

Investigations of the Excitation Energy Transport Mechanism in Donor–Acceptor Systems¹

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Measurements of fluorescence quantum yield η_D/η_{oD} of Na-fluorescein (donor; D) versus concentration of rhodamine B (acceptor; A) in viscous solutions have been carried out. The donor concentration in these solutions was as follows: $C_D = 2 \cdot 10^{-2} M$ (system I), $1.5 \cdot 10^{-2} M$ (II), $10^{-2} M$ (III), $3 \cdot 10^{-3} M$ (IV), and $5 \cdot 10^{-5} M$ (V). The experimental results have been compared with current theories of nonradiative electronic energy transfer (NEET). In the case of very strong migration (systems I, II, and III), a significant influence of correlations (between configurations of D and A molecules in the surroundings of successively excited donors) on quantum yield η_D/η_{oD} has been determined. Experimental values have been found to be clearly higher in comparison with those predicted theoretically. The influence of possible factors on the decrease in the effectiveness of excitation energy transport to traps–acceptors in systems of very strong migration has been discussed.

KEY WORDS: Energy transfer; migration mechanism; quantum yield.

INTRODUCTION

Nonradiative electronic energy transfer (NEET) due to dipole–dipole interactions plays an important role in many natural and artificial systems [1, 2].

The theoretical description of NEET in disordered systems is in general too complicated to be solved exactly. Exact expressions for fluorescence decay $\phi_D(t)$ and quantum yield of donor η_D in the presence of acceptor were obtained by Förster [3] only for the limiting case of neglecting the energy migration in the set of donors.

However, in the case of the donor concentration considerably exceeding the acceptor concentration $C_D \gg C_A$, the energy migration (EM) may have an essential

influence on the luminescent characteristics of these systems [4].

The theoretical results describing NEET in such systems were obtained [5–10] on the assumption that EM takes place in the set of donors without any correlations between D and A molecules before and after the excitation jump. In other words, we assume that EM is a Markov-type process.

Further progress in the NEET theory was made by partial consideration of the above-mentioned correlations and the dependence of the NEET kinetics on the R_{oDA}/R_{oDD} ratio of the critical distances for energy transfer from D^* to D and D^* to A [11–15].

The experimental verification of the latest NEET theories is limited to a few fluorescence decay and emission anisotropy measurements and Monte Carlo simulations of certain luminescent quantities [16–18].

In this paper, we present the results of investigations concerning the influence of energy migration and correlations on fluorescence quantum yield of a donor

¹Dedicated to Professor A. Kowski on the occasion of his 65th birthday.

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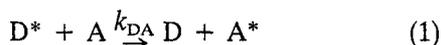
in the presence of an acceptor and compare the obtained results with contemporary NEET theories.

THEORETICAL BACKGROUND

The experimental studies of the NEET process in condensed systems containing statistically distributed D and A molecules are carried out through measurements of luminescent characteristics of these systems for both pulse and continuous excitation. In the latter case, measurements of donor fluorescence quantum yield η_D versus acceptor concentration C_A is also investigated.

Correct interpretation of the obtained results requires the knowledge of the relation between η_D and C_A .

This relation was found by Förster [3] for the limiting case $C_D \ll C_A$ on the assumption that the interaction between D^* and A molecules which leads to NEET according to kinetics,



is a dipole-dipole interaction and that the NEET rate constant from D^* to A equals [19]

$$k_{DA} = \frac{1}{\tau_{oD}} \left(\frac{R_{oDA}}{R} \right)^6 \quad (2)$$

where τ_{oD} denotes the actual lifetime of donor excited state for $C_A = 0$ and R_{oDA} is the critical distance. However, for $C_D \gg C_A$, NEET from D^* to A may occur as a result of subsequent one-stage processes $D^* + D \xrightarrow{k_{DD}} D + D^*$ with the final process (1). In this case the time evolution of excitation energy transport in the set of D and A molecules after pulse excitation may be expressed as follows [5,10]:

$$\phi_D(t) = R_o(t)N_o(t) - \int_0^t \dot{R}_o(t-t') N_o(t-t') \phi_D(t') dt' \quad (3)$$

where

$$N_o(t) = \exp[-2\gamma_A(t/\tau_{oD})^{1/2}] \quad (4)$$

and

$$R_o(t) = \exp[-2\gamma_D(t/\tau_{oD})^{1/2}] \quad (5)$$

Function $\phi_D(t)$ describes the fluorescence decay due to excitation energy migration among donors and its transfer to acceptors, and γ_D and γ_A denote the reduced concentrations of donor and acceptor, respectively [see Eq. (9)]. $N_o(t)$ and $R_o(t)$ describe the deactivation of the excited donor by acceptors and donors, respectively, ran-

domly distributed in the donor surroundings. Function $N_o(t)$ obtained by Förster represents the static fluorescence quenching of the donor by acceptors, whereas function $R_o(t)$ describes the transition of excitation energy from one configuration of donors to another and therefore pictures the rate of excitation energy random walk over configurations.

