Reversible Exciplex Formation Followed Charge Separation

M. V. Petrova

International Tomography Center, Novosibirsk 630090, Russia Novosibirsk State University, Novosibirsk 630090, Russia

A. I. Burshtein*

Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

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The reversible exciplex formation followed by its decomposition into an ion pair is considered, taking into account the subsequent geminate and bulk ion recombination to the triplet and singlet products (in excited and ground states). The integral kinetic equations are derived for all state populations, assuming that the spin conversion is performed by the simplest incoherent (rate) mechanism. When the forward and backward electron transfer is in contact as well as all dissociation/association reactions of heavy particles, the kernels of integral equations are specified and expressed through numerous reaction constants and characteristics of encounter diffusion. The solutions of these equations are used to specify the quantum yields of the excited state and exciplex fluorescence induced by pulse or stationary pumping. In the former case, the yields of the free ions and triplet products are also found, while in the latter case their stationary concentrations are obtained.

I. Introduction

The creation of exciplexes in encounters of excited reactants, A* + D (or D* + A), and their subsequent dissociation into parent particles or a radical ion pair (RIP), is known as "Scheme I" of exciplex formation proposed by Weller[1,2] and is widely accepted.[3–5] It was studied by means of the unified theory (UT) in ref 6, assuming that creation of exciplexes is irreversible. On the contrary, in a very recent article[7] this initial stage was treated as reversible using the integral encounter theory (IET) but neglecting all the subsequent reactions of RIP creation and separation as in Scheme III of ref 8. Here we consider the whole reaction consisting of all its stages as in the later work:[9]

$$\begin{array}{llllll} \mathrm{A}^* & +\,\mathrm{D} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} & [\mathrm{A}^{-\delta}\mathrm{D}^{+\delta}] & \underset{k_a}{\overset{k_d}{\rightleftharpoons}} & [\mathrm{A}^{-}\cdots\mathrm{D}^{+}] & \rightleftharpoons \mathrm{A}^{-}+\mathrm{D}^{+} \\ I\uparrow\downarrow\frac{1}{\tau_A} & & \downarrow 1/\tau_e & & \downarrow k_c & \end{array} \tag{1.1}$$

The exciplex composed from partially charged components ($0 < \delta < 1$) is formed from neutral reactants with the rate constant k_f or by charge association with the rate constant k_a and disappears due to the backward electron transfer with the rate k_b or dissociation into the RIP with the rate k_d

$$k_f = k_b v \exp(-\Delta G_{exc}/T) \tag{1.2}$$
$$k_a = k_d v \exp(-\Delta G_{RIP}/T)$$

where v is approximately the volume of the attached reaction layer.[13,14] According to the energy scheme in Figure 1, the free energy of exciplex formation from the neutral components is $\Delta G_{exc} < 0$, while that from RIP is $\Delta G_{RIP} < 0$ as well (hereafter the Boltzmann constant $k_B = 1$).

The contact recombination of the RIP to the ground state proceeds with the rate constant

$$k_c = k_c^0 \exp\frac{(\varepsilon_S + \Delta G_i - \lambda)^2}{4\lambda T}$$

where ε_S is the excitation energy of singlet ^{1}A* and λ is the reorganization energy of the electron transfer. The RIPs recombination competes with their diffusional separation into free ions. Both A* and the exciplex decay by luminescence, with the rates $1/\tau_A$ and $1/\tau_{exc}$, respectively, which are related by the equation[8,10–12]

$$\frac{1}{\tau_{exc}} = \frac{1}{\tau_A}\frac{1}{1+(\Delta G_{exc}/V)^2} \tag{1.3}$$

where

$$\Delta G_{exc} = \Delta G_i/2 - \sqrt{(\Delta G_i/2)^2 + V^2}$$

Here V is the electron coupling between A*D and A$^-$ D$^+$ and $\Delta G_i < 0$ is the free energy of charge separation (ionization). The light excitation, which is assumed to be rather weak, occurs with the rate IN where $N = [A]$ is the total acceptor concentration.

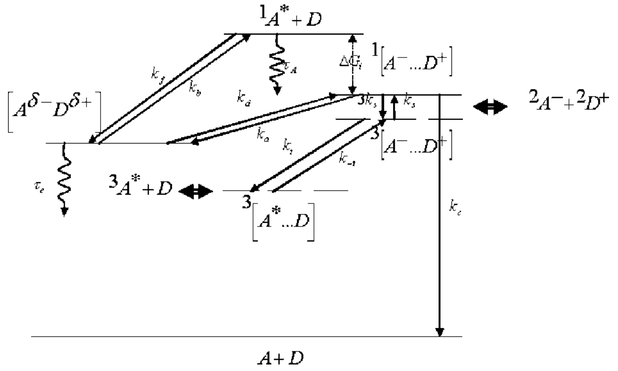

Figure 1. The reversible exciplex formation and dissociation into the RIP converted to triplets or separated into free ions.

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* Corresponding author.

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The luminescence can be detected in two different ways: either after δ-pulse excitation, $I = (N_0/N)\delta(t)$ or under stationary irradiation, $I = I_0 =$ constant. In the former case the initially created excitations $N^*(0) = N_0$ are quenched by exciplex formation and their luminescence allows to trace the decay kinetics $N^*(t) = [A^*]$ in a limited time interval after the pulse. Due to this limitation, the long tail of delayed luminescence resulting from the restoration of A* in the bulk recombination of free ions is cut off and the measured quantum yield,

$$\eta = \frac{\int_0^\infty N^*(t')\,\mathrm{d}t'}{N_0\tau_A} = \frac{1}{1 + c\kappa_g\tau_A} \tag{1.4}$$

obeys the Stern−Volmer dependence on donor concentration $c = [D]$ but with the constant κ_g originating from only the geminate reaction.

