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Examination of a generalized model for radiationless energy transfer in dyes. Comparisons of theory and experiments

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A modified general model for radiationless energy transfer is examined. The model does not rely on selection criteria and is intended to apply over the range of diffusion and resonance energy transfer parameters normally encountered in quenching experiments. Experimental data is compared with theoretical predictions and found to confirm the model's validity for a wide range of physical conditions.

I. INTRODUCTION

The subject of energy transfer between unlike organic dye molecules in solution has received considerable theoretical attention.[1-19] The main mechanisms that have been proposed for such an energy transfer are (1) radiative transfer, i.e., absorption of donor emission by an acceptor, (2) diffusion controlled collisional transfer, and (3) resonance transfer due to long-range dipole–dipole interactions.[2-8] Recently,[20] in an attempt to test the validity and range of applicability of the various models advanced, we have presented a comprehensive theoretical study of radiationless energy transfer mechanisms, applicable to a broad range of experimental situations. Three different theoretical models were presented and examined by carrying out a comprehensive and wider ranging set of comparisons between experimental data and theoretical predictions according to these models. The first model 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. The second model assumes that energy transfer mechanisms may be divided into two Kinetic regimes: pure diffusion, and combined diffusion and long-range (resonance) interactions, with the appropriate kinetics being selected in accordance with Gosele's selection criteria. The third generalized model, Gosele's generalized model, does not rely on selection criteria, and is intended to apply over the whole range of diffusion and resonance energy transfer parameters which are expected to apply in quenching experiments. These comparisons have shown that the first two models, and their criteria for selection of the most appropriate transfer kinetics were applicable only under certain limiting physical conditions, where energy transfer is due either purely to diffusion, or to dipole–dipole resonance mechanisms. It was further shown that, the third generalized model, which did not require selection of specific transfer kinetics, gave in most cases poor agreement with the experimental data and always overestimated the actual values of radiationless transfer efficiency, f_{nr}.

If one tries to avoid complications and uncertainties in the process of selecting the most appropriate kinetics, and giving the fact that the erroneous selection of the appropriate kinetics will result in a significant error in f_{nr} values, then,

the use of a generalized model is a must. However, since the third model examined in[20] (Gosele's generalized model[18]) was found to be inadequate, a modified general model which gives better agreement with experimental data needs to be examined.

In this paper, we examine a modified general 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 are expected to apply in quenching experiments. We test the validity of the modified model by carrying out a comprehensive and wide ranging set of comparisons between the experimental data reported in Ref. 20 and the model's theoretical predictions. To carry out these comparisons, the required analytical expression for the radiationless transfer efficiency f_{nr} is first derived. It is then compared with the equivalent experimental data. The results are discussed below.

II. THEORY

The theoretical model considered permits an expression for the time dependence of the donor concentration $[D^*]$ following instantaneous creation of an initial concentration $[D^*]_0$. After δ excitation of donor molecules at time $t = 0$ the time dependence of the donor fluorescence is obtained from:

$$\frac{d[D^*]}{dt} = -\frac{[D^*]}{T_{0d}} - [D^*][A]F(t) \qquad (1)$$

or in integrated form and for $[A] \gg [D^*]$

$$[D^*] = [D^*]_0 \exp(-t/T_{0d})\exp\{-U(t)[A]\}, \qquad (2)$$

where $U(t)$ is a time-dependent quenching coefficient (due to energy transfer from the donor to the acceptor) given by

$$U(t) = \exp\left[\int_0^t F(t)dt\right],$$

T_{0d} is the excited donor lifetime in the absence of acceptor, $[A]$ is the quencher (acceptor) concentration, and $F(t)$ is the energy transfer rate given[17] by

$$F(t) = 4\pi r_{da}^2 D\left[\frac{dC}{dr}\right]_{r_{da}} + \int_{r=r_{da}}^{\infty} W(r)C(r,t)dV, \qquad (3)$$

where the normalized distribution function $C(r,t)$ satisfies the differential equation

$$\frac{dC(r,t)}{dt} = D \text{ div grad } C - W(r)C$$

and

$$W(r) = (\alpha/R^6) = (R_0^6/R^6 T_{0d}) \tag{4}$$

r_{da} is the distance of closest approach of the donor and acceptor, 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, and 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.

