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RADIATIONLESS INTERMOLECULAR ENERGY TRANSFER WITH PARTICIPATION OF ACCEPTOR EXCITED TRIPLET STATES

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Radiationless energy transfer between like and unlike molecules has been experimentally studied under conditions where acceptor molecules have been excited to the triplet state. Homogeneous singlet–triplet–triplet migration has been discovered in highly concentrated chlorophyll "a" and pheophytin "a" solutions in castor oil at 183 K by measuring the variation of pigment relative quantum yields of fluorescence and triplet state formation as a function of exciting pulse intensity. Heterogeneous singlet–triplet–triplet energy transfer has been observed in solid solutions of different complex organic molecules (perylene + phenanthrene, Na-fluorescein + chlorophyll "a", pyrene + Mg-phthalocyanine) as the fluorescent donor state quenching in the presence of acceptor triplet-excited molecules. Primary emphasis is placed on a direct observation of the effect of energy transfer on the excited-state lifetime of the donor. The benzophenone phosphorescence quenching (shortening of phosphorescence lifetime) in the presence of Mg-mesoporphyrin triplet molecules has been found to be caused by the heterogeneous triplet–triplet–triplet energy transfer. Good agreement of the theoretical and experimental results permits us to conclude that all types of observed transfer processes are described by the Förster–Galanin theory for dipole–dipole radiationless energy transfer with no additional assumptions.

1. Introduction

The majority of experimental investigations of the electronic excitation energy transfer (EEET) in solutions due to the inductive-resonance mechanism of Förster–Galanin [1,2] or electron-exchange interactions of Dexter [3] are devoted to study of electronic energy migration from the lowest electronically excited states of donor molecules (D) to the ground electronic state of acceptor molecules (A) [4,5]. The inductive-resonance theory of EEET is based on the assumption that the leading term in the interaction can be expressed in terms of the dipole-transition moments of D and A, and that the migration efficiency between interacting molecules depends essentially on the allowness of the electronic transitions in A. Provided that the acceptor electronic transition is allowed, the present EEET theories do not exclude the possibility of the participation of short living high-excited states of D and A in migration processes.

Direct evidence for the radiationless transfer from higher triplet levels of organic molecules to solvent molecules was first obtained by Alfimov and co-workers [6,7]. Later on these authors investigated systematically this phenomenon and analyzed the conditions determining efficiency of such a migration [8]. Recently the phenomenon of EEET from a highly excited singlet state of the donor to the singlet ground state of the acceptor was discovered in the crystal matrix [9] and in fluid solutions [10–12]. Kaplan and Jortner [10,11] have extended the Förster–Galanin analysis for the case of EEET from a thermally nonequilibrated vibronic manifold of the donor excited electronic state when the electronic relaxation rate overwhelmed the rate of vibrational relaxation. But in their experiments, the efficiency of the sensitized fluorescence of A (2.5 bis (5′-tertbutyl-2-benzoxazolyl) thiophen) as a result of EEET from D molecules (Rhodamine 6G) was very weak due to the low concentration of A ($< 10^{-4}$ M) and the high probability of back transfer. The most direct experimental evidence of energy transfer from highly excited states of D (9.10-bi-n-propylantracene) was obtained by Ermolaev with co-workers [12,13], who discovered the effective sensitized fluorescence of A (naphthalene), caused by using an intermediate acceptor, i.e. molecules of the solvent (toluene) at room temperature. The probability of such energy transfer was estimated to be 5×10^{12} s^{-1} [13].

For the past 10 years, the methods of nanosecond and picosecond laser spectroscopy permitted the kinetic regularities of EEET to be investigated and the experimental and theoretical results to be compared [14–16]. In some experiments utilizing very high excitation intensities, the interaction of excited states of the donor–acceptor pair was taken into consideration to explain some nonlinear optical effects which were observed under luminescence investigations. For example, the dependence of the luminescence quantum yield (B) and lifetime (τ) of plant objects on the laser pulse intensity [17–20] is explained by the existence of singlet–singlet annihilation and singlet–triplet fusion processes [21,22]. Such effects in which excited state singlets could also interact with one another (singlet–singlet annihilation) were well-documented in organic crystals [23] and in solution [24]. Though the processes with participation of excited states of D and A appear to offer a plausible explanation for the observed dependences of B and τ in vivo, the direct experimental investigation of such a phenomenon has not yet been done. In addition the discovered dependences of B and τ on the laser intensity may be due to the possible influence of stimulated processes (light quenching) which must also be taken into account.

The observation and study of the EEET regularities with participation of acceptor triplet excited molecules are of interest for serveral reasons. First, from the point of view of the luminescence quenching in concentrated solutions of dye and pigment molecules such transfer may be an additional reason for monomer emission quenching, in particular under intense light excitation. Secondly, because of the essential role of triplet molecules in the majority of photochemical reactions, such processes suggest important photochemical implications. For example, it may be a good method for governing the effectivity of some photochemical processes.

Knox et al. [25,26] predicted theoretically the possibility of the EEET by inductive resonance interactions between like molecules according to the scheme:

$$^1D^* + {}^3A^* \rightarrow {}^1D + {}^3A^{**}, \qquad {}^3A^{**} \rightarrow {}^3A^* + \text{heat}. \tag{1}$$

As noted in [26], such a mechanism of singlet–triplet interaction should be effective in concentrated chlorophyll solutions. But the experimental observation and the study of the regularity of this process in the system of like molecules (homogeneous singlet–triplet–triplet (S–T–T) migration) are very difficult due to the existence of some competing processes (photobleaching, triplet–triplet absorption, quenching of triplet states, etc.). In addition in such systems, it is necessary to taken into account the concentration quenching of luminescence and acceptor triplet molecule formation, which influence greatly the efficiency of homogeneous S–T–T EEET. For example, one- and two-laser excitation procedures were employed by Menzel [27,28] to investigate the possibility of S–T fusion in low concentration solution systems (2×10^{-4}–10^{-7} M) of chlorophyll “a” and metal-free phthalocyanine separately at 77 K and 293 K. Weak fluorescence quenching has been observed for both systems under investigation (about 8–10%), which has been attributed to the singlet–triplet fusion process. In spite of the fact that the experimental arrangement utilized in [28] was substantially improved, the inquiry of occurrence of S–T fusion by using only the fluorescence intensity measurements was complicated by experimental difficulties caused by some known effects, competitive with S–T–T energy transfer. Besides, some numerical estimations of triplet molecule concentrations in solutions under question and the proposed features of transfer probability F for the S–T–T EEET, cited in [27,28] do not permit us to conclude that the observed fluorescence intensity quenching is dominantly caused by singlet–triplet fusion at such low concentrations of molecules. More detailed arguments of our point of view will be given below.

