

# Reversible charge separation through exciplex formation

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The Unified Theory of exciplex formation by intermolecular electron transfer or straightforward light excitation of complexes is developed. It includes the reversible dissociation of exciplexes to a singlet ion pair, subjected to spin conversion and recombination to either the ground or triplet state. In the contact approximation the quantum yields of free ions, exciplexes, and triplet products of recombination are calculated analytically. The main results of previous spinless theories are reproduced and shown to be identical to those available with the Integral Encounter Theory.

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## I. INTRODUCTION

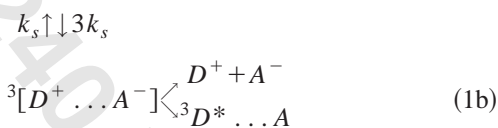
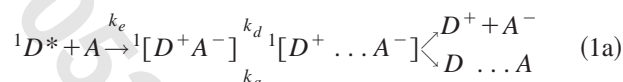
The role of exciplexes in fluorescence quenching by intermolecular electron transfer was recognized long ago.<sup>1</sup> The exciplexes were assumed to be the intermediate products of partial electron transfer from excited donor to acceptor performed at the closest approach distance  $\sigma$ . We denote the exciplexes as  $[D^+A^-]$ , to distinguish them from the ion pair  $[D^+ \dots A^-]$ , produced by their dissociation, and free ions,  $D^+ + A^-$ , which escaped geminate recombination. The contact creation of exciplexes in encounters of excited reactants,  $D^* + A$  (or  $D + A^*$ ), with their subsequent dissociation and recombination, constitutes the reaction which follows "Scheme I" proposed by Weller<sup>2,3</sup> and widely accepted.<sup>4-6</sup> There is also an alternative "Scheme II" which implies that first the remote electron transfer creates the ion pair which later on either associates into exciplex or separates. Scheme II was separately analyzed in Ref. 7 and then incorporated into a more general reaction scheme which includes both competing reaction channels. The latter was considered by means of the Unified Theory (UT) in our original work,<sup>8</sup> as well as in the overview of UT (Chapter IX).<sup>9</sup> Here we will restrict ourselves only to the theory of Scheme I that should be reformulated and generalized.

Modification of the theory allows us to consider exciplexes created not only by encounters of excited reactants but also by straightforward light excitation of existing complexes of the same particles. The photodissociation was often studied experimentally<sup>10-14</sup> and the qualitative difference with bimolecular creation of exciplexes was indicated.<sup>10</sup> Unlike all the rest, the present theory accounts for the spin states of ion pairs and their conversion, which allows subsequent recombination to both the ground and excited triplet state of the products. Setting the rate of spin conversion to zero, the classical spinless theory<sup>15</sup> of reversible dissociation is reproduced. It will be shown that the UT description of the dissociation of exciplexes or stable complexes can be reduced to a single integro-differential equation of the simplest Integral Encounter Theory (IET).<sup>16</sup> The latter is supported by a few more general approaches developed later.<sup>17-21</sup>

The following is an overview of the paper. In the next section the UT approach to the problem will be universally formulated, making the study of exciplex dissociation accessible any way they are prepared. In Sec. III the quantum yields of exciplexes and free ions, as well as the triplet products of the geminate recombination, will be calculated. In the contact approximation they are shown to be identical to our previous results. In Sec. IV the reduction to a spinless theory will be made and a relationship with previous studies of the problem established. The results obtained are summarized in Sec. V.

## II. GENERAL APPROACH

The general Scheme I of bimolecular exciplex formation and subsequent dissociation to an ion pair, subjected to spin-conversion and recombination can be represented as follows:



The basic UT equations for the excited reactant concentration  $N_S = [{}^1D^*]$  at great excess of partners ( $[{}^1D^*] \ll [A] = c = \text{const}$ ) account for the exciplex formation with the rate  $k_e$  at contact distance  $\sigma$

$$\dot{N}_S = -k(t)cN_S - \frac{1}{\tau_S}N_S, \quad (2a)$$

$$k(t) = k_e n(\sigma, t) = 4\pi D r^2 \left. \frac{\partial n(r, t)}{\partial r} \right|_{r=\sigma}, \quad (2b)$$

$$\frac{\partial}{\partial t} n = D \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} n, \quad n(r, 0) = 1, \quad (2c)$$

where  $P_S(t) = N_S(t)/N_S(0)$  is the survival probability of excited state while  $n(r, t)$  is the pair distribution function of the reactants.