The donor quantum yield Φ_d in the presence of the acceptor is then

$$\Phi_d = \int_0^\infty K_{fd}[D^*]\frac{dt}{[D^*]_0} \tag{5}$$

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

$$\frac{\Phi_d}{\Phi_{0d}} = (1/T_{0d}) \int_0^\infty \exp(-t/T_{0d})\exp(-U[A])dt \tag{6}$$

which applies also to steady-state conditions.

Since the nonradiative transfer efficiency f_{nr} is defined as

$$f_{nr} = 1 - \frac{\Phi_d}{\Phi_{0d}} \tag{7}$$

we can substitute Eq. (6) into Eq. (7) to obtain the final expression for the transfer efficiency as

$$f_{nr} = 1 - (1/T_{0d}) \int_0^\infty \exp(-t/T_{0d})\exp(-U[A])dt. \tag{8}$$

In the third model examined in Ref. 20, Gosele et al.[17-19] have proposed the use of a formal effective radius r_{eff} over the whole range of diffusion and resonance energy transfer parameters, repeated here for convenience:

$$r_{eff} = r_{da} + r_f, \tag{9}$$

where

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

Equation (9) is found[20] to be a good approximation for all limiting cases (as, e.g., $D \to 0$, or $\alpha \to 0$), but is a poor approximation for an intermediate region ($Z_0 \approx 1$). Note that the radius r_f accounts for the long-range (resonance) interactions, while the radius r_{da} accounts for the collisional interactions. For both limiting cases (where energy transfer is due either purely to diffusion, or to long range interactions), only one term in Eq. (9) will contribute to the transfer efficiency and the model reduces to a specific kinetic mechanism which is solely responsible for energy transfer. On the other hand, in the intermediate region, both kinetics in Eq. (9) are expected to contribute to the transfer efficiency. Furthermore, as will be shown later, an increase in one kinetic mechanism corresponds to a reduction in the other. However, the general model (Gosele's generalized model) always adds up contributions from both terms in Eq. (9) even

if in fact only one kinetic mechanism is responsible for energy transfer.

One is led to the conclusion[20] that in most of the cases (unless it is a limiting case), this model is always going to overestimate the actual values of radiationless transfer efficiency (f_{nr}). What is needed is an adjustable parameter to be introduced in Eq. (9) to relate both radii r_f and r_{ad}.

To do so, a more accurate expression for r_{eff} may be derived from the limiting value of $F(t)$ at long times (steady state), which is given[19] by

$$r_{eff} = r_f + r_{ad}f(Z_0), \tag{10}$$

where

$$f(Z_0) \approx 0.43Z_0^{1/2}K_{1/4}(z_0)I_{1/4}(z_0), \tag{11}$$

where $K_{1/4}$ and $I_{1/4}$ are modified Bessel functions of order 1/4, and Z_0 is defined as:

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

Since $Z_0 \approx (r_f/r_{ad})$, $f(Z_0)$ is plotted in Fig. 1 as a function of r_f/r_{ad}. It is seen that $r_{ad}f(Z_0)$ may be neglected for all practical purposes if $(r_f/r_{ad}) > 1.5$ (i.e., resonance transfer is the dominant kinetics). If $(r_f/r_{ad}) \approx 0$, $f(Z_0) \approx 1$, and r_{eff} may be fairly well approximated by r_{ad} (i.e., collisional transfer is the dominant kinetics). In the intermediate region, $0 < f(Z_0) < 1$, only a fraction of r_{ad} is added to r_{eff} [i.e., $f(Z_0)$ select the appropriate contribution of each kinetic mechanism, in Eq. (10), to energy transfer]. Thus, the significant advantage of this modified general model, compared to all other models examined in Ref. 20, lies in the adjustable parameter $f(Z_0)$. Not only does $f(Z_0)$ implicitly takes care of the selection criteria, but also it allows for the appropriate contribution of both kinetics in Eq. (9) to energy transfer. In order to fully appreciate this modified general model in comparison to the models previously examined in Ref. 20, one has to understand how the radiationless transfer efficiency (f_{nr}) is evaluated for each model. For the first two models examined in Ref. 20 it was always assumed that there is only
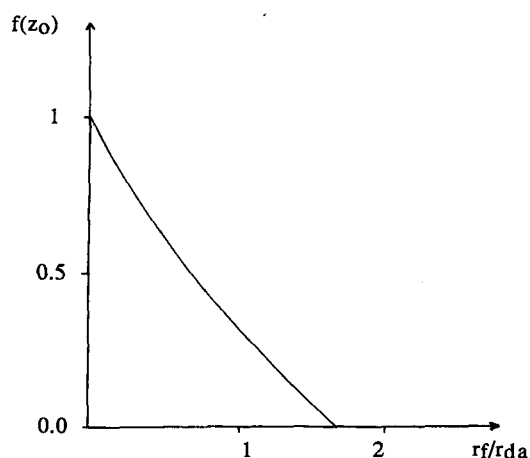