Under stationary irradiation there is the stationary concentration of the luminophore, N_s^*, as well as exciplexes N_s^e and free ions, P_s. The quantum yield of the acceptor luminescence is defined via N_s^*,[15−17]

$$\eta = \frac{N_s^*}{I_0 N\tau_A} = \frac{1}{1 + c\kappa\tau_A} \tag{1.5}$$

where κ is the Stern−Volmer constant accounting for the bulk reactions that contribute to the delayed fluorescence. When the quenching is carried out by the straightforward RIP formation, the simple relationship between κ_g and κ is established[18,19]

$$\kappa = \kappa_g[1 - \chi\bar{\varphi}] \tag{1.6}$$

Here $\bar{\varphi}$ is the yield of free ions produced by the RIP dissociation and χ is the yield of A* restored by the backward electron transfer in the RIPs appearing in the bulk encounters of ions.

The reaction scheme (1.1) is oversimplified. This is the basis for the spin-less theory while in reality the spin state of the RIP can be either singlet or triplet. The general reaction scheme presented in Figure 1 accounts not only for the singlet RIP recombination to the ground state but also for the reversible production of neutral $^3A^*$ from the triplet RIP. Taking into account the singlet−triplet conversion, this final stage of the reaction can be represented as follows The spin conversion is

$$\mathrm{A + D} \xleftarrow{k_c} {}^1[\mathrm{A}^- \cdots \mathrm{D}^+] \rightarrow {}^2\mathrm{A}^- + {}^2\mathrm{D}^+ \tag{1.7a}$$

$$k_s \uparrow\downarrow 3k_s$$

$${}^3\mathrm{A}^* + \mathrm{D} \underset{k_t}{\overset{k_{-t}}{\rightleftharpoons}} {}^3[\mathrm{A}^- \cdots \mathrm{D}^+] \rightarrow {}^2\mathrm{A}^- + {}^2\mathrm{D}^+ \tag{1.7b}$$

considered here and elsewhere[17,20] as a stochastic process performed with the rate k_s. Although this is just the simplest (incoherent) model of the process, it was shown to be rather workable in zero magnetic fields.[21,22] Spin conversion makes possible the subsequent reversible triplet excitation by backward electron transfer, with the rates

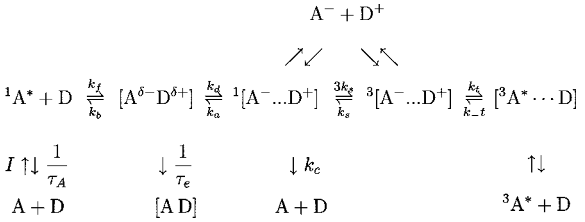
$$k_t = k_t^0 e^{-(\Delta G_t + \lambda)^2/4\lambda T} = k_{-t} \exp \Delta G_t/T \tag{1.8}$$

where the free energy of triplet creation is $\Delta G_t = \varepsilon_T - \varepsilon_S - \Delta G_i < 0$ where ε_T is the excitation energy of triplet excitation, $^3A^*$.

In what follows, we will study the free ions and triplet product yields in line with the excitation and exciplex fluorescence. We will find these quantum yields after pulse excitation, as well as the stationary concentration of all the products under permanent illumination.

II. Integral Encounter Theory of the Phenomenon

A. Integral Equations. The general reaction composed from the reversible exciplex formation and spin-assisted RIP recombination/separation is represented by the following reaction scheme:



(2.1)

The IET kinetic equations have to be written for the densities of the initial excitations (N^*), exciplex intermediate (N^e), and the products of the RIP recombination: counterions density $P = N^- \equiv N^+$ and that of the triplet excitation N^T. For the reversible exciplex formation, they were obtained in ref 7 but the RIP recombination is more often considered in the frame of UT (section XI in ref 17). To derive the full set of IET equations, one has to start from the most general formulation of IET given in ref 23 (eqs 5.4 and 5.7) and specify the Green functions which determine the kernels. Considering the linear in light response, we can keep constant the ground-state densities of the acceptors and donors

$$c = [D] \gg [A^-] \qquad \text{and} \qquad N = [A] \gg [A^*],$$

thus obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}N^* = -c\int_0^t R_{11}(t-\tau)N^*(\tau)\,\mathrm{d}\tau + \int_0^t R_{12}(t-\tau)N_e(\tau)\,\mathrm{d}\tau - \frac{N^*}{\tau_A} + IN \tag{2.2a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}N_e = c\int_0^t R_{11}(t-\tau)N^*(\tau)\,\mathrm{d}\tau - \int_0^t R_{22}(t-\tau)N_e(\tau)\,\mathrm{d}\tau + \int_0^t R_{23}(t-\tau)P^2(\tau)\,\mathrm{d}\tau + c\int_0^t R_{24}(t-\tau)N_T(\tau)\,\mathrm{d}\tau - \frac{N_e}{\tau_{exc}} \tag{2.2b}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}P = \int_0^t R_{32}(t-\tau)N_e(\tau)\,\mathrm{d}\tau - \int_0^t R_{33}(t-\tau)P^2(\tau)\,\mathrm{d}\tau + c\int_0^t R_{34}(t-\tau)N_T(\tau)\,\mathrm{d}\tau \tag{2.2c}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}N_T = \int_0^t R_{42}(t-\tau)N_e(\tau)\,\mathrm{d}\tau + \int_0^t R_{43}(t-\tau)P^2(\tau)\,\mathrm{d}\tau - c\int_0^t R_{44}(t-\tau)N_T(\tau)\,\mathrm{d}\tau \tag{2.2d}$$

All the kernels were defined via the corresponding transfer rates and Green functions that are the solutions of the auxiliary equations accounting for the competing reactions and encounter diffusion.[23]

The quenching of A* by exciplex formation, dissociation, and RIP recombination proceeds starting from the following initial condition to eq 2.2

$$N^*(0) = N_0, \quad N_e(0) = P(0) = N_T(0) = 0 \tag{2.3}$$

The same equations allow study of other reactions at different parameters and initial conditions. For instance, at $k_f = k_b = k_s = 0$ they reduce to a single equation of the spin-less IET of geminate exciplex dissociation considered in ref 7

$$\dot{N}_e = -\int_0^t R_{22}(t-\tau)N_e(\tau)\,d\tau - \frac{N_e}{\tau_{exc}} \qquad (2.4)$$

where

$$N_e(0) = N_0$$

This is exactly the same integral equation as (3.6) in ref 7 where the kernel $F(t) \equiv R_{22}(t)$.