In the only work of Bennet [29] known to us, the heterogeneous S–T–T EEET was achieved in a system composed of perylene ($C_{\text{donor}} = 3 \times 10^{-2}$ M) and phenanthrene · d_{10} ($C_{\text{acceptor}} = 3 \times 10^{-2}$ M) in a cellulose acetate film at 77 K. Such heterogeneous transfer has been discovered by a relative decrease in D fluorescence intensity in the presence of triplet-excited molecules of A. But it should be mentioned that the direct comparison of the experimental results obtained with the theoretical calculations was complicated in this case by the influence of trivial absorption of the perylene fluorescence or screening the perylene excitation by phenanthrene triplet molecules, which would give similar results and by great phosphorescence of A as well. In spite of the fact that these trivial effects were minimized in [29], their role and influence boundaries were not completely defined, and it would be interesting to carry out the total comparison of the inductive resonance theory and the experimental results.

The inductive resonance theory is also directly applicable to the case where the radiative transition $D^* \rightarrow D + h\nu$ is spin-forbidden. The triplet–triplet–triplet (T–T–T) energy transfer may be attributed to those processes which are realized by the scheme:

$$^3D^* + {}^3A^* \rightarrow {}^1D + {}^3A^{**}, \qquad {}^3A^{**} \rightarrow {}^3A^* + \text{heat}. \tag{2}$$

The possibility of such triplet–triplet–triplet migration and triplet-state quenching has been shown by Kellogg [30], who observed that the phosphorescence-to-fluorescence intensity ratio of 10^{-2} M phenanthrene $\cdot$ d_{10} solutions in cellulose acetate films was dependent on both the sample concentration and the exciting light intensity. Unfortunately, the strict division of the energy transfer process and other known phenomena, which can decrease the phosphorescence intensity under cited experimental conditions, was not performed [30], and therefore the results under discussion may be considered as qualitative ones. In addition the Förster–Galanin theory [1,2] does not strictly apply to the case of homogeneous T–T–T EEET due to the fact that concentrations of the excited $^3D^*$ and $^3A^*$ molecules change simultaneously according to the law of phosphorescence decay.

It should be mentioned that most aromatic molecules have overlapping phosphorescence and triplet–triplet absorption spectra, so process (2) is probably a general phenomenon. For example, the long-range dipole–dipole mechanism of the two triplet-excited molecules interaction (T–T annihilation) was suggested by Parker and Joyce [31] for explanation of P-type delayed fluorescence of aromatic molecules in rigid solutions, but direct experimental evidence of existence of such homogeneous T–T–T EEET has not been presented. Besides, for one of the most widely investigated photoactive systems, crystalline anthracene, exciton–exciton interactions, including S–T–T EEET, has been reported to result in charge carrier generation [32].

It is the purpose of the present work to attain conditions and to investigate regularities of the homogeneous and heterogeneous EEET with participation of triplet-excited A molecules (schemes (1) and (2)) in concentrated solutions of complex organic molecules.

As is seen from process schemes (1) and (2) an additional increase in acceptor emission does not take place in such processes. The discovery of this transfer may be possible only under investigation of changes in the spectral-kinetic characteristics of D (the intensity and lifetime of the emission). The most direct and convincing evidence of existence of the S–T–T or T–T–T EEET is a direct observation of the energy transfer effect on the time dependence of the D emission decay following pulsed excitation, because in such experiments all trivial effects are completely excluded. In the present work we use both methods.

2. Homogeneous S–T–T EEET in concentrated solutions of chlorophyll "a" and pheophytin "a"

The present series of measurements have been carried out with solutions of chlorophyll "a" and pheophytin "a" in castor oil at $T = 183$ K, when the solvent is a rigid matrix. Therefore, all diffusion processes, bringing about the deactivation of triplet states, were practically minimized. The experiment was carried out using a standard setup for lamp flash-photolysis. A more detailed description of the experimental setup has been given elsewhere [33,34].

The experimental results for solutions of chlorophyll "a" are given in fig. 1. It is clear by inspection that in dilute pigment solutions ($C \leqslant 1 \times 10^{-4}$ M) relative quantum yields of intersystem crossing and luminescence do not depend on the exciting light intensity. With increasing molecular concentration in solution relative quantum yields increase at $I_{\text{exc}} \to 0$. Also, the steepness of experimental curves increases with concentration. Analogous dependences were discovered for pheophytin "a" solutions. At the same time the experimental dependence of the triplet state lifetime on the exciting light intensity is not observed over the whole range of concentrations under investigation (1×10^{-4} -1×10^{-1} M). This leads to the conclusion that up to $C = 1 \times 10^{-1}$ M the bimolecular processes with participation of the triplet states, followed by their deactivation (T–T transfer to an extraneous quencher, T–T annihilation, concentration quenching of triplet states and so on) are not realized in the systems. Therefore, the I_{exc} dependencies of ΔI_{lum} and γ_{meas} are stipulated by physical processes connected with an additional deactivation of a singlet excited state.

It is interesting to note that these regularities are observed at high concentrations when using samples with low optical densities, but at low concentrations ($C \leqslant 10^{-4}$ M) such effects are unobservable. So far as the triplet–triplet absorption spectra of chlorophyll and pheophytin are known [35], we can estimate the influence of the triplet–triplet absorption related quenching at different pigment concentrations. It was established in our experiments that this influence and a competition of triplet molecules for incident light were minimized when using the samples with fixed and low initial optical densities in the region of the pigment absorption red band ($D = 0.24$ for $\lambda = 669$ nm in chlorophyll solutions). Furthermore, at high pigment concentrations ($C > 10^{-2}$ M) these competitive effects become even smaller ($\leqslant 5\%$) since the concentration quenching of fluorescence and triplet state formation decrease the relative triplet concentration in comparison with the diluted solutions [34].

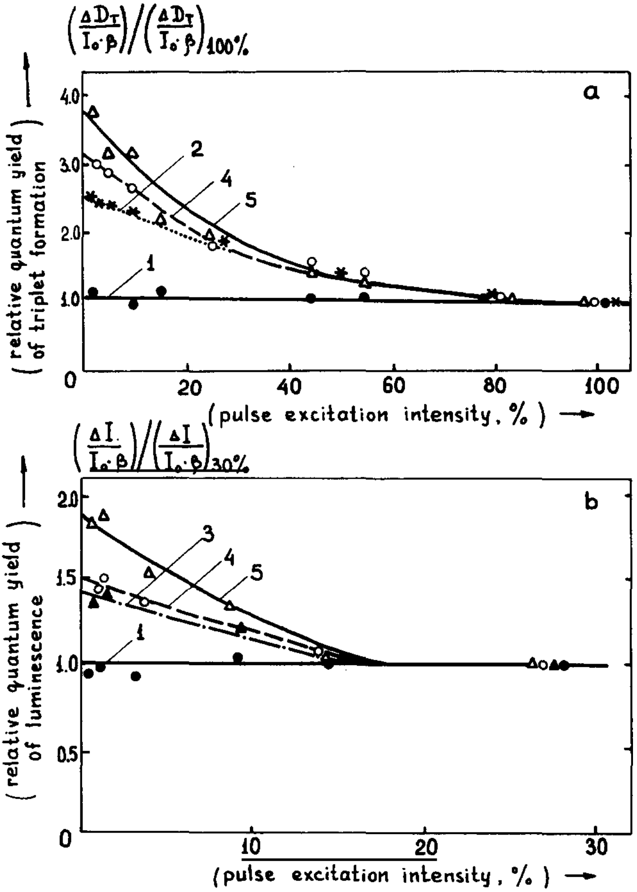

Fig. 1. Dependencies of relative quantum yields of triplet molecule formation (a) and luminescence (b) for chlorophyll "a" solutions in castor oil on pulse photo-excitation intensity at different initial concentrations: 1) 1×10^{-4} M; 2) 1×10^{-3} M; 3) 1×10^{-2} M; 4) 5×10^{-2} M; 5) 1×10^{-1} M. $T=183$ K.