FIG. 1. $f(Z_0)$ as a function of the ratio r_f/r_{da} according to Eq. (11).

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

Solvent\[A] (10^{-3})		0.10	0.20	0.30	0.50	1.00	2.00	3.00	5.00
Benzene									
$n = 0.62$	f_{nr} (exp)	0.170	0.260	0.320	0.430	0.570	0.740	0.810	0.870
$R_0 = 24.2$ Å	theor.	0.170	0.290	0.380	0.510	0.680	0.810	0.860	0.920
Cyclohexane									
$n = 0.98$	f_{nr} (exp)	0.160	0.270	0.330	0.430	0.590	0.750	0.800	0.880
$R_0 = 24.7$ Å	theor.	0.140	0.250	0.330	0.450	0.630	0.770	0.840	0.900
$B(60\%)$									
$C(40\%)$	f_{nr} (exp)	0.090	0.120	0.220	0.300	0.440	0.570	0.720	0.770
$n = 1.57$	theor.	0.080	0.140	0.200	0.300	0.460	0.630	0.720	0.820
$R_0 = 23.4$ Å									
$B(30\%)$									
$C(70\%)$	f_{nr} (exp)	0.050	0.080	0.150	0.190	0.300	0.440	0.520	0.650
$n = 5.89$	theor.	0.030	0.060	0.090	0.140	0.240	0.400	0.500	0.630
$R_0 = 23.4$ Å									
$B(10\%)$									
$C(90\%)$	f_{nr} (exp)	0.040	0.040	0.080	0.080	0.160	0.280	0.390	0.500
$n = 25.2$	theor.	0.014	0.028	0.042	0.069	0.129	0.234	0.318	0.447
$R_0 = 23.5$ Å									
Cyclo-									
hexanol (C)	f_{nr} (exp)	0.030	0.040	0.070	0.060	0.120	0.260	0.290	0.440
$n = 68$	theor.	0.009	0.019	0.028	0.045	0.087	0.164	0.230	0.341
$R_0 = 23.2$ Å									

one kinetic mechanism responsible for energy transfer (assuming it has been properly selected) and that any contributions due to any other kinetic mechanism is totally disregarded. The third generalized model examined in Ref. 20 always added up both kinetic mechanisms in Eq. (9) even if in fact only one kinetic mechanism is responsible for energy transfer.

The time dependent quenching coefficient $U(t)$, over the whole range of diffusion and resonance energy transfer parameters in quenching experiments, is given[20] by

$$U(t) = 4\pi D R_{eff} t\widetilde{N} + 8\pi^{1/2} D^{1/2} R_{eff}^2 t^{1/2}\widetilde{N}, \qquad (12)$$

where R_{eff} is given by Eq. (10), and $\widetilde{N} = N/1000$. This equation represents a more accurate approximation over the whole range of diffusion and resonance energy transfer parameters.