B. Contact Approximation. Since all the reactions of the exciplex are contact, we can consider the electron transfer in the RIP also as contact, making available the exact solution of all the auxiliary equations as in section II of ref 19. By this way we obtained all the integral kernels (memory functions) exactly expressed through the contact reaction constants and parameters of the encounter diffusion in the Coulomb field

$$\tilde{R}_{11}(s) = \frac{k_f}{1+k_f g_1} \qquad (2.5)$$

$$\tilde{R}_{12}(s) = \frac{k_b}{1+k_f g_1}$$

$$\tilde{R}_{22}(s) = \frac{k_b}{1+k_f g_1} + \frac{k_d}{Y}(k_t(g_3+3g_4) + (k_{-t}g_5+1)(4+k_c(3g_3+g_4)) + 4k_c k_t g_3 g_4)$$

$$\tilde{R}_{32}(s) = \frac{4k_d(1+k_t g_3 + k_{-t}g_5)}{Y}$$

$$\tilde{R}_{42}(s) = \frac{3k_d k_t(g_4-g_3)}{Y}$$

$$\tilde{R}_{23}(s) = \frac{k_a(1+k_t g_3+k_{-t}g_5)}{Y}$$

$$\tilde{R}_{33}(s) = \frac{3k_t + (k_a+k_c)(1+4k_t g_3 + k_{-t}g_5)}{Y}$$

$$\tilde{R}_{43}(s) = \frac{3k_t(1+(k_a+k_c)g_3)}{Y}$$

$$\tilde{R}_{24}(s) = \frac{k_a k_{-t}(g_4-g_3)}{Y}$$

$$\tilde{R}_{34}(s) = \frac{4k_{-t}(1+(k_a+k_c)g_3)}{Y}$$

$$\tilde{R}_{44}(s) = \frac{k_{-t}(4+(k_a+k_c)(3g_3+g_4))}{Y}$$

where

$$Y = k_t((g_3+3g_4) + 4(k_a+k_c)g_3g_4) + (k_{-t}g_5+1)(4+(k_a+k_c)(3g_3+g_4))$$

and

$$g_1(s) = \frac{1}{k_D}\frac{1}{1+\sqrt{\tau_d\left(s+\frac{1}{\tau_A}\right)}} \qquad (2.6)$$

$$g_5(s) = \frac{1}{k_D}\frac{1}{1+\sqrt{\tau_d s}}$$

where $k_D = 4\pi\sigma D$ is the diffusional constant of contact reactions, D is an encounter diffusion coefficient considered to be the same for neutral and charged reactants, σ is the contact distance, and $\tau_d = (\sigma^2/D)$ is an encounter time in the free space. The rest of the g-functions

$$g_3(s) = \int u_3(t)e^{-st}\,dt \qquad (2.7)$$

and

$$g_4(s) = \int u_4(t)\mathrm{e}^{-st}\,dt$$

are the Laplace transformations of the Green functions $u_3(t)$ and $u_4(t)$.

The former obeys the following equation

$$\frac{\partial u_3}{\partial t} = -4k_s u_3 + D\frac{1}{r}\frac{\partial}{\partial r}re^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}u_3 \qquad (2.8)$$

with reflecting boundary condition at $r = \sigma$ and initial condition $u_3(0) = \delta(r - r_0)/4\pi rr_0$. Hereafter D is a diffusional constant and $r_c = \mathrm{e}^2/\epsilon T$ is the Onsager radius.

Another Green function obeys the simpler equation

$$\frac{\partial u_4}{\partial t} = D\frac{1}{r}\frac{\partial}{\partial r}re^{r_c/r}\frac{\partial}{\delta r}e^{-r_c/r}u_4 \qquad (2.9)$$

with reflecting boundary condition and the same initial condition: $u_4(0) = \delta(r - r_0)/4\pi rr_0$. It can be solved easily and subjected to the Laplace transformation for getting

$$g_4(0) = \frac{\sigma}{k_D r_c}(e^{r_c/\sigma} - 1) \qquad (2.10)$$

where $k_D = 4\pi\sigma D$ is the diffusional reaction constant of the contact reaction.

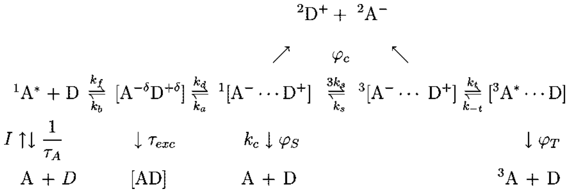
In highly polar solvents there is actually no Coulomb field ($r_c \to 0$), so that g_3 can be easily found from the solution of eq 2.8 in line with the others

$$g_3(s) = \frac{1}{k_D}\frac{1}{1+\sqrt{\tau_d(s+4k_s)}} \tag{2.11a}$$

$$g_4(s) = \frac{1}{k_D}\frac{1}{1+\sqrt{\tau_d s}} \tag{2.11b}$$

III. Pulse Excitation

A. The Geminate Reaction. The luminescence of diluted solutions, detected after pulse excitation in a limited time interval, does not include the delayed luminescence resulting from the ion encounters in a bulk. It obeys the reduced reaction scheme of the process



$$\begin{array}{ccccccccc} & & & & {}^2D^+ + {}^2A^- & & & & \\ & & & \nearrow & \varphi_c & \nwarrow & & & \\ {}^1A^* + D & \underset{k_b}{\overset{k_f}{\rightleftharpoons}} & [A^{-\delta}D^{+\delta}] & \underset{k_a}{\overset{k_d}{\rightleftharpoons}} & {}^1[A^-\cdots D^+] & \underset{k_s}{\overset{3k_s}{\rightleftharpoons}} & {}^3[A^-\cdots D^+] & \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} & [{}^3A^*\cdots D] \\ I\uparrow\downarrow\frac{1}{\tau_A} & & \downarrow\tau_{exc} & & k_c\downarrow\varphi_S & & & & \downarrow\varphi_T \\ A + D & & [AD] & & A + D & & & & {}^3A + D \end{array} \tag{3.1}$$

