^{-12} s.

Research on the photophysical and photochemical properties of organic dye molecules was last reviewed (1967) in a monograph[1]. Since then, an immense number of papers have appeared on the photonics of such molecules. The present Review covers the main results of research on primary photoprocesses in colorant molecules in solution published during the past decade.

II. PHOTOPHYSICAL PROCESSES IN MOLECULES IN A SINGLET EXCITED STATE

The processes occurring in colorant molecules in a singlet excited state (a lower excited state is implied) are extremely diverse. On absorption of a light quantum a molecule usually passes into upper vibrational sublevels of an electronically excited state. The processes following absorption include vibrational and rotational relaxation. The molecule can pass from the singlet excited state to the ground state with emission of a light quantum (fluorescence) or without emission (internal conversion), as well as to a triplet state (intersystem crossing) (Fig.1).

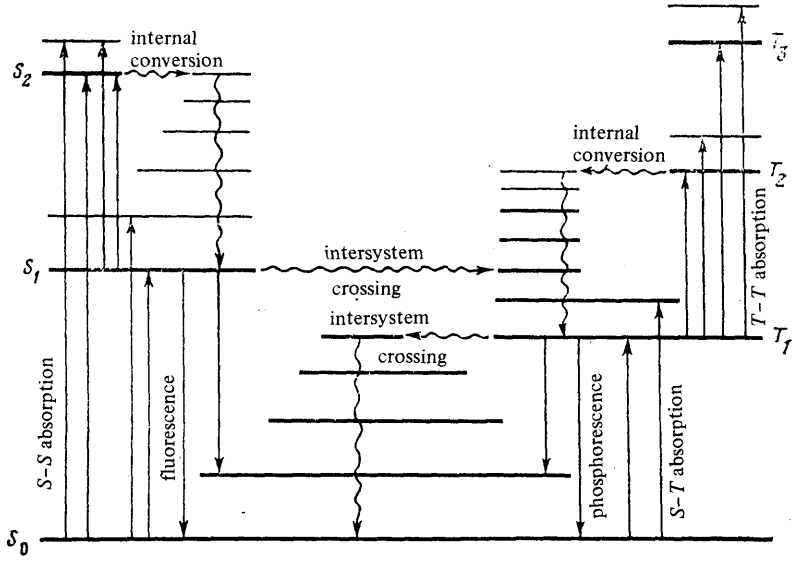


Figure 1. Scheme of energy levels in dye molecules and transitions between them.

Electromagnetic radiation of definite frequency induces forced transitions either to the ground state (amplification of light) or to a higher excited state (absorption of light). These unimolecular processes of deactivation of the singlet excited state may compete with bimolecular processes—energy or electron transfer—stimulated by transitions to ground and triplet states, formation of excimers and excited complexes, etc.

1. Singlet–Singlet Absorption

Absorption from a singlet excited level corresponds to $S_1 \rightarrow S_n$ transitions in the dye molecule (Fig.1). Their experimental investigation has been made possible during recent years by the development of picosecond laser spectroscopy. Spectra or effective $S_1 \rightarrow S_n$ absorption cross-sections have now been determined for several rhodamine[2–7] and cyanine[8–14] dyes, Cresyl Violet[15,16], Acridine Red[17], Nile Blue[6], etc.

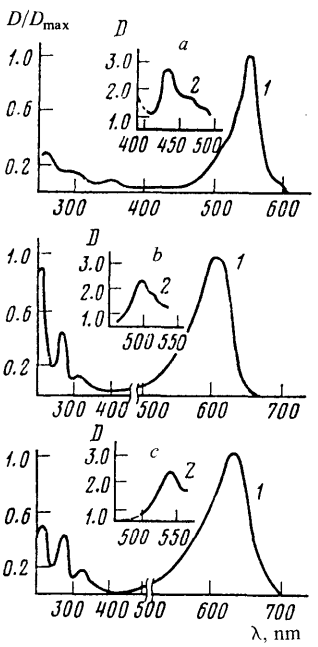


Figure 2. Absorption spectra[6] of ethanolic solutions of: *a*) Rhodamine 3B; *b*) Cresyl Violet; *c*) Nile Blue corresponding to the transitions: 1) $S_0 \rightarrow S_n$; 2) $S_1 \rightarrow S_n$. Optical densities D expressed in relative units.

Thus the $S_1 \rightarrow S_n$ absorption spectra of Rhodamines 6G and 3B in ethanol contain a maximum at 430 nm, but in that of Nile Blue the maximum occurs at 540 nm [6] (Fig.2). The corresponding spectrum of cryptocyanine has a band at 550 nm,[8,9] representing the energy difference between the S_2 and S_1 levels. For Cresyl Violet in methanol and in glycerol the maximum lies at 490–500 nm [6,15] and 430 nm [16] respectively. Here the energy of the $S_1 \rightarrow S_n$ transition does not correspond to any final state involved in absorption from the S_0 ground level. This was explained[15] by a symmetry difference between S_0 and S_1 states, which imposes restrictions on the probability of electron transitions. The absorption spectra of molecules in a singlet excited state give fresh information on the structure of the energy levels in colorant molecules.

2. Vibrational and Rotational Relaxation in a Singlet Excited State

Vibrational relaxation was first recorded in Rhodamine 6G by picosecond laser excitation[18]. The vibrational relaxation time was $\tau_{vibr} \cong 6$ ps, and a similar value 8 ± 3 ps was obtained later[19]; for Rhodamine B $\tau_{vibr} < 2$ ps. Subsequent studies have shown[20–24] that for these two colorants in ethanol, methanol, and water $\tau_{vibr} < 1$ ps, which is apparently the most reliable value.

The vibrational relaxation time for Rhodamine 6G dissolved in glycerol lengthens by only 50% over the temperature range 40–20 °C, while the viscosity increases more than thousandfold[25]. The lack of correlation between this time and the solvent viscosity indicates primarily that vibrational relaxation is due to interaction between solute and solvent molecules. In "isolated" molecules the time of "pure" vibrational relaxation is ~10^{-8} s.[26,27] A relation has been detected also with the quantum efficiency of fluorescence[25]: for Rhodamine B as example the quantum efficiency falls to 0.5 on passing from glycerol to ethanol, while the vibrational relaxation time shortens from 4 ± 1.4 to 0 ± 1.4 ps. The effect on the time was attributed to a difference in mobility of the terminal diethylamino-groups of the dye molecule in the two solvents[25]. An important part in the vibrational relaxation of rhodamines is played by hydrogen bonds between dye and solvent molecules. For the fluorescein group of xanthen colorants (fluorescein, eosin, erythrosin) $\tau_{vibr} < 10$ ps.[28]

The use of picosecond lasers has also enabled rotational or orientational relaxation in colorant molecules to be investigated[29–39]. Most of the measurements of rotational relaxation times have been made on Rhodamine 6G in various solvents. This time is directly proportional[29] to solvent viscosity (as follows from the Debye–Stokes–Einstein hydrodynamic model) and to hydrodynamic volume. Thus for Rhodamine 6G in ethanol the time τ_{rot} fluctuates from 70 to 300 ps according to various workers[29,33,34]. In viscous solvents it increases to 2800 ps [29,31] (or even to 6500 ps [32]) in undecanol and to 2100 ps in ethylene glycol[29,31]. Rotational relaxation times have been measured for Rhodamine 4S in ethanol (250 ps [38]), for Rose Bengal in several organic solvents varying in viscosity (in acetone and ethanol respectively 70 and 450 ps [37]), and for 3,3'-diethyloxadicarbocyanine (160 ps in ethanol[35]). Despite some divergence in the results, it can be accepted that, for the colorants investigated in low-viscosity media at room temperature, orientational equilibrium with the solvent is established before the act of emission.

3. Lifetime and Quantum Efficiency of Fluorescence

The lifetime of a singlet excited state τ_S^* is an important parameter determined by the aggregate of processes deactivating excited molecules. The use of picosecond lasers has enabled it to be found both from the decay of $S_1 \rightarrow S_n$ absorption intensity (for non-fluorescent molecules) and from the decay of fluorescence intensity. Such lifetimes have been measured for rhodamine[32,33,40–44,47,49], xanthen[28,32,41,54–57],

thiazine[58,129,149] azine[44,110], triphenylmethane[57,62,63], indigoid[54–57], coumarin[68,69], polymethine (cyanine)[13,35,70–84,110], and other colorants (Table 1).

Table 1. Lifetime τ_S^* and quantum efficiency ϕ_{fl} of fluorescence of dyes.

Dye	Solvent	τ_S^*, ns	φ_{fl}
Rhodamine 6G	methanol	3.7 [40]; 6.5 [41]	—
	ethanol	3.7 [33]; 4.5 [42, 44]	0.88 [42, 46]
	water	4.0 [44]	0.89 [46]; 0.96 [45]
	acetone	—	0.78 [46]
Rhodamine B	ethanol	3.4 [42]	0.81 [111]; 0.61 [42]; 0.72 [50]
	ethanol + HCl	2.5 [47]	0.49 [48]
	ethanol + KOH	3.1 [47]	0.71 [48]
Rhodamine 3B	ethanol	3.4 [42]	0.7 [111]; 0.68 [42]; 0.42 [46]
	water	—	0.37 [46]
NN'-Diethylrhodamine	ethanol	—	0.94 [42]
Fluorescein	ethanol	—	0.97 [54]
	water	4.0 [41]	—
	water (neutral dye)	—	0.14 [51]; 0.20—0.25 [52]
	water (monoanion)	—	0.26 [51]; 0.25—0.35 [52]
	water (dye cation)	—	0.9—1.0 [52]
	water, pH 9	—	0.92 [53]
	water, 0.05*N* NaOH	4.4 [32]; 3.9 [28]	—
Eosin	methanol	3.3 [54]	0.60 [54]
	ethanol	3.6 [54]	0.53 [111]; 0.69 [54]
	water, pH 7	0.90 [28]	0.19 [28]
	water, pH 9	—	0.19 [53]
	water, pH 9.2	1.4 [54]	0.20 [54]
Erythrosin	methanol	0.14 [55, 56]	0.08 [54]
	ethanol	0.56 [54]; 0.11 [28]	0.08 [54]; 0.02 [28]
	water	0.078 [57]	—
	acetone	2.4 [57]	—
Rose Bengal	methanol	0.66 [54]	0.08 [54]
	ethanol	0.82 [54]	0.11 [54]
	water, pH 9.2	0.095 [54]	0.018 [54]
Phenosafranine	ethanol	2.7 [44]	—
Methylene Blue	methanol	0.3 [58]	—
	water, pH 9	—	0.01 [59]
	water, pH 2.5	0.37 [149]	0.1 [60]
Thionine	water, pH 9	—	0.1 [60]
	water, pH 2.5	0.36 [129]	0.047 [129]
Acridine Orange	ethanol + 0.01M KOH	—	0.2 [61]
	water	1.7 [158]	—
Malachite Green	methanol	0.002 [63]	—
	glycerol	0.090 [57]; 0.010 [62]	—
	water, pH 9	—	0.01 [59]
Crystal Violet	ethanol	0.005 [62]	—
	glycerol	0.010 [62]	—
Thioindigo	toluene	13.0 [64]	—
	benzene	13.4 [66]	0.56 [66]
Indigo	benzene	<1 [67]	—
Coumarin 7	methanol	3.4 [68]	—
	ethanol	3.9 [68]	—
Coumarin 102	methanol	5.2 [68]	—
	ethanol	6.5 [68]	—
Coumarin 120	methanol	3.5 [69]	—
	ethanol	3.1 [69]	—
Pinacyanol (1,1'-diethyl-2,2'-carbocyanin	methanol	0.004 [71]	—
	ethanol	0.009 [71]	—
	glycerol	0.33 [70]	—
Cryptocyanine (1,1'-diethyl-4,4'-carbocyanine)	methanol	0.016 [76]	—
	ethanol	0.037 [71]; 0.080 [72]	0.017 [75]
	glycerol	0.075 [76]; 0.037 [77]	0.007 [77]
1,1'-Diethyl-2,2'-dicarbocyanine	methanol	0.007 [71]	—
	ethanol	0.011 [77]	0.003 [77]
	glycerol	0.145 [71]	—
3,3'-Diethyloxadicarbocyanine	ethanol	1.24 [80]; 1.2 [81, 84]	0.49 [80]; 0.42 [84]
	propan-2-ol	1.6 [35]	—
	water	0.56 [84]	—
3,3'-Diethyl-2,2'-thiatricarbocyanine	methanol	0.090 [13]	—

Note. Numbers in square brackets denote references (Ed. of Translation).

For rhodamine dyes in various solvents (water, methanol, ethanol, glycerol, etc.) the lifetimes lie in the range 2–6 ns. Variations are due to the experimental conditions. For example, τ_S^* falls from 4 to 2 ns with increase in the concentration of Rhodamine 6 G in water from 10^{-5} to 10^{-2} M,[41] which can be explained by singlet–singlet energy transfer from monomers to non-luminescing association complexes[40]. Lifetimes for rhodamine dyes became shorter on heating[85] owing to temperature quenching of fluorescence[86]. Later, however, it was concluded[87] that the excited singlet lifetime did not vary with temperature. Variation has been observed in the presence of detergents[88,89] and also with change in solution acidity[47,90].

Xanthen dyes of the fluorescein group have excited singlet lifetimes of the same order as those of the rhodamine group[28, 32,41,54], except for erythrosin and Rose Bengal, for which they are only around one-tenth[28,54–57]. Such a difference is due not only to the internal effect of the heavy atom[54] but also to a specific solvent effect. Thus these lifetimes for Rose Bengal in proton-donor solvents are some 20% of those in aprotic solvents[91], a difference attributed to the influence of hydrogen bonds on non-radiative transitions.

The shortest excited singlet lifetimes, a few picoseconds, are typical of triarylmethane dyes (Malachite Green, Crystal Violet)[62,63]. The decisive role in ultra-rapid electronic relaxation processes in such molecules belongs to internal conversion and conformational changes[16,63].

Brief lifetimes of singlet excited states have been found also in many polymethine dyes, apparently as a consequence of their capacity for *cis–trans*-photoisomerisation. The lifetimes increase in viscous media[70,71,78]. They depend on the length[92] of the polymethine chain $[CH:CH]_n$, changing approximately tenfold with increase in n from 1 to 3; further increase in n shortens the lifetime, to 50 ps for $n = 5$. The latter effect is explained by narrowing of the energy gap between S_0 and S_1 states and increase in the probability of non-radiative transitions.

An important characteristic of singlet excited states of molecules is the quantum efficiency of fluorescence ϕ_{fl}, which is determined from the singlet lifetime and the fluorescence rate constant k_{fl} by the formula $\phi_{fl} = k_{fl}\tau_S^*$.