Finally, photobleaching arising from triplet population build-up via the intersystem crossing from the first excited singlet state and concomitant depletion of the ground state population for the flash duration at the constant flash intensity must yield concentration independent fluorescence quenching when the quantum yield of triplet state formation is constant. But if one takes into account a decrease in this yield at high pigment concentrations [34], an increase in fluorescence quenching effect in raising the concentration cannot be fully explained by a photobleaching process. Therefore, it may be concluded that the homogeneous S–T–T energy transfer plays an essential role in the fluorescence intensity decreasing with increasing I_{exc}. The calculations which will be made below support this conclusion.

First of all, there is a good overlap of fluorescence and triplet–triplet absorption spectra for both pigments [35], which is necessary for this type of transfer. Secondly, there exists effective singlet–singlet migration between monomeric molecules in these systems [36]. For estimation of the S–T–T EEET influence on the fluorescence quantum yield we used the modification of the Förster transfer model, taking into account the possibility of excitation migration in a donor molecule system with the following trapping by molecules of A [37]. In accordance to [37] the change of the fluorescence relative quantum yield is expressed by the formula

$$\frac{B}{B_0}=\frac{1-\sqrt{\pi}\gamma e^{\gamma^2}[1-\mathrm{erf}(\gamma)]}{1-\alpha_0\sqrt{\pi}\gamma_{\mathrm{D}}e^{\gamma^2}[1-\mathrm{erf}(\gamma)]}, \tag{3}$$

where

$$\gamma=\gamma_{\mathrm{D}}+\gamma_{\mathrm{A}}=\frac{\sqrt{\pi B_0}}{2}\left(\frac{C_{\mathrm{D}}}{C_{\mathrm{D0}}}+\frac{C_{\mathrm{A}}^{\mathrm{T}}}{C_{\mathrm{A0}}^{\mathrm{STT}}}\right);$$

B_0 is the quantum yield of a solution free of triplet molecules; C_{D} and $C_{\mathrm{A}}^{\mathrm{T}}$ are the concentrations of D and triplet-excited molecules of A; C_{D0} and $C_{\mathrm{A0}}^{\mathrm{STT}}$ are the critical concentrations, corresponding with the two types of the transfer $\mathrm{D}^* \rightarrow \mathrm{D}$ and $\mathrm{D}^* \rightarrow \mathrm{A}$; α_0 is the parameter which does not depend on the concentration ($0 \leqslant \alpha_0 \leqslant 1$) and defines the quantum losses in migration acts between monomers; $\mathrm{erf}(\gamma)=(2/\sqrt{\pi})\int_0^{\gamma}e^{-x^2}$ is the error integral. Because all spectral-luminescent parameters of chlorophyll "a" have been studied [36,38,39], we analyzed the experimental and theoretical results for that pigment. In accordance with the inductive resonance theory we calculated the values of the critical transfer distance R_0 (which is connected with C_0 by $C_0=[\frac{4}{3}\pi R_0^3]^{-1}$) from the expression [1,2]:

$$R_0^6=\frac{9000\ln 10\,K^2B_0}{128\pi^5n^4N}\int_0^{\infty}f_{\mathrm{D}}(\nu)\mathcal{E}_{\mathrm{A}}(\nu)\frac{\mathrm{d}\nu}{\nu^4}, \tag{4}$$

where ν is the wavenumber; $\mathcal{E}_{\mathrm{A}}(\nu)$ is the acceptor decimal extinction coefficient; $f_{\mathrm{D}}(\nu)$ is the spectral distribution of the donor molecule fluorescence (measured in quanta and normalized for spectral area to 1 in wavenumber scale); N is the Avogadro number; n is the refraction index of the solvent; B_0 is the donor fluorescence quantum yield in the absence of transfer; K^2 is the orientation factor ($K^2=2/3$ for the isotropic solutions of mean viscosity). Theoretical values of critical distances calculated for S–S and S–T–T EEET in chlorophyll "a" solutions in castor oil are found to be $R_0^{\mathrm{SS}}=54$ Å [39] and $R_0^{\mathrm{STT}}=42$ Å [40]. The triplet-excited molecules concentration at different pulse excitation intensities was measured in T–T bleaching experiments in the main absorption band maximum of chlorophyll "a" ($\lambda = 669$ nm). For all concentrations under investigation, yield of D luminescence in the absence of triplet molecules (B_0) was used in calculations with provision for the concentration fluorescence quenching of chlorophyll "a" in castor oil, which had been experimentally investigated in our earlier works [34,36,39]. The experimental data and the calculation results obtained by using formula (3) are presented in table 1. A satisfactory agreement may be expected when $\alpha_0 = 0.92$, i.e. the existence of quantum losses in migration acts between monomers is assumed to be valid. These losses are assumed to arise from nonideal calculation of trivial competitive effect contributions to observed luminescence quenching, because for the homogeneous S–T–T EEET these effects can be minimized but cannot be fully excluded.

Thus, the existence of the homogeneous S–T–T transfer in concentrated chlorophyll "a" and pheophytin "a" solutions in castor oil at $T = 183$ K is the main explanantion for the observed dependence of quantum yields of fluorescence and intersystem crossing on the pulse excitation intensity. In this respect the absence of such dependence for concentrated solutions of Na-fluorescein in glycerol at $T = 193$ K is due to the low efficiency of the S–T–T transfer in this system because of extremely low concentration of Na-fluorescein triplet-excited molecules at maximum flash excitation intensities caused by low quantum yield of the intersystem crossing in these molecules ($\gamma = 0.008$) [41].