This reaction results in the irreversible free ion and relatively stable triplet production from the RIP (with the yields φ_c and φ_T) not speaking about the yield of the ground-state products, φ_S. Altogether

$$\varphi_S + \varphi_T + \varphi_c = 1 \tag{3.2}$$

but their individual free energy and viscosity dependence is the usual subject of experimental and theoretical investigations.[17,20]

The reduced integral equations not considering any bulk reactions are

$$\frac{d}{dt}N^* = -c\int_0^t R_{11}(t-\tau)N^*(\tau)\,d\tau + \int_0^t R_{12}(t-\tau)N_e(\tau)\,d\tau - \frac{N^*}{\tau_A}$$

$$\frac{d}{dt}N_e = c\int_0^t R_{11}(t-\tau)N^*(\tau)\,d\tau - \int_0^t R_{22}(t-\tau)N_e(\tau)\,d\tau - \frac{N_e}{\tau_{exc}}$$

$$\frac{d}{dt}P = \int_0^t R_{32}(t-\tau)N_e(\tau)\,d\tau$$

$$\frac{d}{dt}N_T = \int_0^t R_{42}(t-\tau)N_e(\tau)\,d\tau$$

The quantum yields of A^* fluorescence is

$$\eta = \frac{\int_0^\infty N^*(t')\,dt'}{N_0\tau_A} = \frac{\tilde{N}^*(0)}{N_0\tau_A} = \frac{1}{1+c\tau_A\kappa_g} \tag{3.3}$$

where

$$\kappa_g = \tilde{R}_{11}(0)\left(1 - \frac{\tilde{R}_{12}(0)}{\tilde{R}_{22}(0)+1/\tau_{exc}}\right) \tag{3.4}$$

The quantum yield of the exciplex luminescence is similarly defined

$$\eta_e = \frac{\int_0^\infty N^e(t')\,dt'}{N_0\tau_{exc}} = \frac{\tilde{N}^e(0)}{N_0\tau_{exc}} = \frac{1-\eta}{1+\tau_{exc}\kappa_e} \tag{3.5}$$

where

$$\kappa_e = \tilde{R}_{22}(0) - \tilde{R}_{12}(0) \tag{3.6}$$

The quantum yields of the free ions and triplet products are

$$\phi_i = P(\infty)/N_0 = (1-\eta)\psi_M\varphi_c \tag{3.7a}$$

$$\phi_T = N_T(\infty)/N_0 = (1-\eta)\psi_M\varphi_T \tag{3.7b}$$

where $1-\eta$ is actually the yield of the primary born exciplexes, while

$$\psi_M = \frac{\kappa_e}{1/\tau_{exc}+\kappa_e} \tag{3.8}$$

is the yield of their transformation into the RIP and

$$\varphi_c = \frac{\tilde{R}_{32}(0)}{\tilde{R}_{22}(0)-\tilde{R}_{12}(0)} \tag{3.9}$$

and

$$\varphi_T = \frac{\tilde{R}_{42}(0)}{\tilde{R}_{22}(0)-\tilde{R}_{12}(0)}$$

are the yields of the RIP separation into charged or neutral (excited triplet) products.

The presence of ψ_M in eqs 3.7a make them differ essentially from their analogues represented the reactions of straightforward electron transfer, from excited reactants to the RIP (see for example eqs 3.17 and 3.24 in ref 19. This factor accounts for the intermediate exciplex formation and the product $\psi_M\varphi_c$ is identical to expression $k_d\tau_E\phi(\sigma)$ from eq 28 of ref 6. The transition to the variables ψ_M and φ_c, φ_T, makes transparent the relationship to any charge separation quantum yields defined earlier. It does not matter how the RIPS were obtained, from exciplex or by straightforward electron transfer,[6] in contact approximation their further evolution is the same

$$\bar{\varphi} = \frac{\tilde{R}^{\dagger}(0)}{\tilde{R}*(0)} \equiv \frac{\tilde{R}_{32}(0)}{\tilde{R}_{22}(0) - \tilde{R}_{12}(0)} = \varphi_c$$

$$\varphi_T = \frac{\tilde{R}^{\dagger}(0)}{\tilde{R}*(0)} = \frac{\tilde{R}_{42}(0)}{\tilde{R}_{22}(0) - \tilde{R}_{12}(0)}$$

B. Contact Approximation. Borrowing the information about the kernels from eq 2.5, we get from eqs 3.4 and 3.6

$$\kappa_g = \frac{\kappa_i}{1 + \kappa_i / K(1/\tau_{exc} + \kappa_e)} \tag{3.10}$$

and

$$\kappa_e = k_d \frac{\kappa_{esc} + k_c}{\kappa_{esc} + k_c + k_a}$$

where

$$\frac{1}{\kappa_i} = \frac{1}{k_f} + \frac{1}{k_D(1 + \sqrt{\tau_d/\tau_A})} \tag{3.11}$$

$$K = \frac{k_f}{k_b} = v e^{-\Delta G_{exc}/T}$$

Here v is the reaction volume and

$$\kappa_{esc} = \frac{k_t(g_3 + 3g_4) + 4(k_{-t}g_5 + 1)}{(3g_3 + g_4)(k_{-t}g_5 + 1) + 4k_t g_3 g_4} \tag{3.12}$$