Rhodamine dyes exhibit intense fluorescence, with quantum efficiencies exceeding 0.5 for most of them[42] (Table 1), which is explained by favourable relative positions of singlet and triplet energy levels[93]. The efficiency is affected by structural features of the rhodamine molecules[94] and also by such experimental conditions as the solvent[47,90], exciting wavelength[95,96], etc. It depends on the temperature: thus for Rhodamine B in alcohol the efficiency increases from 0.4 to 1.0 when the solution is cooled, and falls to a few percent on heating to 78 °C.[97]

The quantum efficiency ϕ_{fl} of the fluorescein group of xanthen dyes varies within wide limits as a consequence both of ionisation of the molecule (with change in solution pH) and of the effect of heavy atoms contained therein (Table 1). It is affected by hydrogen bonding between dye molecule and solvent[98], temperature[99], and deuteration[100].

For triarylmethane dyes the quantum efficiency of fluorescence is low ($\sim 10^{-4}$) in non-viscous media. However, it increases rapidly with the viscosity η, in conformity with the empirical relation $\phi_{fl} = c\eta^{2/3}$,[112] in which c is constant for a given dye.

Research on the spectral luminescent properties of cyanine dyes[75,77,80,84,101,102,110] has revealed a dependence of efficiency on the length of the polymethine chain analogous to the above relation for singlet lifetime[92]. The presence of *meso*-substituents in the chain usually lowers the efficiency. Introduction of a heavy atom into the heterocycle has little

effect[102]. Since polymethine dyes are capable of *cis–trans*-photoisomerisation, the effect of several factors on efficiency is in most cases a consequence of variation in the tendency to photoisomerisation.

Table 2. Quantum efficiencies of intersystem crossing and internal conversion ϕ_{is} and ϕ_{ic} and corresponding rate constants k_{is} and k_{ic} for dyes.

Dye	Solvent	φ_{is}	k_{is}, s^{-1}	φ_{ic}	k_{ic}, s^{-1}
Rhodamine 6G	ethanol	$2\cdot10^{-3}$ [114]; $5.5\cdot10^{-4}$ [111] *	$6.5\cdot10^{6}$ [42]; $1.6\cdot10^{6}$ [113] $4.2\cdot10^{5}$ [114]; $3.2\cdot10^{6}$ [115] $1\cdot10^{5}$ [111, 117] * $6\cdot10^{5}$ [116]	0.17 [119, 120]	$3\,1\cdot10^{7}$ [119, 120]
	methanol	—	$3.4\cdot10^{6}$ [118]	—	—
	bromoform + butanol (1 : 3)	0.12 [119]	$2.2\cdot10^{7}$ [119]	0.08 [119]	$1{,}4\cdot10^{7}$ [119]
	propanol	$3\cdot10^{-3}$ [121]	—	—	—
	water	$8\cdot10^{-3}$ [125]	—	—	—
	water, pH 1.4	$4\cdot10^{-4}$ [122]	—	—	—
	water, pH 5.2	$3\cdot10^{-3}$ [122]	—	—	—
	water, pH 7	$2\cdot10^{-3}$ [123,124]	—	—	—
Rhodamine B	ethanol + HCl	—	—	—	$9{,}7\cdot10^{7}$ [47]
	ethanol + KOH	—	—	—	$2{,}06\cdot10^{8}$ [47]
	ethanol	$3\cdot10^{-3}$ [111] *	$2.8\cdot10^{6}$ [115]; $6.7\cdot10^{5}$ [111] *	0.39 [119]	$1{,}1\cdot10^{8}$ [119]
	water	$6\cdot10^{-3}$ [123]	—	—	—
Rhodamine 3B	ethanol	$3.5\cdot10^{-3}$ [111] *	$1\cdot10^{6}$ [111] *	0.32 [119]	$9{,}4\cdot10^{7}$ [119]
NN'-Diethyl-rhodamine	ethanol	$1.5\cdot10^{-3}$ [111] *	$3.3\cdot10^{5}$ [111] *	0.06 [119]	$1{,}3\cdot10^{7}$ [119]
Fluorescein	water, pH 9	0.07 [53]	—	0.05 [98]	$1{,}4\cdot10^{7}$ [98]
	water, pH 7.2	0.02 [60]	—	—	—
	ethanol + 0.1M KOH	0.035 [61]	—	0.00 [61]	—
Eosin	water, pH 9	0.68 [53]	—	—	—
	water + 0.01M NaOH	0.76 [61]	$7.9\cdot10^{8}$ [118]	0.02 [61]	—
	ethanol	0.34 [126]	—	—	—
Erythrosin	water, pH 9	0.95 [53]	—	—	—
	ethanol	1.05 [60]; 1,0 [126]	—	—	—
Neutral Red	water, pH 9	<0.01 [59]	—	—	—
Methylene Blue	water, pH 9	0.54 [60, 127]	—	0.45—0.36 [59, 60, 127]	—
Thionine	water, pH 7.2	0.55 [60]	—	0.35 [60]	—
Acridine Orange	ethanol + 0.01M HCl	0.10 [61]	$6.8\cdot10^{7}$ [118]	0.44 [61]	—
	ethanol + 0.01M KOH	0.37 [61]; 0.30 [128]	—	0.43 [61]	—
Pinacyanol	methanol	$2.9\cdot10^{-3}$ [130]	—	—	—
	glycerol	$1.1\cdot10^{-2}$ [130]	—	—	$5.1\cdot10^{8}$ [71]
Cryptocyanine	ethanol	$6.3\cdot10^{-4}$ [77]	—	—	—
	glycerol	—	—	—	$6.9\cdot10^{8}$ [71]
1,1'-Diethyl-2,2'-dicarbocyanine	ethanol	$2.6\cdot10^{-4}$ [77]	—	—	—
	glycerol	—	—	—	$9.6\cdot10^{8}$ [71]
3,3'-Diethyl-oxadicarbocyanine	ethanol	$5\cdot10^{-3}$ [80]	—	0.43 [80]	—
3,3'-Diethyl-thiacarbocyanine	ethanol	$1\cdot10^{-2}$ [80]	—	0.52—0.64 [80]	—
	propanol	$1\cdot10^{-3}$ [131]	—	0.00—0.30 [131]	—

* At 77 K.

Note. Numbers in square brackets denote references (Ed. of Translation).

The fluorescence spectrum is characteristic of each dye. With almost all dyes the emission spectrum is located at the longer-wavelength edge of the principal absorption band. In addition to the usual fluorescence arising on transition from a lower singlet excited state to the ground state, a radiative transition from higher excited states is also possible, whose spectrum is displaced to shorter wavelengths (short-wave luminescence). The low quantum efficiencies and short lifetimes make detection of such luminescence difficult For dyes its observation therefore became possible after the creation of powerful laser sources of excitation. Short-wave luminescence has been investigated in solutions of Rhodamines 6G,[103–108], 3B,[109] and B,[104,109] cryptocyanine[78], etc. For these dyes it is characterised by low efficiencies $\phi_{fl} \cong 10^{-4}-10^{-6}$, while the excited states responsible for it are short-lived (~20–0.03 ps).

4. Intersystem Crossing and Internal Conversion

In the absence of processes tending to quench fluorescence and photochemical reactions involving a singlet excited state the non-radiative processes competing with fluorescence are intersystem crossing to a triplet state and internal conversion (Fig.1). Knowledge of quantum efficiencies or rate constants for these processes is necessary mainly because of the involvement of triplet states of colorants in various photoreactions. Methods elaborated for determining quantum efficiencies ϕ_{is} [59] have enabled values to be found for rhodamine[111,114,119,121–125], xanthen[53,60,61,126], thiazine[60,127], polymethine[77,80,110,131–134], and other dyes[59,61,128] in liquid solutions. Efficiencies ϕ_{is} together with rate constants $k_{is} = \phi_{is}\tau_S^{*-1}$ are listed in Table 2 for several dyes.

The efficiency ϕ_{is} of Rhodamine 6G has been determined from measurements of laser generation characteristics[135,136], triplet–triplet absorption[114,120–123,137], phosphorescence[111,117], and yields of photochemical reactions[138], but in several cases results obtained by different methods differed greatly. Those obtained from direct actinometric measurements[114] and by comparison with a standard[121–124] are apparently the most accurate (Table 2). Values of ϕ_{is} remain almost unchanged on passing from alcohol to water[114,123,124], but are appreciably lower in acid media (pH 1.4).[122] A significant increase is observed in media containing heavy atoms[119], as well as when the dye molecules are associated[120,139,140], in the latter case to 0.5. Both effects are due to strengthening of spin–orbit interaction.

The internal effect of a heavy atom in increasing the efficiency ϕ_{is} is especially clear in the series of xanthen dyes of the fluorescein group (Table 2). Thus passing from fluorescein to eosin (tetrabromofluorescein) and erythrosin (tetraiodofluorescein) increases the efficiency by factors of ~35 and ~50 respectively[60].

Low efficiencies $\phi_{is} \cong 10^{-2}-10^{-4}$ characterise many polymethine dyes in non-viscous solutions. Intersystem conversion to a triplet state has *cis–trans*-photoisomerisation as an effective competitor[131–134]. The quantum efficiency ϕ_{is} is significantly higher for dyes containing *meso*-substituents in the polymethine chain[131–134], because of steric hindrance to the competing process. An appreciable increase in efficiency has been observed in viscous media, in which *cis–trans*-isomerisation is likewise hindered[131].

Internal conversion competes with an intersystem transition to a triplet state. In the absence of photochemical reactions involving the singlet excited state the quantum efficiencies in the quenching of fluorescence conform to the relation

$$\varphi_{fl} + \varphi_{is} + \varphi_{ic} = 1 \qquad (1)$$

which enables the quantum efficiency of internal conversion ϕ_{ic} to be found from the observed efficiencies ϕ_{fl} and ϕ_{is}. Table 2 includes values of ϕ_{ic} and the rate constant of internal conversion k_{ic} for xanthen, thiazine, polymethine, and other dyes. It is evident that internal conversion is almost completely absent from fluorescein-group dyes in polar media:

an appreciable contribution by its efficiency has been observed only with fluorescein itself in dimethyl sulphoxide, dimethylformamide, and formamide[98]. The rate constant k_{ic} increases exponentially with decrease in the energy ΔE corresponding to the 0–0 band in the $S_0 \rightarrow S_1$ transition, which is governed by intermolecular interaction in the solute–solvent system[54,98]. Internal conversion is greater in rhodamine dyes, which also can be explained, apparently, in terms of the energetics of intermolecular hydrogen bonding[54].

Internal conversion makes a significant contribution to energy degradation of singlet excited molecules in the case of thiazine, acridine, triarylmethane, and polymethine dyes. It is especially effective in triarylmethane dyes, for which $\phi_{ic} \cong 1$, and $10^{-11}k_{ic}$ is respectively 5 and 2 s^{-1} for methanolic Malachite Green[63] and ethanolic Crystal Violet[62].

5. Quenching of Singlet Excited State

Dynamic quenching of fluorescence can occur mainly as a result of energy transfer, electron transfer, internal conversion or intersystem crossing under the influence of a quenching agent, formation of excimers and excited complexes, and other causes.

Quenching of singlet excited states of dye molecules by compounds having lower S_1 levels results from energy transfer by an inductive–resonance mechanism. Thus energy transfer has been established[141,142] between fluorescein and eosin, and correspondingly erythrosin and Rose Bengal. Picosecond laser technique has enabled such transfer to be investigated between Rhodamine 6G and 3,3'-diethylthiacarbocyanine[143], as well as Malachite Green[144–146]. For the Rhodamine 6G–Malachite Green system the critical energy-transfer radius $R_0 = 53$ Å and the transfer rate constant $k = 3.1 \times 10^{11}$ M^{-1} s^{-1}; for the Rhodamine 6G–3,3'-diethylrhodamine system in water $R_0 = 59$ Å. The efficiency of energy transfer is increased by the presence of a surface-active agent—sodium dodecyl sulphate[143].

Effective quenching of the fluorescence of dyes (Acridine Yellow, Magdala Red, phenosafranine, Rhoduline Red, etc.) by inductive–resonance energy transfer takes place in the presence of rare-earth metals (neodymium, erbium, praseodymium, etc.)[147,148]; the transfer radius is $R_0 = 10–13$ Å.

Many dyes undergo molecular association with increase in concentration[1]. Fluorescence quenching of monomeric dye molecules results from transfer of singlet excitation energy to non-luminescent association complexes. Detailed investigation of such concentration quenching has been made on rhodamine dyes[150–152].

Quenching of fluorescence accompanied by charge-transfer complex formation is assumed in the interaction of singlet excited rhodamine dye molecules with anthracene and its alkyl derivatives[153], as well as of xanthen dyes, Acridine Orange, and 7-hydroxycoumarin with oxygen[154]. Fluorescence quenching of Oxonine by allylthiourea increases the quantum efficiency of intersystem crossing to a triplet state[155], whereas that of Rhodamine 6G by diethylaniline makes internal conversion more probable[156]. Formation of a singlet excited complex is assumed in the fluorescence quenching of Pyronine by potassium iodide[157].

6. Effect of Association on Properties of Molecules in Singlet Excited State

With increase in concentration dyes may associate, which influences the properties of singlet excited states[1]. Thus raising the concentration of Acridine Orange to 0.1 M lengthens the singlet lifetime τ_S^* from 1.7×10^{-9} to 1.6×10^{-8} s.[158] For a pseudocyanine the formation of I-aggregates leads to shortening of this lifetime to 3.5×10^{-11} s, owing to migration of excitation energy within the aggregate[159]. Shortening of the lifetime has been observed also on the aggregation of rhodamine dyes[40,160].

Energy transfer by an inductive–resonance mechanism is possible for associated dye molecules. Such transfer has been observed between *NN'*-dioctadecyloxacyanine and *NN'*-dioctadecylthiacyanine[161]. Formation of excimers has been recorded also for polymethine dyes[162,163].

III. PHOTOPHYSICAL PROCESSES IN MOLECULES IN A TRIPLET STATE

Triplet states of dye molecules have an important role in the degradation of electronic excitation energy and are involved in various photochemical reactions. Triplet–triplet energy transfer is often used to populate the triplet level of molecules having low intersystem quantum efficiencies. Molecules in a triplet state have significantly longer lifetimes than singlet excited dye molecules, so that their spectra can be recorded by flash photoexcitation[164]. Triplet states of dyes are detected also from phosphorescence[1,111,165] and electron spin resonance[165–171] spectra.

