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Comprehensive examination of radiationless energy transfer models in dyes: Comparisons of theory and experiment

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Experimental data on radiationless energy transfer, covering a wide range of physical conditions, was compared with predictions developed from three different theoretical models, to define and determine their respective validities and range of applicability.

I. INTRODUCTION

Despite the interest shown by many authors[1-21] in the theory of radiationless energy transfer mechanisms between unlike organic dye molecules in solution, a comprehensive theoretical study of transfer mechanisms, applicable to a broad range of experimental situations, has not yet been presented. Thus, for instance, while it may sometimes be easy to distinguish between transfer mechanisms in experiments, no generalized theoretical criteria have been established for selection of the most appropriate mechanism under different physical conditions. Two theoretical approaches for selection criteria have been previously discussed by Birks[5,6] and by Gosele et al.[17-19] However, both these approaches, and experimental confirmation of them, are, as will be discussed, applicable only under certain limiting physical conditions, where energy transfer is due either purely to diffusion, or to dipole–dipole resonance mechanisms.

Gosele et al. also introduced[18] a more generalized theoretical model, which does not rely on selection criteria, and which is intended to apply over the whole range of diffusion and resonance energy transfer parameters which could be expected in quenching experiments. So far, however, no attempt has been made to test Gosele's generalized model experimentally. Nor have any quantitative comparisons been carried out to compute theoretical predictions from the model with existing experimental data available in the literature.

Given Gosele's generalized model, in addition to the other theoretical models, and the existence of extensive experimental data,[7-11] it appears timely to test the validity and range of applicability of the various models advanced, by carrying out a comprehensive and wider ranging set of comparisons between experimental data and theoretical predictions.

To carry out these comparisons, the required analytical expresions for the radiationless transfer efficiency f_{nr} were first derived for each of the models examined and for the different experimental regimes being compared. These were then compared with the equivalent experimental data. The results are discussed below.

II. TRANSFER EFFICIENCY

Each theoretical model considered permits an expression for the time dependence donor concentration $[D^*]$ following instantaneous creation of an initial concentration $[D^*]_0$. The general decay function can be written

$$[D^*] = [D^*]_0 \exp(-t/T_{0d})\exp(-U[A]), \quad (1)$$

where U is a time-dependent quenching coefficient (due to energy transfer from the donor to the acceptor), T_{0d} is the excited donor lifetime in the absence of acceptor, and $[A]$ is the quencher (acceptor) concentration. The donor quantum yield Φ_d in the presence of the acceptor is then

$$\Phi_d = \int_0^\infty K_{fd}[D^*]dt / [D^*]_0 \quad (2)$$

in which K_{fd} is the radiative rate constant for the $[D^*]$ decay.

If Φ_{0d} is taken as the quantum yield of the donor in the absence of the acceptor, where $\Phi_{0d} = K_{fd}T_{0d}$ then

$$\frac{\Phi_d}{\Phi_{0d}} = (1/T_{0d}) \int_0^\infty \exp(-t/T_{0d})\exp(-U[A])dt \quad (3)$$

which applies also to steady-state conditions. Since the nonradiative transfer efficiency f_{nr} is defined as

$$f_{nr} = 1 - \frac{\Phi_d}{\Phi_{0d}}, \quad (4)$$

we can substitute Eq. (3) into Eq. (4) to obtain the final expression for the transfer efficiency as

$$f_{nr} = 1 - (1/T_{0d}) \int_0^\infty \exp(-t/T_{0d})\exp(-U[A])dt. \quad (5)$$

III. THE THREE MODELS COMPARED

Three different theoretical models including Gosele's generalized model have been selected for comparison with the experimental data.

A. The first (standard) model

The first model examined assumes that energy transfer mechanisms may be divided into three kinetic regimes: Stern–Volmer kinetics, Forster kinetics, and intermediate kinetics with the appropriate kinetics being selected in accordance with Birk's selection criteria.

1. Diffusion-controlled or Stern–Volmer kinetics

The approximate criterion for the applicability of Stern–Volmer kinetics will be taken as, $r > 3R_0$, where r, is the mean molecular diffusion length, and R_0 is the critical transfer distance at which one-half of the donor molecules decay by energy transfer and one-half decay by the usual radiative and nonradiative rates. The transfer efficiency in this situation is given by[12]

$$f_{nr} = \frac{K_{dif}[A]}{K_{dif}[A] + T_{0d} - 1}, \qquad (6)$$

where K_{dif}, the rate parameter for a diffusion-controlled collision process, is given by[13]

$$k_{dif} = 2 \times 10^5 \, T/\eta. \qquad (7)$$

2. Forster kinetics

The approximate applicable criterion is, $r < R_0$. The transfer efficiency is then given by[1,2]