If the exciplex does not separate in ions, then $\kappa_e = k_d = 0$ and the general expression 3.10 reduces to eq 4.3 of ref 7

$$\kappa_g = \frac{\kappa_i}{1 + \kappa_i \tau_{exc}/K} = \begin{cases} \kappa_i & \text{irreversible} \\ K/\tau_{exc} & \text{reversible} \end{cases} \tag{3.13}$$

This simplest result was a few times obtained earlier, neglecting the exciplex dissociation into RIP from the very beginning.[8,10,12]

In the case of highly polar solvents ($r_c \to 0$), we can use simple expressions to specify this quantity

$$\kappa_{esc} = k_D \left[1 + \frac{3\sqrt{4k_s\tau_d}(k_D + k_t + k_{-t})}{(4(k_D + k_t + k_{-t}) + \sqrt{4k_s\tau_d}(k_D + k_{-t}))} \right] \tag{3.14}$$

The general expression for κ_e obtained from eq 3.10 takes very simple form in two alternative limits, no spin conversion ($k_s = 0$) and ultrafast conversion which immediately equilibrates the spin distribution ($k_s = \infty$)

$$\kappa_e = \begin{cases} k_d \left(1 + \dfrac{k_a}{k_D + k_c} \right)^{-1} & \text{at} \quad k_s = 0 \\ k_d \left(1 + \dfrac{\frac{1}{4}k_a}{k_D + \frac{1}{4}k_c + \frac{3}{4}\dfrac{k_t k_D}{k_D + k_{-t}}} \right)^{-1} & \text{at} \quad k_s = \infty \end{cases} \tag{3.15}$$

In the case of fast equilibration, the recombination reactions from the singlet and triplet states of the RIP are weighted here differently than in the absence of spin conversion. At $k_s = 0$ the expression for the geminate Stern−Volmer constant κ_g in eq 3.10 appears to be the same as for the straightforward RIP formation by electron transfer (eq 3.12 in ref 24), provided k_c in this equation is substituted for $1/\tau_{exc}$ and k_D for κ_e. At highly exergonic triplet production, one can set $k_{-t} = 0$ and the triplet quantum yield thus obtained reduces to that found in ref 6. If there is no triplet production at all ($k_t = 0$), there is the general formula tracing the transition between the limits pointed out in eq 3.15

$$\kappa_e = k_d \left(1 + \frac{k_a}{k_c + k_D \dfrac{1 + \alpha}{1 + \alpha/4}} \right)^{-1} \tag{3.16}$$

where $\alpha = (4k_s\tau_d)^{1/2}$.

The quantum yields of the RIPs separation into free ions or neutral products (singlet and triplet) are usually expressed via efficiencies of RIP recombination through these channels:

$$\varphi_c = \frac{D}{D + Z} = \frac{1}{1 + \tilde{Z}} \tag{3.17a}$$

$$\varphi_T = \frac{Z_T}{D + Z} = \frac{\tilde{Z}_T}{1 + \tilde{Z}} \tag{3.17b}$$

$$\varphi_S = \frac{Z_S}{D + Z} = \frac{\tilde{Z}_S}{1 + \tilde{Z}} \tag{3.17c}$$

where

$$Z = Z_S + Z_T \tag{3.17d}$$

and all the yields obey equality (3.2). Using the definition given to two of them in (3.9) and borrowing the necessary kernels from eq 2.5 we get

$$\tilde{Z} = \frac{k_c}{4}(3g_3 + g_4) + \frac{3}{4}k_t(g_4 - g_3)\frac{1 + k_c g_3}{1 + k_t g_3 + k_{-t} g_5} \tag{3.18a}$$

$$\tilde{Z}_T = \frac{3}{4}\frac{k_t(g_4 - g_3)}{1 + k_t g_3 + k_{-t} g_5} \tag{3.18b}$$

where all g functions are taken at the argument $s = 0$.

Now we turn again to the limiting cases of zero and fast conversion but taking into account for the Coulomb attraction between the ions ($\beta = (r_c/\sigma) \neq 0$). At $k_s = 0$ we obtain from the definitions (3.9) and necessary kernels from contact equations (2.5):

$$\tilde{Z} = \tilde{Z}_S = \frac{k_c}{k_D}\frac{e^{\beta} - 1}{\beta} \tag{3.19}$$

$$\tilde{Z}_T = 0$$

The original efficiency of RIP recombination

$$Z = \tilde{Z}D = z\frac{e^{\beta} - 1}{\beta} \tag{3.20}$$

$$z = \frac{k_c}{4\pi\sigma}$$

appears to be the same as in the widely used spin-less exponential model (EM).[17,20]

In an alternative limit, $k_s = \infty$, there is the triplet production (interrupted by RIP separation) that contributes of in both the ion and triplet efficiencies

$$\tilde{Z} = \frac{e^{\beta} - 1}{\beta}\left(\frac{1}{4}\frac{k_c}{k_D} + \frac{3}{4}\frac{k_t}{k_D + k_{-t}}\right) \tag{3.21a}$$

$$\tilde{Z}_T = \frac{3k_t}{4(k_{-t} + k_D)}\frac{e^{\beta} - 1}{\beta} \tag{3.21b}$$

The transition from one limit to another can be easily traced when there is no recombination to triplets ($k_t = 0$) and no Coulomb attraction ($r_c = 0$)

$$\tilde{Z} = \tilde{Z}_S = z\frac{1 + \alpha/4}{1 + \alpha} \tag{3.22}$$

$$\tilde{Z}_T = 0$$

At zero spin conversion Z reduces to eq 3.19 for the zero field, while at $k_s = \infty$ it becomes identical to eq 3.21a, provided there are no triplets ($k_t = 0$) and no field ($\beta \rightarrow 0$). Figure 2 shows the transition between these limits with increasing spin-conversion. By equilibrating spin distribution, the latter hinders RIP recombination leaving only $^1/_4$ for the reacting singlet state.