1. Triplet–Triplet Absorption

Triplet–triplet ($T–T$) absorption corresponds to permitted transitions between triplet states (Fig. 1). Early work on flash photolysis involved detailed examination of $T–T$ absorption spectra of xanthen dyes of the fluorescein group[172]. During recent years great interest has been taken in triplet states of rhodamine dyes in view of their widespread use in laser technique. The first direct determinations[137] of the corresponding spectrum of Rhodamine 6G with sensitised occupation of the triplet level of the dye molecules in butanol were soon confirmed[120,173]. The spectra of this dye in aqueous and alcoholic solution have been obtained by direct flash photoexcitation[114,116,122–124,140,174]. The $T–T$ absorption band at 600–620 nm, where the laser emission by Rhodamine 6G is located, is accompanied by two additional $T–T$ absorption bands, in the blue and in the infrared (Fig. 3).

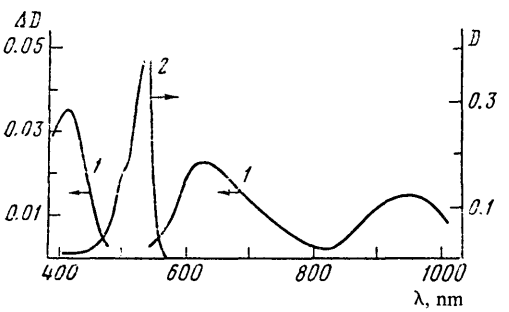


Figure 3. Absorption spectra[123] of aqueous Rhodamine 6G corresponding to the transitions: 1) $T_1 \rightarrow T_n$; 2) $S_0 \rightarrow S_n$.

The triplet–triplet absorption spectra of polymethine dyes have been investigated in detail in connection with their use as active media for optical lasers[11,130,131,133,175–181]. Because

of the low intersystem quantum efficiencies the spectra were obtained for most of these dyes with sensitised excitation. Such spectra have been determined for thiazine dyes (Thionine[182–185], Methylene Blue[186–190], Methylene Green[187]), acridine dyes (Acridine Orange, Acridine Yellow)[191–194], indigoid dyes (thioindigo, 6,6′-diethoxythioindigo)[195,196], coumarin dyes (coumarin, 7-hydroxycoumarin, 7-diethylamino-4-methylcoumarin)[197–199], and other dyes.

2. Deactivation of Triplet States

In photoreactions of dyes the quantum yield of the primary product is directly proportional to the lifetime of the molecule in any triplet state involved. Hence knowledge of the characteristics of processes effecting deactivation of such triplet states is extremely important for assessing the efficiency of photochemical reactions.

A distinction must be made between uni- and bi-molecular deactivation processes. The former include phosphorescence, intersystem crossing, and thermally activated delayed fluorescence (delayed fluorescence of type *E*/200). Among the second are triplet–triplet annihilation fluorescence (delayed fluorescence of type *P*/200), concentration quenching, and electron transfer on disproportionation of two triplet molecules and on interaction of a triplet with an unexcited molecule, as well as deactivation of a triplet state by various quenching agents.

Unimolecular deactivation processes. The lifetime of a molecule in a triplet state is determined by the totality of deactivation processes. In the absence of triplet–triplet annihilation and of concentration and other quenching processes this lifetime is given by

$$\tau_T = (k_{ph} + k_e + k_0 + k_q[Q])^{-1}$$

which takes into account the unimolecular (pseudounimolecular) deactivation processes

$$T \xrightarrow{k_{ph}} S + h\nu_{ph} \qquad (2)$$

$$T \xrightarrow{k_e} S^* \qquad (3)$$

$$T \xrightarrow{k_0} S \qquad (4)$$

$$T + Q \xrightarrow{k_q} S + Q\ . \qquad (5)$$

In most cases phosphorescence (2) cannot be recorded in liquid dye solutions at room temperature, owing to rapid non-radiative deactivation of the triplet state (4) and (5). It has been recorded in solutions of rhodamine dyes in the presence of bromoform (20–30 vol.%), which facilitates transition to a triplet state[209,212,229], the quantum efficiency of phosphorescence being (2–6) × 10^{-5}.[209] Systematic measurements of phosphorescence have been made for xanthen dyes at 77 K.[203,208,230] The longest triplet lifetimes occur in solid matrices—solutions at low temperatures or films (e.g. polyvinyl alcohol)—and are determined from the kinetics of the decay of phosphorescence[203,208], triplet–triplet absorption[198], and the e.s.r. signal[166,169,202,231,232]. Values of τ_T for most colorants under these conditions lie in the range 0.1–1.0 s (Table 3).

Several colorants (e.g. xanthen dyes) exhibit delayed fluorescence of type *E*. This process (3) involves vibrational excitation of T_1 to an isoenergetic level S_1 followed by an intersystem transition at S_1 and loss of excitation by fluorescence (Fig. 1). Delayed fluorescence of this type is observed with compounds having small singlet–triplet separation (2000–3000 cm^{-1}), as well as at high temperatures.

Table 3. Lifetime τ_T and deactivation rate constants of triplet state of dyes.

Dye	Solvent	τ_T, s	k_0, s^{-1}	k_1, s^{-1}	$2k_{TT}$, M^{-1}	k_{TS}, s^{-1}	Ref.
Fluorescein	water, pH 12	—	—	5·10	$1.7\cdot10^9$	$1\cdot10^8$	[59]
	polyvinyl alcohol (pva)	—	7.6	—	—	—	[59]
	ethanol (77 K)	0.18	—	—	—	—	[202]
Eosin	water, pH 9.1	—	—	$5.4\cdot10^2$;	$1.1\cdot10^9$	$3\cdot10^8$	[59]
	water, pH 9.1	—	—	$4.2\cdot10^2$	—	$4\cdot10^8$	[204]
	pva	—	$2.3\cdot10^2$	—	—	—	[59]
	ethanol (77 K)	0.10	—	—	—	—	[202]
	water, pH 7.0	—	—	$4.06\cdot10^2$	—	—	[205]
Erythrosin	water, pH 10	—	—	$3\cdot10^3$	—	—	[59]
	pva	—	$1.6\cdot10^3$	—	—	—	[59]
	water, pH 9.3	—	—	$5.2\cdot10^3$	—	$2.2\cdot10^8$	[204]
Rhodamine 6G	ethanol	—	—	10^3—10^4	$4.1\cdot10^9$	—	[114]
	ethanol (77 K)	1.7	—	—	—	—	[202]
	ethanol + O_2	$0.45\cdot10^{-6}$	—	—	—	—	[114]
		$0.33\cdot10^{-6}$					[115]
	butanol	—	—	$1.7\cdot10^2$	—	—	[210]
	butanol + 20% bromoform	—	—	$1.5\cdot10^3$	—	—	[120]
	propanol + 20% bromoform	—	5·10	—	—	—	[209]
	water, pH 6	—	$4\cdot10^4$	$4\cdot10^2$	$2.8\cdot10^9$	$5\cdot10^7$	[140]
Rhodamine B	butanol + 30% bromoform	—	—	$1.6\cdot10^3$	—	—	[119]
	ethanol (77 K)	1.0	—	—	—	—	[202]
	ethanol + O_2	$0.33\cdot10^{-6}$	—	—	—	—	[115]
	ethylene glycol (90 K)	0.86	—	—	—	—	[169]
Rhodamine 3B	butanol + 30% bromoform	—	—	$2.2\cdot10^3$	—	—	[119]
Thionine	methanol + 20% water (98 K)	$3.5\cdot10^{-3}$	—	—	—	—	[171]
	water, pH 1–8	—	—	$8.5\cdot10^4$	—	—	[215]
	water, pH 1.7	—	—	$1.5\cdot10^5$	—	—	[188]
	water, pH 2.5	$1.6\cdot10^{-5}$	—	—	—	—	[183]
Oxonine	methanol + 20% water (98 K)	$3\cdot10^{-2}$	—	—	—	—	[171]
	water	—	—	$8.3\cdot10^3$	—	—	[217]
Methylene Blue	methanol + 20% water (98 K)	$2\cdot10^{-3}$	—	—	—	—	[171]
	water	$(4\div6)\cdot10^{-5}$	—	$1.52\cdot10^4$**	—	—	[219]
	water, pH 5	—	—	$2.3\cdot10^5$	—	—	[190]
	water, pH 9	—	—	$1.2\cdot10^4$	—	—	[187]
				$0.3\cdot10^5$***	—	—	
	acetonitrile	—	—	$6.5\cdot10^3$	—	$9\cdot10^8$	[189]
Acridine Orange	methanol	—	—	$3.5\cdot10^3$	$5.5\cdot10^9$	—	[194]
	methanol + chloroacetic acid	—	—	—	$1.6\cdot10^9$	—	[194]
	water, pH 12	—	—	$3\cdot10^2$	$5.5\cdot10^9$	$3\cdot10^8$	[192]
	water + 10^{-3}M HCl						
	water, pH 2	—	—	$3\cdot10^2$	$4\cdot10^9$	$\sim10^8$	[228]
		—	—	$2.5\cdot10^3$	$1.5\cdot10^9$	$2.3\cdot10^7$	[221]
	ethanol (77 K)	2.0	—	—	—	—	[202]
	pva	—	11.5	—	—	—	[221]
Acridine Yellow	water, pH 11	—	—	$6\cdot10^2$	$3.1\cdot10^9$	$7.6\cdot10^8$	[221]
	water, pH 2	—	—	$1.9\cdot10^3$	$3.8\cdot10^9$	$2.0\cdot10^8$	[221]
	ethanol (77 K)	3.1	—	—	—	—	[202]
	pva	—	1.5–4.2	—	—	—	[221]
3,3′-Diethylthiadicarbocyanine	propanol	—	—	$2.3\cdot10^2$	$2.6\cdot10^9$	$4.0\cdot10^7$	[222]
	butanol	—	—	$4.6\cdot10^2$	—	—	[133]
	pva	—	$1.5\cdot10^2$	—	—	—	[223]
3,3′-Diethylthiadicarbocyanine	propanol	—	—	$3.0\cdot10^2$	$2.4\cdot10^9$	$1.3\cdot10^7$	[222]
				$5.4\cdot10^2$****			
	pva	—	$2.5\cdot10^2$	—	—	—	[223]
Cryptocyanine	ethanol	—	—	$9.1\cdot10^2$	—	—	[77]
	glycerol + O_2	$4\cdot10^{-5}$	—	—	—	—	[226]
Pinacyanol	methanol	—	—	$5.3\cdot10^3$	—	—	[130]
8,9-Difluorothiacarbocyanine	propanol + O_2	$4.2\cdot10^{-6}$	—	$9.3\cdot10^5$	—	—	[175]
3,3′-Diethyl-9-methoxythiacarbocyanine	Propanol	—	—	$4\cdot10^2$	$2\cdot10^9$	$1.9\cdot10^7$	[222]
7-Hydroxycoumarin	ether + isopentane + ethanol (5 : 5 : 2) (77 K)	0.90	—	—	—	—	[198]
	ditto (117 K)	0.10	—	—	—	—	[197]
Thioindigo	benzene	$1.35\cdot10^{-7}$;	—	—	—	—	[227]
	benzene	$2.79\cdot10^{-7}$	—	—	—	—	[196]

*Ref. 116.
**Ref. 218.
***Ref. 190.
****Ref. 224.

In deoxygenated liquid solutions the chief processes deactivating a triplet state are non-radiative degradation (4) and quenching by uncontrollable impurities (5). Table 3 lists rate constants k_0 and $k_1 = k_0 + k_Q[Q]$ for various classes of dyes, and Table 4 gives positions of the triplet level E_T for the molecules. Several conclusions follow from these data: (i) k_1 exceeds k_0 for all the compounds investigated (the difference between them is due mainly to quenching by residual oxygen, whose concentration is estimated as $(1-2) \times 10^{-7}$ M); (ii) k_0 and k_1 increase with the number of heavy atoms in xanthen dye molecules in the sequence—fluorescein < eosin < erythrosin—and also in polymethine dyes (internal heavy-atom effect)[102]; (iii) k_1 for the rhodamine group of xanthen dyes is greater in media containing heavy atoms, e.g. bromoform (external heavy-atom effect); (iv) protonation of thiazine and acridine dye molecules increases k_1, as a consequence of the position of the triplet level in protonated molecules; (v) the high values $k_1 \cong (2-3) \times 10^8$ s^{-1} for thioindigoid dyes are due to the involvement of the triplet state in photoisomerisation; and (vi) k_1 for triarylmethane dyes increases on passing from a solid matrix to a solution, as conformational changes and additional rotational modes become possible.

Table 4. Triplet levels E_T of dye molecules.

Dye	Solvent	E_T, cm^{-1}	Ref.
Fluorescein	*	16500	[201]
»	ethanol	18000	[203]
Eosin	ethanol	15600	[203]
»	*	15900	[206]
»	*	14800	[207]
Erythrosin	water, pH 9	14700	[213]
Rhodamine 6G	ethanol	15100	[203, 208]
»	propanol + 20% bromoform	14400	[209]
»	propan-2-ol	14650	[211]
»	propanol + 30% bromoform	14900	[212]
Rhodamine B	propanol + 20% bromoform	14300	[209]
»	ethanol	14890	[203]
Rhodamine 3B	ethanol	14870	[203]
Thionine	water + KOH	13700	[214]
»	water + HCl	10500	[214]
»	*	13900	[216]
Methylene Blue	water + KOH	11640	[220]
»	water + HCl	8220	[220]
Acridine Orange	*	17100	[111]
Acridine Yellow	*	18350	[111]
3,3'-Diethylthiacarbocyanine	propanol	13750	[225]
3,3'-Diethylthiadicarbocyanine	propanol	<12600	[225]

*Solvent not stated.

Triplet–triplet annihilation and concentration quenching. Bimolecular processes include triplet–triplet interaction (at high concentrations of triplet molecules) and concentration quenching. Provided that the singlet–triplet splitting in the molecule is less than the separation between triplet and ground levels, excitation energy can be transferred between two triplet molecules with transition of one of them to a singlet excited state followed by fluorescence (delayed fluorescence of type P). Other possible results of triplet–triplet interaction may be non-radiative degradation[200, 233] and electron transfer[59,234]:

$$T + T \xrightarrow{k_{TT}} \begin{cases} \rightarrow S^* + S & (6) \\ \rightarrow \tilde{S} + S & (7) \\ \rightarrow R^{\cdot} + R^{\cdot} . & (8) \end{cases}$$

The triplet–triplet interaction rate constant k_{TT} is usually found from the rate of decay of triplet–triplet absorption intensity. Table 3 gives values of k_{TT} for individual xanthen, acridine, and polymethine dyes; high values indicate that triplet–triplet interaction is occurring in the diffusion range.