Our experimental results and calculations permit us to ananlyze some data and estimations in [27,28], where low concentrated ($C_{s_0} \leqslant 2 \times 10^{-4}$ M) rigid solutions of chlorophyll "a" and metal-free phthalocyanine have been separately investigated under laser excitation generating low concentration of triplet-excited molecules ($C_T \simeq 0.06$–$0.1\ C_{s_0}$). Since the values of critical transfer distance R_0 of S–T–T EEET and the theoretical calculations for

Table 1
Influence of chlorophyll "a" triplet-excited molecule concentration on fluorescence quantum yield in castor oil at $T = 183$ K

C (M)	C_A^T (M)	Initial quantum yield B_0	$(B/B_0)^{\text{theor}}$	$(B/B_0)^{\text{expt}}$
1×10^{-3}	0	0.32	1.0	1.0
1×10^{-3}	1×10^{-5}	0.32	0.97	1.0
1×10^{-3}	3×10^{-4}	0.32	0.92	0.97
5×10^{-2}	0	0.018	1.0	1.0
5×10^{-2}	3×10^{-4}	0.018	0.50	0.70
5×10^{-2}	2.5×10^{-3}	0.018	0.44	0.50
1×10^{-1}	0	0.002	1.0	1.0
1×10^{-1}	3×10^{-4}	0.002	0.68	0.60
1×10^{-1}	1×10^{-3}	0.002	0.62	0.59

chlorophyll "a" solutions have not been given in [27], we used for our calculation the value of $R_0^{\mathrm{STT}} = 42$ Å from [40] and estimated an expected efficiency of quenching for conditions cited in [27] by using formula (3). These calculations show the absence of quenching fluorescence effect for $C_{s_0} = 2 \times 10^{-4}$ M and $C_T = 2 \times 10^{-5}$ M ($B/B_0 = 0.99$).

It should be mentioned that the Förster–Galanin treatment of the problem of singlet excitation migration via the dipole–dipole interaction mechanism conformed well with numerous experimental works even in the case of weak fluorescent or nonfluorescent acceptor molecules and in the experiments on sensitized fluorescence when the energy gap $\Delta E = E_D^{S_1} - E_A^{S_1}$ excludes the back transfer [2,4,5]. Therefore, there are no good grounds for modifying the main equation of the inductive-resonance theory as it has been done in [28]. It is further alleged in [28] that the critical distance for S–T fusion is a property of the molecular system and the irradiation conditions of the particular experimental configuration employed. This point of view is not obvious because it is well known that the critical distance for any energy transfer via inductive resonance interactions is determined only by molecular orientation, fluorescence quantum yield of a D molecule, refractive index of the medium and overlap integral of spectra (see eq. (4)). But the efficiency of the S–T–T transfer is certain to depend on the triplet concentration, i.e. on the incident light intensity. Therefore, the energy transfer with participation of triplet-excited molecules may be fully described by the Förster–Galanin theory without any additonal assumptions. This is well documented in [25,26,29]. Thus, the value of about 200 Å for the critical distance found in [28] for metal-free phthalocyanine solutions of low concentrations is surprisingly large.

3. Influence of heterogeneous S–T–T EEET on donor fluorescence intensity

For this experiment we developed a procedure which permitted us to investigate completely all trivial processes, to estimate their influence on measured parameters and to isolate the pure transfer phenomenon (fig. 2). The sample fluorescence is excited by a source S (a tungsten lamp 17 V, 100 W with a dc source) through the glass and interference optical filter system F_1 selecting a required spectral region. The D luminescence is recorded by the experimental setup including an optical filter system F_2, a prism monochromator UM-2, a photomultiplier FEU-38 and a CI-42 storage oscilloscope operating in the driven sweep regime. The A molecules are pumped to a triplet state via a singlet state by light pulses from two IFP-2000 flash lamps ($\tau_{1/2} \simeq 2 \times 10^{-5}$ s) using a light filter system F_3. The samples investigated (thin films) are arranged as shown in fig. 2. Having placed the source S in position B and changing the light filters F_1 and F_2 and the monochromator wavelength in recording we can determine a real concentration of the A triplet-excited molecules at the same

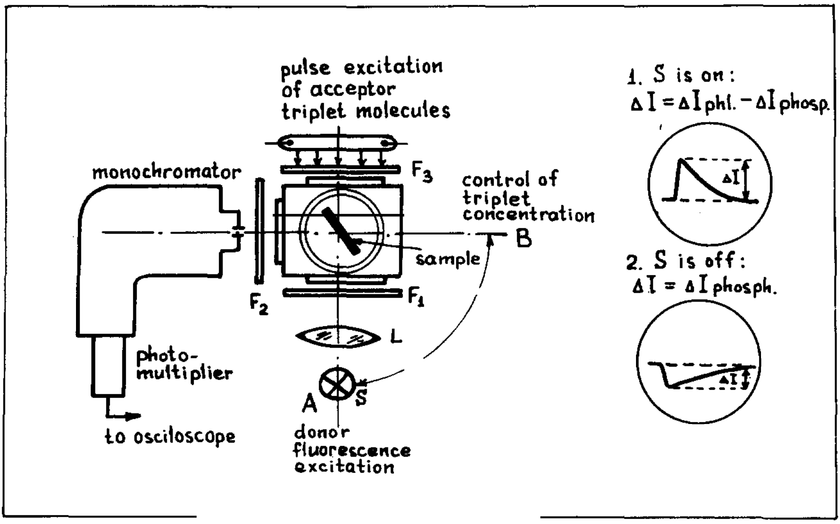

Fig. 2. Schematic of the experimental arrangement for investigation of the dependence of the donor fluorescence intensity on the acceptor triplet-excited molecule concentration.

experimental conditions and use the value of C_A^T for calculations according to the inductive resonance theory. Then, by switching off the source S and pumping the samples by light pulses we can measure directly the A phosphorescence (if it exists) which can affect the measurement of the D fluorescence change.

The primary intention of this stage of the experiments was to reexamine Bennett's system [29] perylene + phenanthrene but only in polyvinylbuthyral films with the exclusion of trivial effects and direct comparing experimental results with theoretical calculations. The second donor–acceptor pair was the Na-fluorescein + chlorophyll "a" system in polyvinylbuthyral films. The electronic spectra of both systems are shown in fig. 3 and the main spectral-luminescent characteristics and calculated transfer parameters are presented in table 2. The values of the orientational factor K^2 in eq. (4) were calculated for an isotropic distribution of molecules in a rigid solvent [5]. A relative change of the D luminescence intensity was measured in the experiments when the concentrations of the A triplet molecules in solutions were known. At such conditions, the quenching of D luminescence correlated in time with the deactivation kinetics of the A triplet states. The experimental values of ΔI_{fl} were found by extrapolation to an exciting pulse maximum. All measurements were made in a quartz Dewar at 77 K. The low concentration ($C \leqslant 10^{-5}$ M) ethanolic solutions of the donor–acceptor pairs investigated at 77 K were examined to estimate a direct influence of the exciting light and D fluorescence absorption by A triplet-excited molecules. In these systems the energy transfer