Following the general approach developed in Sec. II in Ref. 20, if we substitute Eq. (12) into Eq. (8), we obtain the modified general expression for radiationless transfer efficiency (f_{nr}) as

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

Solvent\[A] (10^{-3})		2	3	4	5	7
Cyclohexane						
$n = 0.98$	f_{nr} (exp)	0.340	0.440	0.520	0.580	0.700
$R_0 = 35.6$ Å	theor.	0.410	0.530	0.620	0.680	0.760
Cyclohexanol						
$n = 68$	f_{nr} (exp)	0.280	0.400	0.490	0.540	0.660
$R_0 = 34.8$ Å	theor.	0.280	0.380	0.460	0.530	0.640

$$f_{nr} = 1 - \frac{K_0}{K} + \frac{K_0}{K^{3/2}}\pi^{1/2}A$$
$$\times \exp\left(\frac{A^2}{K}\right)[1 - \mathrm{erf}(A/K^{1/2})], \qquad (13)$$

where

$$K = K_0 + 4\pi D R_{eff}\widetilde{N}[A],$$

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

and

$$K_0 = 1/T_{0d}.$$

III. EXPERIMENTAL DATA: RESULTS AND ANALYSIS

Seven different sets of experimental data for quantum efficiency of radiationless energy transfer, reported in Ref. 20, were selected for comparisons with theoretical results calculated in accordance with theoretical results calculated in accordance with the modified model.

Tables I–VII shows the experimental results[20] and our theoretical calculations for f_{nr} from Eq. (13). The critical transfer distance R_0, is also included in all tables.

Figures 2–4 are typical curves which show comparisons between the theoretical predictions of the four models (the modified general Model and the previously three models examined in Ref. 20), along with the corresponding experimental results under three different physical conditions.

IV. DISCUSSION AND CONCLUSION

The theoretically calculated values for f_{nr} according to the modified general Model (Tables I–VII) and the pre-

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

Solvent\\[A] (10^{-3})		0.313	0.625	1.250	2.500	5.000
Ethyleneglycol						
$n = 26.09$	f_{nr} (exp)%	16.4 ± 3	27.2 ± 3	47.7 ± 6	72.0 ± 7	81.5 ± 9
$R_0 = 56$ Å	theor.	0.190	0.330	0.540	0.750	0.900

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

Solvent\\[A](10^{-3})		0.313	0.625	1.250	2.500	5.000
Ethyleneglycol						
$n = 26.09$	f_{nr} (exp)%	15 ± 4	20 ± 1	41 ± 5	64 ± 4	81 ± 6
$R_0 = 56$ Å	theor.	0.170	0.310	0.510	0.720	0.880

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

Solvent\\[A] (10^{-3})		5	2	1
Methanol				
$n = 0.6$	f_{nr} (exp)	0.920	0.830	0.660
$R_0 = 22.8$ Å	theor.	0.900	0.780	0.630
Tert-butanol				
$n = 4.8$	f_{nr} (exp)	0.780	0.600	0.450
$R_0 = 22.4$ Å	theor.	0.640	0.510	0.254
Glycerol				
$n = 1000$	f_{nr} (exp)	0.390	0.280	
$R_0 = 22.4$ Å	theor.	0.242	0.108	
Cyclohexanol				
$n = 65$	f_{nr} (exp)	0.530		
$R_0 = 22.2$ Å	theor.	0.341		
Ethyleneglycol				
$n = 17.4$	f_{nr} (exp)	0.560		
$R_0 = 23.5$ Å	theor.	0.448		
Amylalchol				
$n = 4.3$	f_{nr} (exp)	0.770		
$R_0 = 23$ A	theor.	0.710		
n-Butanol				
$n = 2.8$	f_{nr} (exp)	0.860		
$R_0 = 22.2$ Å	theor.	0.730		
Isopropanol				
$n = 1.95$	f_{nr} (exp)	0.840		
$R_0 = 22.6$ Å	theor.	0.790		
Ethanol				
$n = 1.2$	f_{nr} (exp)	0.900		
$R_0 = 23$ Å	theor.	0.850		
Isobutanol				
$n = 4.1$	f_{nr} (exp)	0.760		
$R_0 = 23.2$ Å	theor.	0.720		