Here should be mentioned that the charge separation yield, obtained from the measured quantities

$$\frac{\phi_i}{(1 - \eta)} = \psi_M\varphi_c = \frac{\kappa_e\varphi_c}{1/\tau_{exc} + \kappa_e} \tag{3.23}$$

does not equal to φ_c as usual but differs from it by the multiplier ψ_M first appeared in the present work, eq 3.8. As a result, what is actually measured depends not only on the loose ion pair (LIP) recombination constant $k_c \equiv k_{CR}^{LIP}$ via φ_c but also on the natural exciplex decay $1/\tau_{exc}$. Moreover, the true decay of the exciplex or contact ion pair (CIP) is composed from a natural one, $1/\tau_{exc}$, and the intersystem charge recombination k_{CR}^{CIP} that we neglected from the very beginning for simplicity. To take it into account posteriori, one has just to substitute the sum $(1/\tau_{exc}) + k_{CR}^{CIP}$ for $(1/\tau_{exc})$ in eq 3.23. Only then the isotope effect obtained in ref 9 could be explained: the charge separation yield depends on deuterium substitution of any reactants because it affects neither k_c nor φ_c but k_{CR}^{CIP}.

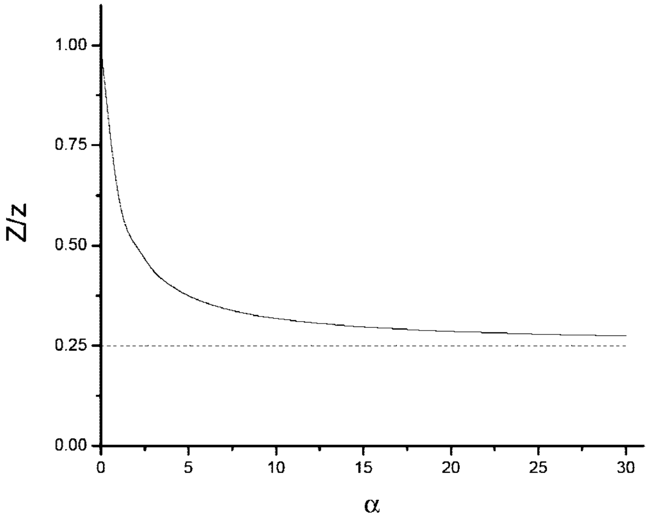


Figure 2. The efficiency of RIP dissociation into free ions, reduced by spin conversion.

The efficiency of exciplex formation is also affected by Coulomb attraction between ions. Accounting for it, we have to substitute eqs 3.15 by the following set

$$\kappa_e = k_d\left(1 + \frac{k_a}{k_c + k_D\dfrac{\beta}{e^{\beta} - 1}}\right)^{-1} \tag{3.24a}$$

$$k_s = 0$$

$$\kappa_e = k_d\left(1 + \frac{\dfrac{1}{4}k_a}{\dfrac{1}{4}k_c + k_D\left(\dfrac{\beta}{e^{\beta} - 1} + \dfrac{3}{4}\dfrac{k_t}{k_{-t} + k_D}\right)}\right)^{-1} \tag{3.24b}$$

$$k_s = \infty$$

C. Diffusional Exciplex Formation. The exciplex formation is often considered as diffusion controlled reaction which at any contact between either neutral or charged components. Hence the exciplex reaction surface being isotropic is black like in an original Smoluchowski model. To reduce to this limit from our general consideration, we have to set

$$k_f \propto k_b \rightarrow \infty \tag{3.25}$$

and

$$k_{\mathrm{d}} \propto k_{\mathrm{a}} \rightarrow \infty$$

After that we obtain from eqs 3.11 and 3.10

$$\kappa_{\mathrm{i}} = k_{\mathrm{D}}(1 + \sqrt{\tau_{\mathrm{d}}/\tau_{\mathrm{A}}}) \tag{3.26}$$

$$\kappa_{\mathrm{e}} = (\kappa_{\mathrm{esc}} + k_{\mathrm{c}})\frac{k_{\mathrm{d}}}{k_{\mathrm{a}}}$$

where

$$\frac{k_{\mathrm{d}}}{k_{\mathrm{a}}} = \frac{e^{(\Delta G_{\mathrm{exc}} - \Delta G_{\mathrm{i}})/T}}{\upsilon} \tag{3.27}$$

Then instead of eq 3.15 we obtain

$$\kappa_{\mathrm{e}} = \begin{cases} (k_{\mathrm{D}} + k_{\mathrm{c}})\dfrac{k_{\mathrm{d}}}{k_{\mathrm{a}}} & \text{at} \quad k_{\mathrm{s}} = 0 \\ \left(4k_{\mathrm{D}} + k_{\mathrm{c}} + \dfrac{3k_{\mathrm{t}}k_{\mathrm{D}}}{k_{\mathrm{D}} + k_{-\mathrm{t}}}\right)\dfrac{k_{\mathrm{d}}}{k_{\mathrm{a}}} & \text{at} \quad k_{\mathrm{s}} = \infty \end{cases} \tag{3.28}$$

while from eq 3.10 follows

$$\kappa_{\mathrm{g}} = \begin{cases} k_{\mathrm{D}}(1 + \sqrt{\tau_{\mathrm{d}}/\tau_{\mathrm{A}}}) & \text{irreversible } (\textit{ionization control}) \\ K\left(\dfrac{1}{\tau_{\mathrm{exc}}} + \kappa_{\mathrm{e}}\right) & \text{reversible } (\textit{dissipation control}) \end{cases} \tag{3.29}$$

The highly exergonic transfer is irreversible, forming a diffusional plateau of the Rehm–Weller dependence, but in the downhill endergonic branch of this curve, it becomes endergonic and reversible, being limited by the exciplex dissipation. Contrary to the conventional result (3.13) the exciplex decay is not only a natural one but includes also RIPs recombination (k_c) and their escape from the cage (κ_{esc}) that weighted with equilibrium exciplex-RIP constant, eq 3.27, constitute κ_{e} in eq 3.26.