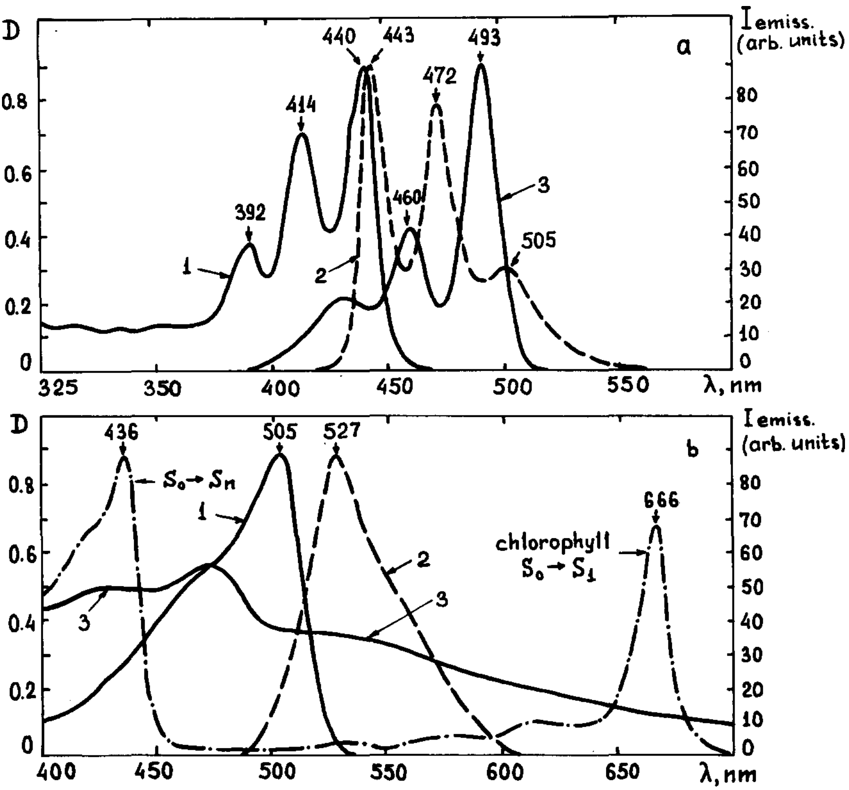

Fig. 3. Absorption (1) and emission (2) spectra of donor molecules and triplet–triplet absorption spectra (3) of acceptor molecules in polyvinylbuthyral films at 77 K: (a) perylene + phenanthrene; (b) Na-fluorescein + chlorophyll "a".

had been entirely excluded. Furthermore, such examination was carried out with double polyvinylbuthyral films, containing separately D and A molecules at the same concentrations as in mixed solutions. The results obtained permitted us to calculate a true decrease in D fluorescence which was solely due to the transfer process for different optical densities of the triplet–triplet absorption.

The theoretical alternation of a relative fluorescence quantum yield of D in the presence of A triplet-excited molecules was calculated by the formula [1,2]:

$$\frac{B}{B_0} = 1 - \sqrt{\pi}\, q\, e^{q^2}\left(1 - \int_0^q e^{-x^2}\,dx\right), \tag{5}$$

where $q \simeq 3.14\, R_0^3 C_A^T$ for rigid solutions [5]. The comparison of the experimental and theoretical results are presented in table 3. As one can see from table 3 there is a close conformity between the theory and the experimental studies for

Table 2
Spectral-luminescent characteristics and values of S–T–T energy-transfer parameters for the system of fig. 3

Donor–acceptor pair	Refraction index of solvent n	Quantum yield of D emission B_0	E_A^{triplet} (ν) ($\text{cm}^{-1}\text{M}^{-1}$)	Overlap integral ($\text{cm}^{-4}\text{M}^{-1}$)	τ_T^A (s)	R_0^{theor} (Å)
Perylene + phenanthrene	1.489	0.94 [45]	27000 (ν=20300 cm^{-1}) [42,43]	0.37×10^{-13}	4.4	39
Na-fluorescein + chlorophyll “a”	1.489	0.97	20000 (ν=20000 cm^{-1}) [44]	1.44×10^{-13}	2×10^{-3}	48

Table 3
Comparison of experimental and theoretical results of investigation of S–T–T EEET in polyvinylbuthyral films

Donor–acceptor pair	C_D (M)	C_A (M)	C_A^T (M)	D_A^S	$(B/B_0)^{\text{meas}}$	Influence of T–T reabsorpt. (%)	$(B/B_0)^{\text{exp}}$	$(B/B_0)^{\text{theor}}$
				0.21	0.42	19	0.52	0.57
Perylene +				0.26	0.38	30	0.54	0.57
phenanthrene	5.2×10^{-3}	2.3×10^{-2}	3.1×10^{-3}	0.42	0.26	47	0.49	0.57
				1.24	0.35	71	0.60	0.57
Na-fluorescein +	2×10^{-2}	1×10^{-3}	2.5×10^{-4}	0.40	0.88	6	0.94	0.92
chlorophyll “a”	2×10^{-2}	5×10^{-3}	5×10^{-4}	0.98	0.70	16	0.83	0.84

* Values of acceptor optical densities D_A^S in the singlet state were measured for phenanthrene at $\lambda=394$ nm and for chlorophyll “a” at $\lambda=669$ nm.

the systems. For the perylene + phenanthrene pair this conformity is insensitive to the recording wavelengths ($\lambda_1 = 492$ nm, $\lambda = 474$ nm, $\lambda_3 = 450$ nm), i.e. the D fluorescence quenching effect is not selective in character. Hence we can consider these results as direct evidence of the energy transfer while the reabsorption effect depends on a spectral distribution of a triplet–triplet absorption of A and must change in variation with a recording wavelength.

4. Influence of heterogeneous S–T–T EEET on decay kinetics of donor fluorescence

The experiments of this type have been carried out by using the nanosecond kinetic spectroscopy method. For this purpose an experimental setup with separate and simultaneous selective laser pumping of a donor–acceptor pair was used which permitted us to record the D fluorescence decay kinetics in the absence and presence of A triplet-excited molecules. A more detailed description of the experimental apparatus based on a double frequency Q-switched ruby laser has been given in [46]. When exciting the donor–acceptor system by a 347 nm laser pulse ($\tau_{1/2} = 25$ ns, $E_1 = 0.05$ J) we measure the D fluorescence lifetime in the absence of A triplet molecules. In exciting simultaneously this system by two laser pulses ($\lambda_2 = 694$ nm and $\lambda_1 = 347$ nm) we measured the D fluorescence lifetime in the presence of A triplet molecules pumped to the triplet state by a 694 nm laser pulse ($\tau_{1/2} = 25$ ns, $E_2 = 1.1$ J). In this case the existence of the S–T–T energy transfer can be found by decreasing the D fluorescence lifetime in the presence of the A triplet molecules, and thus one can investigate the regularities and mechanism of such a transfer. All measure-