Expression (3) was found by Vugmeister [20] otherwise when investigating the spatial and spectral spin diffusion in diluted paramagnetics and discussed by Burshtein [14,21]. The integral equation (3) allows one to evaluate the fluorescence quantum yield η_D from the following expression:

$$\eta_D = k_F \int_0^\infty \exp(-t/\tau_{oD}) \phi_D(t) dt = k_F \hat{\phi}_D(s = \tau_{oD}^{-1}) \quad (6)$$

where k_F is the rate constant for fluorescence emission.

Calculation of Laplace transform $\hat{\phi}(s)$ leads to the formula [5,10]

$$\eta_D = \eta_{oD} [1 - f(\gamma)]/[1 - \alpha \cdot f(\gamma)] \quad (7)$$

where

$$f(\gamma) = \pi^{1/2} \gamma \exp(\gamma^2) [1 - \text{erf}(\gamma)] \quad (8)$$

$$\gamma = \gamma_D + \gamma_A = \frac{1}{2} \pi^{1/2} (C_D/C_{oDD} + C_A/C_{oDA}), \quad \alpha = \gamma_D/\gamma \quad (9)$$

η_{oD} is the absolute quantum yield of donor fluorescence for $\gamma \rightarrow 0$, and C_{oDD} and C_{oDA} denote critical concentrations for NEET from molecules D^* to D and D^* to A, respectively.

It should be emphasized that Eq. (3) and subsequently Eq. (7) were obtained on the assumption that the configurations of D and A in the surroundings of the excited donor D^* are independent before and after the excitation energy jump. Partial consideration of the correlations may be achieved [22] when $R_o(t)$ is replaced by a function,

$$R(t) = \exp[-2(2^{-1/2}\gamma_D)(t/\tau_{oD})^{1/2}] \quad (10)$$

obtained by Huber *et al.* [23].

Inserting (10) in (3) gives [14]

$$\eta_D = \eta_{oD} [1 - f(\gamma')]/[1 - \alpha' f(\gamma')] \quad (11)$$

where

$$\gamma' = 2^{-1/2}\gamma_D + \gamma_A, \quad \alpha' = 2^{-1/2}\gamma_D (2^{-1/2}\gamma_D + \gamma_A)^{-1} \quad (12)$$

Equations (7) and (11) differ only in substitution of lower concentration $2^{-1/2}\gamma_D$ for γ_D .

Hence the above correction decreases the effective range of excitation energy migration and trapping by acceptors and consequently increases the donor fluorescence quantum yield. A numerical analysis of Eqs. (7) and (11) leads to the conclusion that the most significant influence of the correlations on the quantum yield η_D may be expected in systems of a high donor concentration.

However, it is well-known that formation of dimers or statistical pairs of dye molecules playing the role of excitation energy traps is a major obstacle in investigations of the NEET process for high donor concentrations.

EXPERIMENTAL

In order to determine the influence of the correlations on the donor quantum yield in a two-component system, five glycerol-alcohol solutions of Na-fluorescein (donor) and rhodamine B (acceptor) were prepared. The donor concentrations C_D for systems I-V were fixed at $2 \cdot 10^{-2}$, $1.5 \cdot 10^{-2}$, 10^{-2} , $3 \cdot 10^{-3}$, and $5 \cdot 10^{-5}$ M, respectively. The acceptor concentration C_A varied from 10^{-5} to $6.3 \cdot 10^{-3}$ M in all the systems.

Na-fluorescein (POCH; Gliwice, Poland) was purified by recrystallization in air from a mixture of ethyl alcohol and ethyl acetate. Rhodamine B (Schuchardt) was purified by multiple crystallization from ethyl alcohol and evaporation in vacuum. Anhydrous glycerol (Fluka AG) and spectrally pure ethanol were used as solvents without any additional purification. Table I presents certain data referring to investigated systems.

