Exciplex Formation Accompanied with Excitation Quenching

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Exciplex Formation Accompanied with Excitation Quenching

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The competence of the reversible exciplex formation and parallel quenching of excitation (by electron or energy transfer) was considered using a non-Markovian π-forms approach, identical to integral encounter theory (IET). General equations accounting for the reversible quenching and exciplex formation are derived in the contact approximation. Their general solution was obtained and adopted to the most common case when the ground state particles are in great excess. Particular cases of only photoionization or just exciplex formation separately studied earlier by means of IET are reproduced. In the case of the irreversible excitation quenching, the theory allows specifying the yields of the fluorescence and exciplex luminescence, as well as the long time kinetics of excitation and exciplex decays, in the absence of quenching. The theory distinguishes between the alternative regimes of (a) fast equilibration between excitations and exciplexes followed by their decay with a common average rate and (b) the fastest and deep excitation decay followed by the weaker and slower delayed fluorescence, backed by exciplex dissociation.

I. Introduction

The irreversible quenching of the excited donor D* by electron acceptor A is studied in the wide class of transfer reactions, D* + A → D⁺ + A⁻, either exergonic or endergonic. Moreover, the famous Rehm−Weller dependence[1] of the stationary quenching rate k_i on the free energy of electron transfer, ΔG_I greater than or less than 0, was finally plausibly explained[2] within the differential encounter theory (DET).[3]

However, this theory does not work in a narrow strip near the resonance where $\Delta G_I(\sigma) = 0$, provided the electron tunneling $V(\sigma) = V_0$ at contact distance σ is rather strong. The exciplex $E = [A^{\delta-}D^{\delta+}]$ (with partial charge separation δ) is formed there from the contact pair of neutral reactants [AD*], while the full electron transfer occurs between the space separated reactants. It proceeds with the distance-dependent rate $W(r)$ which is usually specified by the second-order perturbation theory with respect to $V(r)$. The quasi-resonance case is an exceptional one due to the reversibility of the electron transfer that cannot be accounted for with DET but only with IET (integral encounter theory) or its modified version (MET).

The quasi-resonant electron transfer results in either the exciplex or the free ion $(A^- \cdots D^+)$ formation (Figure 1) according to Scheme 1.

The rates of the forward and backward electron transfer obey the detailed balance principle

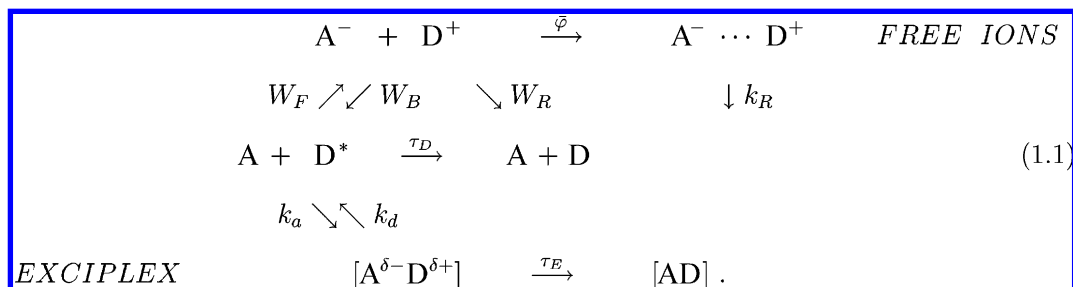$$W_F(r) = W_B(r) \exp(-\Delta G_I/T) \qquad (1.2)$$

as well as the rates of association and dissociation of exciplex compounds
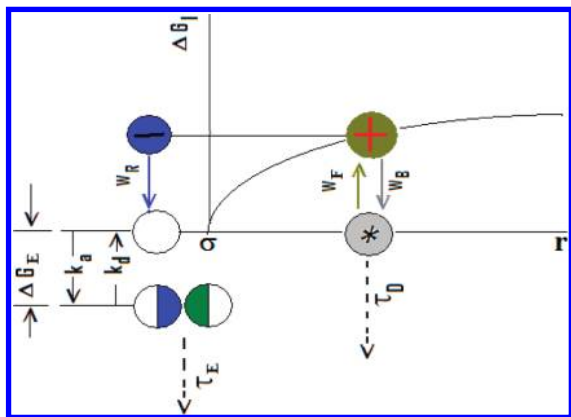
$$k_a/k_d = v \exp(-\Delta G_E/T) \qquad (1.3)$$

Here the Boltzmann constant $k_B = 1$, v is the reaction volume, and the free energy of the resonant exciplex formation is known to be[4−6] $\Delta G_E = -V_c$, where V_c is the electron coupling between the resonant states D*A and D⁺A⁻ at contact.

The exciplex formation and dissociation is contact by definition, but the electron transfer (especially proceeding in the normal Marcus region) is often fashioned as an exponential one[3,7,8]

SCHEME 1

$$
\begin{array}{cccc}
A^- \;+\; D^+ & \xrightarrow{\;\bar{\varphi}\;} & A^- \cdots D^+ & \textit{FREE IONS} \\[4pt]
W_F \nearrow\!\swarrow W_B \quad \searrow W_R & & \downarrow k_R & \\[4pt]
A \;+\; D^* & \xrightarrow{\;\tau_D\;} & A \;+\; D & \qquad(1.1) \\[4pt]
k_a \searrow\!\nwarrow k_d & & & \\[4pt]
\textit{EXCIPLEX} \qquad [A^{\delta-}D^{\delta+}] & \xrightarrow{\;\tau_E\;} & [AD]\;. &
\end{array}
$$

Exciplex Formation with Excitation Quenching

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Figure 1. The space dependence of ionization free energy $\Delta G_I = r_c/\sigma - r_c/r$ at resonant exciplex formation. The spheres positioned on the abscisses present the reactants separated by distance r which become the counterions (shown above) as a result of the electron transfer at this distance. The excited donor and the exciplex formed at contact decay with the times τ_D and τ_E, respectively. The rates of reversible free ions formation are W_I and W_B, while W_R is the rate of ion recombination to the reactants ground state. The rate constants of exciplex association and dissociation are k_a and k_d, respectively.
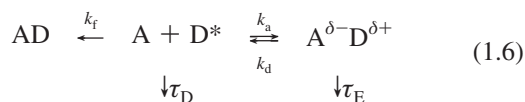
$$W(r) = W_0 \exp\left(-\frac{2(r-\sigma)}{l}\right) \quad (1.4)$$