$$f_{nr} = \pi^{1/2} \, \Omega \, \exp(\Omega)^2 (1 - \mathrm{erf}\, \Omega), \qquad (8)$$

where

$$\mathrm{erf}(X) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-t^2)\,dt$$

and

$$\Omega = [A]/[A]_0 \quad \text{and} \quad [A]_0 = 3000/2\pi^{3/2}NR_0^3.$$

3. Intermediate kinetics

The approximate applicable criterion is, $3R_0 > r > R_0$. For this situation, the time-dependent quenching coefficient (U) introduced by Voltz et al.[16] is

$$U = 2\pi \, \widetilde{N}DR_0 t + 4\widetilde{N}R_0^2 (\pi Dt)^{1/2}, \qquad (9)$$

where

$$\widetilde{N} = N/1000.$$

Substituting from Eq. (9) into Eq. (5) after carrying out the integration we get (see the Appendix)

$$f_{nr} = 1 - \frac{K_0}{K_v} + \frac{K_0}{K_v^{3/2}} \pi^{1/2} A_v$$
$$\times \exp(A_v^2/K_v)[1 - \mathrm{erf}(A_v/K_v^{1/2})], \qquad (10)$$

where

$$K_v = K_0 + 3.78 \times 10^{21} DR_0[A]$$

and

$$A_v = 2.134 \times 10^{21} \sqrt{D}\, R_0^2 [A],$$

$K_0 = 1/T_{0d}$, and where the diffusion coefficient D is given by $D = D_d + D_a$, where D_d and D_a are the diffusion coefficients of donor and acceptor.

B. The second model

This model assumes that energy transfer mechanisms may be divided into two kinetic regimes: Pure diffusion, combined diffusion, and long-range (resonance) interactions, with the appropriate kinetics being selected in accordance with Gosele's selection criteria.

1. Pure diffusion kinetics

Gosele et al.[17-19] introduced a dimensionless parameter Z_0 defined as

$$Z_0 = \left[\frac{1}{2r_{ad}^2}\right] \left[\frac{R_0^6}{T_{0d}D}\right]^{1/2},$$

where r_{da} is the distance of closest approach of the donor and acceptor. For the pure diffusion case, the approximate criterion applicable will be taken as $z_0 \ll 1$. The time dependent quenching coefficient $U(t)$ is given by the usual expression for pure diffusion,[17]

$$U(t) = 4\pi D r_{ad}\widetilde{N}t + 4\pi r_{ad}^2 \widetilde{N}(Dt/\pi)^{1/2}. \qquad (11)$$

Following the general approach developed in Sec. II, if we substitute Eq. (11) into Eq. (5) we get

$$f_{nr} = 1 - \frac{K_0}{K_2} + \frac{K_0}{K_2^{3/2}} \pi_2^1 A_2 \exp(A_2^2/K_2)$$
$$\times [1 - \mathrm{erf}(A_2/K_2^{1/2})], \qquad (12)$$

where

$$K_2 = K_0 + 4\pi r_{ad}\widetilde{N}[A]D$$

and

$$A_2 = 2(\pi D)^{1/2} r_{ad}^2 \widetilde{N}[A].$$

Note that these kinetics corresponds to the Stern–Volmer kinetics introduced in the first model.

2. Combined diffusion and long-range (resonance) interactions

The approximate criterion applicable for this situation will be taken as, $Z_0 \gg 1$. The time dependent quenching coefficient $U(t)$ is then given by[17]

$$U(t) = 4\pi D r_f \widetilde{N}t + (4/3)\pi^{3/2}\widetilde{N}R_0^3 [t/T_{0d}]^{1/2}, \qquad (13)$$

where

$$r_f = 0.676(R_0^6/T_{0d}D)^{1/4}.$$

Substituting Eq. (13) into Eq. (5), then gives

$$f_{nr} = 1 - \frac{K_0}{K_g} + \frac{K_0}{K_g^{3/2}}\pi 1/2 A_g \, \exp(A_g^2/K_g)$$
$$\times [1 - \mathrm{erf}(A_g/K_g^{1/2})], \qquad (14)$$

where

$$K_g = K_0 + 4\pi D r_f \widetilde{N}[A]$$

and

$$A_g = (2/3)\pi^{3/2}\widetilde{N}R_0^3[A]K_0^{1/2} = \Omega K_0^{1/2}.$$

Note that these kinetics combine both Forster and the intermediate kinetics. Therefore as $D \to 0$, $K_g = K_0$, Eq. (14) reduces to

$$f_{nr} = \pi 1/2 \, \Omega \, \exp(\Omega^2)[1 - \mathrm{erf}(\Omega)] \qquad (8)$$

which is exactly the same as the transfer efficiency for the Forster kinetic.