Delayed fluorescence of type P, resulting from triplet–triplet annihilation, is observed in liquid dye solutions. That of butanolic Rhodamine 6G in the presence of bromoform[229] is assumed to involve formation of a ternary complex of two triplet dye molecules and one bromoform molecule. With photoexcitation sensitised by triplet–triplet energy transfer account must be taken also of delayed fluorescence due to triplet–triplet annihilation of mixed type[224,235].

Concentration quenching of triplet states arises from interaction of a triplet with an unexcited molecule. Its mechanism has not been finally established, but it apparently results from formation of a vibrationally excited molecule in the ground state[236], excimer phosphorescence[59], and electron transfer[59,172,234]:

$$T + S \xrightarrow{k_{TS}} \begin{cases} \rightarrow \tilde{S} + S & (9) \\ \rightarrow [T_2] \rightarrow S + S + h\nu & (10) \\ \rightarrow R^{\cdot} + R^{\cdot} & (11) \end{cases}$$

Table 3 includes concentration-quenching rate constants k_{TS} for several dyes. Comparison of k_{TS} and k_{TT} indicates that concentration quenching is substantially less effective than triplet–triplet interaction.

3. Quenching of the Triplet State

A distinction is made between static and dynamic quenching of triplet states. The former involves a decrease in concentration of triplet molecules unaccompanied by change in their lifetime. Static quenching corresponds to equilibrium between molecules unperturbed by the quenching agent and those that have been affected by the quencher (complex formation with the latter, association, etc.) and have a lower intersystem quantum efficiency ϕ_{is}. Dynamic quenching of the triplet state occurs in encounters of triplet with quencher molecules and shortens their lifetime.

A distinction is made also between "physical" and "chemical" quenching: the former yields the initial molecules in a ground (vibrationally excited) or an electronically excited state, but the latter gives intermediate products, e.g. free radicals. Physical quenching includes triplet–triplet interaction, concentration quenching, and quenching by heavy atoms; quenching by electron donors and acceptors, etc. must be regarded as chemical.

The chief processes for quenching the triplet state of dye molecules are triplet–triplet energy transfer, electron transfer, quenching by an "external" heavy-atom mechanism, and paramagnetic quenching.

Triplet–triplet energy transfer is one way in which the triplet state of a donor is quenched by an energy acceptor[233, 237]. Measurements of such transfer have revealed that the rate constant depends on the separation ΔE_T between the triplet levels of donor and acceptor. With large $\Delta E_T \geq 1500$ cm^{-1} the rate constant remains almost unchanged, close

to the diffusion constant; with decrease in the separation the rate constant k_q decreases; and with $\Delta E_T < 0$ there is a linear dependence of $\ln k_q$ on ΔE_T.[238,239]

Table 5. Triplet–triplet energy-transfer quenching rate constants for dyes.

Dye	Quencher	Solvent	k_q, M^{-1} s^{-1}	Ref.
Fluorescein	O_2	water, pH 12	$1.6 \cdot 10^9$	[204]
Eosin	O_2	water, pH 8.6	$1.1 \cdot 10^9$	[204]
»	O_2	water	$(1.1–2.0) \cdot 10^9$	[240]
»	Cu^{2+}	water, pH 6.2	$5.6 \cdot 10^8$	[255]
»	anthracene	ethanol	$5.1 \cdot 10^8$	[207]
Erythrosin	anthracene	ethanol	$7.3 \cdot 10^8$	[207]
Rhodamine 6G	O_2	ethanol	$2.5 \cdot 10^8$	[241]
»	O_2	ethanol	$1.6 \cdot 10^9$	[114]
»	O_2	methanol	$3.3 \cdot 10^9$	[242]
»	O_2	water	$6 \cdot 10^8$	[116]
»	cyclo-octatetraene	ethanol	$7.0 \cdot 10^8$	[114]
»	Co^{2+}	water	$2.6 \cdot 10^7$	[124]
Thionine	O_2	water, pH 4.6	$2.6 \cdot 10^8$	[215]
»	O_2	water, pH 8	$4.5 \cdot 10^8$	[183]
»	Co^{2+}	water, pH 2.5	$5 \cdot 10^5$	[243]
Methylene Blue	O_2	water	$3 \cdot 10^9$	[219]
3,3′-Diethylthia-carbocyanine	naphthacene	butanol	$1 \cdot 10^9$	[180]
3,3′-Diethyl-9-methoxythia-carbocyanine	naphthacene	propanol	$3.7 \cdot 10^9$	[134]

Table 6. Rate constants k_q for quenching of the triplet state of dyes by compounds containing heavy atoms.

Dye	Solvent	Quencher	k_q, M^{-1} s^{-1}	Ref.
Rhodamine 6G	ethanol	KI	$2 \cdot 10^9$	[244]
»	ethanol	KI	$1.1 \cdot 10^9$	[115]
»	propanol	LiBr	$5 \cdot 10^3$	[212]
»	propanol	CBr_4	$4.6 \cdot 10^4$	[212]
»	propanol	$CHBr_3$	$2 \cdot 10^2$	[212]
Rhodamine B	ethanol	KI	$2.2 \cdot 10^8$	[115]
Eosin	water, pH 6.5	KI	$1.5 \cdot 10^7$	[245]
»	water, pH 6.2	KI	$1.5 \cdot 10^7$	[246]
»	water, pH 7.1	KI	$1.9 \cdot 10^7$	[247]
»	water	$HgCl_2$	$5 \cdot 10^8$	[219]
»	water	TlCl	$2 \cdot 10^7$	[219]
»	water	CsCl	10^5	[219]
Thionine	methanol	C_6H_5Br	$4 \cdot 10^4$	[248]
»	water, pH 7.1	KI	$4.7 \cdot 10^9$	[247]
Methylene Blue	water	KI	$1 \cdot 10^7$	[219]
»	water	CsCl	$2 \cdot 10^6$	[219]
»	water	$HgCl_2$	$2 \cdot 10^9$	[219]
»	water	TlCl	$2 \cdot 10^8$	[219]
Safranine T	water, pH 9	KI	$1 \cdot 10^8$	[59]
3,3′-Diethyl-9-methoxythia-carbocyanine	butanol	$CHBr_3$	$2.5 \cdot 10^5$	[134]

Energy acceptors in the quenching of triplet states of dyes include oxygen molecules, aromatic hydrocarbon molecules, and inorganic ions. Quenching by oxygen has been studied in the greatest detail: it is generally accepted that quenching results in the formation of singlet oxygen[237], but electron transfer is also possible[204,249]. Table 5 gives triplet-quenching rate constants for various energy acceptors.

Compounds containing heavy atoms (bromobenzene, bromoform, alkali-metal bromides and iodides, hetero-organic compounds of tin, lead, mercury, etc.) facilitate intersystem transitions and lead to triplet quenching in both liquid and solid solutions[59]. Those in Table 6 can be arbitrarily divided into two groups according as k_q lies in the ranges 10^2–10^5 and 10^7–10^9 M^{-1} s^{-1}. Differences in the values of k_q are due to different quenching mechanisms: weak quenching (by bromoform, bromobenzene, caesium chloride, lithium bromide) is caused by direct spin–orbit interaction, but effective quenching by potassium iodide and by mercury(II) and thallium(I) chlorides involves electron transfer.

4. Triplet States of Association Complexes

At high dye concentrations association complexes are formed in polar solvents, in micellar solutions by interaction with macromolecular compounds, and also in mixtures of a polar and a non-polar solvent[1]. Association is accompanied by change in the spectral luminescent properties of the molecules.

Triplet states of association complexes have been investigated mainly on the rhodamine group of xanthen dyes[120,140,210,250–254]. Association of Rhodamine 6G in tetrachloromethane, cyclohexane, benzene, etc. in the presence of 0.1–0.2% of a polar solvent (association complexes of type I), as well as in aqueous solution in the presence of polymethacrylic acid (association complexes of type II) increases significantly the quantum efficiency of intersystem crossing in the triplet state relative to that of the dye monomers (ϕ_T respectively ~0.2 and ~0.5 for types I and II). The quantum efficiency of internal conversion also increases, and that of fluorescence decreases. The increase in ϕ_T accompanying association of Rhodamine 6G may be due to strengthening of spin–orbit interaction on aggregation and narrowing of singlet–triplet separation[252].

The triplet state of associated Rhodamine 6G is deactivated in uni- and bi-molecular processes. In 0.2% butanol–99.8% tetrachloromethane mixtures both delayed fluorescence of type *E* and phosphorescence are observed[250,251]. Measurements of the lifetime of the triplet state have shown that the deactivation rate constant k_1 increases from 200 to 3000 s^{-1} on passing from type II to type I association complexes[254]. The longer lifetime for the former is probably due to stabilisation of the complexes by the polymer. An analogous stabilising effect of polymethacrylic acid has been found for monomeric Rhodamine 6G.[140] The rate constant k_1 depends on the nature of the polar component of the mixture (viscosity and capacity for hydrogen bonding)[140,254]. Associated Rhodamine 6G can undergo triplet concentration quenching and triplet–triplet interaction[254], the latter accompanied by delayed fluorescence of type *P*.[210]

Many dyes are ionic compounds[1]. At certain solution concentrations charged dye ions are able to form ionic association complexes with a gegenion. Photophysical processes have been investigated in ionic association complexes of xanthen dyes of the fluorescein series with transition and rare-earth metal ions[256–261]. The measured phosphorescence lifetimes of the dye complexes with rare-earth metal ions in ethanol at 77 K indicate transfer of the triplet excitation energy to the metal ion. Sensitised luminescence of the trebly charged ytterbium cation has been detected in associated dyes in liquid solutions. The nature of the gegenion influences the relative quantum efficiencies of fluorescence and phosphorescence in the association complexes: thus the phosphorescence of eosin completely vanishes in complexes with the ytterbium(III) cation, whereas its quantum efficiency increases in the presence of trebly charged europium, gadolinium, terbium, and cerium cations.

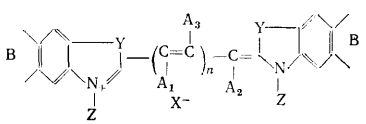
IV. PRIMARY PHOTOCHEMICAL REACTIONS OF DYES

Dyes undergo various photochemical reactions in solutions[1]. Primary photochemical processes can occur at any stage in degradation of the energy of singlet and triplet excitation.

Three types of reaction can be distinguished, independently of the multiplicity of the excited state[262]: reactions of type A take place in a vibronic state immediately after absorption of a light quantum, those of type B follow vibrational relaxation, and type C occur after transition to a vibrationally excited level of the ground state, or to a triplet state. Type A reactions, proceeding from an unrelaxed vibrationally excited state, should have rate constants exceeding 10^{11}–10^{13} s^{-1}; they include photodissociation and photoisomerisation. Such reactions are unimolecular, with kinetics depending on temperature and exciting wavelength. Type B—electron, proton, etc. transfer—are of great interest for the photochemistry of dyes. The main factors influencing the reactivity of molecules are energy, multiplicity, distribution of electron density, and orbital symmetry.

1. *cis–trans*-Photoisomerisation

cis–trans-Photoisomerisation has been studied in greatest detail on cyanine (polymethine) dyes of structure



Y=O, S, $C(CH_3)_2$; Z=CH_3, C_2H_5; A_1, A_2=H, CH_3, F;
A_3=H, F, CH_3, C_2H_5, OCH_3, NH_2;
n = 0, 1, 2, 3; B = H, 5-NO_2, 5-H_2CO,
6-$N(CH_3)_2$, 6-Br, 6-NH_2OH, OCH_3, I, NO_2;
X=I, CH_3SO_4, Br, ClO_4

It has been investigated in solid matrices[265] and in liquid solutions with flash (microsecond)[130–132,134,175,180,263,264,268,270] and laser (nanosecond[266,267,269,273–276] and picosecond[176,271,272]) excitation.

In the ground state polymethine dye molecules may occur in either the *trans* or the *cis* form. Photoexcitation may correspondingly involve *trans* → *cis* or *cis* → *trans* transitions. Thus 3,3'-diethylthiacarbocyanine, which has an unsubstituted polymethine chain, on excitation passes from the *trans* into the *cis* form[264]. *trans–cis*-Isomerisation takes place about the $C_{(2)}$–$C_{(8)}$ bond in the unsubstituted and 10-substituted polymethine chain, and about the $C_{(8)}$–$C_{(9)}$ bond in *meso*-substituted dyes[270].

cis–trans-Photoisomerisation of polymethine dyes takes place in the singlet state S_1,[266,277] as indicated primarily by triplet–triplet energy transfer results. Sensitised population of the triplet level of these dyes gives a triplet–triplet absorption spectrum markedly different from that of the photoisomers[130,131,134,175,180,264,269,273]. Furthermore, the fluorescence of 3,3'-diethylthiacarbocyanine decays and its *cis*-isomer accumulates within the same time (300 ps).[272] However, *cis–trans*-photoisomerisation from the triplet state is possible with 8,9-difluorothiacarbocyanine[274].

On excitation in the $S_0 \rightarrow S_n$ transition band, isomerisation follows internal conversion $S_n \rightarrow \tilde{S}_1$ and vibrational relaxation $\tilde{S}_1 \rightarrow S_1$.[267,278] However, picosecond laser excitation enabled isomerisation to be recorded in the S_2 state of 3,3'-diethyl-2,2'-thiacarbocyanine[12]. The rate constant in methanol is 3.2×10^{10} s^{-1}, which ensures that isomerisation can compete successfully with internal conversion ($k_{ic} = 1.8 \times 10^{10}$ s^{-1}).

Fig. 4 shows the transitions in substituted thiacarbocyanines when the initial form is a *cis*-isomer. The absorption and fluorescence spectra of isomers usually differ insignificantly, with shifts of 5–20 nm. Extinction coefficients are also closely similar[176,266,272].

Polymethine dyes are usually characterised by high quantum efficiencies of photoisomerisation ϕ_{isom}. Table 7 lists quantum efficiencies ϕ_{fl}, ϕ_{is}, and ϕ_{isom}, rate constants of triplet deactivation k_1 and relaxation of the photoisomer k_{relax}, and also activation energies of relaxation E_a for 3,3'-diethylthiacarbocyanine and its substituted derivatives. It is evident that non-radiative degradation of the energy of singlet excited states is effected mainly by isomerisation with characteristics (ϕ_{isom}, k_{relax}, E_a) depending on the presence in the polymethine chain of substituents capable of offering steric hindrance to rotation on isomerisation. Replacement of one hydrogen atom at position 8 or 9 by a fluorine atom does not produce significant steric hindrance, so that long-lived photoisomers are formed (lifetime 10^{-3}–10^{-2} s) with an angle of rotation of the chain $\alpha = 180°$. Replacing two or three hydrogen atoms leads to marked steric hindrance, with the angle decreasing to 90°, the photoisomer relaxation rate constant increasing abruptly, and the activation energy of relaxation simultaneously diminishing. Analysis of Stuart–Briegleb models shows that similar changes in k_{relax}, E_a, and α always accompany steric hindrance[273]. If such hindrance is sufficiently great, photoisomerisation may be completely suppressed[279].