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Equations (2) should be supplemented with the equation for exciplex concentration:

$$\dot{P}_e = ck_e n(\sigma, t) P_S(t) + k_a g_S(\sigma, t) - \frac{1}{\tau_E} P_e. \quad (3)$$

Through  $1/\tau_E = 1/\tau_{exc} + k_d$  the dissociation of the exciplex with a rate  $k_d$  and its decay with time  $\tau_{exc}$  are incorporated. Besides, in this equation the backward reaction of ion association into exciplex is accounted for. The association rate is a product of the rate constant  $k_a$  and the pair correlation function  $g = cm$  ( $m$  in our previous notations<sup>8,9</sup>).

The set of equations for ion pairs in the singlet and triplet states, given by their pair distributions  $g_S$  and  $g_T$ , can be obtained from Eqs. (9.6) of Ref. 9, provided that the rate of remote ionization is substituted by the exciplex dissociation rate  $k_d P_e$  multiplied by the contact distribution of charged products  $f_e(r)$

$$\begin{aligned} \dot{g}_S = & k_s g_T - 3k_s g_S + \tilde{D} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} \\ & \times e^{-r_c/r} g_S - W_R^0 g_S + k_d f_e(r) P_e(t), \end{aligned} \quad (4a)$$

$$\begin{aligned} \dot{g}_T = & -k_s g_T + 3k_s g_S + \tilde{D} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} \\ & \times e^{-r_c/r} g_T - W_R^T g_T, \end{aligned} \quad (4b)$$

where  $g_S(r, 0) = g_T(r, 0) = 0$  and  $f_e(r) = \delta(r - \sigma)/4\pi r^2$ . Advantage is taken in here of the simplest but popular model of incoherent spin conversion.<sup>22-26</sup> The latter is represented as a stochastic process which proceeds with the rate  $k_s$  from triplet to singlet state of ion pair and  $3k_s$  in the backward direction.

The boundary conditions for these equations have to account for only the charge annihilation to an exciplex at the contact distance available for singlet pairs:

$$4\pi\sigma^2 \tilde{D} \frac{\partial}{\partial r} e^{-r_c/r} g_S(r, t) \Big|_{r=\sigma} = k_a g_S(\sigma, t), \quad (5a)$$

$$4\pi\sigma^2 \tilde{D} \frac{\partial}{\partial r} e^{-r_c/r} g_T(r, t) \Big|_{r=\sigma} = 0. \quad (5b)$$

The present formulation of the problem differs essentially from that used earlier.<sup>8,9</sup> There starting from the so called ‘‘radiation desorption’’ boundary condition, proposed for reversible aggregation,<sup>27</sup> we made a trick which discriminates between the primary exciplexes formed from neutral reactants and those which result from the geminate annihilation of ions. Dissociation of the former was accounted for by a contact pumping term in the kinetic equation for the singlet pair distribution, while dissociation of the latter was left in the boundary condition to this equation. Now we go further: including both of them into Eq. (4a) through  $P_e(t)$  we make the boundary conditions (5a) identical to ‘‘radiation’’ one (for the irreversible annihilation of ions).

This rearrangement makes possible the universal consideration of either bimolecular generation of exciplexes, or

their creation by a straightforward and instantaneous light excitation. In the former case their time dependence is given by the solution to Eq. (3):

$$\begin{aligned} P_e(t) = & \int_0^t \exp -\frac{t-t'}{\tau_E} [ck_e n(\sigma, t') P_S(t') \\ & + k_a g_S(\sigma, t')] dt', \end{aligned} \quad (6)$$

while in the latter case it is the solution of the same equation, but for  $k_e = 0$  and the initial condition  $P_e(0) = 1$ :

$$P_e(t) = e^{-t/\tau_E} + k_a \int_0^t \exp -\frac{t-t'}{\tau_E} g_S(\sigma, t') dt'. \quad (7)$$

Leaving analysis of instantaneous photoexcitation of exciplexes for Sec. IV let us first confirm the results of our previous investigation of bimolecular exciplex formation and charge separation.