C. The third model (Gosele's generalized model)

In this section we derive a general expression for the nonradiative transfer efficiency (f_{nr}) valid for all kinetics,

over the whole range of Z_0 and D. Gosele et al.[17-19] introduced a rough approximation for the time dependent quenching coefficient $U(t)$, over the whole range of diffusion and resonance energy transfer parameters in quenching experiments, given by

$$U(t) = 4\pi DR_{eff} t\widetilde{N} + 8\pi 1/2\, D\, 1/2\, R_{eff}^2 t\, 1/2\, \widetilde{N}, \quad (15)$$

where

$$R_{eff} = r_{ad} + 0.724\left[\frac{R_0^6 K_0}{D}\right]^{1/4}.$$

Equation (15) covers all limiting cases, such as

$D \to 0$, $R_0 \to 0$, D very large or R_0 very large,

$t \to 0$ or $t \to \infty$.

This equation represents a useful approximation over the whole range of diffusion and resonance energy transfer parameters.

Following the general approach developed in Sec. II, if we substitute Eq. (15) into Eq. (5), we obtain

$$f_{nr} = 1 - \frac{K_0}{K_3} + \frac{K_0}{K_3^{3/2}}\,\pi 1/2\, A_3 \exp(A_3^2/K_3)$$

$$\times\left[1 - \mathrm{erf}(A_3/K_3^{1/2})\right], \quad (16)$$

where

$$K_3 = K_0 + 4\pi DR_{eff}\widetilde{N}[A]$$

and

$$A_3 = 4\pi\tfrac{1}{2}\, D\tfrac{1}{2}\, R_{eff}^2\widetilde{N}[A].$$

IV. EXPERIMENTAL DATA: RESULTS AND ANALYSIS

Seven different sets of experimental data for quantum efficiency of radiationless energy transfer, reported in the literature,[7-11] have been selected for comparisons with theoretical results calculated according to the three models introduced in the previous section.

The first and second sets of experimental data were reported by Birks et al.,[7] where the yield of nonradiative energy transfer was measured for the following pair of dyes:

TABLE I. Transfer quantum efficiency (f_{nr}) in napthalene (0.1 M)–DPA [A] solutions.

Solvent \ [A] (10^{-3} M)			0.10	0.20	0.30	0.50	1.00	2.00	3.00	5.00
	f_{nr}	(exp)	0.170	0.260	0.320	0.430	0.570	0.740	0.810	0.870
Benzene	Mod 1	(Stern)	0.100	0.176	0.242	0.347	0.515	0.680	0.761	0.842
$\cap = 0.62$	Mod 2	> (Diff)	0.150	0.265	0.350	0.470	0.640	0.785	0.846	0.900
$Z_0 = 0.97$		> (Res)	0.140	0.250	0.330	0.460	0.630	0.776	0.840	0.899
$R_0 = 24.2$ Å	Mod		0.276	0.435	0.538	0.663	0.802	0.894	0.929	0.958
	f_{nr}	(exp)	0.160	0.270	0.330	0.430	0.590	0.750	0.800	0.880
Cyclohexane	Mod 1	(Stern)	0.080	0.140	0.200	0.290	0.450	0.620	0.710	0.800
$\cap = 0.98$	Mod 2	> (Diff)	0.120	0.215	0.290	0.410	0.580	0.735	0.800	0.880
$Z_0 = 1.2$		> (Res)	0.125	0.220	0.300	0.420	0.590	0.750	0.818	0.884
$R_0 = 24.7$ Å	Mod 3		0.237	0.385	0.487	0.616	0.767	0.874	0.915	0.948
	f_{nr}	(exp)	0.090	0.120	0.220	0.300	0.440	0.570	0.720	0.770
B(60%) C(40%)	Mod 1	(Stern)	0.036	0.070	0.100	0.157	0.270	0.430	0.530	0.650
$\cap = 1.57$	Mod 2	> (Diff)	0.060	0.100	0.160	0.240	0.390	0.560	0.660	0.766
$Z_0 = 1.5$		> (Res)	0.070	0.130	0.190	0.280	0.440	0.610	0.700	0.800
$R_0 = 23.4$ Å	Mod 3		0.136	0.242	0.325	0.448	0.626	0.777	0.845	0.906
	f_{nr}	(exp)	0.050	0.080	0.150	0.190	0.300	0.440	0.520	0.650
B(30%) C(70%)	Mod 1	(Stern)	0.010	0.020	0.030	0.048	0.090	0.170	0.234	0.337
$\cap = 5.89$	Mod 2	> (Diff)	0.017	0.030	0.050	0.080	0.150	0.260	0.350	0.470
$Z_0 = 2.9$		> (Res)	0.030	0.060	0.090	0.140	0.240	0.400	0.500	0.630
$R_0 = 23.4$ Å	Mod 3		0.056	0.107	0.153	0.234	0.385	0.567	0.671	0.785
	f_{nr}	(exp)	0.040	0.040	0.080	0.080	0.160	0.280	0.390	0.500
B(10%) C(90%)	Mod 1	(Voltz)	0.010	0.027	0.040	0.060	0.130	0.230	0.310	0.440
$\cap = 25.2$	Mod 2	(Res)	0.014	0.028	0.042	0.069	0.129	0.234	0.318	0.447
$Z_0 = 6$	Mod 3		0.024	0.047	0.069	0.110	0.202	0.345	0.450	0.593
$R_0 = 23.5$ Å										
Cyclo-	f_{nr}	(exp)	0.030	0.040	0.070	0.060	0.120	0.260	0.290	0.440
hexanol (C)	Mod 1	(Voltz)	0.006	0.013	0.019	0.030	0.060	0.120	0.170	0.260
$\cap = 68.0$	Mod 2	(Res)	0.009	0.019	0.028	0.045	0.087	0.164	0.230	0.341
$Z_0 = 10$	Mod 3		0.015	0.029	0.043	0.070	0.133	0.241	0.329	0.466
$R_0 = 23.3$ Å										