The absorption spectra were measured on the Speccord M-40 spectrophotometer. Both fluorescence spectra and relative quantum yields were measured for frontal excitation and sample observation using the apparatus described in Ref. 24. The quantum yield was measured in the spectral range of (520 ± 1) nm by using the method proposed by Förster [3], which is based on com-

parison of the donor fluorescence intensity of the D and A systems of different acceptor densities in layers of the same optical density. If I_1 and I_2 are the observed fluorescence intensities corresponding to the acceptor concentrations C_1 and C_2 for luminophore layers of thicknesses d_1 and d_2 , ensuring the same absorption, then the intensity ratio I_1^0/I_2^0 , reduced to the surface layer, can be found from the relation

$$I_1^0/I_2^0 = (I_1/I_2) F(\xi)$$

where

$$F(\xi) = [1 - \beta d_2 g(\xi)]/[1 - \beta d_1 g(\xi)]$$

$$g(\xi) = [1 - (1 + \xi) \exp(-\xi)]/\{\xi [1 - \exp(-\xi)]\},$$

$$\xi = \ln 10 (\epsilon_{\text{exc}} + \epsilon_{\text{obs}}) Cd$$

ϵ_{exc} and ϵ_{obs} denote the decimal molar extinction coefficients for the exciting and observed light, respectively, and β is the optical system constant. The intensity ratio I_1^0/I_2^0 is equal to the fluorescence yield ratio for the investigated system of concentrations C_1 and C_2 , respectively. For extremely low acceptor concentrations the quantum yield η_D is constant and equal to the limiting value η_{0D} .

In systems of high D and A concentrations, overlapping of the absorption and fluorescence bands leads to reabsorption and secondary fluorescence, influencing the quantum yield η_D .

In order to obtain the true values of fluorescence yield η_D , one should use sufficiently thin samples of thickness d fulfilling the condition [25]

$$C \cdot \epsilon_{\text{max}} \cdot d < 0.1 \quad (13)$$

where C is the dye concentration, and ϵ_{max} is its maximum value of extinction. In our case, because of high concentrations $C_D = 10^{-2}$ M and $\epsilon_{\text{max}} = 0.7 \cdot 10^5$ M⁻¹ cm⁻¹, fulfillment of condition (13) would require cuvettes of thicknesses $d \sim 1$ μ m. However, as has recently been shown [26], the adsorption of dye molecules and their increased concentration in the surface layer may

Table I. Data Characterizing Na-Fluorescein and Rhodamine B Systems in Solutions

Donor	Acceptor	Solvent	T (K)	n	Viscosity (P·s)	λ_{EX} (nm)	λ_{OB} (nm)
Na-fluorescein, C ₂₀ H ₁₀ O ₅ N ₂ , MW 376.29	Rhodamine B, C ₂₈ H ₃₁ O ₃ N ₂ Cl, MW 479.03	Glycerol + 10% ethanol + 0.1 N NaOH	300	1.4657	0.630	500	520

influence the measurement results. Therefore the quantum yield measurements were carried out in cuvettes thick enough ($d = 0.053$ cm) to neglect the effects mentioned above.

The influence of reabsorption and secondary fluorescence on the quantum yield η_D was taken into account by applying the Budo and Ketskemety theory [27]. Calculations of the ratio of secondary to primary fluorescence for individual concentrations were performed on the following assumptions:

- (1) nonradiative and radiative excitation energy transfer from A^* to D does not take place, and
- (2) fluorescence is registered in the region of no acceptor fluorescence.

Both conditions were fulfilled (cf. Fig. 1). The true values of η_D were obtained using the self-consistent method with an accuracy of 10^{-4} . All the calculations considering secondary effects were computed numerically.

The values of η_D were also corrected for the spatial anisotropy distribution of the polarized fluorescence (cf. Refs. 28 and 29).

RESULTS AND DISCUSSION

Figure 1 presents the absorption and emission spectra of Na-fluorescein and rhodamine B in glycerol-alcohol solutions. It has been found that the absorption

spectra of both dyes do not change with increasing concentrations up to 10^{-2} M. Lutz *et al.* have shown [16] that for Na-fluorescein in ethanol the presence of dimers may be neglected up to $3 \cdot 10^{-2}$ M. Hence the presence of fluorescence quenching centers in the investigated range of concentrations may be neglected. One can see from Fig. 1 that the overlapping of the acceptor fluorescence (Rh B) and the donor absorption (Na-Fl) spectra may be practically neglected, and so the nonradiative and radiative back transfer of the excitation energy from A^* to D can be left out of account.