The general solution of Eqs. (4) can be represented as follows:

$$g_S(r, t) = k_d \int_0^t G^{SS}(r, t - \tau) P_e(\tau) d\tau, \quad (8a)$$

$$g_T(r, t) = k_d \int_0^t G^{ST}(r, t - \tau) P_e(\tau) d\tau. \quad (8b)$$

Here  $G^{SS}(r, t) \equiv G^{SS}(r, \sigma, t)$  and  $G^{ST}(r, t) \equiv G^{ST}(r, \sigma, t)$  are the Green functions for the ion pair distributions proceeding from the contact singlet pair:  $G^{SS}(r, \sigma, 0) = \delta(r - \sigma)$ ,  $G^{ST}(r, \sigma, 0) = 0$ . They obey the homogeneous equations following from Eqs. (4), whose Laplace transformation can be presented as follows:

$$\begin{aligned} -\delta(r - \sigma)/4\pi r^2 + s \tilde{G}^{SS} \\ = k_s \tilde{G}^{ST} - 3k_s \tilde{G}^{SS} + \mathbf{L} \tilde{G}^{SS} - W_R^0(r) \tilde{G}^{SS} \end{aligned} \quad (9a)$$

$$s \tilde{G}^{ST} = -k_s \tilde{G}^{ST} + 3k_s \tilde{G}^{SS} + \mathbf{L} \tilde{G}^{ST} - W_R^T(r) \tilde{G}^{ST}, \quad (9b)$$

where the encounter diffusion of ions with coefficient  $\tilde{D}$  is represented by operator

$$\mathbf{L} = \tilde{D} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} e^{-r_c/r}.$$

The boundary conditions are the Laplace transformed Eqs. (5) with  $G$  substituted for  $g$ .

In the contact approximation the recombination rates of the singlet and triplet radical ion pairs are zero everywhere, except the closest approach distance where they are represented by kinetic reaction constants:

$$k_r^S = \int W_R^0(r) d^3 r,$$

and

$$k_r^T = \int W_R^T(r) d^3 r. \quad (10)$$

In this approximation, Eqs. (9) are made much simpler for an analytic solution:

$$-\delta(r-\sigma)/4\pi r^2 + s\tilde{G}^{SS} = k_s\tilde{G}^{ST} - 3k_s\tilde{G}^{SS} + \mathbf{L}\tilde{G}^{SS} \quad (11a)$$

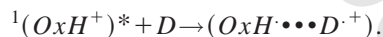
$$s\tilde{G}_{ST} = -k_s\tilde{G}^{ST} + 3k_s\tilde{G}^{SS} + \mathbf{L}\tilde{G}^{ST}. \quad (11b)$$

However, the boundary conditions for them are changed, including the contact recombination not only to an exciplex, but to the ground and triplet states as well

$$4\pi\sigma^2\tilde{D}\left.\frac{\partial}{\partial r}e^{-r_c/r}\tilde{G}^{SS}(r,s)\right|_{r=\sigma} = [k_a + k_r^S]\tilde{G}^{SS}(\sigma,s), \quad (12a)$$

$$4\pi\sigma^2\tilde{D}\left.\frac{\partial}{\partial r}e^{-r_c/r}\tilde{G}^{ST}(r,s)\right|_{r=\sigma} = k_r^T\tilde{G}^{ST}(r,s). \quad (12b)$$

The electron transfer represented by the Scheme (1a) is just an example of reaction leading to exciplex formation. Another reaction studied in Ref. 28 also results in formation of exciplex though of a different kind:



Such exciplexes are bounded by only covalent forces and their energy diagram was presented and analyzed in detail in the same work. The present theory is applied to this reaction equally well and the absence of Coulomb interaction between reactants and products makes it even simpler: the Onsager radius  $r_c = e^2/\epsilon k_B T$  turns to zero.