TABLE II. Transfer quantum efficiency (f_{nr}) in PPO (10^{-2} M)–DPA [A] solutions.

Solvent \ [A] (10^{-3} M)		2	3	4	5	7
Cyclohexane	f_{nr} (exp)	0.340	0.440	0.520	0.580	0.700
$\cap = 0.98$	Mod 1 (Forst	0.290	0.390	0.480	0.550	0.650
$Z_0 = 25$	Mod 2 (Res)	0.410	0.530	0.620	0.680	0.760
$R_0 = 35.6$ Å	Mod 3	0.500	0.620	0.710	0.760	0.830
Cyclohexanol	f_{nr} (exp)	0.280	0.400	0.490	0.540	0.660
$\cap = 68$	Mod 1 (Forst)	0.270	0.370	0.450	0.520	0.630
$Z_0 = 205$	Mod 2 (Res)	0.280	0.380	0.460	0.530	0.640
$R_0 = 34.8$ Å	Mod 3	0.310	0.420	0.500	0.570	0.680

TABLE III. Transfer quantum efficiency (f_{nr}) in Rh6G (1.25×10^{-3} M)–O×4 [A] solutions.

Solvent \ [A] (10^{-3} M)		0.313	0.625	1.25	2.50	5.0
Ethyleneglycol	f_{nr} (exp) %	16.4 ± 3	27.2 ± 3	47.7 ± 6	72.0 ± 7	81.5 ± 9
$\cap = 26.09$	Mod 1 (Fors)	0.180	0.330	0.530	0.740	0.890
$R_0 = 56$ Å	Mod 2 (Res)	0.190	0.330	0.540	0.750	0.900
$Z_0 = 620$	Mod 3	0.200	0.360	0.560	0.770	0.920

TABLE IV. Transfer quantum efficiency (f_{nr}) in RhB (1.25×10^{-3} M)–NB [A] solutions.

Solvent \ [A] (10^{-3} M)		0.313	0.625	1.25	2.50	5.0
Ethyleneglycol	f_{nr} (exp) %	15 ± 4	20 ± 1	41 ± 5	64 ± 4	81 ± 6
$\cap = 26.09$	Mod 1 (Fors)	0.170	0.310	0.500	0.720	0.880
$R_0 = 54$ Å	Mod 2 (Res)	0.170	0.310	0.510	0.720	0.880
$Z_0 = 621$	Mod 3	0.190	0.330	0.530	0.750	0.900

(1) Naphthalene (the donor) and 9,10 diphenylanthracene (the acceptor) in six different solvents with viscosities ranging from $\eta = 0.62$ CP to 68 CP at a fixed donor concentration, [D] = 0.1 M and various acceptor concentrations ranging from [A] = 10^{-4} to 5×10^{-3} M.

(2) 2,5 Diphenyloxazole (the donor) and 9,10 diphenylanthracene (the acceptor) in two different solvents at a fixed donor concentration, [D] = 0.01 M and various acceptor concentrations ranging from [A] = 10^{-4} to 5×10^{-3} M.

Table I lists the values of energy transfer efficiency f_{nr} obtained experimentally for different N–DPA solutions, f_{nr} values calculated according to the three theoretical models discussed above are also tabulated. These calculated values for f_{nr} depend on the kinetics selected according to the Birks criteria for the first model, and according to the Gosele criteria for the second model. Whenever it was not clear which kinetics would be applicable in the second model, i.e., when $1 \ll Z_0 \gg 1$, we have tabulated two values for f_{nr}, one value corresponding to resonance kinetics, while the other value corresponds to diffusion kinetics.