Figure 2a shows the experimental results of the fluorescence quantum yield of donor η_D for system I as well as the theoretical curves calculated from Eqs. (7) and (11) for critical concentrations listed in Table II. Curve 2 corresponds to the case in which correlations have been partially taken into account. It describes the experimental results better than curve 1, which has been calculated assuming that no correlations exist. However, in both cases the theoretical curves considerably differ from the experimental points. If one measures the influence of correlations on the excitation energy transfer by means of the differences of quantum yield η_D/η_{0D} calculated from Eqs. (11) and (7) (curves 2 and 1), it is evident that these differences are prominent within the range of moderate concentrations and disappear for very high and very low concentrations C_A . It should be emphasized that curves 1 and 2 were calculated with no fitting parameters.

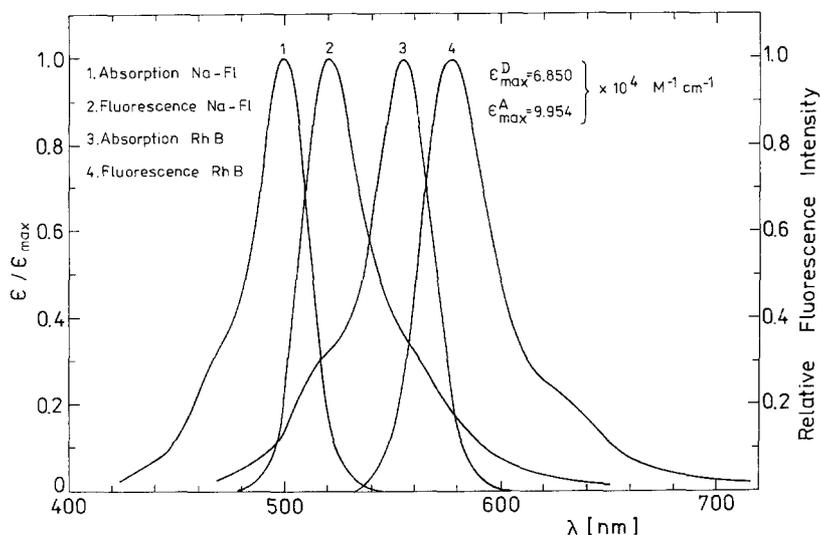


Fig. 1. Electronic absorption and fluorescence spectra of Na-fluorescein (donor) and rhodamine B (acceptor) in glycerol-ethanol solutions.