### III. QUANTUM YIELDS

#### A. Fluorescence quantum yield

According to the previously given definition, the quantum yield of exciplex fluorescence is<sup>9</sup>

$$\phi_e = \eta_0\varphi_E, \quad (13)$$

where  $\eta_0 = W_f\tau_{exc}$  is the quantum yield of fluorescence, provided that the exciplex does not dissociate and  $W_f$  is the rate of light emission. Then

$$\varphi_E = \tilde{P}_e(0)/\tau_{exc} \quad (14)$$

is the exciplex quantum yield expressed through its integral population,  $\int_0^\infty P_e(t)dt = \tilde{P}_e(0)$ . The latter in its turn can be found from either Eq. (6) or Eq. (7) depending on how exciplexes are formed:

$$\tilde{P}_e(0) = \begin{cases} \tau_E[\psi_e + \psi_a] & \text{by bimolecular electron transfer,} \\ \tau_E[1 + \psi_a] & \text{by light excitation of complexes.} \end{cases} \quad (15)$$

The first term in this expression is the quantum yield of primary created exciplexes (from neutral reactants):<sup>9</sup>

$$\psi_e = ck_e \int_0^\infty n(\sigma,t)P_S(t)dt, \quad (16)$$

while the last one accounts for those exciplexes which appear as a result of ion association:

$$\psi_a = k_a\tilde{g}_S(\sigma,0) = k_a k_d \tilde{G}^{SS}(\sigma,0)\tilde{P}_e(0). \quad (17)$$

Inserting Eqs. (16) and (17) into Eq. (15) we can resolve the latter regarding  $\tilde{P}_e(0)$ :

$$\tilde{P}_e(0) = \frac{\tau_E\psi_e}{1 - \tau_E k_a k_d \tilde{G}^{SS}(\sigma,0)}, \quad (18)$$

where  $\psi_e$  should be substituted by 1 if exciplexes are created by a straightforward complex excitation.

The quantum yield of exciplexes produced by forward electron transfer, Eq. (15), can be represented exactly as in Eq. (9.35) of Ref. 9:

$$\varphi_E = \psi_e \left[ \frac{1}{1 + k_d\tau_{exc}} + \frac{k_d\tau_{exc}}{1 + k_d\tau_{exc}} \chi_E \right], \quad (19)$$

but  $\chi_E$  acquires an alternative definition:

$$\chi_E = \frac{k_a\tilde{G}^{SS}(\sigma,0)}{1 + k_d\tau_{exc}(1 - k_a\tilde{G}^{SS}(\sigma,0))}. \quad (20)$$

#### B. Charge separation quantum yield

The same is true for the quantum yield of free ions which is evidently

$$\begin{aligned} \phi &= \int [g_S(r,\infty) + g_T(r,\infty)]d^3r \\ &= \int d^3r \lim_{s \rightarrow 0} s[\tilde{g}_S(r,s) + \tilde{g}_T(r,s)]. \end{aligned} \quad (21)$$

Making the Laplace transformation of Eqs. (8) we have:

$$\begin{aligned} \tilde{g}_S(r,s) &= k_d\tilde{G}^{SS}(r,s)\tilde{P}_e(s), \\ \tilde{g}_T(r,s) &= k_d\tilde{G}^{ST}(r,s)\tilde{P}_e(s). \end{aligned} \quad (22)$$

Inserting these results into Eq. (21) we obtain

$$\phi = k_d\varphi_i\tilde{P}_e(0), \quad (23)$$

where  $\varphi_i$  is the separation yield of ions, starting from the contact and recombining there irreversibly through all the channels:

$$\varphi_i = \int d^3r \lim_{s \rightarrow 0} s[\tilde{G}^{SS}(r,s) + \tilde{G}^{ST}(r,s)]. \quad (24)$$

From Eqs. (23) and (18) we obtain for the quantum yield of free ions produced by bimolecular photoionization the very same expression as in Ref. 9

$$\phi = k_d\tau_E\psi_e\varphi(\sigma), \quad (25)$$

but the charge separation quantum yield acquires an alternative definition:

$$\varphi(\sigma) = \frac{\varphi_i}{1 - \tau_E k_d k_a \tilde{G}^{SS}(\sigma,0)}, \quad (26)$$

where the same quantity for the irreversible ion pair recombination is

$$\varphi_i = 1 - (k_a + k_r^S)\tilde{G}^{SS}(\sigma,0) - k_r^T\tilde{G}^{ST}(\sigma,0). \quad (27)$$

The latter expression can be derived from Eq. (24) and the general solution of Eqs. (11) in the same very way as Eq. (4.2) of Ref. 7.

If the free ions appear due to dissociation of excited complex then their quantum yield differs slightly from Eq. (25):

$$\phi = k_d \tau_E \varphi(\sigma) = \frac{k_d \tau_{\text{exc}}}{1 + k_d \tau_{\text{exc}}} \varphi(\sigma). \quad (28)$$

For long lived exciplexes  $\phi \approx \varphi(\sigma)$ .