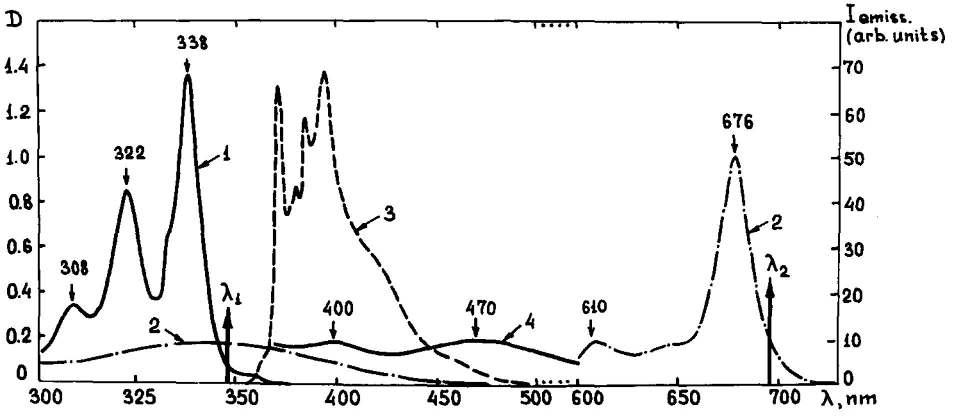

Fig. 4. Absorption (1) and luminescence (3) spectra of pyrene and S_0-S_n (2) and T_1-T_n (4) spectra of Mg-phthalocyanine in polyvinylbuthyral films at 293 K. $\lambda_1 = 347$ nm and $\lambda_2 = 694$ nm are the laser excitation wavelengths.

ments have been carried out at room temperature.

The donor–acceptor pair studied is pyrene (D) + Mg-phthalocyanine (A) in polyvinylbuthyral films. The electronic spectra and the main spectral and luminescence characteristics of these molecules are presented in fig. 4 and table 4. The chosen donor–acceptor system satisfies the following conditions: (1) the overlap of D fluorescence and A singlet–singlet absorption spectra is less than the analogous D fluorescence and the same A triplet–triplet absorption spectra overlap (fig. 4, table 4), i.e. the conditions are secured for a preferable realization of the S–T–T transfer; (2) the probability of A molecule intersystem crossing to the triplet state ($r_A \simeq 10^8$ s^{-1}) exceeds the deactivation probability of the D singlet-excited state ($f_D = 2.6 \times 10^6$ s^{-1}), i.e. the A triplet-excited molecule concentration is not equal to zero at the beginning of the D fluorescence emission; (3) the A molecule triplet lifetime ($\tau_T = 1 \times 10^{-5}$ s) is considerably greater than the D fluorescence lifetime ($\tau_S = 3.8 \times 10^{-7}$ s), i.e. the A triplet-excited molecule concentration is constant and not equal to zero during the whole D fluorescence lifetime. The latter condition enables us to use the equations of the inductive resonance theory with no additional assumptions [49].

Both sample constituents have been incorporated into a polyvinylbuthyral

Table 4
Spectral-luminescent characteristics and values of energy-transfer parameters of pyrene + Mg-phthalocyanine system in polyvinylbuthyral films ($n = 1.489$; $C_D = 1 \times 10^{-2}$ M; $C_A = 2.25 \times 10^{-3}$ M; $B_0 = 0.72$ [47])

Singlet–singlet transfer	
$\mathcal{E}_A^S$ ($\lambda = 400$ nm)	0.9×10^4 cm^{-1} M^{-1} [48]
$\int_0^\infty f_D(\nu)\mathcal{E}_A^S(\nu)\frac{d\nu}{\nu^4}$	2.7×10^{-14} cm^{-4} M^{-1}
$(R_0^{SS})^{theor}$	35 Å
$(R_0^{SS})^{exp}$	36 Å
$(\tau/\tau_0)^{exp\ a)}$	0.86
$(B/B_0)^{exp}$	0.71
$(\tau/\tau_0)^{theor}$	0.84
$(B/B_0)^{theor}$	0.60
Singlet–triplet–triplet transfer	
$\mathcal{E}_A^T$ ($\lambda = 400$ nm)	2×10^4 cm^{-1} M^{-1} [48]
$\int_0^\infty f_D(\nu)\mathcal{E}_A^T(\nu)\frac{d\nu}{\nu^4}$	5.2×10^{-14} cm^{-4} M^{-1}
$(R_0^{STT})^{theor}$	40 Å
$(R_0^{STT})^{exp}$	40 Å
$(\tau/\tau_0)^{exp\ b)}$	0.71
$(\tau/\tau_0)^{theor}$	0.76

a,b) Donor fluorescence lifetime $\tau_0 = 440$ ns, in the absence of both types of transfer; when singlet–singlet transfer is operating, then $\tau_0 = 380$ ns.

film at the concentrations of pyrene, $C_D = 1 \times 10^{-2}$ M, and Mg-phthalocyanine, $C_A = 2.3 \times 10^{-3}$ M. The selection of a rigid polymer film as a solvent excluded the possible participation of different diffusion processes in the phenomenon under investigation and decreases essentially the influence of oxygen on the triplet state deactivation. In our investigation special experiments using both laser and lamp flash photolysis show that the laser excitation pumps practically all acceptor molecules (~ 100%) to the triplet state. Consequently, in our calculations we use the value of triplet molecule concentration equal to 2.3×10^{-3} M.

The results of the lifetime measurements are shown in fig. 5. It is evident from fig. 5 that in the presence of A triplet molecules the D fluorescence mean lifetime becomes shorter. Furthermore, noticeable deviations from exponential decay are observed at the initial stage of the time dependence of the D fluorescence decay. It must be noted that the exciting laser pulse duration $t \ll \tau$ in order to cause perturbations in the range of interest. Therefore, as was predicted by the Förster–Galanin theory, the observed deviation is due to statistical fluctuations in the distribution of molecules by distances in rigid solutions which lead to the dependence of transfer probability on the time t passing from the excitation instant (i.e. $F_{D^* \to A} \sim \sqrt{(t)^{-1}}$). From fig. 4 it is seen that there are two types of EEET which are observed in the system investigated: (1) S–S transfer to nonexcited singlet A molecules and (2) S–T–T transfer to the triplet-excited A molecules. The homogeneous S–S migration between D molecules may be excluded because of a negligible overlap of the pyrene fluorenscence and absorption spectra. We can therefore apply the equations of the inductive resonance theory [1–5]. The analysis of the theoretical and experimental results for both types of EEET has been carried out using the formulae:

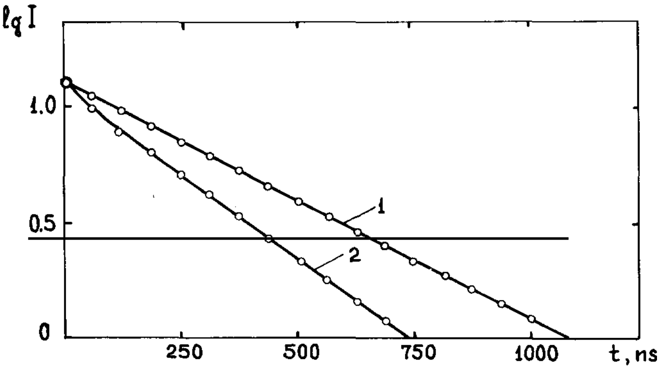

Fig. 5. Time dependence of the pyrene fluorescence decay ($C = 1 \times 10^{-2}$ M) in the absence (1) and in the presence (2) of triplet-excited molecules of Mg-phthalocyanine in polyvinylbuthyral films at 293 K.