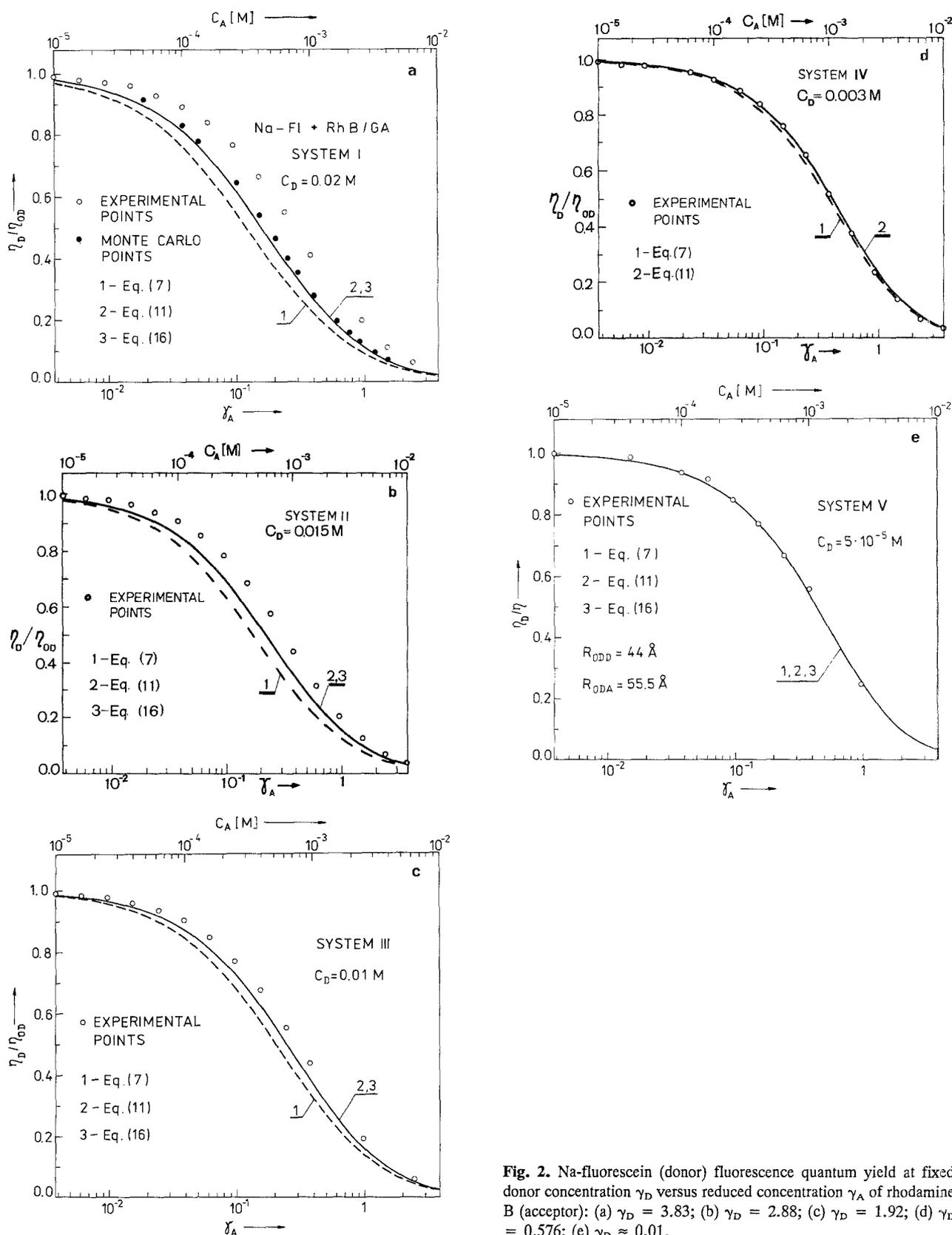


Fig. 2. Na-fluorescein (donor) fluorescence quantum yield at fixed donor concentration γ_D versus reduced concentration γ_A of rhodamine B (acceptor): (a) $\gamma_D = 3.83$; (b) $\gamma_D = 2.88$; (c) $\gamma_D = 1.92$; (d) $\gamma_D = 0.576$; (e) $\gamma_D \approx 0.01$.

Table II. Values of Electronic Energy Transfer Parameters for the Systems Investigated

C_{oDD} $10^{-3} M$	C_{oDA} $10^{-3} M$	R_{oDD} (Å)	R_{oDA} (Å)	\bar{k}^2	$\bar{\gamma}^2$	$z = \frac{R_{oDA}}{R_{oDD}}$	η_{oD}	τ_{oD} (ns)
4.63	2.32	44.0	55.5	0.476	<1	1.26	0.9 ^a	3.69 ^b

^a Based on Ref. 30.

^b Based on Ref. 29.

The critical concentrations were evaluated from relation [19]:

$$C_{oDX} = 4.23 \cdot 10^{-10} n^2 (\eta_{oD} \bar{k}_{DX}^2 I_{DX})^{-1/2},$$

$$X = D, A \quad (14)$$

where n is the refractive index, η_{oD} is the absolute quantum yield of donor fluorescence, and I_{DX} is the overlap integral. \bar{k}_{DX}^2 is the orientation factor, representing the effect of mutual orientation of D^* and X molecules and is usually expressed as

$$\bar{k}_{DX}^2 = (\cos\theta_T - 3 \cos\theta_D \cos\theta_X)^2 \quad (15)$$

where θ_T is the angle between dipole moment vectors of D emission and A absorption, whereas θ_D and θ_X are the angles between these dipoles and the separation vector \bar{R}_{DX} . The absolute yield of Na-fluorescein was taken as $\eta_{oD} = 0.9$ [30]. Similar values in the range 0.9 ± 0.05 were obtained by other authors by means of different measurement methods [31]. We assume that $\bar{k}_{DD}^2 = \bar{k}_{DA}^2 = \bar{k}^2 = 0.476$, a value corresponding to the statical distribution of immobile molecular dipoles [32]. Because of the incomplete rigidity of the medium, the dipoles can slightly reorient themselves within the excited donor lifetime τ_{oD} . An increase in \bar{k}^2 in relation to the limiting value 0.476 calculated as in Ref. 24 for $\tau_{oD} = 3.69$ ns [29] and D molecule rotation time $\tau_r = 250$ ns does not exceed 0.003. The rotation time τ_r was obtained from the Stokes–Einstein relation for the radius of the Na-fluorescein molecule $r = 0.5$ nm and viscosity and temperature T listed in Table I. Finally, the relative change in critical concentrations C_{oDD} and C_{oDA} , caused by \bar{k}^2 increase and η_{oD} deviations, does not exceed 3% and may be neglected. We also neglected the translational diffusion of D and A molecules since the mean diffusion length $\sqrt{\bar{r}^2} < 1 \text{ Å} \ll R_{oDX}$.