### C. Triplet yield

The quantum yield of triplet products of ion pair recombination is given by the definition

$$\varphi_T = \frac{1}{\tau_T} \int_0^\infty P_T(t) dt = \frac{\tilde{P}_T(0)}{\tau_T}, \quad (29)$$

where  $\tau_T$  is the lifetime of the triplet products of charge recombination,  ${}^3D^*$ , and  $P_T$  is their probability which obeys the evident equation:

$$\dot{P}_T = \int W_R^T(r) g_T(r, t) d^3r - \frac{1}{\tau_T} P_T. \quad (30)$$

If recombination to the triplet is contact it follows from Eqs. (29), (30), and (18) that

$$\varphi_T = k_r^T k_d \tilde{G}^{ST}(\sigma, 0) \tilde{P}_e(0) = \psi_T k_d \tau_E \psi_T. \quad (31)$$

Formally this is exactly the same result as obtained in Refs. 7 and 9, but  $\psi_T$  acquires an alternative definition

$$\psi_T = \frac{k_r^T \tilde{G}^{ST}(\sigma, 0)}{1 - \tau_E k_d k_d \tilde{G}^{SS}(\sigma, 0)}. \quad (32)$$

Hence we see that all quantities of interest  $\chi_E$ ,  $\varphi(\sigma)$ , and  $\psi_T$ , are expressed in Eqs. (20), (26), and (32) through the new Green functions easily related to those used previously:  $\tilde{G}^{SS}(\sigma, 0) = \tilde{p}_{SS}(\sigma, \sigma, 0)|_{k_d=0}$  and  $\tilde{G}^{ST}(\sigma, 0) = \tilde{p}_{ST}(\sigma, \sigma, 0)|_{k_d=0}$ . Since the expressions for the old Green functions  $\tilde{p}_{SS}(\sigma, \sigma, 0)$  and  $\tilde{p}_{ST}(\sigma, \sigma, 0)$  are available from Refs. 8 and 9, we present here the values of the new ones without proof:

$$\begin{aligned} m \tilde{G}^{SS}(\sigma, 0) &= \frac{\tilde{G}_0(\sigma, 0) - 3k_s J_0(\sigma, 0)}{1 + 3k_s k_r^T J_0(\sigma, 0) + (k_a + k_r^S) [\tilde{G}_0(\sigma, 0) - 3k_s J_0(\sigma, 0)]}, \end{aligned} \quad (33a)$$

$$\begin{aligned} \tilde{G}^{ST}(\sigma, 0) &= \frac{3k_s J_0(\sigma, 0)}{1 + 3k_s k_r^T J_0(\sigma, 0) + (k_a + k_r^S) [\tilde{G}_0(\sigma, 0) - 3k_s J_0(\sigma, 0)]}. \end{aligned} \quad (33b)$$

Here  $\tilde{G}_0(\sigma, s) \equiv \tilde{G}_0(\sigma, \sigma, s)$  is the Green function of diffusional equations (11) with reflecting boundary conditions and  $k_s = 0$ . The auxiliary function  $J_0(\sigma, 0)$  introduced in Refs. 8 and 9 is defined through two values of  $\tilde{G}_0(\sigma, s)$ , at  $s = 0$  and  $s = 4k_s$

$$J_0(\sigma, 0) = \frac{\tilde{G}_0(\sigma, 0) - \tilde{G}_0(\sigma, 4k_s)}{4k_s [1 + k_r^T \tilde{G}_0(\sigma, 4k_s)]}. \quad (34)$$

### D. Quantum yields dependence on spin conversion

Substituting the new Green function Eq. (33a) into the new definition Eq. (20), we obtain the final expression for  $\chi_E$  which is in fact identical to Eq. (9.36) of Ref. 9:

$$\chi_E = \frac{k_a^R [\tilde{G}_0(\sigma, 0) - 3k_s J_0(\sigma, 0)]}{1 + (k_a^R + k_r^S) \tilde{G}_0(\sigma, 0) + 3k_s J_0(\sigma, 0) [k_r^T - (k_a^R + k_r^S)]}, \quad (35)$$

where the renormalized annihilation constant  $k_a^R = k_a / (1 + k_d \tau_{\text{exc}})$  accounts for the reverse exciplex dissociation to the ion pair. Similarly we obtain from Eqs. (26), (27), and (33) the charge separation quantum yield