All the parameters could be different for W_F, W_B, and W_R except the common contact radius σ. Moreover, for the sake of simplicity the electron transfer is sometimes considered as a contact one.[3,7] In this approximation it is accounted for (via boundary conditions) by the corresponding kinetic rate constants

$$k_f = \int W_F(r) \, d^3r$$

$$k_b = \int W_B(r) e^{r_c/r} \, d^3r \quad (1.5)$$

$$k_r = \int W_R(r) e^{r_c/r} \, d^3r$$

where $r_c = e^2/\varepsilon T$ is the Onsager radius of the Coulomb attraction. According to Figure 1 the ionization preceding exciplex formation is an endergonic one and therefore essentially reversible ($k_b > k_f$).
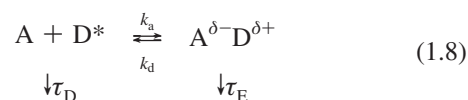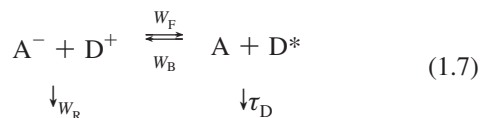
However, the quenching of the excitation by dipole–dipole (Foerster) or exchange (Dexter) mechanisms is usually irreversible.[9] The exchange rate has an exponential shape like (1.4) and therefore is often considered as a contact one. The double-channel reaction including the irreversible energy quenching in line with reversible exciplex formation proceeds according to the scheme:

$$\text{AD} \xleftarrow{k_f} \text{A} + \text{D*} \underset{k_d}{\overset{k_a}{\rightleftarrows}} \text{A}^{\delta-}\text{D}^{\delta+} \quad (1.6)$$
$$\downarrow \tau_D \qquad\qquad \downarrow \tau_E$$

This is the simplest particular case of two competing contact reactions, reversible exciplex formation and irreversible excita-

tion quenching. Their relative yields and kinetics are subjected to analytical investigation in section IV.

Until now the energy (fluorescence) quenching by either electron transfer or exciplex formation was considered only separately according to the reduced reaction schemes

$$\text{A}^- + \text{D}^+ \underset{W_B}{\overset{W_F}{\rightleftarrows}} \text{A} + \text{D*} \quad (1.7)$$
$$\downarrow W_R \qquad\qquad \downarrow \tau_D$$

$$\text{A} + \text{D*} \underset{k_d}{\overset{k_a}{\rightleftarrows}} \text{A}^{\delta-}\text{D}^{\delta+} \quad (1.8)$$
$$\downarrow \tau_D \qquad\qquad \downarrow \tau_E$$

The former was considered first by means of conventional IET accounting for the space dependence of all the transfer rates but only for the geminate reaction (neglecting charge recombination in the bulk).[10] In the next article it was taken into consideration[11] but for only the irreversible ionization ($W_B = 0$). The general IET equations obtained and studied in ref.12 account for both: the reversible geminate photo-ionization and the bulk reaction of charged products. The latter is responsible for the delayed fluorescence and spin conversion effects that were studied in ref 13 using the contact approximation in the basic equations. All these results are reviewed in ref 7.

The reversible dissociation of the stable complex ($\tau_E = \infty$) was first studied by Berg.[14] The extension of this theory to the reversible exciplex dissociation made in ref 15 showed its identity with the IET analogue of the monomolecular exciplex dissociation: from right to left of reaction scheme 1.8. The IET equations for reverse reaction of bimolecular exciplex formation—from left to right of reaction scheme 1.8—were obtained in ref 16 and reproduced numerously. Then the theory was extended to account for both: the reversible exciplex dissociation and the backward bimolecular exciplex formation.[18] The same results reviewed in refs 7 and 8 were obtained independently by other methods in refs 20–24.

The original method proposed in the last work allows the easiest extension of the theory to the general reaction (Scheme 1) that appears in the next section. There the non-Markovian kinetic equations for all the particle concentrations and for the π-forms of reacting pairs will be obtained in the contact approximation. Their general solution in the case of equal particle mobilities and zero Coulomb fields will be presented in section III. It was shown to obey the corresponding IET equations whose kernels are specified via reaction constants and the diffusion coefficient. In the particular cases (1.7) and (1.8) these equations reduce to already known ones. In the last section we concentrate on the reaction 1.6 looking for the fluorescence yields and decay kinetics of the excited donor and exciplex.

II. Kinetic Equations

A. Reaction under Kinetic Control. In the kinetic limit (at the highest diffusion) one can use the conventional set of chemical kinetic equations for particle concentrations

$$\frac{d[D^*]_t}{dt} = -(k_f + k_a)[D^*]_t[A]_t + k_b[D^+]_t[A^-]_t + k_d[E]_t - \frac{1}{\tau_D}[D^*]_t \tag{2.1}$$

$$\frac{d[A]_t}{dt} = -(k_f + k_a)[D^*]_t[A]_t + (k_b + k_r)[D^+]_t[A^-]_t + \left(k_d + \frac{1}{\tau_E}\right)[E]_t \tag{2.2}$$

$$\frac{d[D^+]_t}{dt} = \frac{d[A^-]_t}{dt} = k_f[D^*]_t[A]_t - (k_b + k_r)[D^+]_t[A^-]_t \tag{2.3}$$

$$\frac{d[D]_t}{dt} = k_r[D^+]_t[A^-]_t + \frac{1}{\tau_D}[D^*]_t + \frac{1}{\tau_E}[E]_t \tag{2.4}$$

$$\frac{d[E]_t}{dt} = k_a[D^*]_t[A]_t - \left(k_d + \frac{1}{\tau_E}\right)[E]_t \tag{2.5}$$

The conservation laws for the particles participating in these reactions demands that

$$[D^*]_t + [D^+]_t + [D]_t + [E]_t = \text{constant}, \quad [A^-]_t + [A]_t + [E]_t = \text{constant} \tag{2.6}$$

Therefore we have to keep only three independent equations, (2.1), (2.3), and (2.5), omitting all the rest.

B. Non-Markovian Equations Based on π-Forms. In the case of moderate mobilities the multiparticle correlations have to be taken into consideration. Formally exact kinetic equations for the concentrations $[X_i]_t$ should account for the π-forms,[22] $P_{ij}(r,t) = \rho_{ij}(r,t) - [X_i]_t[X_j]_t$, i.e., for the deviations of the pair distribution functions $\rho_{ij}(r,t)$ from the products of the corresponding concentrations[24]

$$\frac{d[X_i]_t}{dt} = -\sum_{m \geq n} \Phi_{imn}([X_m]_t[X_n]_t + P_{mn}(R,t)) - \sum_n (\Omega_{in} + Q_{in})[X_n]_t \tag{2.7}$$

Here the first sum collects all the quadratic in concentration terms while the second contains the linear terms: dissociation $\{\Omega_{in}\}$ and relaxation $\{Q_{in}\}$ ($N \times N$) matrixes, provided N is a number of reactants.

In the simplest approximation corresponding to the integral encounter theory π-forms satisfy the following matrix reaction-diffusion equations

$$\frac{\partial P}{\partial t} = L(DP + PD) - QP - PQ^T \tag{2.8}$$

here **D** is the diagonal matrix of the diffusion coefficients and L_{ij} are the stochastic motion operators, while

$$\Omega = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -k_d \\ 0 & 0 & 0 & 0 & 0 & -k_d \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & k_d \end{bmatrix} \quad Q = \begin{bmatrix} \tau_D^{-1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\tau_E^{-1} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -\tau_D^{-1} & 0 & 0 & 0 & 0 & -\tau_E^{-1} \\ 0 & 0 & 0 & 0 & 0 & \tau_E^{-1} \end{bmatrix} \tag{2.9}$$

For the reaction under study there are only 3 independent equations from the set 2.7:

$$\frac{d[D^*]_t}{dt} = -(k_f + k_a)([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) + k_b([D^+]_t[A^-]_t + P_{D^+A^-}(\sigma, t)) + k_d[E]_t - \frac{1}{\tau_D}[D^*]_t \tag{2.10}$$

$$\frac{d[D^+]_t}{dt} = \frac{d[A^-]_t}{dt} = k_f([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) - (k_b + k_r)([D^+]_t[A^-]_t + P_{D^+A^-}(\sigma, t)) \tag{2.11}$$

$$\frac{d[E]_t}{dt} = k_a([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) - \left(k_d + \frac{1}{\tau_E}\right)[E]_t \tag{2.12}$$

Since initially the particles are assumed to be randomly distributed, the deviations $P_{ij}(r,t = 0) = 0$. Accordingly, the correlations become negligible for the large distances: $P_{ij}(r \rightarrow \infty, t) = 0$.