Table II lists the experimental results[7] and our theoretical calculations for f_{nr} for different PPO–DPA solutions.

The third and fourth sets of experimental data were re-

ported by Alfano et al.,[9] where the yield of nonradiative energy transfer was determined for the following pair of dyes:

(1) Rhodamine-6G (the donor) and oxazine-4 perchlorate (the acceptor).

(2) Rhodamine-B (the donor) and nile blue A perchlorate (the acceptor).

In both mixtures ethyleneglycol was used as the solvent at a fixed donor concentration, [D] = 1.25×10^{-3} M and various acceptor concentrations ranging from [A] = 3.13×10^{-4}–5×10^{-3} M. Tables III and IV list the experimental results[9] and our theoretical calculations for f_{nr} for the Rh6G-O×4 and RhB-NB solutions in ethyleneglycol.

The fifth set of experimental data were reported by Elkana et al.,[10] where the yield of nonradiative energy transfer from naphthalene (the donor) to anthranilic acid (the acceptor) was calculated at ten different solvents with viscosities ranging from $\eta = 0.6$ to 1000 CP at a fixed donor concentration, [D] = 5×10^{-3} M and various acceptor concentrations ranging from : [A] = 10^{-3}–5×10^{-3} M. Table V lists the experimental results[10] and our theoretical calculations for f_{nr} for different N–anthranilic acid solutions.

The sixth set of experimental data were reported by Birks et al.,[8] where the yield of nonradiative energy transfer

TABLE V. Transfer quantum efficiency (f_{nr}) in napthalene (0.1 M)–anthranilic acid [A] solutions.

Solvent \ [A] (10^{-3} M)			5	2	1
	f_{nr}	(exp)	0.920	0.830	0.660
Methanol	Mod 1	(Stern)	0.810	0.650	0.460
$\cap = 0.6$	Mod 2	$\gg$ (Diff)	0.881	0.745	0.592
$Z_0 = 1$		$\gg$ (Res)	0.886	0.750	0.600
$R_0 = 22.8$ Å	Mod 3		0.950	0.875	0.769
	f_{nr}	(exp)	0.780	0.600	0.450
Tert-butanol	Mod 1	(Stern)	0.340	0.170	0.094
$\cap = 4.8$	Mod 2	$\gg$ (Diff)	0.479	0.267	0.154
$Z_0 = 2.9$		$\gg$ (Res)	0.640	0.510	0.254
$R_0 = 22.4$ Å	Mod 3		0.787	0.570	0.388
	f_{nr}	(exp)	0.390	0.280	
Glycerol	Mod 1	(Forst)	0.230	0.100	
$\cap = 1000$	Mod 2	(Res)	0.242	0.108	
$Z_0 = 40$	Mod 3		0.310	0.141	
$R_0 = 22.4$ Å					
	f_{nr}	(exp)	0.530		
Cyclohexanol	Mod 1	(Voltz)	0.270		
$\cap = 65$	Mod 2	(Res)	0.341		
$Z_0 = 9.2$	Mod 3		0.468		
$R_0 = 22.2$ Å					
	f_{nr}	(exp)	0.560		
Ethyleneglycol	Mod 1	(Voltz)	0.465		
$\cap = 17.4$	Mod 2	$\gg$ (Diff)	0.210		
$Z_0 = 4.9$		$\gg$ (Res)	0.448		
$R_0 = 23.5$ Å	Mod 3		0.602		
	f_{nr}	(exp)	0.770		
Amylalcohol	Mod 1	(Stern)	0.425		
$\cap = 4.3$	Mod 2	$\gg$ (Diff)	0.567		
$Z_0 = 2.6$		$\gg$ (Res)	0.710		
$R_0 = 23$ Å	Mod 3		0.831		
	f_{nr}	(exp)	0.860		
n-Butanol	Mod 1	(Stern)	0.485		
$\cap = 2.8$	Mod 2	$\gg$ (Diff)	0.624		
$Z_0 = 2.1$		$\gg$ (Res)	0.726		
$R_0 = 22.2$ Å	Mod 3		0.850		
	f_{nr}	(exp)	0.840		
Isopropanol	Mod 1	(Stern)	0.580		
$\cap = 1.95$	Mod 2	$\gg$ (Diff)	0.706		
$Z_0 = 1.8$		$\gg$ (Res)	0.790		
$R_0 = 22.6$ Å	Mod 3		0.885		
	f_{nr}	(exp)	0.900		
Ethanol	Mod 1	(Stern)	0.710		
$\cap = 1.2$	Mod 2	$\gg$ (Diff)	0.807		
$Z_0 = 1.47$		$\gg$ (Res)	0.840		
$R_0 = 23$ Å	Mod 3		0.924		
	f_{nr}	(exp)	0.760		
Isobutanol	Mod 1	(Stern)	0.440		
$\cap = 4.1$	Mod 2	$\gg$ (Diff)	0.580		
$Z_0 = 2.6$		$\gg$ (Res)	0.720		
$R_0 = 23.2$	Mod 3		0.830		

TABLE VI. Transfer quantum efficiency (f_{nr}) in napthalene (0.05 M)–biacetyl [A] solutions.