(a) a critical transfer distance (rigid solutions),

$$(R_0^{\text{theor}})^6 = \frac{9000 \ln 10 \, (K^2 0.845) B_0}{128 \pi^5 n^4 N_A} \int_0^\infty f_D(\nu) \mathcal{E}_A(\nu) \frac{d\nu}{\nu^4}; \tag{4a}$$

(b) quenching of the D molecule fluorescence quantum yield, eq. (5) in this paper;

(c) shortening the D fluorescence mean lifetime,

$$\left(\frac{\tau}{\tau_0}\right) = \tfrac{3}{2} + q^2 - \tfrac{1}{2}\left[1 - \sqrt{\pi}\, q\, e^{q^2}\left(1 - \frac{2}{\sqrt{\pi}} \int_0^q e^{-x^2}\, dx\right)\right]; \tag{6}$$

(d) a critical transfer distance (analysis of the D fluorescence decay curves in the presence of A molecules)

$$(R_0^{\text{expt}})^3 = \left[-\ln\frac{n(t)}{n_0} - \frac{t}{\tau_0}\right] \Big/ \left(6.28 C_A \sqrt{t/\tau_0}\right). \tag{7}$$

The physical meaning of the majority of parameters entering eqs. (4–7) is cited above in this paper. Here the value of C_A is measured by the number of particles/cm^3 and the value of R_0 is measured in cm. τ_0 is the D emission lifetime in the absence of A molecules and τ is the D emission lifetime in the presence of A molecules. n_0 denotes the number of excited D molecules at the exciting pulse maximum, $n(t)$, is the same value for the instant time t, passed from the moment of the pulse maximum. Both of these values (n_0 and $n(t)$) are proportional to the corresponding donor emission intensities on the decay curve.

The numerical results are given in table 4. As is evident from table 4 there is good conformity between R_0^{theor} and R_0^{expt}, obtained for the S–S and S–T–T energy transfer. A close agreement is also observed between the theoretical and experimental results for resonance quenching of a donor luminescence in the presence of triplet acceptor molecules. In conclusion, when Cu-phthalocyanine is used as an acceptor we cannot observe any shortening of the pyrene fluorescence lifetime at the same D and A concentrations, practically equal overlap of spectra and the same pulse excitation intensities. This fact corresponds with the third condition: since the lifetime of Cu-phthalocyanine triplet molecules ($\tau_T = 35$ ns [50]) is smaller than the pyrene fluorescence lifetime ($\tau_S = 3.8 \times 10^{-7}$ s), the possibility of observing the S–T–T transfer in the above case is practically absent.

5. Influence of heterogeneous T–T–T EEET on decay kinetics of donor phosphorescence

For a successful realization of the heterogeneous T–T–T transfer, the selection of D and A (benzophenone + Mg-mesoporphyrin in ethanol at 77 K) has been made with provision for the following requirements. Firstly, the overlap of the D phosphorescence and T–T absorption spectra of A is greater than the analogous overlap with singlet–singlet absorption spectrum of the same A (fig. 6, table 5). In this case, the T–T–T transfer is more effective in comparison with the long-range triplet–singlet radiationless energy transfer discovered first in [51]. Secondly the lifetime of A triplet-excited molecules ($\tau_T = 1.10 \times 10^{-1}$ s) is significantly greater than the D phosphorescence lifetime ($\tau_{ph} = 5.3 \times 10^{-3}$ s). The above requirement is necessary for a strict application of theoretical calculations according to the resonance theory and creates advantages for realization and observation of a heterogeneous T–T–T transfer in comparison with a homogeneous one.

The concentration of benzophenone is $C_D = 1.5 \times 10^{-2}$ M and the concentration of Mg-mesoporphyrin is $C_A = 4.4 \times 10^{-3}$ M. To use higher A concentrations is unreasonable since a great concentration quenching of a triplet state formation has been observed for these compounds at $C \geqslant 5 \times 10^{-3}$ M [33,34]. Separate and simultaneous excitation of D and A molecules has been carried out by using two pulse lamps (IFP-2000, $\tau_{1/2} = 7 \times 10^{-5}$ s) with proper filtering of the exciting light and phosphorescence emission. A detailed description of the experimental apparatus and conditions can be found in [52]. Solutions of the compounds under study are placed between quartz glasses with layer thickness $l = 3$–4×10^{-5} M. These samples are located in a quartz Dewar at $\alpha = 45°$ to the pulse radiation. The time dependence of the D molecule phosphorescence decay in the absence and presence of A

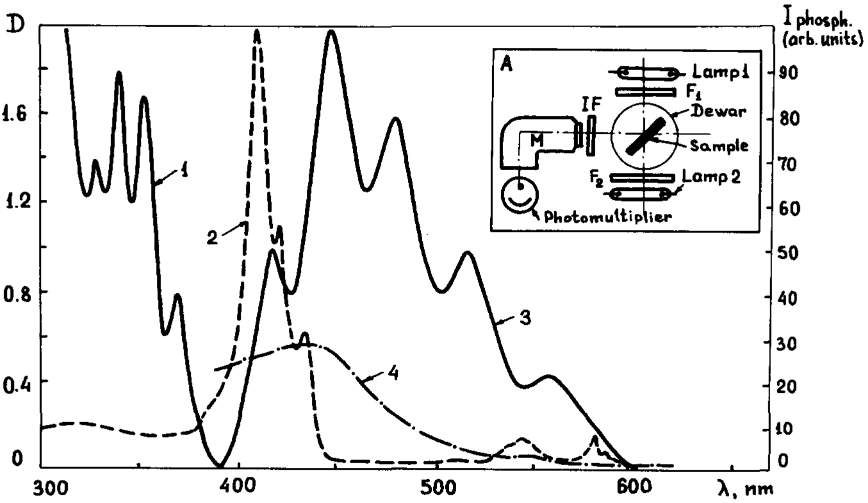

Fig. 6. The normalized absorption (1) and phosphorescence (3) spectra of benzophenone and S_0–S_n (2) and T_1–T_n (4) absorption bands of Mg-mesoporphyrin in ethanol at 77 K. A – schematic of the experiment.