Due to the symmetry relationship, $P_{ij}(r,t) = P_{ji}(r,t)$, the matrix eq 2.8 consist actually of 21 equations for independent π-forms but only three of them are coupled and necessary for solving the present problem

$$\frac{\partial P_{D^*A}}{\partial t} = D_{D^*A}L_{D^*A}P_{D^*A} - \frac{1}{\tau_D}P_{D^*A} + \frac{1}{\tau_E}P_{ED^*} \tag{2.13}$$

$$\frac{\partial P_{D^+A^-}}{\partial t} = D_{D^+A^-}L_{D^+A^-}P_{D^+A^-} \tag{2.14}$$

$$\frac{\partial P_{ED^*}}{\partial t} = D_{ED^*}L_{ED^*}P_{ED^*} - \frac{1}{\tau_D}P_{ED^*} - \frac{1}{\tau_E}P_{ED^*} \tag{2.15}$$

It is assumed here that all the reactions occur only at contact radius σ and the corresponding reaction fluxes are incorporated into the boundary conditions for the reacting pairs

$$D_{D^*A}4\pi\sigma^2\frac{\partial P_{D^*A}}{\partial r}\bigg|_{r=\sigma} = (k_f + k_a)([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) - k_b([D^+]_t[A^-]_t + P_{D^+A^-}(\sigma, t)) - k_d[E]_t \tag{2.16}$$

$$D_{D^+A^-}4\pi\sigma^2e^{-\beta U(\sigma)}\frac{\partial}{\partial r}e^{\beta U(r)}P_{D^+A^-}\bigg|_{r=\sigma} = (k_b + k_R)([D^+]_t[A^-]_t + P_{D^+A^-}(\sigma, t)) - k_f([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) \tag{2.17}$$

where $U(r)$ is the Coulomb potential acting between the counterions. For the unreactive ED* pair there is the reflecting boundary condition

$$D_{ED^*}4\pi\sigma^2\frac{\partial P_{ED^*}}{\partial r}\bigg|_{r=\sigma} = 0 \tag{2.18}$$

It is easy to see that eq 2.15 with the boundary condition (2.18) has zero solution. So we can omit the last term of the right-hand side of eq 2.13 and retain only two coupled equations (2.13) and (2.14).

C. Reactions in Highly Polar Solvents. In solvents of high polarity one can set $U(r) = 0$ and, assuming for simplicity equal mobilities in any reactive pairs, introduce the following simplification

$$D_{D^*A} = D_{D^+A^-} = D, \quad L_{D^*A} = L_{D^+A^-} = \nabla^2 \tag{2.19}$$

After that we have the following equations

$$\frac{\partial}{\partial t}P_{D^*A}(r, t) = D\nabla^2 P_{D^*A}(r, t) - \frac{1}{\tau_D}P_{D^*A}(r, t) \tag{2.20}$$

$$\frac{\partial}{\partial t}P_{D^+A^-}(r, t) = D\nabla^2 P_{D^+A^-}(r, t) \tag{2.21}$$

From their Laplace transformation we get

$$s\tilde{P}_{D^*A}(r, s) = D\nabla^2\tilde{P}_{D^*A}(r, s) - \frac{1}{\tau_D}\tilde{P}_{D^*A}(r, s) \tag{2.22}$$

$$s\tilde{P}_{D^+A^-}(r, s) = D\nabla^2\tilde{P}_{D^+A^-}(r, s) \tag{2.23}$$

while the boundary conditions are

$$D4\pi\sigma^2\frac{\partial\tilde{P}_{D^*A}(r, s)}{\partial r}\bigg|_{r=\sigma} = (k_f + k_a)(\tilde{F}_{D^*A} + \tilde{P}_{D^*A}(\sigma, s)) - k_b(\tilde{F}_{D^+A^-} + \tilde{P}_{D^+A^-}(\sigma, s)) - k_d\tilde{E}(s) \tag{2.24}$$

$$D4\pi\sigma^2\frac{\partial\tilde{P}_{D^+A^-}(r, s)}{\partial r}\bigg|_{r=\sigma} = (k_b + k_r)(\tilde{F}_{D^+A^-} + \tilde{P}_{D^+A^-}(\sigma, s)) - k_f(\tilde{F}_{D^*A} + \tilde{P}_{D^*A}(\sigma, s)) \tag{2.25}$$

where $\tilde{F}_{D^*A}$, $\tilde{F}_{D^+A^-}$, and $\tilde{E}(s)$ are the Laplace images of $[D^*]_t[A]_t$, $[D^+]_t[A^-]_t$, and $[E]_t$, correspondingly.

So the formulation of the problem for a double channel contact reaction includes eqs 2.10−2.12 for the concentrations and (corresponding to the accuracy of IET) eqs 2.20−2.25 for the π-forms of the reactive pairs. In the next section we will solve the problem in general and illustrate it by reactions of separate formation of ions and exciplex (1.7) and (1.8) that have been well studied previously.[3,7,8]

III. Competition of Photoionization and Exciplex Formation

A. General Solution. Now we start to investigate the general reaction (Scheme 1) solving eqs 2.22 and 2.23 with the boundary conditions (2.24) and (2.25). Thus we obtain π-forms at the contact distance

$$\tilde{P}_{D*A}(R, s) = A\tilde{F}_{D*A} + B\tilde{E}(s) + C\tilde{F}_{D+A-} \tag{3.1}$$

$$\tilde{P}_{D+A^-}(R, s) = A_1\tilde{F}_{D*A} + B_1\tilde{E}(s) + C_1\tilde{F}_{D+A-} \tag{3.2}$$

Here

$$A = -\left[\frac{k_f + k_a}{s_1\tilde{k}_D(s_1)} + \frac{k_f k_r + k_a(k_b + k_r)}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right]\frac{1}{Z}, \quad A_1 = \frac{k_f}{s\tilde{k}_D(s)}\frac{1}{Z} \tag{3.3}$$

$$B = \frac{k_d(s\tilde{k}_D(s) + k_b + k_r)}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\frac{1}{Z}, \quad B_1 = \frac{k_d k_f}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\frac{1}{Z} \tag{3.4}$$

$$C = \frac{k_b}{s_1\tilde{k}_D(s_1)}\frac{1}{Z}, \quad C_1 = -\left[\frac{k_b + k_r}{s\tilde{k}_D(s)} + \frac{k_f k_r + k_a(k_b + k_r)}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right]\frac{1}{Z} \tag{3.5}$$

where

$$\tilde{k}_D(s) = \frac{k_D}{s}\left(1 + \sigma\sqrt{\frac{s}{D}}\right), \quad k_D = 4\pi\sigma D, \quad s_1 = s + 1/\tau_D \tag{3.6}$$

and

$$Z = \frac{k_b}{s\tilde{k}_D(s)} + \left(1 + \frac{k_f}{s_1\tilde{k}_D(s_1)}\right)\left(1 + \frac{k_r}{s\tilde{k}_D(s)}\right) + \frac{k_a}{s_1\tilde{k}_D(s_1)}\left(1 + \frac{k_b + k_r}{s\tilde{k}_D(s)}\right) \tag{3.7}$$