Figures 2b–2e present results for systems of lower donor concentrations. As one can see, the influence of correlations on the excitation energy transport decreases with concentration C_D and disappears in system V, in which there is no energy migration. In this case the theoretical curves practically overlap in the whole range of

C_A concentration. The most interesting is the observed deviation of experimental points from the theoretical curves for systems of $C_D \geq 10^{-2} M$.

Systems I, II, and III differ from systems IV and V in that the former have high concentrations of donor molecules. In such systems the effect of a finite volume of D and A molecules may lead to an increase in quantum yield η_D/η_{oD} . As has recently been shown [33] in the case of organic dye solutions for which the critical distances R_{oDD} and R_{oDA} are considerably larger than the distances r_{DD} and r_{DA} of closest approach of interacting molecules, the effect mentioned above may be entirely neglected for $\gamma \leq 10$ if $R_{oDX} \gg 5 \cdot r_{DX}$ ($x = D, A$). Our systems fulfill these conditions and $\gamma_{\max} < 6$. Let us add that Eqs. (7) and (11) were obtained within the frame of hopping approximation, which is suitable for systems with $z = R_{oDA}/R_{oDD} \leq 1$ [11, 15], while for the investigated system $z = 1.26$. Therefore higher than expected experimental values of η_D/η_{oD} may be related to a non-hopping mechanism of the excitation energy transfer [18].

In order to explain this problem, in Fig. 2 the experimental results have been compared also with the theory elaborated by Loring, Anderson, and Fayer (LAF) [13], which, unlike other theories, contains evident dependence of theoretical results on the ratio of critical distances $z = R_{oDA}/R_{oDD}$ and therefore includes not only the hopping ($z \leq 1$) but also the diffusive ($z \gg 1$) mechanism of energy migration [11, 15].

Curve 3 was calculated from Eq. (16) obtained within the three-body approximation of the LAF theory [13]:

$$\eta_D/\eta_{oD} = q(r/r_o)^{-1} \quad (16)$$

where

$$r/r_o = 1 - (\pi/2) (q/2)^{1/2} \gamma'_D + 0.1887 \cdot q$$

$$\cdot \gamma'_D + (0.3832 - \alpha) \cdot q$$

$$\cdot \gamma'_D \cdot \gamma'_A$$

$$q = \left[\frac{-x + (x^2 + y)^{1/2}}{y} \right]^2$$

$$x = (\pi/4) \cdot (\gamma'_D \cdot 2^{-1/2} + \gamma'_A)$$

$$y = 1 - 0.3371 \gamma'_A + 0.1887 \gamma'_D$$

$$- (0.13716 - \alpha + \beta) \gamma'_D \cdot \gamma'_A$$

$$\gamma'_D = 2 \pi^{-1/2} \gamma_D, \quad \gamma'_A = 2 \pi^{-1/2} \gamma_A$$

α and β are functions of $z = R_{oDA}/R_{oDD}$. Their values for chosen z are listed in Ref. 13. Curve 3 was calculated for $\alpha = 0.28939$ and $\beta = 0.67027$, which correspond

to $z = 1.26$. It practically overlaps curve 2 over the whole range of concentrations. The maximum differences of η_D/η_{OD} values computed from Eqs. (11) and (16) do not exceed 0.016 and 0.014 for systems I and II, respectively. That is why the energy migration mechanism in the investigated systems is still a hopping one, although R_{oDA} clearly surpasses R_{oDD} . Let us point out that for systems of $z \approx 1$, Eqs. (11) and (16) predict practically identical concentrational changes of the quantum yield for any values of γ_D and γ_A . However, unlike Eq. (16), the analytical form of Eq. (11) is much simpler. The experimental results are still considerably higher than the theoretical results. This cannot be interpreted as a result of the measurement accuracy (dimensions of circles take into account the standard deviations).

Therefore we consider one more reason which may be responsible for these discrepancies between experimental and theoretical curves, i.e., the application of the mean value of the orientation factor \bar{k}^2 when deriving Eqs. (7), (11), and (16). It is usually assumed that $\bar{k}_d^2 = 2/3$ [19] for sufficiently fast rotational Brownian motion of D* and A molecules and $|\bar{k}_s|^2 = 0.476$ [34,35] for a statistical distribution of fixed molecular dipoles. In solutions of high viscosity every act of excitation energy transfer proceeds for a fixed mutual distance and orientation of the interacting molecular dipoles [cf. Eq. (15)].