$$\begin{aligned} \varphi(\sigma) &= \frac{1}{1 + (k_a^R + k_r^S) \tilde{G}_0(\sigma, 0) + 3k_s J_0(\sigma, 0) [k_r^T - (k_a^R + k_r^S)]}, \end{aligned} \quad (36)$$

and from Eq. (32) the triplet one

$$\psi_T = \frac{3k_s k_r^T J_0(\sigma, 0)}{1 + (k_a^R + k_r^S) \tilde{G}_0(\sigma, 0) + 3k_s J_0(\sigma, 0) [k_r^T - (k_a^R + k_r^S)]}. \quad (37)$$

The latter vanishes if there is no spin conversion in the ion pair ( $k_s = 0$ ). However, this only means that triplets are not produced during geminate recombination which is the only one incorporated into the reaction scheme (1). In reality they should be generated even in this case by the free ion recombination in a bulk that follows the geminate one.<sup>29</sup>

The rate of spin conversion  $k_s$  affects all the yields directly and indirectly, through  $J_0(\sigma, 0)$  which depends on  $\tilde{G}_0(\sigma, 4k_s)$ . To illustrate this phenomenon let us concentrate on fluorescence yield which is affected through  $\chi_E(k_s)$  and charge separation quantum yield  $\varphi(\sigma)$  which is also the function of  $k_s$ . It is easier to compare the quantum yields in two opposite limiting cases:

- (1) in the absence of recombination to triplet products ( $k_r^T = 0$ ), or
- (2) in the case of extremely fast recombination to them ( $k_r^T = \infty$ ).

Using the definition of  $J_0(\sigma, 0)$  given in Eq. (34) and  $\tilde{G}_0(\sigma, s) = [4\pi\sigma\tilde{D}(1 + \sigma\sqrt{s/\tilde{D}})]^{-1}$  we obtain from Eqs. (35) and (36) for the case 1 ( $k_r^T = 0$ ):

$$\chi_E = \frac{k_a^R}{k_a^R + k_r^S + 4k_D q}, \quad \varphi(\sigma) = \frac{4k_D q}{k_a^R + k_r^S + 4k_D q}, \quad (38)$$

where  $q = (1 + \alpha)/(4 + \alpha)$  and

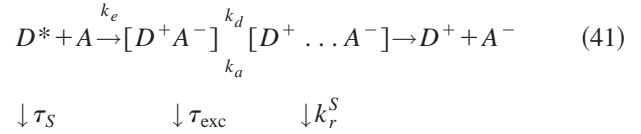
$$\alpha = \sqrt{4k_s \sigma^2 / \tilde{D}}. \quad (39)$$

the ion recombination through triplet channel is faster than through singlet one. More particularly,  $k_r^T > k_a + k_r^S$  and the situation is closer to case (2) than to case (1). Even more straight evidence in favor of the recombination to triplet state was obtained by heavy atom substitution into the fluorescence quencher which also enhances the rate of spin conversion. By measuring the transient absorption of both ion radicals and triplet products of their recombination it was demonstrated that the quantum yield of triplets  $\psi_T$  increases when the charge separation yield  $\varphi(\sigma)$  decreases due to heavy atom substitution.<sup>31</sup> As was shown in Fig. 1,  $\varphi(\sigma)$  decreases with  $k_s$  if recombination to triplet is faster than to singlet states, while the quantum yield of triplets Eq. (37) always increases with  $k_s$ . Hence these data also indicate that the triplet channel of recombination is the most efficient.

#### IV. REDUCTION TO THE SPINLESS THEORY

##### A. Charge recombination through the exciplex

If there is no spin conversion in the ion pairs then the spin states of the reactants and products may be ignored and the reaction scheme (1) simplified to the following one:



As follows from Eqs. (35) and (36) in this particular case we have

$$\chi_E = \frac{k_a^R \tilde{G}_0(\sigma, 0)}{1 + (k_a^R + k_r^S) \tilde{G}_0(\sigma, 0)}, \quad (42a)$$

$$\varphi(\sigma) = \frac{1}{1 + (k_a^R + k_r^S) \tilde{G}_0(\sigma, 0)}, \quad (42b)$$

where  $\tilde{G}_0(\sigma, 0)$  is well known and may be expressed through the separation rate  $k_{sep}$  of the so called ‘‘exponential model’’ (EM)<sup>9</sup>

$$\begin{aligned} \tilde{G}_0(\sigma, 0) &= \frac{1}{4\pi r_c \bar{D}} \left[ \exp\left(\frac{r_c}{\sigma}\right) - 1 \right] \\ &= \frac{1}{(4\pi\sigma^3/3) k_{sep}}, \end{aligned} \quad (43)$$

where  $r_c = e^2/k_B T$  is the Onsager radius of the interion Coulomb attraction.