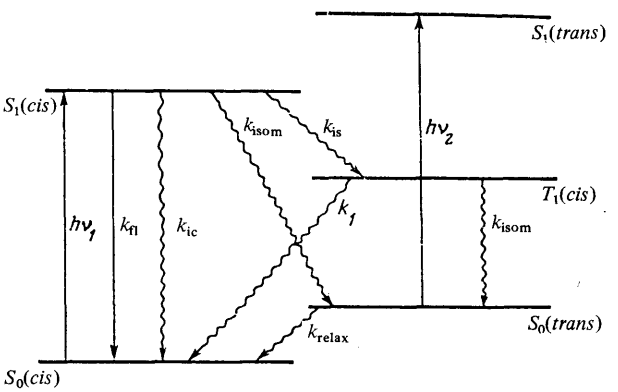


Figure 4. Scheme of energy levels and transitions between them for *cis*- and *trans*-isomers of thiacarbocyanines.

Replacement of hydrogen atoms in polymethine dyes by halogens leads to a redistribution of probabilities of singlet deactivation of excited states as a consequence not only of steric hindrance but also of an internal heavy-atom effect. Thus for 9-iodothiacarbocyanine $\phi_{is} = 1$ but $\phi_{isom} \cong 0$.[102].

Photoexcitation of indoleninedicarbocyanines initially in *cis*-form gives long-lived *trans*-isomers together with short-lived di-*cis*-isomers (k_{relax} respectively ~10^2 and ~10^6 s^{-1}).[132,269]. The latter are sterically hindered and are found in low quantum yields (0.01–0.1). Dyes having a shorter polymethine chain can also form sterically hindered di-*cis*-photoisomers[275].

The efficiency of photoisomerisation effected by rotation of large fragments of the molecule is substantially dependent on the viscosity of the medium: increase in viscosity diminishes the probability of formation of a photoisomer[131,272] and its rate of relaxation[276]. Photoisomerisation is influenced also by the temperature[276] and the solvent[271,279]. Thus a ketocyanine isomerises in a non-polar solvent ($\phi_{isom} = 0.5$) but

not in alcohol[279], owing to predominance of the non-polar structure of the photoisomer.

Merocyanine dyes, like carbocyanines, are capable of photoisomerisation[280–282]. From a singlet excited state both short- and long-lived photoisomers are formed (k_{relax} respectively ~100 and ~1 s^{-1}), whereas a triplet state yields only the latter[280,281]. They are formed by rotation about the $C_{(2')}$–$C_{(8')}$ and $C_{(5)}$–$C_{(9')}$ bonds respectively[281]. The photoisomerisation rate constant depends on the proton-donor power and the polarity of the solvent[282].

Table 7. Influence of substituents in polymethine chain of 3,3'-diethylthiacarbocyanine on quantum efficiences, rate constants, and activation energies of *cis–trans*-photoisomerisation[131–134,175,264,274].

Substituents	Isomer	φfl	$\varphi$is	φisom	k_1, s^{-1}	k_{relax}, s^{-1}	E_a, kcal mole^{-1}
None	*cis*	0.05	<0.001	0.95	$4.6\cdot10^2$	$1.6\cdot10^2$	15
9-Methoxy	*cis*	0.015	0.20	<0.001	$3.3\cdot10^3$	—	—
8-Fluoro	*trans*	0.03	<0.001	0.99	$1.6\cdot10^4$	$1.9\cdot10^2$	13.3
9-Fluoro	*cis*	0.55	0.03	0.4	$8.2\cdot10^2$	$3.2\cdot10^3$	11.3
8,9-Difluoro	*trans*	0.005	0.16	0.83	$9.3\cdot10^5$	$1.0\cdot10^5$	9.6
8,9,10-Trifluoro	*trans*	≤0.0005	—	0.6	≫$3\cdot10^5$	$5.0\cdot10^6$	7.3
8,10-Dimethyl	—	0.0024	0.005	0.9	—	$1.8\cdot10^4$	10.5

Thioindigo and its derivatives are capable of *cis–trans*-photoisomerisation[65,66,195,196,227,283–287]. With thioindigo and 6,6'-diethoxythioindigo the reaction involves a triplet state common to *cis*- and *trans*-forms. In the triplet state fragments of the molecule are turned through 90° relative to the ethylenic bond[196]. Involvement of the triplet state of thioindigo in isomerisation follows from results on sensitised population of the triplet level of the dye molecule[286] and on inhibition of the *trans* → *cis* transition by oxygen[227,287], as well as from comparison of rates of triplet deactivation and photoisomer accumulation[196]. However, recent work[307,308] on the mechanism of the photoisomerisation of *trans*-thioindigo using a picosecond laser casts doubt on involvement of a triplet state in isomerisation.

Azomethine dyes undergo *syn–anti*-isomerisation about the carbon–nitrogen double bond[288]. Two mechanisms are possible, one (torsion) consisting in rotation about this bond, and the other (inversion) in rotation of a fragment in the plane of the molecule through 120° about the nitrogen atom. Experimental results indicate that both mechanisms operate[289], isomerisation occurring in both singlet excited and triplet states[290,291]. In azo-dyes of the Picramine R group[292] *cis–trans*-photoisomerisation takes place from a singlet excited state[191].

2. Electron Transfer

Electron transfer is the most common photochemical reaction of dyes[234]. It can occur in both singlet excited and triplet states. Interaction of excited molecules with electron donors or acceptors will inevitably produce additional paths for degradation of the excitation energy. Thus a consequence of electron transfer is to shorten the lifetime of excited molecules in the presence of a quenching additive, in conformity with the Stern–Volmer equation. Thus the singlet lifetime τ_S^* of Thionine is shorter in the presence of iron(II) chloride or sulphate in aqueous solution at pH 2.[129]

Study of the quenching of singlet excited states usually involves measurement of the relative fall in efficiency or intensity of fluorescence. If the dye molecules do not form non-luminescent complexes with quenching additives, the fall in efficiency and the shortening of the lifetime τ_S^* are described by the same Stern–Volmer formula. A fall in fluorescence efficiency has been found for Thionine in the presence of iron(II), manganese(II), cerium(III), and caesium(I) in water at pH 2.5,[293] Rhodamine 101 in the presence of methanolic amines[294], and Methylene Blue in the presence of iron(II) in 0.01 M hydrochloric acid[149]. The rate constant for the quenching of singlet excited states of Thionine molecules by iron(II) cations is $k_q = 3.5 \times 10^9$ M^{-1} s^{-1},[129] identical with the 3.6×10^9 M^{-1} s^{-1} calculated from the Stern–Volmer dependence for the fall in fluorescence efficiency[293] and for the lifetime of these singlet states[129]. Thus quenching of fluorescence in the Thionine–iron(II) system is due solely to electron transfer. Formation of complexes in the ground state is possible between Thionine and the sulphate anion[293].

Table 8. Rate constants k_q for quenching of the triplet state of dyes by electron donors and acceptors.

Dye	Solvent	Donor	Acceptor	k_q, M^{-1} s^{-1}	Ref.
Eosin	water, pH 7.1	(-)-tryptophan	—	$8.4\cdot10^8$	[247]
»	water, pH 6.2	—	ferricyanide	$7.5\cdot10^8$	[246]
»	water, pH 7.2	edta	—	$5.0\cdot10^5$	[60]
»	water, pH 7.2	allylthiourea	—	$3.4\cdot10^5$	[60]
Rhodamine 6G	water, pH 6	—	*p*-benzoquinone	$2.5\cdot10^9$	[116, 124]
»	water, pH 6	ascorbic acid	—	$8.0\cdot10^8$	[116, 124]
»	water, pH 6	hydroquinone	—	$2.0\cdot10^9$	[116, 124]
»	water, pH 6	ferrocyanide	—	$8.0\cdot10^9$	[116, 124]
»	water, pH 6	—	ferricyanide	$5.0\cdot10^9$	[116, 124]
Thionine	water, pH 7.1	(-)-tryptophan	—	$3.9\cdot10^9$	[247]
»	water, pH 7.1	allylthiourea	—	$1.1\cdot10^7$	[247]
»	water, pH 2.5	—	Fe^{3+}	$9.0\cdot10^4$	[183]
»	water, pH 2.5	Fe^{2+}	—	$6.1\cdot10^7$	[183]
»	methanol, pH 8.6	hydroquinone	—	$2.5\cdot10^9$	[248]
»	methanol, pH 8.6	thiourea	—	$7.5\cdot10^6$	[248]
»	acetonitrile	*p*-phenylenediamine	—	$5.9\cdot10^9$	[185]
Methylene Blue	water, 0.01M H_2SO_4	Fe^{2+}	—	$5.5\cdot10^6$	[220]
»	water, 0.04M KH_2PO_4	—	ferricyanide	$1.4\cdot10^{10}$	[220]
»	methanol	triethylamine	—	$4.7\cdot10^7$	[295]
»	methanol	aniline	—	$1.1\cdot10^{10}$	[295]
»	acetonitrile	*p*-phenylene-diamine	—	$1.4\cdot10^{10}$	[189]
»	acetonitrile	perylene	—	$3.2\cdot10^9$	[189]
»	acetonitrile	9,10-dimethy-lanthracene	—	$3.7\cdot10^7$	[189]
Oxonine	water, pH 8	edta	—	$1.5\cdot10^7$	[296]
»	methanol	allylthiourea	—	$1.8\cdot10^6$	[182]
Biscyanine	propanol	—	nitroxyl	$(1—10)\cdot10^7$	[225]
3,3'-Diethyl-9-methoxy-carbocyanine	propanol	ascorbic acid	—	$2.5\cdot10^8$	[181]
»	propanol	2-naphthylamine	—	$2.0\cdot10^6$	[181]
»	propanol	—	*p*-benzoquinone	$6.7\cdot10^8$	[181]
»	propanol	—	*m*-dinitro-benzene	$2.2\cdot10^9$	[181]
»	propanol	—	methylviologen	$1.4\cdot10^8$	[181]

Quenching of triplet states by electron donors and acceptors has been investigated in thiazine[171,182–189,215,218,220,247,248,295,296], xanthen[59,60,116,124,246,247,297], acridine[192–194], polymethine[131,181,225], and other dyes[234] (Table 8).

The Stern–Volmer type of linear dependence found experimentally between the relative shortening of the lifetime of singlet and triplet molecules and the concentration of the

quenching additive is a direct indication of the possibility of electron transfer. It must be borne in mind that this type of relationship is satisfied by other processes, e.g. energy or hydrogen transfer. Electron transfer involving excited dye molecules is characterised firstly by the formation of solvated radical-ions (or radicals) and secondly by a correlation between the quenching rate constant and the donor or acceptor properties of the quencher.

Flash and laser photolysis have been used to determine the absorption spectra of one-electron oxidation and reduction products of fluorescein[297], rhodamine[116,123,124,298], thiazine[182–185,187–189,295], acridine[182,228], polymethine[131,181,225], and other dyes.

In polar media electron transfer between a triplet dye molecule (acceptor) and a quencher molecule (donor) leads to formation of a solvent-separated radical-pair[234]:

$$A(T) + D \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A(T)\ldots D \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} A^{\cdot-}\ldots D^{\cdot+} \begin{cases} \xrightarrow{k_{30}} A + D \\ \xrightarrow{k_{34}} A^{\cdot-} + D^{\cdot+} \end{cases}$$

This either dissociates into solvated radical-ions or recombines with formation of the original reactants in the ground state; involvement of a triplet excited complex has also been suggested[184,248,301].

The quenching rate constant is given by the formula[301]

$$k_q = k_{12}\left[1 + \frac{k_{21}}{k_{30}}\exp\left(\frac{\Delta G_{23}^{\neq}}{RT}\right) + \frac{k_{21}}{k_{30}+k_{34}}\exp\left(\frac{\Delta G_{23}}{RT}\right)\right]^{-1}, \qquad (12)$$

The relation between the free energy of activation $\Delta G_{23}^{\neq}$ and the change in free energy of electron transfer ΔG_{23} is established by means of the correlation[299]

$$\Delta G_{23}^{\neq} = \frac{\Delta G_{23}}{2} + \left[\left(\frac{\Delta G_{23}}{2}\right)^2 + (\Delta G_{23}^{\neq}(0))^2\right]^{1/2} \qquad (13)$$

in which $\Delta G_{23}^{\neq}(0)$ is the free energy of activation when $\Delta G_{23} = 0$. It follows from (12) and (13) that k_q is independent of ΔG_{23} for exothermic reactions ($\Delta G_{23} < 0$), whereas $\ln k_q$ decreases linearly with increase in ΔG_{23} for endothermic reactions ($\Delta G_{23} > 0$). Good agreement has been found between the experimental and the calculated dependence of k_q on ΔG_{23} over wide ranges of the latter for Thionine[185,300], Methylene Blue[189,220], eosin[255], Acridine Orange[194,301] and its 10-methyl derivative[194], and *o*-methylfluorescein methyl ester[185], which confirms the electron-transfer mechanism of quenching of the triplet state.

Electron transfer can occur in both singlet excited and triplet states. With dilute solutions and low concentrations of quenching additives it takes place solely in the triplet state. Evidence of involvement of this state of dye molecules in electron transfer is provided by quenching results and by kinetic analysis of its deactivation and the accumulation of radical-ions (or radicals), which are products of electron transfer[234]. The role of the triplet state has been demonstrated in one-electron oxidation and reduction reactions of Thionine[171,182–184,215,248], Methylene Blue[185–189,218,295], fluorescein[59,204,297], eosin[204,246], erythrosin[59], Safranine T,[172] phenosafranine[172], Oxonine[296], Acridine Orange[192–194], Rhodamine 6G,[116,123,124] polymethine dyes[131,181], etc.

Electron transfer can occur not only as a result of diffusional encounters of a triplet dye molecule with an unexcited partner molecule (exogenous electron donor or acceptor) but also in the absence of foreign donor or acceptor molecules. In the latter case the partner may be another triplet molecule [triplet–triplet interactions (8)] or an unexcited molecule of the same dye [triplet–singlet interaction (11)]. Electron transfer by reactions (8) and (11) has been established for fluorescein[204], eosin[204], Rhodamine 6G,[116,123,124], and thiazine[187,204] and polymethine[131 222] dyes.