Solvent \ [A] $(10^{-3}$ M)			0.1	0.5	1.0	3.0	5.0
Hexane	f_{nr}	(exp)	0.020	0.080	0.155	0.355	0.480
$\cap = 0.34$	Mod 1	(Stern)	0.015	0.070	0.130	0.310	0.430
$R_0 = 4.2$ Å	Mod 2	(Diff)	0.025	0.110	0.200	0.440	0.566
$Z_0 = 0.01$	Mod 3		0.030	0.130	0.230	0.480	0.600
Benzene	f_{nr}	(exp)	0.026	0.120	0.210	0.440	0.570
$\cap = 0.62$	Mod 1	(Stern)	0.020	0.080	0.150	0.350	0.470
$R_0 = 4.8$ Å	Mod 2	(Diff)	0.030	0.130	0.230	0.480	0.600
$Z_0 = 0.02$	Mod 3		0.035	0.150	0.270	0.530	0.650
ISO (50%)	f_{nr}	(exp)	0.010	0.050	0.090	0.230	0.330
C (50%)	Mod 1	(Stern)	0.003	0.010	0.030	0.080	0.120
$\cap = 10$	Mod 2	(Diff)	0.005	0.025	0.050	0.130	0.200
$R_0 = 5.6$ Å	Mod 3		0.007	0.035	0.070	0.180	0.275
$Z_0 = 0.07$							
Liquid paraffin	f_{nr}	(exp)	0.005	0.020	0.040	0.120	0.180
$\cap = 172$	Mod 1	(Voltz)	0.00036	0.002	0.004	0.010	0.018
$Z_0 = 0.28$	Mod 2	≫ (Res)	0.00032	0.0016	0.003	0.0095	0.016
$R_0 = 5.9$ Å		≫ (Diff)	0.0006	0.003	0.006	0.020	0.030
	Mod 3		0.001	0.007	0.014	0.040	0.060

from naphthalene (the donor) to biacetyl (the acceptor) was determined at four different solvents with viscosities ranging from $\eta = 0.34$ to 172 CP at a fixed donor concentration, [D] $= 5 \times 10^{-3}$ M and various acceptor concentrations ranging from [A] $= 10^{-4}$–5×10^{-3} M. Table VI lists

the experimental results[8] and our theoretical calculations for f_{nr} for different N–biacetyl solutions.

Finally the last set of experimental data were reported by Feitelson,[11] where the yield of nonradiative energy transfer from P-terphenyl (the donor) to 9-methylanthracene

TABLE VII. Transfer quantum efficiency (f_{nr}) in terphenyl (5×10^{-4}) M–9 methylanthracene [A] solutions.

Solvent \ [A] (10^{-3})			0.5	1.0	2.0	5.0
Cyclohexane	f_{nr}	(exp)	0.110	0.170	0.280	0.530
$\cap = 1$ CP	Mod 1	(Forst)	0.040	0.080	0.160	0.350
$Z_0 = 21$	Mod 2	(Res)	0.070	0.130	0.230	0.450
$R_0 = 28.1$ Å	Mod 3		0.090	0.170	0.300	0.550
Methanol	f_{nr}	(exp)	0.120	0.200	0.310	0.540
$\cap = 0.6$ CP	Mod 1	(Forst)	0.050	0.100	0.190	0.400
$Z_0 = 19$	Mod 2	(Res)	0.090	0.160	0.290	0.530
$R_0 = 29.7$ Å	Mod 3		0.120	0.220	0.370	0.640
Iso-propanol	f_{nr}	(exp)	0.100	0.170	0.290	0.530
$\cap = 2.3$ CP	Mod 1	(Forst)	0.048	0.090	0.180	0.380
$Z_0 = 36$	Mod 2	(Res)	0.060	0.120	0.220	0.450
$T_0 = 29$ Å	Mod 3		0.080	0.150	0.270	0.520
Tert-butanol	f_{nr}	(exp)	0.090	0.200	0.300	0.500
$\cap = 4.1$ CP	Mod 1	(Forst)	0.045	0.090	0.170	0.350
$Z_0 = 43$	Mod 2	(Res)	0.050	0.100	0.190	0.390
$R_0 = 28.7$ Å	Mod 3		0.070	0.130	0.230	0.470
Cyclohexanol	f_{nr}	(exp)	0.080	0.140	0.230	0.440
$\cap = 68$ CP	Mod 1	(Forst)	0.040	0.080	0.150	0.330
$Z_0 = 165$	Mod 2	(Res)	0.040	0.081	0.154	0.332
$R_0 = 27.8$ Å	Mod 3		0.050	0.090	0.180	0.370

(the acceptor) was determined at five different solvents with viscosities ranging from $\eta = 0.6$ to 68 CP at a fixed donor concentration, $[D] = 5 \times 10^{-4}$ M and acceptors at various concentrations ranging from $[A] = 5 \times 10^{-4} - 5 \times 10^{-3}$ M. Table VII lists the experimental results[11] and our theoretical calculations for f_{nr} for different PT–9M solutions.