In terms of EM the charge separation yield is usually

For the alternative case 2 ( $k_r^T = \infty$ ):

$$\chi_E = \frac{k_a^R}{k_a^R + k_r^S + k_D \kappa}, \quad \varphi(\sigma) = \frac{k_D}{k_a^R + k_r^S + k_D \kappa}, \quad (40)$$

where  $\kappa = 1 + \frac{3}{4}\alpha$ . These formulas establish the upper and lower limits for  $\alpha$  dependence of  $\chi_E$ , [see Fig. 1(a) and  $\varphi(\sigma)$ , Fig. 1(b)]. The curves for the intermediate values of  $k_r^T$  can be obtained from the general Eqs. (35) and (36). For instance, it follows from Eq. (36) that for  $k_r^T = k_a + k_r^S$  the charge separation quantum yield unlike all the rest does not depend on spin conversion at all [the horizontal dashed line in Fig. 1(b)]. The spin conversion makes no difference between recombination of singlet and triplet RIPs if they occur with the same rate.

Since  $\chi_E$  decreases with  $k_s$  in both (1) and (2) cases the same is true for the exciplex yield and its fluorescence. However, the quantum yield of free ions  $\varphi(\sigma)$  exhibits the opposite behavior in these two limits: it increases with  $\alpha$  in case (1) but decreases in case (2). This means that only in case (2) both  $\chi_E$  and  $\varphi(\sigma)$  decrease with spin conversion rate  $k_s$ . If in H-substituted species the spin conversion is faster than in deuterated ones both fluorescence and free ion yields should be sensitive to this difference. As was indicated in Ref. 30 in H-containing species relative to deuterated ones the quantum yield of free ions measured by ion conductivity is lower and the lifetime of exciplex is shorter that makes the fluorescence quantum yield smaller. The simultaneous reduction of both these quantities in RIPs composed of 9,10-dicyanoanthracene and durenene as well as in other pairs<sup>30</sup> points out that

$$k_r^S = k_0 \exp[-(\Delta G_r + \lambda_c)^2 / 4k_B T \lambda_c], \quad (46)$$

where  $\Delta G_r$  is the free energy of backward electron transfer in the nearest but solvent separated pair and  $\lambda_c$  is the corresponding reorganization energy. If to the contrary this rate constant is negligibly small, then the whole backward recombination proceeds through the exciplex with the rate constant  $k_a^R$  which may have a qualitatively different free energy dependence.

This was proved by a straightforward excitation of complexes and experimental study of their subsequent dissociation.<sup>10,32</sup> In the limit of long lived exciplexes ( $k_d \tau_{\text{exc}} \gg 1$ ) the free ion yield  $\phi = \varphi(\sigma)$  and

$$k_a^R = \frac{K}{\tau_{\text{exc}}}, \quad (47)$$

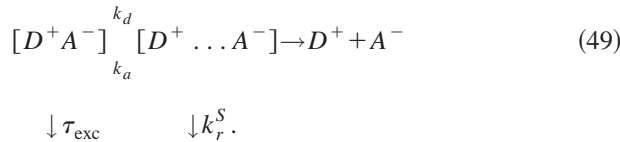
where the equilibrium constant  $K = k_a / k_d \propto \exp(-\Delta G_a / k_B T)$  is an exponential function of the free energy of ion association into the exciplex  $\Delta G_a$ . As a matter of fact,  $\Delta G_r = \Delta G_a + \Delta G_e$  where  $\Delta G_e$  is the free energy of intraexciplex electron transfer responsible for the radiationless decay of the exciplex with the rate  $1/\tau_{\text{exc}}$ . In the balance of large quantities  $|\Delta G_a|$  is negligibly small and can be neglected as in Refs. 10. Setting it at zero we have to identify  $\Delta G_r$  and  $\Delta G_e$  and put  $K = 1$ . Then the ion recombination rate

$$\frac{1}{\tau_{\text{exc}}} = \alpha \exp(\beta \Delta G_r) \quad (48)$$

does not depend on temperature but it exponentially decreases with  $|\Delta G_r| = |\Delta G_e|$  as was established experimentally and theoretically in Ref. 32. The log of this rate is a linear function of the free energy unlike the recombination rate of solvent separated ions, Eq. (46), which is a parabolic one in accordance with Marcus free energy gap law.