3. Other Reactions

Proton phototransfer involving dye molecules has been considerably less studied. The acid–base properties in both ground and electronically excited states are characterised by the protolytic equilibrium exponent pK. Values of $pK_{S_0,T}$ in ground and triplet states are usually determined from the pH dependence of the $S_0 \to S_n$ and $T_1 \to T_n$ absorption spectra, and those of pK_{S*} in the singlet excited state from that of the fluorescence spectra. Determinations of pK_{S_0}, pK_{S*}, and pK_T have been made on xanthen, thiazine, azine, and other dyes[59]. It follows from Table 9 that excitation of thiazine dye molecules to a triplet state appreciably facilitates proton addition to the cation with formation of the protonated form. Data on acid–base equilibrium constants for thiazine dyes and the relative proton affinities estimated therefrom for molecules in ground and triplet states are confirmed by calculations of the distribution of electron density for Thionine in ground, singlet excited, and triplet states[302]. These show that the basic properties of Thionine are significantly stronger in the triplet than in the unexcited state, with the singlet excited state occupying an intermediate position. A similar situation is found for other thiazine dyes.

Table 9. Acid–base equilibrium constants of dye molecules in ground, singlet excited, and triplet states[59].

Dye	pK_{S_0}	pK_{S^*}	pK_T
Fluorescein (monoanion)	6.7	—	7.0
Eosin (monoanion)	4.3	—	<4
Erythrosin (monoanion)	5	—	5
Thionine	−0.33	3.1	6.3
Methylene Blue	<1	—	6.7
Methylene Green	<1	—	7.5
New Methylene Blue	<1	—	7.5
Azure	<1	—	7.7
Safranine T	0.1	—	6
Phenosafranine	0	—	6

A substantial difference between pK_T and pK_{S_0} is observed also with azine dyes (Safranine T, phenosafranine). Their example also reveals a higher basicity of molecules in the triplet state than in the singlet states S_0 and S_1. However, the above rule does not hold for xanthen dye molecules: pK_T and pK_{S_0} have closely similar values (Table 9).

Laser excitation has been used[303] for the direct determination of kinetic parameters of proton transfer involving triplet Thionine. The rate constant is found to be close to the diffusion constant[303,304].

Among little investigated but important photoreactions of dyes is photodissociation. It has been shown for leuco-cyanides of triarylmethane dyes (Malachite Green, Brilliant Green) that a coloured form—the dye cation—appears on ultraviolet exposure of solutions in polar media[305,306]. From direct measurements of the rate of formation of the cation of Malachite Green[305] and data on the sensitised population of the triplet level of the leuco-cyanide of Brilliant Green[306] it is concluded that a singlet excited state is involved in photodissociation.

Photodissociation of the *p*-azido-derivative of Malachite Green has been studied in an alcohol–ether matrix at 77 and 300 K.[309] At the latter temperature the quantum efficiency

of the photoelimination of nitrogen increases from 0.001 to 0.1 with change in the exciting wavelength from 600 to below 350 nm. A predissociation mechanism of rupture of the nitrogen–nitrogen bond is regarded as the most probable.

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Thus laser techniques have permitted the investigation in dye molecules of many primary photoprocesses lasting as little as 10^{-12} s. The laws of photophysical and primary photochemical reactions established for dyes of various classes are common to many organic compounds and biologically active substances. Research on primary photoprocesses in dye molecules constitutes an important branch of photochemistry–molecular photonics.

REFERENCES

1. A.N.Terenin, "Fotonika Molekul Krasitelei i Rodstvennykh Organicheskikh Soedinenii" (Photonics of Molecules of Colorants and Related Organic Compounds), Nauka, Leningrad, 1967.
2. E.Sakor and D.Treves, IEEE J.Quant.Electron., 1977, 13, 962.
3. S.Mory, D.Leupold, and R.König, Opt.Comm., 1972, 6, 394.
4. G.Dolan and C.R.Goldschmidt, Chem.Phys.Letters, 1976, **39**, 320.
5. A.V.Aristov and V.S.Shevandin, Optika i Spektrosk., 1977, **42**, 201.
6. A.N.Rubinov, B.A.Bushuk, and A.P.Stupak, Acta Phys.et Chem.Szeged., 1978, **24**, 391.
7. O.Teschke and A.Dienes, Appl.Phys.Letters, 1975, **26**, 13.
8. M.D.Galanin and Z.A.Chizhikova, Optika i Spektrosk., 1973, **34**, 197.
9. A.Müller and E.Pflüger, Chem.Phys.Letters, 1968, 2, 155.
10. B.Voight, R.Menzel, D.Leupold, and R.König, Opt.Comm., 1973, 9, 274.
11. J.-P.Fouassier, D.-J.Lougnot, and J.Faure, Chem. Phys.Letters, 1975, **35**, 189.
12. T.Kobayashi and S.Nagakura, Chem.Phys., 1977, **23**, 153.
13. H.Tashiro and T.Yajima, Chem.Phys.Letters, 1974, **25**, 582.
14. J.Faure, J.-P.Fouassier, and D.-J.Lougnot, Phys. Letters, 1974, **A50**, 319.
15. J.Shah and R.F.Leheny, Appl.Phys.Letters, 1974, **24**, 562.
16. D.A.Cremers and M.W.Windsor, Chem.Phys.Letters, 1980, **71**, 27.
17. E.Sahar and I.Wieder, Chem.Phys.Letters, 1973, **23**, 518.
18. P.M.Rentzepis, M.R.Topp, R.P.Jones, and J.Jortner, Phys.Rev.Letters, 1970, **25**, 1742.
19. D.Ricard, W.H.Lowdermilk, and J.Ducuing, Chem. Phys.Letters, 1972, **16**, 617.
20. G.Mourou and M.M.Malley, Chem.Phys.Letters, 1975, **32**, 476.
21. A.Penzkofer , W.Falkenstein, and W.Kaiser, Chem. Phys.Letters, 1976, **44**, 82.
22. A.Penzkofer and W.Falkenstein, Chem.Phys.Letters, 1976, **44**, 547.
23. B.Kapainsky and W.Kaiser, Opt.Comm., 1978, **26**, 219.
24. L.D.Dergacheva and V.A.Petukhov, Optika i Spektrosk., 1978, **45**, 891.
25. D.Ricard, J.Chem.Phys., 1975, **63**, 3841.
26. S.F.Fischer and E.W.Schlag, Chem.Phys.Letters, 1969, **4**, 333.
27. C.J.Werkhoven, T.Deinum, J.Langlaar, P.H.Rettschniek, and J.D.W.Van Woorst, Chem.Phys.Letters, 1975, **30**, 504.
28. G.Porter, E.S.Reid, and C.J.Tredwell, Chem.Phys. Letters, 1974, **29**, 469.
29. T.J.Chuang and K.B.Eisenthal, Chem.Phys.Letters, 1971, **11**, 368.
30. G.Mourou, B.Drouin, M.Bergeron, and M.M.Dekariez-Roberge, IEEE J.Quant.Electron., 1973, **9**, 745.
31. K.B.Eisenthal, Acc.Chem.Res., 1975, **8**, 118.
32. A.Heiss, F.Dörr, and I.Kühn, Ber.Bunsenges.phys. Chem., 1975, **79**, 294.
33. D.W.Phillion, D.J.Kuizenga, and A.E.Siegman, Appl. Phys.Letters, 1975, **27**, 85.
34. H.Inomata and T.Igarashi, Japan J.Appl.Phys., 1976, **15**, 669.
35. G.R.Fleming, A.E.W.Knight, J.M.Morris, R.J.Robbins, and G.W.Robinson, Chem.Phys.Letters, 1977, **49**, 1.
36. G.Porter, P.J.Sadkowski, and C.J.Tredwell, Chem. Phys.Letters, 1977, **49**, 416.
37. K.G.Spears and L.E.Cramer, Chem.Phys., 1978, **30**, 1.
38. A.N.Rubinov, B.A.Bushuk, A.P.Stupak, and D.Schubert, Zhur.Prikl.Spektrosk., 1979, **31**, 246.
39. T.Gillbro and V.Sundström, Chem.Phys.Letters, 1980, **74**, 188.
40. K.A.Selanger, J.Falnes, and T.Sikkeland, J.Phys. Chem., 1977, **81**, 1960.
41. P.Peretti, P.Parson, and R.Dupearat, Compt.rend., 1970, **270B**, 710.
42. E.N.Viktorova and I.A.Gofman, Zhur.Fiz.Khim., 1965, **39**, 2643 [Russ.J.Phys.Chem., 1965(11)].
43. R.E.Lessing, E.Lippert, and W.Rapp, Chem.Phys. Letters, 1970, 7, 247.
44. V.V.Arsen'ev, V.A.Gavanin, V.Z.Pashchenko, S.P.Protasov, L.B.Rubin, and A.B.Rubin, Zhur. Prikl.Spektrosk., 1973, **18**, 1093.
45. W.Lahmann and H.J.Ludewig, Chem.Phys.Letters, 1977, **45**, 117.
46. V.K.Runov, A.P.Golovina, L.P.Savvina, and I.P.Alimarin, Vestnik Moskov.Univ., Khim., 1974, **15**, 378.
47. P.J.Sadkowski and G.R.Fleming, Chem.Phys.Letters, 1978, **57**, 526.
48. J.Ferguson and A.W.H.Man, Austral.J.Chem., 1973, **26**, 1617.
49. H.R.Stadelmann, J.Luminescence, 1970, **3**, 143.
50. R.A.Velapoldi, J.Res.Natl.Bur.Stad., 1972, **76A**, 642.
51. G.Guvot, R.Arnaud, and J.Lemaire, J.Chim.phys. Phys.-chim.biol., 1975, **72**, 647.
52. M.M.Martin and L.Lindqvist, J.Luminescence, 1975, **10**, 381.
53. P.G.Bowers and G.Porter, Proc.Roy.Soc., 1967, **A299**, 348.
54. G.R.Fleming, A.W.E.Knight, J.M.Morris, R.J.S.Morrison, and G.W.Robinson, J.Amer.Chem. Soc., 1977, **99**, 4306.
55. G.Mourou and M.M.Malley, Opt.Comm., 1974, **11**, 282.
56. H.Al-Obaidi and G.A.Olderskaw, J.Photochem., 1976, **6**, 153.
57. W.Yu, F.Pollegrino, M.Grant, and R.R.Alfano, J.Chem.Phys., 1977, **67**, 1766.