Making the inverse Laplace transformation over (3.1) and (3.2)

$$P_{D*A}(R, t) = \int_0^t d\tau A(t - \tau)[D*]_\tau[A]_\tau + \int_0^t d\tau B(t - \tau)[E]_\tau + \int_0^t d\tau C(t - \tau)[D^+]_\tau[A^-]_\tau$$

$$P_{D+A^-}(R, t) = \int_0^t d\tau A_1(t - \tau)[D*]_\tau[A]_\tau + \int_0^t d\tau B_1(t - \tau)[E]_\tau + \int_0^t d\tau C_1(t - \tau)[D^+]_\tau[A^-]_\tau$$

and substituting the result into (2.10)−(2.12) we obtain the integro-differential equations for the problem (Scheme 1)

$$\frac{d[D*]_t}{dt} = -\int_0^t d\tau R_1(t - \tau)[D*]_\tau[A]_\tau + \int_0^t d\tau R_2(t - \tau)[E]_\tau + \int_0^t d\tau R_3(t - \tau)[D^+]_\tau[A^-]_\tau - \frac{[D*]_t}{\tau_D} \tag{3.8}$$

$$\frac{d[D^+]_t}{dt} = \int_0^t d\tau R_4(t - \tau)[D*]_\tau[A]_\tau + \int_0^t d\tau R_5(t - \tau)[E]_\tau - \int_0^t d\tau R_6(t - \tau)[D^+]_\tau[A^-]_\tau \tag{3.9}$$

$$\frac{d[E]_t}{dt} = \int_0^t d\tau R_7(t - \tau)[D*]_\tau[A]_\tau - \int_0^t d\tau R_8(t - \tau)[E]_\tau + \int_0^t d\tau R_9(t - \tau)[D^+]_\tau[A^-]_\tau - \frac{[E]_t}{\tau_E} \tag{3.10}$$

where the kernels are defined in the Laplace representation

$$\tilde{R}_1(s) = (k_f + k_a)(1 + A) - k_b A_1, \quad \tilde{R}_2(s) = -(k_f + k_a)B + k_b B_1 + k_d \tag{3.11}$$

$$\tilde{R}_3(s) = -(k_f + k_a)C + k_b(1 + C_1), \quad \tilde{R}_4(s) = k_f(1 + A) - (k_b + k_r)A_1 \tag{3.12}$$

$$\tilde{R}_5(s) = k_f B - (k_b + k_r)B_1, \quad \tilde{R}_6(s) = -k_f C + (k_b + k_r)(1 + C_1) \tag{3.13}$$

$$\tilde{R}_7(s) = k_a(1 + A), \quad \tilde{R}_8(s) = -k_a B + k_d, \quad \tilde{R}_9(s) = k_a C \tag{3.14}$$

This is the complete collection of the contact problem solution.

B. The Ground State Particles in Great Excess. For further consideration, we introduce the following dimensionless values

$$N*(t) = [D*]_t/[D*]_0, \quad N^\pm(t) = [D^+]_t/[D*]_0 = [D^-]_t/[D*]_0, \quad N_E(t) = [E]_t/[D*]_0 \tag{3.15}$$

and take into account that concentrations of acceptor and donors are time independent: $[A]_t \approx [A]_0 = c$, $[D]_t \approx [D]_0 = \rho$, provided acceptors are in great excess and the excitation is relatively low, $\varepsilon = [D*]_0/[D]_0 \ll 1$. In such a case eqs 3.8−3.10 take the form

$$\dot{N}*(t) = -c\int_0^t d\tau R_1(t - \tau)N*(\tau) + \int_0^t d\tau R_2(t - \tau)N_E(\tau) + \varepsilon\rho\int_0^t d\tau R_3(t - \tau)[N^\pm(\tau)]^2 - \frac{N*(t)}{\tau_D} \tag{3.16}$$

$$\dot{N}^\pm(t) = c\int_0^t d\tau R_4(t - \tau)N*(\tau) + \int_0^t d\tau R_5(t - \tau)N_E(\tau) - \varepsilon\rho\int_0^t d\tau R_6(t - \tau)[N^\pm(\tau)]^2 \tag{3.17}$$

$$\dot{N}_E(t) = c \int_0^t d\tau R_7(t - \tau)N^*(\tau) - \int_0^t d\tau R_8(t - \tau)N_E(\tau) + \varepsilon\rho \int_0^t d\tau R_9(t - \tau)[N^{\pm}(\tau)]^2 - \frac{N_E(t)}{\tau_E} \tag{3.18}$$

where the kernels in the Laplace representation after some algebra are the following

$$\tilde{R}_1(s) = (k_f + k_a)\left[1 - \frac{(k_f + k_a)[s\tilde{k}_D(s) + k_r] + k_a k_b}{Zs\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right] - \frac{k_b k_f}{Zs\tilde{k}_D(s)} \tag{3.19}$$

$$\tilde{R}_2(s) = k_d\left[1 - \frac{(k_f + k_a)[s\tilde{k}_D(s) + k_r] + k_a k_b}{Zs\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right] \tag{3.20}$$

$$\tilde{R}_3(s) = k_b\left[1 - \frac{1}{Z}\left(\frac{k_f + k_a}{s_1\tilde{k}_D(s_1)} + \frac{(k_b + k_r)[s_1\tilde{k}_D(s_1) + k_a] + k_f k_a}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right)\right] \tag{3.21}$$

$$\tilde{R}_4(s) = k_f\left[1 - \frac{1}{Z}\left(\frac{k_f + k_a}{s_1\tilde{k}_D(s_1)} + \frac{k_b + k_r}{s\tilde{k}_D(s)} + \frac{k_a(k_b + k_r) + k_f k_r}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right)\right] \tag{3.22}$$

$$\tilde{R}_5(s) = \frac{1}{Z}\frac{k_f k_d}{s_1\tilde{k}_D(s_1)} \tag{3.23}$$

$$\tilde{R}_6(s) = (k_b + k_r)\left[1 - \frac{1}{Z}\left(\frac{k_b + k_r}{s\tilde{k}_D(s)} + \frac{k_a(k_b + k_r) + k_f k_r}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right)\right] - \frac{k_f k_b}{Zs_1\tilde{k}_D(s_1)} \tag{3.24}$$

$$\tilde{R}_7(s) = k_a\left[1 - \frac{1}{Z}\left(\frac{k_f + k_a}{s_1\tilde{k}_D(s_1)} + \frac{k_a(k_b + k_r) + k_f k_r}{s\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right)\right] \tag{3.25}$$

$$\tilde{R}_8(s) = k_d\left[1 - \frac{k_b + k_r + s\tilde{k}_D(s)}{Zs\tilde{k}_D(s)s_1\tilde{k}_D(s_1)}\right], \quad \tilde{R}_9(s) = \frac{k_a k_b}{Zs_1\tilde{k}_D(s_1)} \tag{3.26}$$