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

Solvent\[A] (10^{-3})		0.1	0.5	1.0	3.0	5.0
Hexane						
$n = 0.34$	f_{nr} (exp)	0.020	0.080	0.155	0.355	0.480
$R_0 = 4.2$ Å	theor.	0.025	0.110	0.200	0.440	0.566
Benzene						
$n = 0.62$	f_{nr} (exp)	0.026	0.120	0.210	0.440	0.570
$R_0 = 4.8$ Å	theor.	0.030	0.130	0.230	0.480	0.600
ISO (50%)						
C (50%)	f_{nr} (exp)	0.010	0.050	0.090	0.230	0.330
$n = 10$	theor.	0.005	0.025	0.050	0.130	0.200
$R_0 = 5.6$ Å						
Liquid paraffin						
$n = 172$	f_{nr} (exp)	0.005	0.020	0.040	0.120	0.180
$R_0 = $ Å	theor.	0.0006	0.003	0.006	0.020	0.030

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

Solvent\[A] (10^{-3})		0.5	1.0	2.0	5.0
Cyclohexane					
$\eta = 1$ CP	f_{nr} (exp)	0.110	0.170	0.280	0.530
$R_0 = 28.2$ Å	theor.	0.070	0.130	0.230	0.450
Mehtanol					
$\eta = 0.6$ CP	f_{nr} (exp)	0.120	0.200	0.310	0.540
$R_0 = 29.7$ Å	theor.	0.090	0.160	0.290	0.530
Isoporpanol					
$\eta = 2.3$ CP	f_{nr} (exp)	0.100	0.170	0.290	0.530
$R_0 = 29$ Å	theor.	0.060	0.120	0.220	0.450
Tert-butanol					
$\eta = 4.1$	f_{nr} (exp)	0.090	0.200	0.300	0.500
$R_0 = 28.7$ Å	theor.	0.050	0.100	0.190	0.390
Cyclohexanol					
$\eta = 68$	f_{nr} (exp)	0.080	0.140	0.230	0.440
$R_0 = 27.8$ Å	theor.	0.040	0.081	0.154	0.332
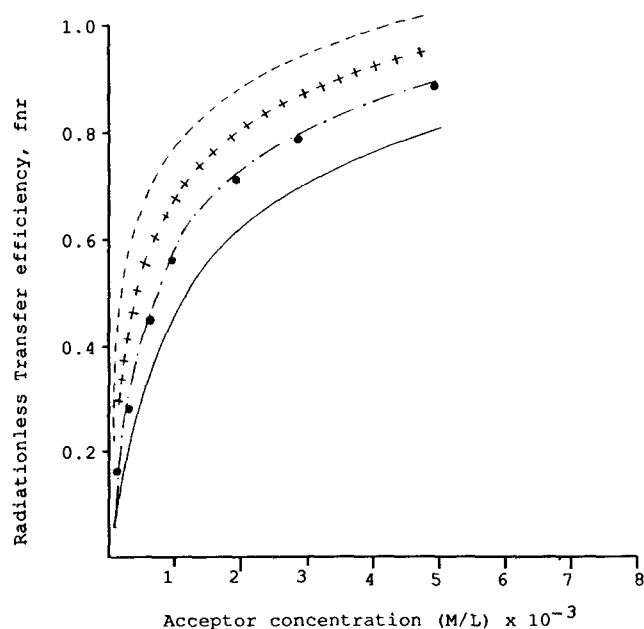
FIG. 2. Napthalene–anthranilic acid in methanol f_{nr} vs [anth. acid]. — Model 1 (diffusion, $\cdots$ experimental, $---$ model 3, $+++$ model 4 (modified model), $-\cdot\cdot-$ model 2 (combined diff. and resonance).
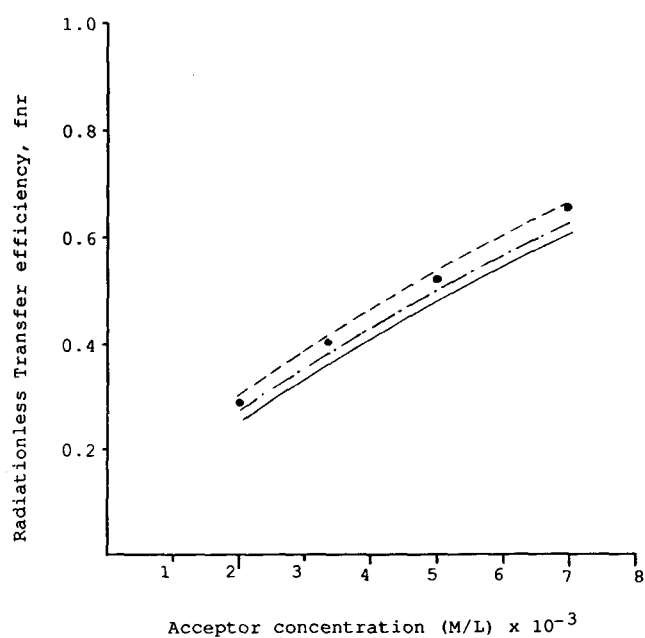
FIG. 3. PPO-DPA in cyclohexanol. f_{nr} vs [DPA]. — Model 1 (Forster), $---$ model 3, $\cdots$ experimental, $-\cdot\cdot-$ model 2 (resonance) and model 4.
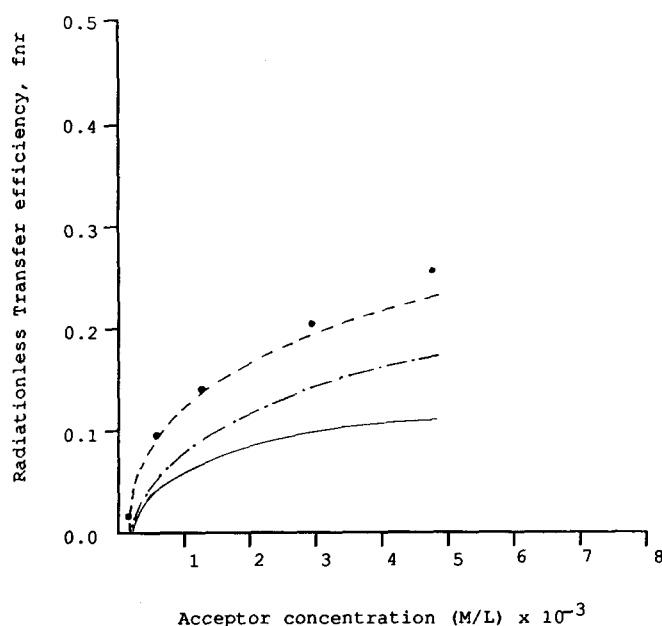
FIG. 4. Napthalene–Biacetyl in isopropanol. f_{nr} vs [biacetyl]. — Model 1 (Stern–Volmer), --- model 3, -·- model 2 (diffusion) and model 4, ··· experimental.