58. V.V.Danilov, Yu.T.Mazurenko, and S.I.Vorontsova, Opt.Comm., 1973, **9**, 283.
59. A.K.Chibisov, Khim.Vysok.Energii, 1976, **10**, 3.
60. M.Nemoto, H.Kokubun, and M.Koizumi, Bull.Chem. Soc.Japan, 1969, **42**, 1223, 2464.
61. B.Soep, A.Kellmann, M.Martin, and L.Lindqvist, Chem.Phys.Letters, 1972, **13**, 241.
62. P.Wirth, S.Schneider, and E.Dörr, Ber.Bunsenges. phys.Chem., 1977, **81**, 1127.
63. E.P.Ippen, C.V.Shank, and A.Bergman, Chem.Phys. Letters, 1976, **38**, 611.
64. G.Maucke, M.Erler, R.Paetgold, A.B.Demyashkevich, and M.G.Kuz'min, Vestnik Moskov.Univ., Khim., 1976, **17**, 190.
65. T.Karstens, K.Kobs, R.Memming, and F.Schröppel, Chem.Phys.Letters, 1977, **48**, 540.
66. G.M.Wyman and B.M.Zarnegar, J.Phys.Chem., 1973, **77**, 831.
67. W.Windhager, S.Schneider, and F.Dörr, Z.Naturforsch., 1977, **32a**, 876.
68. J.H.Richardson, L.L.Steinmetz, S.B.Deutscher, W.A.Bookless, and W.L.Schmelzinger, Z.Naturforsch., 1978, **33a**, 1592.
69. S.L.Shapiro and K.R.Winn, Chem.Phys.Letters, 1980, **71**, 440.
70. J.-C.Mialoco, J.Jaraudias, and P.Goujon, Chem. Phys.Letters, 1977, **47**, 123.
71. A.T.Eske and K.Razi Naqvi, Chem.Phys.Letters, 1979, **63**, 128.
72. H.Paerschke, K.-E.Süsse, D.-G.Welsch, and M.Süsse, Chem.Phys.Letters, 1979, **66**, 376.
73. C.J.Tredwell and C.M.Keary, Chem.Phys., 1979, **43**, 307.
74. H.Tashiro and T.Yajema, Chem.Phys.Letters, 1976, **42**, 553.
75. S.A.Batishche and V.A.Mostovnikov, Izv.Akad.Nauk SSSR, Ser.Fiz., 1975, **39**, 2254.
76. J.-P.Fouassier, D.-J.Lougnot, and J.Faure, Chem. Phys.Letters, 1975, **30**, 448.
77. D.N.Dempster, T.Morrow, R.Rankin, and G.F.Thompson, Chem.Phys.Letters, 1973, **18**, 488.
78. K.Razi Naqvi, D.K.Sharma, and G.J.Hoytink, Chem.Phys.Letters, 1973, **22**, 222.
79. A.M.Bonch-Bruevich, I.N.Zatsepina, T.K.Razumova, G.M.Rubanova, I.F.Tupitsyn, and V.N.Shuvalova, Optika i Spektrosk., 1970, **28**, 100.
80. D.N.Dempster, T.Morrow, R.Rankin, and G.F.Thompson, J.Chem.Soc., Faraday Trans.II, 1972, **68**, 1479.
81. J.Jaraudias, P.Goujou, and J.C.Mialoco, Chem. Phys.Letters, 1977, **45**, 107.
82. E.G.Arthurs, D.J.Bradley, and A.G.Roddie, Chem. Phys.Letters, 1973, **22**, 230.
83. D.Madge and M.W.Windsor, Chem.Phys.Letters, 1974, **27**, 31.
84. J.-C.Mialoco, A.W.Boyd, J.Jaraudias, and J.Sutton, Chem.Phys.Letters, 1976, **37**, 236.
85. F.-J.Theiss and J.Weber, Opt.Comm., 1974, **12**, 368.
86. A.V.Aristov and E.N.Viktorova, Izv.Akad.Nauk SSSR, Ser.Fiz., 1970, **34**, 645.
87. J.Knof, F.-J.Theiss, and J.Weber, Opt.Comm., 1976, **17**, 264.
88. R.R.Alfano, S.L.Shapiro, and W.Yu, Opt.Comm., 1973, **7**, 191.
89. E.Lehoczki, E.Balint, J.Hevesi, and E.Bor, Zhur. Prikl.Spektrosk., 1973, **19**, 68.
90. M.I.Snegov, I.I.Reznikova, and A.S.Cherkasov, Optika i Spektrosk.,1974, **36**, 96.
91. L.E.Cramer and K.G.Spears, J.Amer.Chem.Soc., 1978, **100**, 221.
92. L.D.Dergacheva, V.A.Petukhov, and E.G.Trenev, Optika i Spektrosk., 1976, **41**, 971.
93. R.N.Nurmukhametov, "Pogloshchenie i Lyuminestsentsiya Aromaticheskikh Soedinenii" (Absorption and Luminescence of Aromatic Compounds), Khimiya, Moscow, 1971.
94. I.A.Gofman, Zhur.Prikl.Spektrosk., 1970, **13**, 1011.
95. M.I.Snegov and A.S.Cherkasov, Izv.Akad.Nauk SSSR, Ser.Fiz., 1975, **39**, 2249.
96. I.Kecskemeti, L.Kozma, and E.Farkas, Zhur.Prikl. Khim., 1972, **17**, 59.
97. K.H.Drezhage, Laser Focus, 1973, **9**, 35.
98. M.M.Martin, Chem.Phys.Letters, 1975, **35**, 105.
99. M.M.Martin, Chem.Phys.Letters, 1976, **43**, 332.
100. M.M.Martin and L.Lindqvist, Chem.Phys.Letters, 1973, **22**, 309.
101. V.A.Mostovnikov, A.N.Rubinov, M.A.Al'perovich, V.I.Avdeeva, I.I.Levkoev, and M.M.Loikov, Zhur. Prikl.Spektrosk., 1974, **20**, 42.
102. V.A.Kuz'min, A.P.Darmanyan, N.I.Shirokova, M.A.Al'perovich, and I.I.Levkoev, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 581.
103. M.D.Galanin and Z.A.Chizhikova, Izv.Akad.Nauk SSSR, Ser.Fiz., 1972, **36**, 941.
104. G.C.Orner and M.R.Topp, Chem.Phys.Letters, 1975, **36**, 295.
105. V.L.Bogdanov, V.P.Klochkov, and B.S.Neporent, Optika i Spektrosk., 1977, **43**, 1184.
106. V.L.Bogdanov and V.P.Klochkov, Optika i Spektrosk., 1978, **44**, 707.
107. A.V.Aristov and V.S.Shevandin, Optika i Spektrosk., 1978, **44**, 473.
108. I.Kaplan and J.Jortner, Chem.Phys., 1978, **32**, 381.
109. A.V.Aristov and V.S.Shevandin, Optika i Spektrosk., 1978, **45**, 1015.
110. D.F.O'Brien, T.M.Kelly, and L.F.Costa, Photogr. Science Engineer., 1974, **18**, 76.
111. N.I.Kunavin, Candidate's Thesis, Karpov Physicochemical Scientific Research Institute, Moscow, 1979.
112. T.Förster and G.Hoffmann, Z.phys.Chem.(Frankfurt), 1971, **75**, 63.
113. A.V.Aristov, M.B.Levin, and A.S.Cherkasov, Optika i Spektrosk., 1977, **43**, 1067.
114. D.N.Dempster, T.Morrow, and M.F.Quinn, J.Photochem., 1973–74, **2**, 343.
115. A.V.Aristov and Yu.S.Maslyukov, Izv.Akad.Nauk SSSR, Ser.Fiz., 1978, **42**, 524.
116. V.E.Korobov and A.K.Chibisov, Khim.Vysok. Energii, 1976, **10**, 177.
117. N.I.Kunavin and R.N.Nurmukhametov, Zhur.Prikl. Spektrosk., 1977, **26**, 1120.
118. M.Yamashita, A.Kuniyasu, and H.Kashiwagi, J.Chem. Phys., 1977, **66**, 986.
119. A.K.Chibisov, H.A.Kezle, L.V.Levshin, and T.D.Slavnova, Chem.Comm., 1972, 1292.
120. G.A.Ketsle, L.V.Levshin, T.D.Slavnova, and A.K.Chibisov, Izv.Akad.Nauk SSSR, Ser.Fiz., 1972, **36**, 1078.
121. V.E.Korobov and A.K.Chibisov, Optika i Spektrosk., 1975, **38**, 1221.
122. V.E.Korobov and A.K.Chibisov, Zhur.Prikl. Spektrosk., 1976, **24**, 28.
123. V.E.Korobov, V.V.Shubin, and A.K.Chibisov, Chem. Phys.Letters, 1977, **45**, 498.
124. V.E.Korobov and A.K.Chibisov, J.Photochem., 1978, **9**, 411.

125. G.A.Ketsle, L.V.Levshin, and V.V.Bryukhanov, Zhur.Prikl.Spektrosk., 1976, **24**, 809.
126. H.E.Lessing, J.A.von Jena, and M.Reichert, Chem. Phys.Letters, 1976, **42**, 218.
127. A.K.Chibisov and G.P.Roitman, Zhur.Prikl. Spektrosk., 1972, **17**, 443.
128. M.Nemoto, H.Kokubun, and M.Koizumi, Chem.Comm., 1969, 1095.
129. M.D.Archer, I.C.Ferreira, G.Porter, and G.Tredwell, Nouv.J.Chim., 1977, **1**, 9.
130. M.Arvis and J.-C.Mialoco, J.Chem.Soc., Faraday Trans.II, 1979, **75**, 415.
131. A.K.Chibisov, J.Photochem., 1977, **6**, 199.
132. V.A.Kuzmin and A.P.Darmanyan, Chem.Phys.Letters, 1978, **54**, 159.
133. Yu.I.Lifanov, V.A.Kuz'min, A.K.Chibisov, and I.I.Levkoev, Khim.Vysok.Energii, 1973, **7**, 321.
134. Yu.I.Lifanov, V.A.Kuz'min, A.K.Chibisov, I.I.Levkoev, and A.V.Karyakin, Zhur.Prikl. Spektrosk.,1974, **20**, 221.
135. J.P.Webb, W.C.McColgin, O.G.Peterson, D.L.Stockman, and J.H.Eberly, J.Chem.Phys., 1970, **53**, 4227.
136. N.A.Borisevich, V.V.Gruzinskii, and S.V.Davydov, Kvant.Elektron., 1974, 1717.
137. G.A.Ketsle, L.V.Levshin, T.D.Slavnova, and A.K.Chibisov, Dokl.Akad.Nauk SSSR, 1971, **201**, 60.
138. O.M.Petsol'd, I.M.Byteva, and G.P.Gurinovich, Optika i Spektrosk., 1973, **34**, 599.
139. A.K.Chibisov, G.A.Ketsle, L.V.Levshin, and T.D.Slavnova, Optika i Spektrosk., 1975, **38**, 83.
140. V.L.Pugachev, T.D.Slavnova, A.K.Chibisov, A.V.Karyakin, and V.E.Korobov, Izv.Akad.Nauk SSSR, Ser.Fiz., 1975, **39**, 2363.
141. K.K.Rohatgi-Mukherjee and A.K.Mukhopadhyay, Indian J.Pure Appl.Phys., 1976, **14**, 481.
142. U.Satmanta and K.K.Rohatgi-Mukherjee, Indian J. Chem, 1978, **16A**, 729.
143. H.Sato, Y.Kusumoto, N.Nakashima, and K.Yoshihara, Chem.Phys.Letters, 1980, **71**, 326.
144. G.Porter and C.J.Tredwell, Chem.Phys.Letters, 1978, **56**, 278.
145. D.Rehm and K.B.Eisenthal, Chem.Phys.Letters, 1971, **9**, 387.
146. K.B.Eisenthal, in "Ultrashort Light Pulses" (Translated into Russian), Mir, Moscow, 1981, p.350.
147. T.A.Shakhverdov, Optika i Spektrosk., 1975, **38**, 1228.
148. V.L.Ermolaev, E.B.Sveshnikova, and T.A.Shakhverdov, Uspekhi Khim., 1976, **45**, 1753 [Russ.Chem. Rev., 1976(10)].
149. T.L.Osif, N.N.Lichtin, M.Z.Hoffman, and S.Ray, J.Phys.Chem., 1980, **84**, 410.
150. C.Bojarski, J.Kusba, and G.Obermüller, Z.Naturforsch., 1971, **26a**, 255.
151. L.V.Levshin, E.Yu.Bekhli, T.D.Slavnova, and V.I.Yuzhakov, Optika i Spektrosk., 1974, **36**, 503.
152. N.R.Senatorova, L.V.Levshin, and B.D.Ryzhikov, Zhur.Prikl.Spektrosk., 1979, **30**, 658.
153. M.I.Snegov and A.S.Cherkasov, Optika i Spektrosk., 1971, **31**, 835.
154. J.Olmsted, Chem.Phys.Letters, 1974, **26**, 33.
155. E.Vogelmann and H.E.A.Kramer, Photochem.Photobiol., 1976, **24**, 595.
156. A.N.Rubinov, B.A.Bushuk, and A.P.Stupak, Izv. Akad.Nauk SSSR, Ser.Fiz., 1978, **42**, 2584.
157. T.Nagabhushanam, K.T.Joseph, and M.Sautappa, Indian J.Chem., 1974, **12**, 1205.
158. K.Teuchner, B.Bornowski, W.Becker, and S.Dähne, Z.Chem., 1976, **16**, 449.
159. F.Fink, E.Klose, and S.Dähne, Chem.Phys.Letters, 1977, **45**, 548.
160. J.Knof, F.-J.Theiss, and J.Weber, Z.Naturforsch., 1978, **33a**, 98.
161. D.Möblus, Ber.Bunsenges.phys.Chem., 1978, **82**, 867.
162. W.Cooper and N.B.Liebert, Photogr.Science Engineer., 1972, **16**, 25.
163. J.T.Knudtson and E.M.Eyring, J.Phys.Chem., 1974, **78**, 2355.
164. A.K.Chibisov, Uspekhi Khim., 1970, **39**, 1886 [Russ. Chem.Rev., 1970(10)].
165. S.P.McGlynn, T.Azumi, and M.Kinoshita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Mir, Moscow, 1972.
166. F.R.Antonucci and L.G.Tolley, J.Phys.Chem., 1973, **77**, 2712.
167. A.P.Marchett, J.F.Landry, and D.S.Tinti, J.Chem. Phys., 1974, **61**, 1086.
168. R.A.Pierce and R.A.Berg, J.Chem.Phys., 1972, **56**, 5087.
169. I.H.Leaver, Photochem.Photobiol., 1974, **19**, 309.
170. H.Schmidt, Photochem.Photobiol., 1970, **11**, 17.
171. E.Vogelmann, H.Schmidt, U.Steiner, and H.E.A.Kramer, Z.phys.Chem.(Frankfurt), 1975, **94**, 101.
172. A.K.Chibisov and A.V.Karyakin, in "Molekulyarnaya Fotonika" (Molecular Photonics), Nauka, Leningrad, 1970, p.231.
173. I.V.Antonov, V.E.Korobov, V.S.Prokudin, and A.V.Chibisov, Zhur.Prikl.Spektrosk., 1972, **17**, 170.
174. V.A.Kuznetsov, K.A.Kostylev, and V.N.Shamraev, Zhur.Prikl.Spektrosk., 1980, **32**, 493.
175. A.P.Darmanyan and V.A.Kuz'min, Dokl.Akad.Nauk SSSR, 1976, **227**, 1139.
176. J.-P.Fouassier, D.-J.Lougnot, and J.Faure, Opt. Comm., 1976, **18**, 263.
177. A.M.Bonch-Bruevich, T.K.Razumova, and G.M.Rubinova, Optika i Spektrosk., 1973, **35**, 832.
178. V.A.Kuz'min, Yu.E.Borisevich, G.G.Duadyusha, and F.A.Mikhailenko, Dokl.Akad.Nauk SSSR, 1976, **229**, 131.
179. L.A.Shvedova, A.S.Tatikolov, S.M.Makin, N.I.Romanov, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 749.
180. A.K.Chibisov, V.A.Kuz'min, G.P.Roitman, I.I.Levkoev, and A.V.Karyakin, Izv.Akad.Nauk SSSR, Ser.Fiz., 1970, **34**, 1288.
181. Yu.I.Lifanov, V.E.Korobov, A.V.Karyakin, and A.K.Chibisov, Khim.Vysok.Energii, 1975, **9**, 265.
182. E.Vogelmann and H.E.A.Kramer, Photochem. Photobiol., 1976, **23**, 383.
183. M.I.C.Ferreira and A.Harriman, J.Chem.Soc., Faraday Trans.I, 1977, **73**, 1085.
184. U.Steiner, G.Winter, and H.E.A.Kramer, J.Phys. Chem., 1977, **81**, 1104.
185. S.-I.Tamura, K.Kikuchi, and H.Kokubun, Z.phys. Chem.(Frankfurt), 1978, 111, 7.
186. A.K.Chibisov, G.P.Roitman, and A.V.Karyakin, Khim.Vysok.Energii, 1970, **4**, 273.
187. G.P.Roitman and A.K.Chibisov, Teor.Eksper.Khim., 1971, **7**, 54.
188. P.D.Wildes, N.N.Lichtin, M.Z.Hoffman, L.Andrews, and H.Linschitz, Photochem.Photobiol., 1977, **25**, 21.
189. K.Kikuchi, S.-I.Tamura, C.Iwanoga, and H.Kokubun, Z.phys.Chem.(Frankfurt), 1977, **106**, 17.