C. Only Exciplex Formation. Since in the case of the particular reaction 1.8 $k_f = k_b = k_r = 0$, only four kernels remain nonzero and all of them could be expressed via the universal one, $\tilde{Y}(s)$

$$\tilde{Y}(s) = \frac{\tilde{R}_1(s)}{k_a} = \frac{\tilde{R}_7(s)}{k_a} = \frac{\tilde{R}_2(s)}{k_d} = \frac{\tilde{R}_8(s)}{k_d} = \frac{1}{1 + k_a/[s_1\tilde{k}_D(s_1)]} \tag{3.27}$$

Thus we obtain the integro-differential equations

$$\frac{dN^*}{dt} = -ck_a\int_0^t d\tau Y(t - \tau)N^*(\tau) + k_d\int_0^t d\tau Y(t - \tau)N_E(\tau) - \frac{N^*(t)}{\tau_D} \tag{3.28}$$

$$\frac{dN_E}{dt} = ck_a\int_0^t d\tau Y(t - \tau)N^*(\tau) - k_d\int_0^t d\tau Y(t - \tau)N_E(\tau) - \frac{N_E(t)}{\tau_E} \tag{3.29}$$

The set of these equations with their kernel (3.27) are identical to IET equations derived in ref 17 (eqs 4.1 with kernels 3.15) and their analogues postulated in ref 18. They are also in agreement with some particular results obtained earlier.[19-23]

D. Only Photoionization. Turning to reaction 1.7 we have to set $k_a = k_d = 0$ and keep only the nonzero kernels defined in the Laplace representation

$$\tilde{R}^*(s) = \tilde{R}_1(s) = k_f\left(1 + \frac{k_r}{s\tilde{k}_D(s)}\right)\frac{1}{Z}, \quad \tilde{R}^{\#}(s) = \tilde{R}_3(s) = \frac{k_b}{Z} \tag{3.30}$$

$$\tilde{R}^{\dagger}(s) = \tilde{R}_4(s) = \frac{k_f}{Z}, \quad \tilde{R}^{\ddagger}(s) = \tilde{R}_6(s) = \left(k_b + k_r + \frac{k_f k_r}{s_1\tilde{k}_D(s_1)}\right)\frac{1}{Z} \tag{3.31}$$

where

$$Z = \frac{k_b}{s\tilde{k}_D(s)} + \left(1 + \frac{k_f}{s_1\tilde{k}_D(s_1)}\right)\left(1 + \frac{k_r}{s\tilde{k}_D(s)}\right) \tag{3.32}$$

With these kernels the IET integro-differential equations take the form common for all previous studies

$$\frac{dN^*}{dt} = -c \int_0^t d\tau R^*(t - \tau)N^*(\tau) + \varepsilon\rho \int_0^t d\tau R^{\#}(t - \tau)[N^{\pm}(\tau)]^2 - \frac{N^*(t)}{\tau_D} \tag{3.33}$$

$$\frac{dN^{\pm}}{dt} = c \int_0^t d\tau R^{\dagger}(t - \tau)N^*(\tau) - \varepsilon\rho \int_0^t d\tau R^{\ddagger}(t - \tau)[N^{\pm}(\tau)]^2 \tag{3.34}$$

In particular eqs 3.33 and 3.34 identically coincide with eqs 3.358 and 3.369 of the review[7] where a number of their applications are also considered.

IV. Irreversible Energy Quenching and Exciplex Formation

Let us consider, as the simplest application of the theory, the irreversible energy quenching competing with reversible exciplex formation, according to (1.6). In this particular situation $k_b = k_r = 0$ and the kernels $\tilde{R}_3(s)$, $\tilde{R}_9(s)$ turn to zero while the necessary ones are

$$\tilde{R}_1(s) = \frac{k_f + k_a}{Y}, \quad \tilde{R}_2(s) = \frac{k_d}{Y} \tag{4.1}$$

$$\tilde{R}_7(s) = \frac{k_a}{Y}, \quad \tilde{R}_8(s) = \frac{k_d}{Y}\left(1 + \frac{k_f}{s_1\tilde{k}_D(s_1)}\right) \tag{4.2}$$

where

$$Y = 1 + \frac{k_f + k_a}{s_1\tilde{k}_D(s_1)} \tag{4.3}$$

Ignoring the ground state product of energy quenching, we have to write only two kinetic equations for $N^*(t)$ and $N_E(t)$ which follow from eqs 3.16 and 3.18, after neglecting there the recombination terms

$$\dot{N}^*(t) = -c \int_0^t d\tau R_1(t - \tau)N^*(\tau) + \int_0^t d\tau R_2(t - \tau)N_E(\tau) - \frac{N^*(t)}{\tau_D} \tag{4.4}$$

$$\dot{N}_E(t) = c \int_0^t d\tau R_7(t - \tau)N^*(\tau) - \int_0^t d\tau R_8(t - \tau)N_E(\tau) - \frac{N_E(t)}{\tau_E} \tag{4.5}$$

Making Laplace transformations of these equations we obtain

$$\tilde{N}^*(s) = \frac{1}{s + \tau_D^{-1} + c\tilde{\Sigma}(s)}, \quad \tilde{N}_E(s) = \frac{c\tilde{R}_7(s)}{s + 1/\tau_E + \tilde{R}_8(s)}\tilde{N}^*(s) \tag{4.6}$$

where the "mass operator" equals

$$\tilde{\Sigma}(s) = \tilde{R}_1(s) - \frac{\tilde{R}_2(s)\tilde{R}_7(s)}{s + 1/\tau_E + \tilde{R}_8(s)} = \frac{k_f + k_a}{Y}\left[\frac{s + \tau_E^{-1} + k_dk_f/(k_f + k_a)}{s + \tau_E^{-1} + \frac{k_dk_f}{Y}\left(\frac{1}{s_1\tilde{k}_D(s_1)} + \frac{1}{k_f}\right)}\right] \tag{4.7}$$

A. The Luminescence Quantum Yields. The excitation fluorescence quantum yield

$$\eta = \int_0^{\infty} N^*(t)\, dt/\tau_D = \frac{\tilde{N}^*(0)}{\tau_D} = \frac{1}{1 + c\kappa\tau_D} \tag{4.8}$$

obeys the Stern–Folmer law, whose constant κ can be easily found using eq 4.7

$$\kappa = \tilde{\Sigma}(0) = \tilde{R}_1(0) - \frac{\tilde{R}_2(0)\tilde{R}_7(0)}{1/\tau_E + \tilde{R}_8(0)} \tag{4.9}$$

and the quantum yield of the exciplex fluorescence can be specified using eq 4.6

$$\eta_E = \frac{\tilde{N}_E(0)}{\tau_E} = \frac{\phi_E}{\tau_E}\tilde{N}^*(0) \tag{4.10}$$

It is seen that the expression

$$\phi_E = \frac{\tilde{N}_E(0)}{\tilde{N}^*(0)} = \frac{c\tilde{R}_7(0)}{1/\tau_E + \tilde{R}_8(0)} \tag{4.11}$$

is just the fraction of the exciplexes transformed from excitations.