The black sphere approximation (3.25) is valid in a restricted region of ionization free energies. As a matter of fact the A^* and exciplex luminescence lines are separable if their separation $|\Delta G_{\mathrm{exc}}|$ is larger than their width Γ. According to eq 1.3, the former is equal to $V^2/\Delta G_{\mathrm{i}}$ at positive ΔG_{i} and relatively small V, that is

$$|\Delta G_{\mathrm{exc}}| \approx V^2/\Delta G_{\mathrm{i}} \gg \Gamma \tag{3.30}$$

or

$$\Delta G_{\mathrm{i}} \ll V^2/\Gamma$$

This is the limitation of ΔG_{i} from above. However, being negative it is also limited from below by the accuracy of intensity measurements. At high-frequency splitting, the intensity of exciplex luminescence turns to be small and finally invisible. Hence the formation of exciplexes can be ignored at too large $|\Delta G_{\mathrm{i}}|$. It is commonly accepted that the narrow strip where the exciplex should be accounted for is restricted by the inequality $|\Delta G_{\mathrm{i}}| < 0.5$ eV.

IV. Stationary Illumination

Under stationary illumination there are stationary concentrations of all reactants and products in the solution, N_{s}^{*}, $N_{\mathrm{e}}^{\mathrm{s}}$, P_{s}, $N_{\mathrm{T}}^{\mathrm{s}}$. They can be found from eqs 2.2a by setting all time derivations to zero and solving the thus obtained algebraic equations

$$N_{\mathrm{S}}^{*} = \frac{I_0 \tau_{\mathrm{A}} N}{1 + c\kappa\tau_{\mathrm{A}}} \tag{4.1a}$$

$$\kappa = \tilde{R}_{11} \times \left(1 - \frac{\tilde{R}_{12}}{\dfrac{1}{\tau_{\mathrm{exc}}} + \tilde{R}_{22} - \dfrac{\tilde{R}_{24}\tilde{R}_{33}\tilde{R}_{42} + \tilde{R}_{24}\tilde{R}_{32}\tilde{R}_{43} + \tilde{R}_{23}\tilde{R}_{34}\tilde{R}_{42} + \tilde{R}_{23}\tilde{R}_{32}\tilde{R}_{44}}{\tilde{R}_{33}\tilde{R}_{44} - \tilde{R}_{34}\tilde{R}_{43}}}\right)_{s=0}$$

$$N_{\mathrm{e}}^{\mathrm{s}} = \left(\frac{c\tilde{R}_{11}N_{\mathrm{s}}^{*}}{\dfrac{1}{\tau_{\mathrm{exc}}} + \tilde{R}_{22} - \dfrac{\tilde{R}_{24}\tilde{R}_{33}\tilde{R}_{42} + \tilde{R}_{23}\tilde{R}_{34}\tilde{R}_{42} + \tilde{R}_{24}\tilde{R}_{32}\tilde{R}_{43} + \tilde{R}_{23}\tilde{R}_{32}\tilde{R}_{44}}{\tilde{R}_{33}\tilde{R}_{44} - \tilde{R}_{34}\tilde{R}_{43}}}\right)_{s=0} \tag{4.1b}$$

$$cN_{\mathrm{T}}^{\mathrm{s}} = \frac{\tilde{R}_{32}(0)\tilde{R}_{43}(0) + \tilde{R}_{33}(0)\tilde{R}_{42}(0)}{\tilde{R}_{33}(0)\tilde{R}_{44}(0) - \tilde{R}_{34}(0)\tilde{R}_{43}(0)} N_{\mathrm{e}}^{\mathrm{s}} \tag{4.1c}$$

$$P_{\mathrm{s}}^{2} = \frac{\tilde{R}_{32}(0)}{\tilde{R}_{33}(0)} N_{\mathrm{e}}^{\mathrm{s}} + \frac{\tilde{R}_{34}(0)}{\tilde{R}_{33}(0)} cN_{\mathrm{T}}^{\mathrm{s}} \tag{4.1d}$$

In the contact approximation for charge transfer, the Stern–Volmer constant of stationary quenching of luminescence is

$$\kappa = \frac{\kappa_{\mathrm{i}}}{1 + \kappa_{i}/K(1/\tau_{\mathrm{exc}} + \kappa_0)} \tag{4.2}$$

where

$$\kappa_0 = k_{\mathrm{d}} \frac{k_{\mathrm{c}}}{k_{\mathrm{a}} + k_{\mathrm{c}}} \tag{4.2.1}$$

The only difference between the stationary κ_0 appearing in eq 4.2 and the geminate κ_{e} obtained in eq 3.10 is the absence in the stationary parameter κ_0 of the term κ_{esc}, representing the irreversible escape from the cage of either ions or triplets. Under stationary conditions such an escape is not the irreversible process because the products of geminate reaction are subjected