Such an exact treatment of the orientation factor was considered in the Monte Carlo simulation of the fluorescence quantum yield of system I. The simulation has been conducted in the similar fashion as presented in Refs. 17 and 18. To avoid finite-system size effects, periodic boundary conditions have been imposed. Taking into account the convergence tests, the number 200 was chosen as an appropriate quantity of donor molecules in one configuration. Simulations have been sampled until the maximum value of the standard deviation of quantum yield was less than 0.5%. The results of simulations carried out for the values of η_{OD} and R_{oDD}^6/k^2 , R_{oDA}^6/k^2 listed in Table II are presented in Fig. 2a as filled circles.

They clearly exceed the theoretical results but to a considerably lesser extent than the experimental data.

The calculations of concentrational changes of emission anisotropy r/r_o carried out by Bodunov [36] using the Monte Carlo method with the exact treatment of the orientation factor also gave similar results; i.e., the values r/r_o exceeded those obtained for the mean value of the orientation factor \bar{k}^2 by about 10%.

The results show that replacing the mean value of orientation factor by its actual value in η_D/η_{OD} calculations reduces the excitation energy migration just as in

the case when correlations in the process of excitation energy among donors are considered. As one can see from Fig. 2a, the orientation factor effect cannot explain the discrepancies between the theory and the experimental results.

Finally, let us consider the influence of Na-fluorescein dimers on the fluorescence quantum yield η_D/η_{OD} of the studied systems. As the absorption spectra of Na-fluorescein in glycerol–ethanol solutions were practically unchanged up to $C_D = 10^{-2} M$, the dimerization constant κ was determined on the basis of concentration-dependent variations of the emission anisotropy and the quantum yield, according to the method described in [37]. The obtained value of $\kappa = 0.21 M^{-1}$ is consistent with the value of $\kappa < 0.6 M^{-1}$ estimated for Na-fluorescein in ethanol by Lutz *et al.* [16]. The concentration of dimers C'' in the studied systems as well as values of quantum yield η_D/η_{OD} (for $C_A = 0$) are presented in Table III.

The influence of dimer presence on quantum yield η_D/η_{OD} in systems I and II is considerable. Figure 3 shows the concentrational changes of quantum yield η_D/η_{OD} in systems I and II, considering the presence of dimers. Theoretical curves have been calculated from Eq. (11) and (16), in which γ_D was replaced by $\gamma' + \gamma''$, where $\gamma' = \sqrt{(\pi/2)} (C'/C_o)$ plays the hitherto role of reduced donor concentration and $\gamma'' = \sqrt{(\pi/2)} (C''/C_o)$ is the reduced concentration of dimers–additional acceptors. $C_o = C_{OMM}$, $C_o' = C_{OMM}/p = 3.26 \cdot 10^{-3} M$, and $p = 1.42$, taken from Bojarski and Dudkiewicz [4].

As Fig. 3 shows, the discrepancies between experimental points and theoretical curves cannot be ascribed to dimer formation.

The above analysis of the influence of different factors on the fluorescence quantum yield η_D in the high concentration range leads to the conclusion that the cause of the discrepancy found between experimental data and the NEET theory should be attributed to the weak points of the latter.

Gomez-Jahn *et al.* [38], who carried out direct mea-

Table III. Dimer Concentrations C'' and Values of Fluorescence Quantum Yield η_D/η_{OD} (for $C_A = 0$) of Na-Fluorescein in Glycerol–Ethanol Solutions

	System				
	I	II	III	IV	V
$C_D(10^{-2} M)$	2	1.5	1	0.3	0.005
$C''(10^{-5} M)$	8.26	4.67	2.08	0.19	0.002
η_D/η_{OD}	0.890	0.947	0.980	1.00	1.00