The critical transfer distance R_0, and the dimensionless parameter Z_0 are included in all tables. It is informative and important to note that in all the experimental data reported here, the donor concentrations were chosen such that, concentratin quenching, self-absorption, and migration of the donor excitation, which would increase the effective transfer efficiency, are all absent. All data required for the calculations of f_{nr} values for the three models are obtained from the same reference where the experimental data are reported.

V. DISCUSSION AND CONCLUSION

A comparison of the calculated values of f_{nr} for the three models given in Tables I–VII with the corresponding experimental values given in the first row of every table reveals that:

(1) When R_0 is high ($R_0 > 30$ Å), Tables II–IV, it appears that the first (standard) model agrees closely with the experimental data as long as the Forster kinetics is selected and diffusion does not play a major role. The second model gives almost the same results as the first model provided that diffusion effects are not significant, it also appears as though it would overestimate the actual values of f_{nr} when diffusion effects are significant. The third model shows poor agreement with the experimental data and always overestimates the actual values of f_{nr}. Under these conditions where R_0 is high meaning that $Z_0 \gg 1$, the Gosele criteria are the most appropriate.

(2) When R_0 has an intermediate value (20 Å $< R_0 < 30$ Å), Tables I, V, and VII, with lower viscosity, and when diffusion plays a major role, the second model appears to agree closely with the experimental data. As the viscosity gets higher, the third model appears to have the edge in getting the closest fit to the experimental results.

In general, at very high viscosity, where energy transfer is expected to proceed according to the theory of Forster, all models including the third model underestimate the actual values of f_{nr}. This may be due to the neglect of higher multipole–multipole terms in the evaluation of R_0. Obviously the effects of neglecting such terms will be more important when R_0 is small. What is needed is an extension of the Forster theory to allow for the effects of higher multipole–multipole interaction terms on the magnitude of R_0.

For the less viscous solution, the f_{nr} values, although sensitive to D, are relatively insensitive to R_0. A careful inspection of all the Z_0 values listed in Table I and Table V clearly indicates that the Gosele criterion for the applicability of long-range (resonance) kinetics, may be modified to $Z_0 > 1$, and not $Z_0 \gg 1$.

A comparison of the theoretically calculated values for f_{nr} using the first model (with Stern–Volmer diffusion kinetics selected) and the second model, with experimental values (Tables I and V), show that, the second model, with resonance kinetics selected, gives the best fit with the experimen-

tal data. One is then led to the conclusion that the Birk's criterion, for the applicability of diffusion kinetics can not be considered as a valid general rule. This conclusion is even more accurate when $Z_0 > 2$, and R_0 is large and long-range kinetics contribute significantly to the transfer efficiency.

(3) When R_0 is small, with a value between the collisional interaction radius ($R = 5$–6 Å) and the electron-exchange interaction radius ($R = 6$–12 Å), Table VI, energy transfer should proceed as a diffusion controlled process and long-range mechanism can be expected to have almost no effect on energy transfer.

For lower viscosity solvents, Table VI shows that, when, for instance, hexane was the solvent, the diffusion kinetics of the first model, Stern–Volmer, gave the closest fit to the experimental data. When the solvent was benzene, the diffusion kinetics of the second model gave the closest fit to the experimental results.

As the viscosity got high, all three models, as expected, underestimated the actual values of f_{nr}. The reason for this is that none of the three models includes a term to account for short range electron-exchange interactions. It is also clear that under these circumstances, the Birk's criterion for the Stern–Volmer diffusion kinetics is not going to be invalidated, since long-range mechanisms do not contribute at all to the transfer efficiency. This is also true for the Gosele diffusion criterion, sinze $Z_0 \ll 1$ for all values listed in Table VI.

In conclusion, it appears that at lower viscosities, one of the three models presented, will give a fair agreement between experimental data and theoretical predictions. As the viscosity is increased, and the Forster distance R_0 is reduced, all three models presented underestimate the experimental data. The reason for this is that because contributions from additional terms in the dipole expansion and/or short range electron-exchange mechanisms, are not considered in the models. To allow for these, a theoretical model which takes into account contributions from higher multipole–multipole and/or exchange interaction terms is required.