For a better understanding of the quenching phenomenon, it is useful to present eqs 4.9 in the following form

$$c\kappa = c\tilde{R}_1(0) - \tilde{R}_2(0)\phi_E \tag{4.12}$$

The first term in the right-hand side of this expression is the sum of the rates of energy transfer and irreversible exciplex formation

$$c\tilde{R}_1(0) = c\left[\frac{k_f}{Y_0} + \frac{k_a}{Y_0}\right], \quad Y_0 = 1 + \frac{k_f + k_a}{k_D(1 + \sqrt{\tau_c/\tau_D})} \tag{4.13}$$

where $\tau_c = \sigma^2/D$ is the encounter time. Just this term, $c\tilde{R}_1(0)$, turns to be linear in k_D when the quenching becomes diffusional

$$c\tilde{R}_1(0) \approx k_D(1 + \sqrt{\tau_c/\tau_D}) \quad \text{at} \quad k_f + k_a \gg k_D$$

The second term in eq 4.12 is the rate of the reverse electron transfer (from the exciplex to the excited donor) which initiates the delayed fluorescence. It is equal to the share of exciplexes ϕ_E multiplied by the rate of their dissociation into the fluorescence pair, $\tilde{R}_2(0)$. In diffusion limit the second term is quadratic in k_D, i.e., rather small, but restores partially the density of the excitations reducing the Stern–Volmer constant.

In the opposite kinetic limit ($D \to \infty$, $Y_0 \to 1$) one can obtain

$$\phi_E = ck_E\tau_E \quad \text{and} \quad \kappa = k_f + k_E \tag{4.14}$$

where the effective rate constant of the exciplex formation is

$$k_E = \left(\frac{1}{k_a} + \frac{k_d}{k_a}\tau_E\right)^{-1} = \begin{cases} k_a & \text{at} \quad k_d\tau_E \ll 1 \\ K_{eq}\tau_E^{-1} & \text{at} \quad k_d\tau_E \gg 1 \end{cases} \tag{4.15}$$

The latter integrates the processes occurring at different times: the upper estimate relates to the initial stage of exciplex formation proceeding irreversibly while the lower one relates to the final stage of the exciplex decay, after equilibration between them and their precursors determined by the equilibrium constant $K_{eq} = k_a/k_d$.

As can be seen from Figure 2, between the diffusional and kinetic limits of quenching, the Stern–Volmer constant is the monotonously growing function of diffusion

$$k_D(1 + \sqrt{\tau_c/\tau_D}) \le \kappa(D) \le k_f + k_E \tag{4.16}$$

As well as $\kappa(D)$, the exciplex yield monotonously grows with diffusion between the diffusional and kinetic limits (Figure 3)

$$\frac{k_E}{k_f + k_E}ck_D(1 + \sqrt{\tau_c/\tau_D})\eta\tau_D \ll \eta_E \ll ck_E\eta\tau_D \tag{4.17}$$

In the kinetic limit the exciplexes are produced with the effective rate constant k_E, while in the diffusional limit k_E determines just the exciplex share $(k_E)/(k_f + k_E)$ from the products of diffusional quenching (with the rate ck_D). This share is not affected by diffusion, but this independence is a price for the contact approximation. If the quenching is distant, being diffusional, it proceeds far from the contact. In particular the remote diffusional ionization screens the contact from the excitations approaching it, thus preventing any contact reactions.[26]

B. Kinetics. As a rule the exciplex lives longer than the primary excitation ($\tau_E > \tau_D$), pumping the latter by dissociation and thus prolonging its delayed fluorescence. The latter follows closely the initial stage of the excitation quenching, due to exciplex association/dissociation. To study such a process of energy dissipation and conservation, we can restrict ourself to rather long times (small s), where one can expand the kernels defined in eqs 4.1 and 4.2, leaving only the smallest nonstationary corrections. In diffusion limit they are

$$\tilde{R}_j(s) \approx \tilde{R}_j(0)\left[1 + \frac{s}{2}\left(\frac{\sqrt{\tau_c\tau_D}}{1 + \sqrt{\tau_c/\tau_D}}\right)\right] \sim \tilde{R}_j(0)[1 + o(st_b)] \tag{4.18}$$

where $\tau_c = \sigma^2/D$. The correction, which is linear in s, does not influence the long time kinetics. Being small at $st_b \ll 1$ it defines the boundary time t_b that restricts the validity limit of such an approximation

$$t \gg t_b = \frac{\sqrt{\tau_c\tau_D}}{1 + \sqrt{\tau_c/\tau_D}} \tag{4.19}$$

Just in this time interval the integral eqs 4.4 and 4.5 are simplified to the differential ones with the time-independent coefficients $\tilde{R}_j(0)$. The "mass operator" (4.7) also becomes much simpler in this approximation

$$\tilde{\Sigma}(s) = \tilde{R}_1(0)\left(\frac{s + \tau_E^{-1} + \vartheta}{s + \tau_E^{-1} + \theta}\right) \tag{4.20}$$

where
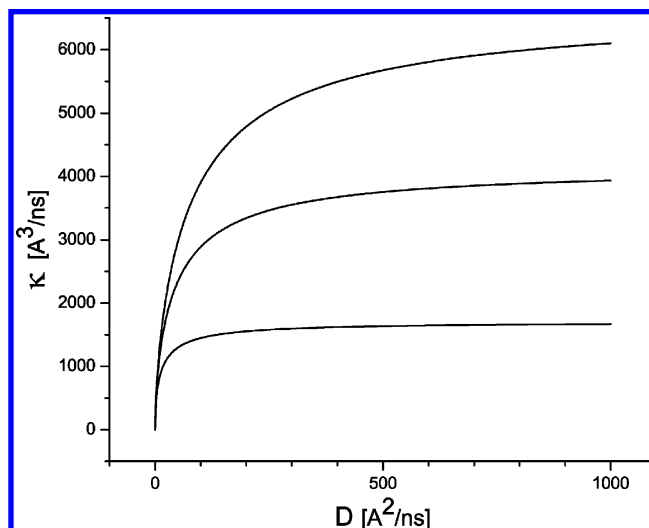
Figure 2. The Stern−Volmer constant diffusional dependence in the case of irreversible (upper curve, $k_d\tau_E = 0$) and reversible exciplex formation: $k_d\tau_E = 1$ (intermediate), $k_d\tau_E = 100$ (ground one). Other parameters: $\tau_D = 1$ ns, $k_f = 1660$ Å^3 /ns, $k_a = 5000$ Å^3/ns.
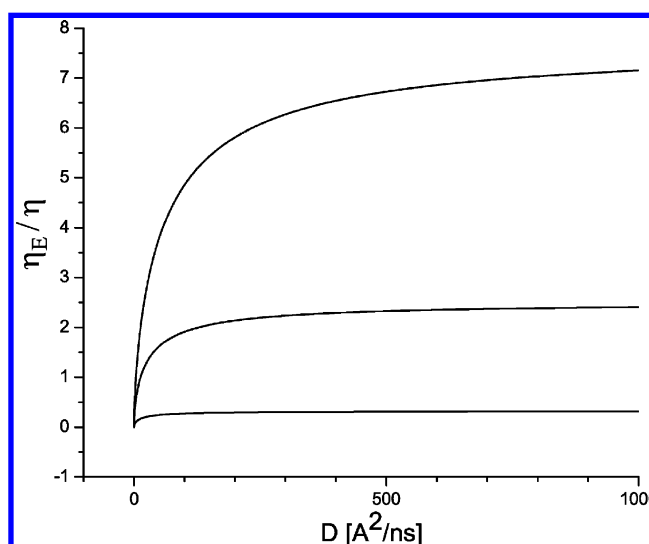
Figure 3. The ratio of the luminescence yields changing with diffusion from the diffusional to kinetic control, at different reversibility of exciplex formation: $k_d\tau_E = 0.3$ (upper curve); $k_d\tau_E = 3$ (intermediate); $k_d\tau_E = 30$ (ground one). The rest of parameters are: $\tau_D = 1$ ns, $\tau_E = 10$ ns, $k_f = 1660$ Å^3/ns, $k_a = 5000$ Å^3/ns.