Table 5

Spectral-luminescent characteristics and values of energy-transfer parameters of benzophenone + Mg-mesoporphyrin system in ethanol ($T = 77$ K; $n = 1.3623$; $C_D = 1.5 \times 10^{-2}$ M; $B_0 = 0.74$ [47,53])

Triplet–singlet transfer		
$\int_0^\infty f_D^T(\nu)\mathcal{E}_A^S(\nu)\frac{d\nu}{\nu^4}$	1.2×10^{-13} cm^{-4} M^{-1}	
C_A^S	1.6×10^{-4} M	4.4×10^{-3} M
C_A^T	0	0
$(R_0^{TS})^{theor}$		50 Å
$(R_0^{TS})^{exp}$		50 Å
$(\tau/\tau_0)^{theor}$	0.97	0.43 [a]
$(\tau/\tau_0)^{exp}$	1.0	0.41
Triplet–triplet–triplet transfer		
$\int_0^\infty f_D^T(\nu)\mathcal{E}_A^T(\nu)\frac{d\nu}{\nu^4}$	2.1×10^{-13} cm^{-4} M^{-1}	
C_A^S	0	1.2×10^{-3} M
C_A^T	1.6×10^{-4} M	3.2×10^{-3} M
$(R_0^{TTT})^{theor}$		55 Å
$(R_0^{TTT})^{exp}$		57 Å
$(\tau/\tau_0)^{theor}$	0.96	0.44 [b]
$(\tau/\tau_0)^{exp}$	0.95	0.40

[a,b] Benzophenone phosphorescence lifetime $\tau_0 = 5.3 \times 10^{-3}$ s in the absence of both types of transfer. At $C_A^S = 1.2 \times 10^{-3}$ M benzophenone phosphorescence lifetime in the absence of T–T–T transfer is $\tau_{initial} = 4.1 \times 10^{-3}$ S in accordance with the theory [1,2]. Mg-mesoporphyrin triplet state lifetime at 77 K is $\tau_T = 1.1 \times 10^{-1}$ s.

singlet and triplet molecules is shown in fig. 7. The comparison of τ_{phosph} of a single D ($C = 1.5 \times 10^{-2}$ M) and in a mixture with A in excitation of D molecules only (by one pulse lamp) allows us to assume the existence of the singlet–triplet EEET in the system investigated. Besides, the shortening of the D phosphorescence lifetime in the presence of A triplet-excited molecules serves as a direct illustration of the T–T–T transfer at these conditions. It may be mentioned that deviations from an exponential decay of D phosphorescence are observed in the presence of A molecules for both types of transfer (fig. 7). The physical reason for this effect has been discussed in section 4. The comparison of the theoretical and experimental results has been carried out using eqs. (4–7) in the present work and replacing the D normalized fluorescence spectrum by the normalized phosphorescence spectrum in the overlap integral, and taking B_0 as a quantum yield of D phosphorescence. The direct experiments with flash photolysis of the donor–acceptor pair investigated shows that under our experimental conditions 75% of A molecules are pumped to the triplet state. Therefore, when T–T–T transfer was investigated [52], the above fact was taken into account in calculation of the $(\tau/\tau_0)^{theor}$ values and determination of R_0^{expt} from analysis of D phosphorescence decay curves. The

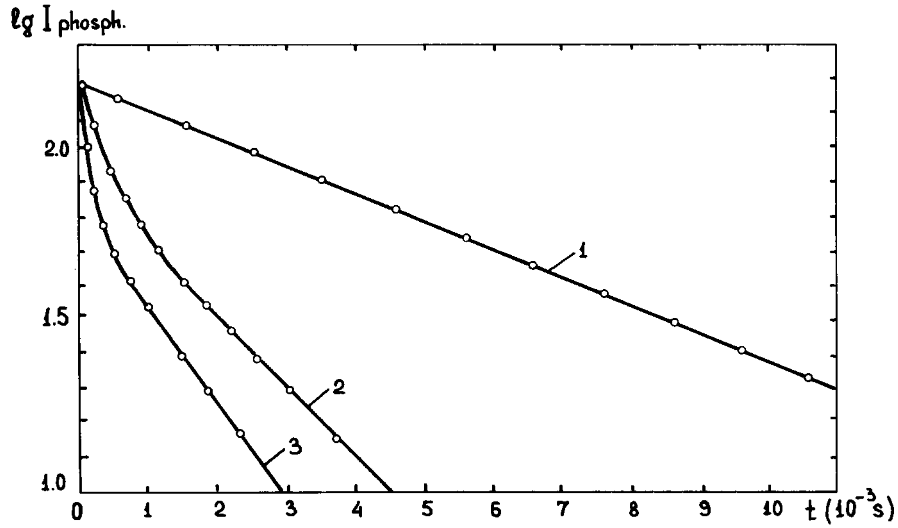

Fig. 7. Observed decay curves for the system of fig. 6: 1 – pure benzophenone ($C_D = 1.5 \times 10^{-2}$ M); 2 – benzophenone and singlet molecules of Mg-mesoporphyrin ($C_A^S = 4.4 \times 10^{-3}$ M); 3 – benzophenone and triplet-excited molecules of Mg-mesoprophyrin ($C_A^T = 3.2 \times 10^{-3}$ M) $T = 77$ K.

numerical results are tabulated in table 5. From analysis of the data obtained we conclude that there is good agreement between the experimental results and the calculations according to the inductive resonance theory. At the same time a decrease in pulse excitation intensity or dilution of D and A concentrated solutions up to $C_D = 1.4 \times 10^{-4}$ M and $C_A = 4.2 \times 10^{-5}$ M results in the disappearance of the dependence of the D phosphorescence decay on the presence of A triplet molecules. Thus, it is evident from the above that the efficiency of the observed process depends essentially on the A triplet-excited molecule concentration.

6. Conclusion

Homogeneous and heterogeneous long-range radiationless transfer with participation of triplet-excited acceptor molecules leads to reduction of quantum yield (sects. 2 and 3) and donor emission lifetime (sects. 4 and 5) with no additional change of acceptor emission. It has been directly shown that the energy transfer from donor excited singlet or triplet levels to acceptor excited triplet levels in a rigid condensed medium can be reasonably explained by the Förster–Galanin dipole–dipole inductive-resonance mechanism. Supporting evidence is given in sects. 4 and 5 of this paper where a direct experimental and theoretical verification has been carried out by investigation of time dependence of the donor emission decay following a pulse excitation. Such a transfer can take place even in the case where the radiative transition in donor molecules is spin-forbidden. Even though the donor dipole transition moment is of extremely small magnitude, a long-range radiationless transfer is significant in donor de-excitation due to the equally forbidden nature of all competing processes.

The observed phenomenon must take place in all molecular systems excited by an intense light flux and also in the case of an effective energy migration where the meeting of two or more excitons can lead to their interaction (high concentrated solutions, molecular crystals, photosynthetic apparatus of plants and so on).

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