APPENDIX

$$f_{nr} = 1 - K_0 \int_0^\infty \exp(-tK_0)\exp(-U[A])dt$$

$$= 1 - K_0 \int_0^\infty \exp(-tK_0)\exp[-\{2\pi\tilde{N}DR_0[A]t + 4\tilde{N}R_0^2(\pi D)^{1/2}[A]t^{1/2}\}],$$

$$f_{nr} = 1 - K_0 \int_0^\infty \exp[K_0 + 2\pi\tilde{N}DR_0[A]]t$$

$$\times \exp - [4\tilde{N}R_0^2(\pi D)^{1/2}[A]t^{1/2}]$$

$$= 1 - K_0 \int_0^\infty \exp(-K_v t)\exp(-2A_v t^{1/2})dt,$$

where

$$K_v = K_0 + 2\pi \widetilde{N} D R_0 [\text{A}],$$

$$A_v = 2\widetilde{N} R_0^2 (\pi D)^{1/2} [\text{A}].$$

Let

$$Y = \int_0^\infty \exp[-(K_v t + 2A_v t^{\frac{1}{2}})]\, dt,$$

now

$$x = t^{\frac{1}{2}} \rightarrow dx = \frac{dt}{2t^{\frac{1}{2}}} = \frac{dt}{2x}$$

$$\rightarrow dt = 2x\, dx,$$

$$t = 0 \rightarrow x = 0,$$

$$t = \infty \rightarrow x = \infty,$$

$$Y = 2\int_0^\infty \exp[-(K_v x^2 + 2A_v x)]dx,$$

$$Y = 2\exp(A_v^2/K_v)\int_0^\infty x$$

$$\times \exp[-(K_v^{1/2}x + A_v/K_v^{1/2})^2]\, dx,$$

$$Y = 2\exp(A_v^2/K_v)\int_0^\infty x\exp\left[\frac{K_v x + A_v}{K_v^{1/2}}\right]^2 dx.$$

Let

$$\left[\frac{K_v x + A_v}{K_v^{1/2}}\right] = r,$$

$$K_v x + A_v = rK_v^{1/2} \rightarrow dx = dr/K_v^{1/2},$$

$$X = \left[\frac{r}{K_v^{1/2}} - \frac{A_v}{K_v}\right] \rightarrow \begin{array}{l} x = 0 \rightarrow \quad r = A_v/K_v^{1/2} \\ x = \infty \rightarrow \quad r = \infty \end{array},$$

$$Y = \frac{2\exp(A_v^2/K_v)}{K_v^{1/2}}\int_{A_v/K_v^{1/2}}^\infty \left[\frac{r}{K_v^{1/2}} - \frac{A_v}{K_v}\right]$$

$$\times \exp(-r^2)dr,$$

$$Y = \frac{2\exp(A_v^2/K_v)}{K_v}\int_{A_v/K_v^{1/2}}^\infty r\exp(-r^2)dr$$

$$- \frac{2A_v \exp(A_v^2/K_v)}{K_v^{3/2}}\int_{A_v/K_v^{1/2}}^\infty \exp(-r^2)dr,$$

$$Y = \frac{\exp(A_v^2/K_v)}{K_v}\int_{A_v/K_v^{1/2}}^\infty 2r\exp(-r^2)dr$$

$$- \frac{\pi^{1/2}}{K_v^{3/2}}A_v\exp(A_v^2/K_v)\frac{2}{\pi^{1/2}}$$

$$\times \int_{A_v/K_v^{1/2}}^\infty \exp(-r^2)dr.$$

Let

$$y = r^2,$$

$$Y = \frac{\exp(A_v^2/K_v)}{K_v}\int_{A_v/K_v^{1/2}}^\infty \exp(-y)dy$$

$$- \frac{\pi^{1/2}}{K_v^{3/2}}A_v\exp(A_v^2/K_v)[1 - \text{erf}(A_v/K_v^{1/2})],$$

$$Y = \frac{1}{K_v} - \frac{\pi^{1/2}}{K_v^{3/2}}A_v\exp(A_v^2/K_v)[1 - \text{erf}(A_v/K_v^{1/2})],$$

$$f_{\text{nr}} = 1 - K_0\left[\frac{1}{K_v} - \frac{\pi^{1/2}}{K_v^{3/2}}A_v\right.$$

$$\left.\times \exp(A_v^2/K_v)(1 - \text{erf}(A_v/K_v^{1/2}))\right],$$

$$f_{\text{nr}} = 1 - \frac{K_0}{K_v} + \frac{K_0}{K_v^{3/2}}\pi^{1/2}A_v$$

$$\times \exp(A_v^2/K_v)[1 - \text{erf}(A_v/K_v^{1/2})].$$

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