$$\vartheta = \frac{k_d k_f}{k_f + k_a}, \quad \theta = \tilde{R}_8(0) = \frac{k_d}{Y_0}\left(1 + \frac{k_f}{k_D(1 + \sqrt{\tau_c/\tau_D})}\right) \tag{4.21}$$

So in a time interval $t \gg \tau_b$, the general results obtained in eqs 4.6 can be represented as the sum of the common fractions

$$\tilde{N}^*(s) \approx \frac{A_1}{s - s_1} + \frac{A_2}{s - s_2}, \quad \tilde{N}_E(s) \approx \frac{c\tilde{R}_7(0)}{s + \tau_E^{-1} + \theta}\tilde{N}^*(s) \tag{4.22}$$

This can be easily inverted analytically

$$N^*(t) \approx A_1 \exp(s_1 t) + A_2 \exp(s_2 t) \tag{4.23}$$

$$N_E(t) \approx \frac{c\tilde{R}_7(0)}{(s_1 - s_2)}[\exp(s_1 t) - \exp(s_2 t)] \tag{4.24}$$

Hence, the time dependence of the survival probabilities $N^*(t)$ and $N_E(t)$ has the biexponential form specified by the following coefficients

$$A_1 = \frac{\tau_E^{-1} + \theta + s_1}{s_1 - s_2}, \quad A_2 = \frac{\tau_E^{-1} + \theta + s_2}{s_2 - s_1} \tag{4.25}$$

and

$$s_{1,2} = \frac{1}{2}(-b \pm \sqrt{b^2 - 4d}) \tag{4.26}$$

are the roots of the corresponding quadratic equation which has the following coefficients

$$b = \frac{1}{\tau_D} + \frac{1}{\tau_E} + \theta + c\tilde{R}_1(0), \quad d = \frac{1}{\tau_D}\left(\frac{1}{\tau_E} + \theta\right) + c\tilde{R}_1(0)\left(\frac{1}{\tau_E} + \vartheta\right)$$

1. Only Exciplex Formation. Let us illustrate these results by the simplest particular case of reversible exciplex formation without any additional quenching ($k_f = 0$). Then

$$\tilde{R}_1(0) = \frac{k_a}{Y_0} \equiv R, \quad \vartheta = 0, \quad \theta = \frac{k_d}{Y_0}$$

It is also convenient to introduce the new notations for this particular problem

$$\delta = \frac{1}{\tau_D} - \frac{1}{\tau_E}, \quad \gamma = \frac{k_d}{ck_a}, \quad \lambda = c(1 + \gamma)R \tag{4.27}$$

In these notations the roots (4.26) take the following form

$$s_{1,2} = -\frac{1}{\tau_D} + \frac{\delta - \lambda \pm \sqrt{(\delta + \lambda)^2 - 4\gamma cR\delta}}{2} \tag{4.28}$$

From now on one has to distinguish between two alternative limits:
1. Fast exciplex/excitation equilibration compared to natural decay ($\lambda \gg \delta \approx 1/\tau_D$).
2. Fast natural decay compared to association and dissociation ($\lambda \ll \delta \approx 1/\tau_D$)
In the former case one can expand expressions 4.28 into the small parameter $\delta/\lambda \ll 1$

$$s_1 \approx -\left(\frac{1}{1+\gamma}\right)\frac{1}{\tau_E} - \left(\frac{\gamma}{1+\gamma}\right)\frac{1}{\tau_D} + \left(\frac{\gamma}{1+\gamma}\right)\frac{\delta^2}{\lambda} \tag{4.29}$$

$$s_2 \approx -\lambda - \left(\frac{1}{1+\gamma}\right)\frac{1}{\tau_D} - \left(\frac{\gamma}{1+\gamma}\right)\frac{1}{\tau_E} - \left(\frac{\gamma}{1+\gamma}\right)\frac{\delta^2}{\lambda} \tag{4.30}$$

Correspondingly, the weight coefficients A_i are found to be

$$A_1 \approx \left(\frac{\gamma}{1+\gamma}\right)\left[1 + 2\left(\frac{1}{1+\gamma}\right)\frac{\delta}{\lambda}\right], \quad A_2 \approx \left(\frac{1}{1+\gamma}\right)\left[1 - 2\left(\frac{1}{1+\gamma}\right)\frac{\delta}{\lambda}\right] \tag{4.31}$$

Note, that in the case of the stable reaction partners, $\tau_E = \tau_D = \infty$, their populations after equilibration gain the equilibrium values, $N^*(\infty) = \mathcal{N}$ and $N_E(\infty) = \mathcal{N}_E$, which are

$$\mathcal{N} = \frac{\gamma}{1+\gamma}, \quad \mathcal{N}_E = \frac{1}{1+\gamma} \tag{4.32}$$

Making use of these definitions and omitting the small corrections in δ/λ in the eqs 4.29–4.31, we obtain the results for the expressions 4.23 and 4.24:

$$N^*(t) \approx \mathcal{N}e^{-((\mathcal{N}/\tau_D)+(\mathcal{N}_E/\tau_E))t} + \mathcal{N}_E e^{-(\lambda+((\mathcal{N}_E/\tau_D)+(\mathcal{N}/\tau_E))t} \tag{4.33}$$

$$N_E(t) \approx \mathcal{N}_E[e^{-((\mathcal{N}/\tau_D)+(\mathcal{N}_E/\tau_E))t} - e^{-(\lambda+((\mathcal{N}_E/\tau_D)+(\mathcal{N}/\tau_E))t}] \tag{4.34}$$