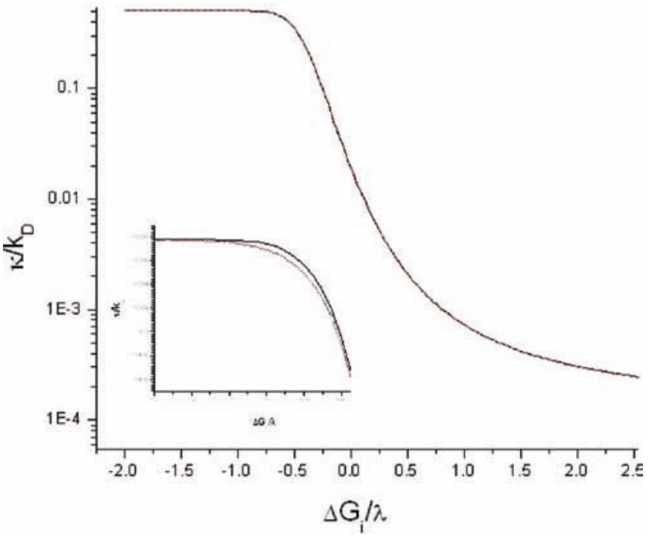


Figure 3. The free energy dependence of the stationary Stern−Volmer constants. The present one from eq 4.2 given by solid line is compared to that obtained earlier,[7] neglecting exciplex dissociation into ions (dashed line). Here $\kappa_i = 7.3 \times 10^3$ Å^3/ns, $\tau_A = 10$ ns, $k_D = 6.3 \times 10^3$ Å^3/ns, $k_c^0 = 10^5$ Å^3/ns. More particularly: $\varepsilon_S = 1.3$ eV, $V = 0.05$ eV, $\lambda = 0.375$ eV, $\upsilon = 310$ Å^3.

to subsequent encounters in the bulk that restore the exciplex and initial excitation as well. This is the reason why the very complex formula for κ in eq 4.1a reduces to such a simple expression as (4.2).

In the black sphere approximation (3.25) we have

$$\kappa_0 = \frac{k_c}{\upsilon} \exp(\Delta G_{exc} - \Delta G_i)/T \tag{4.3}$$

that should be used for estimating the Stern−Volmer constant κ in eq 4.2. This is κ_0 that differs our general result from a canonical one, eq 3.13, that neglects the RIP formation from the exciplex. In fact, the RIP recombination contributes into exciplex decay, but just a little, so that the difference in κ is seen only in a narrow quasi-resonance region (Figure 3). Hence, the widely ignored exciplex dissociation into ions[10,12,25,26,7] appears to be a rather good approximation.

The difference between FEG law obtained from the pulse experiment and from the permanent (stationary) detection of fluorescence is much more pronounced. Their Stern−Volmer constants, found from eqs 3.10 and 4.2, are both shown in Figure 4. The constant obtained after pulse excitation is larger and decays sharper with increasing the free energy than that resulting from stationary fluorescence. That is because $\kappa_e > \kappa_0$. The former accounts for both RIP recombination (k_c) and their separation (k_{esc}) while the latter only for ion recombination due to restoration of the excitations in bulk encounters.

The stationary concentration of ions responsible for the stationary photoconductivity is

$$P = 2\sqrt{\frac{I_0 N}{k_c} \frac{c\kappa\tau_A}{1 + c\kappa\tau_A} \frac{\kappa_0\tau_{exc}}{1 + \kappa_0\tau_{exc}}} \tag{4.4}$$

The stationary photocurrent is proportional to $\sqrt{I_0}$ and saturates with increasing quencher concentration c. As to the stationary concentration of triplets that can be measured from either phosphorescence or triplet absorption, it can be expressed via P

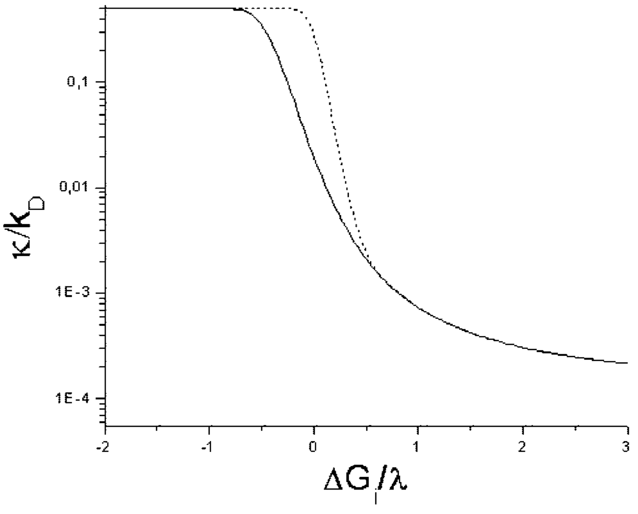


Figure 4. The stationary Stern−Volmer constant (4.2) (solid line) compared to the geminate one (3.10) (dashed line) at different ionization free energies. Here $k_t^0 = 10^5$ Å^3/ns, $4k_{sd}^{\tau} = 1$, and the energy of the excited triplet $\varepsilon_T = 2.3$ eV, while $\varepsilon_S = 3.5$ eV, $\lambda = 1.5$ eV, $V = 0.1$ eV. The rest of the parameters are the same as in Figure 3.

$$cN_T^s = \frac{3k_t}{4k_{-t}} P^2 \tag{4.5}$$

The intensity of triplet absorption or emission is linear in I_0 and monotonously reduces with c due to impurity quenching.

V. Conclusions

Integral encounter theory is a unique method of studying reversible non-Markovian processes, like bimolecular exciplex formation from either neutral or charged components. Here both of them were accounted for in line with the spin-conversion in RIPs and their recombination/separation to free ions and triplet products. In contact approximation the quantum yield of luminescence quenching was specified for two alternative cases: pulse and stationary light excitation.

Taking into account the reversible exciplex−RIP transformation, we essentially corrected the FEG law for the Stern−Volmer constant of pulse-induced luminescence which is usually obtained neglecting this channel of exciplex decomposition. The stationary luminescence is less affected by this phenomenon due to free ion recombination in the bulk restoring the exciplex. The IET is the only non-Markovian theory that correctly describes such a phenomenon.

The quantum yields of the free ions and triplets appearing after quenching the pulse-induced luminescence were also shown to be different from those obtained within the simple exponential model ignoring the exciplex−RIP conversion. Under permanent illumination there are stationary concentrations of all these products that were also specified in line with the Stern−Volmer constant of stationary quenching.

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