190. T.Ohno, T.L.Osif, and N.N.Lichtin, Photochem. Photobiol., 1979, **30**, 541.
191. L.N.Rugalov, A.V.Karyakin, and A.K.Chibisov, Teor.Eksper.Khim., 1972, **8**, 391.
192. A.Kellmann, Photochem.Photobiol., 1971, **14**, 85.
193. A.Kellmann and Y.Lion, Photochem.Photobiol., 1979, **29**, 217.
194. E.Vogelmann, W.Rauscher, and H.E.A.Kramer, Photochem.Photobiol., 1979, **29**, 776.
195. T.Karstens, K.Kobs, and R.Memming, Ber. Bunsenges.phys.Chem., 1979, **83**, 504.
196. K.-H.Grellmann and P.Hentzchel, Chem.Phys.Letters, 1978, **53**, 545.
197. P.Crozet, Chem.Phys.Letters, 1974, **25**, 114.
198. B.R.Henry and E.A.Lawler, J.Mol.Spectrosc., 1973, **48**, 117.
199. D.N.Dempster, T.Morrow, and M.F.Quinn, J.Photochem., 1974, **2**, 329.
200. C.A.Parker, "Photoluminescence of Solutions" (Translated into Russian), Mir, Moscow, 1972.
201. R.W.Chambers and D.R.Kearns, Photochem.Photobiol., 1969, **10**, 215.
202. M.Yamashita, H.Okeda, and H.Kashiwagi, J.Chem. Phys., 1975, **63**, 1127.
203. N.I.Kunavin, R.N.Nurmukhametov, and T.G.Khachaturova, Zhur.Prikl.Spektrosk., 1977, **26**, 1023.
204. M.Koizumi and Y.Usui, Mol.Photochem., 1972, **4**, 57.
205. T.Akiyama, M.Kamiya, and Y.Akahori, Bull.Chem. Soc.Japan, 1975, **48**, 1033.
206. L.I.Grossweiner and A.G.Kepka, Photochem. Photobiol., 1972, **16**, 305.
207. K.Kikuchi, H.Kokubun, and M.Koizumi, Bull.Chem. Soc.Japan, 1970, **43**, 2732.
208. V.A.Kuznetsov, N.N.Kunavin, and V.N.Shamraev, Zhur.Prikl.Spektrosk., 1974, **20**, 800.
209. V.V.Bryukhanov, G.A.Ketsle, and L.V.Levshin, Optika i Spektrosk., 1978, **44**, 392.
210. V.V.Bryukhanov, G.A.Ketsle, and L.V.Levshin, Zhur.Prikl.Spektrosk., 1978, **28**, 262.
211. G.A.Ketsle, L.V.Levshin, and Yu.A.Soinikov, Izv. Akad.Nauk SSSR, Ser.Fiz., 1975, **39**, 1840.
212. V.V.Bryukhanov, L.V.Levshin, and G.A.Ketsle, Zhur.Prikl.Spektrosk., 1977, **27**, 66.
213. Yu.A.Soinikov, G.A.Ketsle, and L.V.Levshin, Zhur. Prikl.Spektrosk., 1979, **30**, 446.
214. H.E.A.Kramer, Z.phys.Chem., 1969, **66**, 73.
215. H.E.A.Kramer and A.Maute, Photochem.Photobiol., 1972, **15**, 7.
216. H.E.A.Kramer, M.Hafner, and M.Zügel, Z.phys. Chem., 1969, **65**, 276.
217. J.Joussot-Dubien, R.Bonneau, P.Fordier de Violet, R.Koussini, and R.Lapouyde, Pure Appl.Chem., 1979, **51**, 271.
218. A.Knowles and S.Gurnani, Photochem.Photobiol., 1972, **16**, 95.
219. R.Nilsson, P.B.Merkel, and D.R.Kearns, Photochem. Photobiol., 1972, **16**, 109.
220. T.Ohno and N.N.Lichtin, J.Amer.Chem.Soc., 1980, **102**, 4636.
221. V.L.Pugachev, A.V.Karyakin, and A.K.Chibisov, Zhur.Prikl.Spektrosk., 1974, **21**, 481.
222. Yu.I.Lifanov and A.K.Chibisov, Khim.Vysok.Energii, 1974, **8**, 418.
223. R.A.Pierce and R.A.Berg, J.Chem.Phys., 1969, **51**, 1267.
224. A.K.Chibisov, V.A.Kuz'min, and Yu.I.Lifanov, Optika i Spektrosk., 1974, **36**, 919.
225. V.A.Kuzmin, A.S.Tatikolov, and Yu.E.Borisevich, Chem.Phys.Letters, 1978, **53**, 52.
226. A.M.Bonch-Bruevich, T.K.Razumova, and G.M.Rubanova, Optika i Spektrosk., 1973, **34**, 305.
227. A.D.Kirsch and G.M.Wyman, J.Phys.Chem., 1975, **79**, 543.
228. A.Kellmann, Photochem.Photobiol., 1974, **20**, 103.
229. V.V.Bryukhanov, G.A.Ketsle, L.V.Levshin, and B.F.Minaev, Optika i Spektrosk., 1978, **45**, 1090.
230. R.N.Nurmukhametov, N.I.Kunavin, and G.T.Khachaturova, Izv.Akad.Nauk SSSR, Ser.Fiz., 1978, **42**, 517.
231. J.-Ph.Grivet, Chem.Phys.Letters, 1971, **11**, 267.
232. M.Yamashita and H.Kashiwagi, Japan J.Appl.Phys., 1975, **14**, 421.
233. V.L.Ermolaev, in "Elementarnye Fotoprotsessy v Molekulakh" (Primary Photoprocesses in Molecules), Nauka, Moscow and Leningrad, 1966, p.147.
234. A.K.Chibisov, Uspkhi Khim., 1981, **50**, 1169 [Russ. Chem.Rev., 1981(7)].
235. K.Kikuchi, H.Kokubun, and M.Koizumi, Bull.Chem. Soc.Japan, 1971, **44**, 1527.
236. J.B.Birks, "Photophysics of Aromatic Molecules", Wiley Intersci., New York, 1970.
237. V.L.Ermolaev, E.N.Bodunov, E.B.Sveshnikova, and T.A.Shekhverdov, "Bezizluchatel'nyi Perenos Energii Elektronnogo Vozbuzhdeniya" (Non-radiative Transfer of Electronic Excitation Energy), Nauka, Leningrad, 1977, p.311.
238. G.Porter and F.Wilkinson, Proc.Roy.Soc., 1961, **A264**, 1.
239. V.Balzani, F.Bolletta, and F.Scandola, J.Amer.Chem. Soc., 1980, **102**, 2152.
240. K.S.Marshall and F.Wilkinson, Z.phys.Chem.(Frankfurt), 1976, **101**, 67.
241. T.N.Smol'skaya, A.N.Rubinov, and M.M.Asimov, Optika i Spektrosk., 1973, **34**, 410.
242. F.P.Schäfer and L.Ringwelski, Z.Naturforsch., 1973, **20a**, 792.
243. H.Fischer, H.E.A.Kramer, and A.Maute, Z.phys. Chem.(Frankfurt), 1970, **69**, 113.
244. A.V.Aristov and Yu.S.Maslyukov, Optika i Spektrosk., 1973, **35**, 1138.
245. G.Prell and V.Zanker, Ber.Bunsenges.phys.Chem., 1972, **76**, 39.
246. A.G.Kepke and L.I.Grossweiner, Photochem.Photobiol., 1971, **14**, 621.
247. I.Kraljic and L.Lindqvist, Photochem.Photobiol., 1974, **20**, 351.
248. U.Steiner, G.Winter, and H.E.A.Kramer, Z.Naturforsch., 1976, **13a**, 1019.
249. V.S.Srinivasan, D.Podolski, N.J.Westriek, and N.Neckers, J.Amer.Chem.Soc., 1978, **100**, 6513.
250. V.V.Bryukhanov, G.A.Ketsle, and L.V.Levshin, Izv.Akad.Nauk SSSR, Ser.Fiz., 1978, **42**, 393.
251. V.V.Bryukhanov, G.A.Ketsle, and L.V.Levshin, Zhur.Prikl.Spektrosk., 1978, **28**, 741.
252. A.K.Chibisov, G.A.Ketsle, L.V.Levshin, and T.D.Slavnova, Optika i Spektrosk., 1975, **38**, 83.
253. V.L.Pugachev, T.D.Slavnova, and A.K.Chibisov, Khim.Vysok.Energii, 1977, **11**, 355.
254. A.K.Chibisov and T.D.Slavnova, J.Photochem., 1978, **8**, 285.
255. G.V.Zakharova, Yu.I.Lifanov, and A.K.Chibisov, Khim.Vysok.Energii, 1981, **15**, 68.
256. T.A.Shakhverdov and Z.N.Turaeva, Izv.Akad.Nauk SSSR, Ser.Fiz., 1975, **39**, 1952.

257. T.A.Shakhverdov and Z.N.Turaeva, Optika i Spektrosk., 1976, 41, 1082.
258. T.A.Shakhverdov, S.S.Tibilov, Z.N.Turaeva, and R.Ergashev, Izv.Akad.Nauk SSSR, Ser.Fiz., 1978, 42, 399.
259. T.A.Shakhverdov, Z.N.Turaeva, V.L.Ermolaev, and N.Nizamov, Teor.Eksper.Khim., 1979, 15, 382.
260. T.A.Shakhverdov, Z.N.Turaeva, and N.Nizamov, Optika i Spektrosk., 1979, 47, 803.
261. V.L.Ermolaev, I.P.Kotlyar, Z.N.Turaeva, and T.A.Shakhverdov, Zhur.Prikl.Spektrosk., 1980, 32, 869.
262. G.Porter, in "Introduction to Photobiology", Prentice-Hall, Newark, N.J., 1969, p.1.
263. D.N.Dempster, T.Morrow, R.Rankin, and G.F.Thompson, J.Chem.Soc., Faraday Trans.II, 1972, 68, 1479.
264. Yu.I.Lifanov, V.A.Kuz'min, A.V.Karyakin, A.K.Chibisov, and I.I.Levkoev, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 787.
265. W.Cooper and K.A.Rome, J.Phys.Chem., 1974, 78, 16.
266. A.P.Darmanyan, V.A.Kuz'min, and Yu.E.Borisevich, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 349.
267. E.N.Kalitievskaya and T.K.Razumova, Optika i Spektrosk., 1977, 43, 671.
268. A.K.Chibisov, Teor.Eksper.Khim., 1966, 2, 825.
269. A.P.Darmanyan and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 587.
270. V.A.Kuz'min, A.M.Vinogradov, M.A.Al'perovich, and I.I.Levkoev, Dokl.Akad.Nauk SSSR, 1975, 224, 139.
271. J.-P.Fouassier, D.J.Lougnot, and J.Faure, Opt. Comm., 1977, 23, 393.
272. A.N.Rubinov, B.A.Bushuk, A.P.Stupak, and M.A.Al'perovich, Izv.Akad.Nauk SSSR, Ser.Fiz., 1978, 42, 554.
273. A.P.Darmanyan, V.A.Kuz'min, N.I.Romanov, and F.S.Babichev, Dokl.Akad.Nauk SSSR, 1976, 229, 1367.
274. V.A.Kuz'min, A.P.Darmanyan, and M.M.Kul'chitskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2392.
275. A.P.Darmanyan, V.A.Kuz'min, and L.M.Popova, 1978, 691.
276. O.V.Przhonskaya, Yu.L.Slonimskii, and E.A.Tikhonov, Izv.Akad.Nauk SSSR, Ser.Fiz., 1978, 42, 557.
277. A.M.Vinogradov, V.A.Kuz'min, M.A.Al'perovich, I.I.Levkoev, and I.I.Zil'berman, Dokl.Akad.Nauk SSSR, 1976, 227, 642.
278. A.M.Vinogradov and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2613.
279. G.G.Dyadyusha, A.A.Rykov, and Yu.L.Slonimskii, Teor.Eksper.Khim., 1977, 13, 539.
280. V.A.Kuz'min, Ya.N.Malkin, M.A.Al'perovich, and I.I.Levkoev, Dokl.Akad.Nauk SSSR, 1976, 227, 380.
281. V.A.Kuz'min, A.M.Vinogradov, N.N.Romanov, M.A.Al'perovich, I.I.Levkoev, and F.S.Babichev, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1864.
282. A.M.Vinogradov, V.A.Kuz'min, M.A.Al'perovich, N.N.Sveshnikov, and I.I.Levkoev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1497.
283. M.A.Mostoslavskii, V.V.Yadrikhinskii, and O.K.Yadrikhinskaya, Zhur.Fiz.Khim., 1970, 44, 2979 [Russ.J.Phys.Chem., 1970(12)].
284. Z.V.Zhidkova, Zhur.Prikl.Spektrosk., 1975, 22, 861.
285. D.L.Ross, Appl.Opt., 1971, 10, 571.
286. G.M.Wyman, B.M.Zarnegar, and D.G.Whitten, J.Phys.Chem., 1973, 77, 2584.
287. A.D.Kirsch and G.M.Wyman, J.Phys.Chem., 1977, 81, 413.
288. W.G.Herkstroeter, Mol.Photochem., 1971, 3, 181.
289. W.G.Herkstroeter, J.Amer.Chem.Soc., 1973, 95, 8686.
290. W.G.Herkstroeter, J.Amer.Chem.Soc., 1976, 98, 6210.
291. V.A.Kuz'min, A.M.Vinogradov, M.A.Al'perovich, and I.I.Levkoev, Khim.Vysok.Energii, 1977, 11, 38.
292. A.K.Chibisov, L.N.Rygalov, Yu.M.Dedkov, A.V.Karyakin, and A.N.Ermakov, Zhur.Prikl. Spektrosk., 1971, 14, 826.
293. G.Köhler, S.Solar, and N.Getoff, Z.Naturforsch., 1980, 35a, 1201.
294. A.J.Frank, J.W.Otvos, and M.Calvin, J.Phys.Chem., 1979, 83, 716.
295. R.H.Kayser and R.H.Young, Photochem.Photobiol., 1976, 24, 395.
296. R.Bonneau, Photochem.Photobiol., 1977, 25, 129.
297. U.Krüger and R.Memming, Ber.Bunsenges.phys. Chem., 1974, 78, 670.
298. U.Krüger and R.Memming, Ber.Bunsenges.phys., 1974, 78, 679.
299. D.Rehm and A.Weller, Ber.Bunsenges.phys.,1969, 73, 834.
300. E.Vogelmann, S.Schreiner, W.Rauscher, and H.E.A.Kramer, Z.phys.Chem.(Frankfurt), 1976, 101, 321.
301. E.Vogelmann, W.Rauscher, R.Traber, and H.E.Kramer, Z.phys.Chem.(Frankfurt), 1981, 124, 13.
302. U.Sommer and H.E.A.Kramer, Photochem.Photobiol., 1971, 13, 387.
303. R.Bonneau and R.D.S.Stevens, Chem.Phys.Letters, 1972, 13, 376.
304. G.M.Wyman, Chem.Comm., 1971, 1332.
305. R.G.Brown and J.Cosa, Chem.Phys.Letters, 1977, 45, 429.
306. M.W.Geiger, N.J.Turro, and W.H.Waddell, Photochem.Photobiol., 1977, 25, 15.
307. S.A.Krysanov and M.V.Alfimov, Chem.Phys.Letters, 1980, 76, 221.
308. S.A.Krysanov and M.V.Alfimov, Dokl.Akad.Nauk SSSR, 1981, 258, 665.
309. V.A.Smirnov, S.B.Brichkin, M.V.Alfimov, L.I.Tyltina, and L.F.Avramenko, Khim.Vysok. Energii, 1979, 79, 156.

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