The last terms in these expressions account for the fast equilibration during encounters. When they vanish the remaining terms determine the final decay of the excited state and exciplex with one and the same average rate

$$w_0 = \frac{\mathcal{N}}{\tau_D} + \frac{\mathcal{N}_E}{\tau_E} \tag{4.35}$$

though with different amplitudes, $\mathcal{N}$ and $\mathcal{N}_E$. As these populations are equilibrated
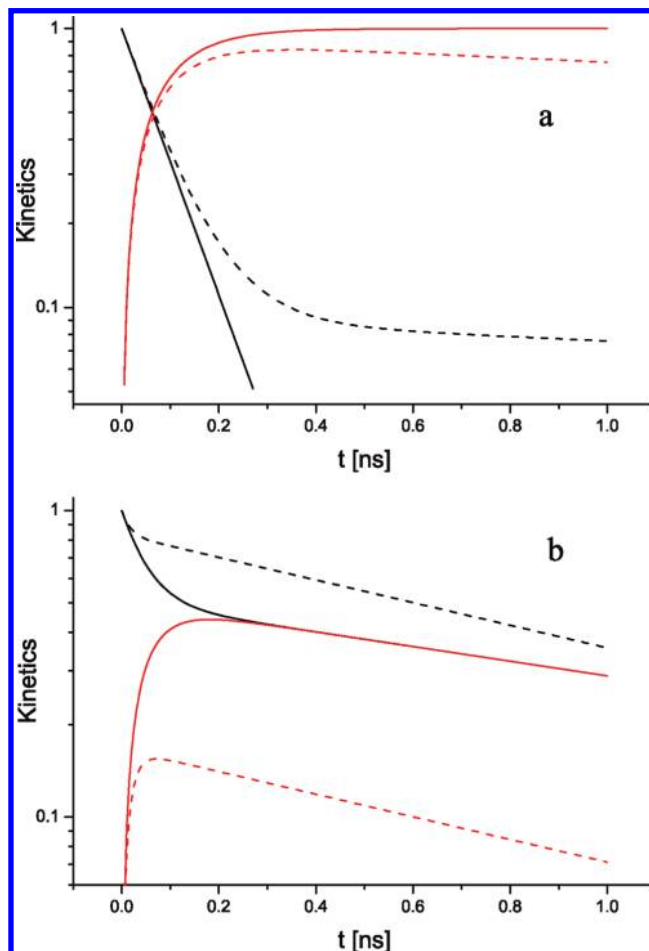
Figure 4. Slow donor decay $\tau_D = 1$ ns and fast equilibration $cR = 10$ ns^{-1} (black curves) compared to exciplex accumulation (red curves) whose lifetime is $\tau_E = 10$ ns. (a)The irreversible reaction (solid curves), proceeding at $\gamma = 0$, and weakly reversible (dashed curves), corresponding to $\gamma = 0.1$. (b) The same for the larger reversibility, $\gamma = 1$ (solid lines) and for $\gamma = 5$ resulting in pronounced delayed fluorescence (dashed lines).

$$N = \gamma N_E, \quad \gamma = \frac{\exp(\Delta G_E/T)}{cv}$$

where γ is a measure of the reaction reversibility. Figure 4 demonstrates the typical kinetics of fast equilibration followed by delayed fluorescence with an average rate (4.35).

In the opposite limiting case of fast excitation decay, $\lambda \ll \delta$, it follows from eq 4.28

$$s_1 \approx -cR - \frac{1}{\tau_D} + \gamma cR\frac{\lambda}{\delta}, \quad s_2 \approx -\gamma cR - \frac{1}{\tau_E} - \gamma cR\frac{\lambda}{\delta} \tag{4.36}$$

$$A_1 \approx 1 - \gamma cR\frac{\lambda}{\delta^2}, \quad A_2 \approx \gamma cR\frac{\lambda}{\delta^2} \tag{4.37}$$

Thus the kinetics of the donor and exciplex dissipation takes the following form

$$N^*(t) \approx A_1 e^{-((1/\tau_D)+cR)t} + A_2 e^{-((1/\tau_E)+\gamma cR)t} \tag{4.38}$$

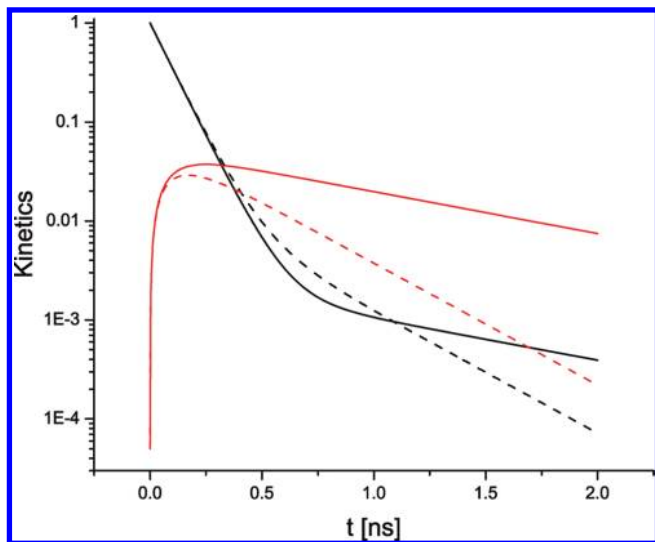$$N_E(t) \approx \frac{cR}{\delta}[e^{-((1/\tau_E)+\gamma cR)t} - e^{-((1/\tau_D)+cR)t}] \tag{4.39}$$

The fast and deep initial decay of the donor occurs with the rate

$$w_D = \frac{1}{\tau_D} + cR \tag{4.40}$$

which is slightly accelerated by irreversible exciplex formation. It then gives way to a weak delayed fluorescence whose decay rate

$$w_E = \frac{1}{\tau_E} + \gamma cR \tag{4.41}$$

is also slightly accelerated by the irreversible exciplex dissociation (Figure 5).

Figure 5. Fast donor decay $\tau_D = 0.1$ ns, $cR = 0.5$ ns^{-1} (black curves) compared to slow mixing, resulting in weakly accumulated exciplexes (red curves) whose lifetime is $\tau_E = 2$ ns (a) at $\gamma = 1$ (solid lines) and (b) at $\gamma = 5$ (dashed lines).

V. Concluding Remarks

The pioneering investigation of the distant (exponential) quenching parallel to the contact one[25] was made with the DET valid for only irreversible transfer

$$\overset{W_F}{\leftarrow} A + D^* \overset{k_a}{\longrightarrow} \atop \downarrow_{\tau_D} \qquad (5.41)$$

Moreover, all the results obtained there were derived within Markovian approximation ignoring the transient effects. Just recently the non-Markovian extension of this very theory was proposed[26] which stresses the determinative role of the distant and especially nonstationary (non-Markovian) quenching in screening the contact reaction.

The same should take place when the contact reaction is actually the reversible exciplex formation

$$\overset{W_F}{\leftarrow} A + D^* \overset{k_a}{\underset{k_d}{\rightleftarrows}} A^{\delta-}D^{\delta+} \atop \downarrow_{\tau_D} \qquad \downarrow_{\tau_E} \qquad (5.2)$$
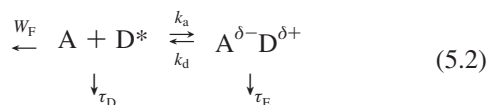
To account for this reversibility, DET should be replaced by the IET or any approach which is equivalent to it. This is even more so when the distant quenching or ionization is reversible as well as shown in Scheme 1. This is what we plan to do next.

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