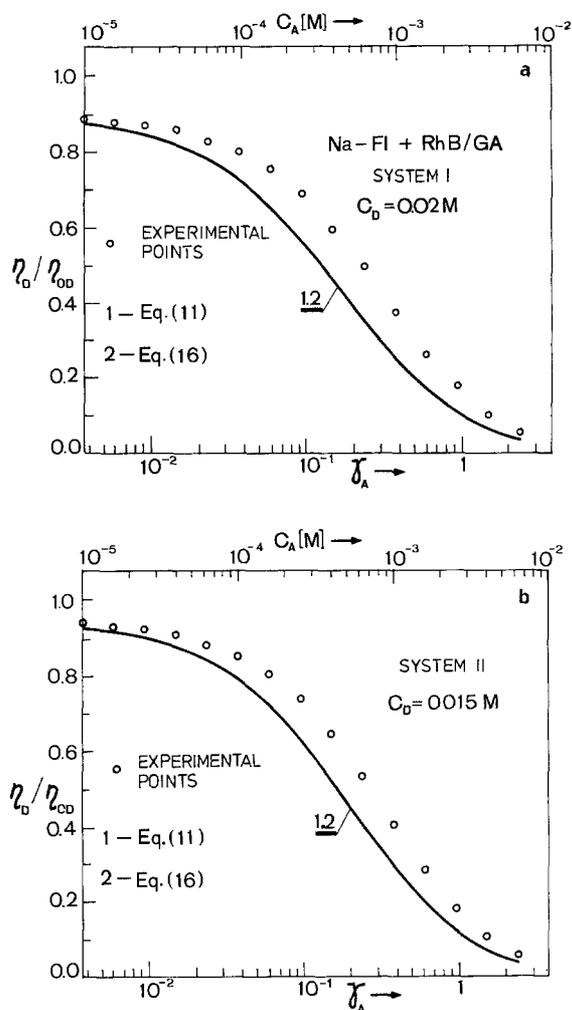


Fig. 3. Concentration changes of fluorescence quantum yield of Na-fluorescein as in Fig. 2, taking into account the presence of Na-fluorescein dimers; equilibrium constant $\kappa = 0.21 \text{ M}^{-1}$ at 300 K.

measurements of excitation energy transport in concentrated ethanolic solutions of Na-fluorescein, also arrived at the similar conclusion. Using the picosecond transient grating technique, they were able to determine the excitation diffusion constant from the grating decays as a function of the reduced concentration. For moderate concentrations, the diffusion constant scales linearly with reduced concentration $\gamma_D^{4/3}$ as theoretically predicted.

However, for higher concentrations they noticed a significant deviation from linear behavior and slower concentrational dependence of the energy transport. We find this effect to be closely connected with ours, because in both cases hampering of energy migration in concentrated solutions was observed.

The authors of Ref. 38 maintain that the mentioned

discrepancy is due to the finite volume effect of the dye molecules, which was neglected in theoretical models; i.e., the interacting molecules were treated as point dipoles.

We have already discussed this problem earlier on and have shown that the finite volume of D and A molecules was not the source of error in our experiment. However, the finite volume of these molecules also denotes their finite number, N_D and N_A , respectively, in the sample of volume V . It should be emphasized that in the Förster theory as well as in NEET theories of other authors, arriving at analytical expressions for the decay function $\phi_D(t)$ or other observables is done by using the transition to infinity with volume V and numbers N_D and N_A , so that $\lim_{V \rightarrow \infty} \frac{N_D}{V} = C_D$ and $\lim_{V \rightarrow \infty} \frac{N_A}{V} = C_A$. In fact, the excited donor interacts with a finite number of donors and acceptors.

Very recently Borshchagovsky [39] discussed the mathematical limitations for the applicability of the Förster decay kinetics, i.e., the case when a single donor interacts with an infinite number of acceptors. The time-dependent correction of the Förster kinetics was obtained, and the limiting acceptor concentration above which this correction should be considered was estimated. The corrected fluorescence decay appeared slower for a system with a finite number of acceptors compared to that for a system with an infinite number of acceptors. One should expect that in donor-acceptor systems with strong energy migration, the influence of the mentioned correction on the fluorescence decay $\phi_D(t)$ and quantum yield η_D will increase as multiple-step excitation transport to the acceptor is considered.

The discussed discrepancy between experimental data and theoretical results can be formally explained if one assumes that in systems of extremely strong migration such as systems I, II, and III, pairs of monomer molecules may be formed, which do not degrade the excitation energy but only confine it and then cause the fluorescence emission. This kind of assumption was put forward in order to explain the mechanism of concentrational fluorescence quenching in solutions [40].

Systems of strong migration with a high donor-to-acceptor concentration ratio are not uncommon. Among them are organic dye solutions, weakly inclined toward aggregation, in which monomers play the role of donors and dimers the role of acceptors as well as natural biological systems.

Further investigations of the mechanism of excitation energy transport in such systems and the explanation of discrepancies between theory and experiment would be useful.

CONCLUSIONS

In this paper we have presented the results of investigations of NEET in donor-acceptor systems of very strong energy migration. We have found a considerable influence of correlations on the donor quantum yield and a significant deviation of the experimental points from the theoretical curves calculated within the framework of current NEET theories. The observed discrepancies have been partially explained as the result of applying the mean value of the orientation factor k^2 in the NEET theories. These theories, developed for systems with infinite number of donors and acceptors, cannot explain the luminescent observables of highly concentrated solutions. A satisfactory explanation of the above-mentioned discrepancies demands further investigations.

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