viously three models examined in Ref. 20 were compared with each other and with corresponding experimental results, these comparisons reveal that:

(1) The modified general model gives much better agreement with experimental data than the previous generalized model examined in Ref. 20.

(2) In the two limiting cases (where energy transfer is due either purely to diffusion, or to dipole–dipole resonance mechanisms), the modified model gives exactly the same results at the second model examined in Ref. 20. This is not surprising since for the modified model, the modified effective interaction radius, r_{eff} [Eq. (10)], conbines both the long range interaction radius (r_f) and the collision radius (r_{da}) of the second model.

If $f(Z_0) \approx 0$ (i.e., long-range resonance transfer dominates), then, $r_{\text{eff}} \approx r_f$ and the modified model reduces to the second kinetics (combined diffusion and long-range interactions) of the second model. On the other hand, if $f(Z_0) \approx 1$ (i.e., energy transfer is mainly due to pure diffusion), then,

$r_{\text{eff}} \approx r_{da}$ and the modified model reduces to the first kinetics (pure diffusion) of the second model.

(3) As the viscosity is increased, and the Forster distance R_0 is reduced, this modified model, as expected, also underestimates the experimental data. The reason for this is because contributions from additional terms in the dipole expansion and/or short range electron-exchange mechanisms, are not considered in the model.

In conclusion, it appears that the modified model gives much better agreement with experimental data, than the previous general model examined in Ref. 20. Furthermore, it is superior to the first two models examined in Ref. 20, in that it can be used directly without the uncertainties attending the use of these models, of which need to correctly select the transfer kinetics most appropriate to each different physical situation.

ACKNOWLEDGMENTS

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