## B. Kinetics of exciplex dissociation

If exciplexes were created by instantaneous light excitation acting in the charge transfer absorption band of complex  $[DA]$ , then their subsequent reversible dissociation is described by the reduced reaction scheme:



This process is governed by Eqs. (7) and (8a), where the kernel indexes are omitted as superfluous:

$$P_e = e^{-t/\tau_E} + k_a \int_0^t e^{-(t-t')/\tau_E} g(\sigma, t') dt', \quad (50a)$$

$$g(\sigma, t) = k_d \int_0^t G(\sigma, t - \tau) P_e(\tau) d\tau. \quad (50b)$$

The Green function  $G(r, t)$  yields the conventional diffusion equation for contact born ions:

$$\begin{aligned} \dot{G} &= \tilde{D} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} e^{-r_c/r} G \\ &\text{at } G(r, 0) = \delta(r - \sigma) / 4\pi r^2, \end{aligned} \quad (51)$$

with the boundary condition identical to Eq. (5)

$$4\pi\sigma^2 \tilde{D} \frac{\partial}{\partial r} e^{-r_c/r} G(r, t) \Big|_{r=\sigma} = k_a G(\sigma, t). \quad (52)$$

From the set of Eqs. (50) we obtain the single integral equation for exciplex concentration:

$$\begin{aligned} P_e(t) &= e^{-t/\tau_E} + k_a k_d \int_0^t e^{-(t-t')/\tau_E} dt' \\ &\times \int_0^{t'} G(\sigma, t' - \tau) P_e(\tau) d\tau. \end{aligned} \quad (53)$$

This expression is composed from two parts: initial irreversible decay/dissociation which proceeds exponentially with the rate  $1/\tau_E$  and subsequent dissipation of exciplexes restored by backward electron transfer. The differentiation of this equation transforms it to integro-differential one:

$$\dot{P}_e = -\frac{P_e}{\tau_E} + k_d \int_0^t \mathcal{F}(t - \tau) P_e(\tau) d\tau, \quad (54)$$

where the kernel

$$\mathcal{F}(t) = k_a G(\sigma, t). \quad (55)$$

The Green function can be defined by its Laplace transformation  $\tilde{G}(\sigma, s)$ , related to  $\tilde{G}_0(\sigma, s)$  by Eq. (5.10) of Ref. 9 similar to Eq. (33a):

$$\tilde{G}(\sigma, s) = \frac{\tilde{G}_0(\sigma, s)}{1 + (k_a + k_r^S) \tilde{G}_0(\sigma, s)}. \quad (56)$$

Using an explicit expression for

$$\tilde{G}_0(\sigma, s) = \frac{1}{4\pi\sigma\tilde{D}(1 + \sqrt{\sigma^2/\tilde{D}})},$$

followed from Eq. (8.28) of Ref. 9 for highly polar solvents ( $r_c = 0$ ), we obtain for the Laplace transformation of the kernel Eq. (55):

$$\frac{1}{\tilde{\mathcal{F}}(s)} = 1 + (k_a + k_r^S)$$

where

$$\tilde{F}(s) = 1 - \tilde{\mathcal{F}}(s) = 1 - k_a \tilde{G}(\sigma, s). \quad (59)$$

As follows from Eqs. (59) and (56) in highly polar solvents

$$\frac{1}{\tilde{F}(s)} = 1 + \frac{k_a}{k_D(1 + \sqrt{s}\tau_d) + k_r^S}. \quad (60)$$

With this new kernel Eq. (54) may be given a form inherent to IET:<sup>16</sup>

$$\dot{P}_e = -\frac{P_e}{\tau_{\text{exc}}} - k_d \int_0^t F(t-\tau) P_e(\tau) d\tau. \quad (61)$$

The IET equation appears here regularly. It is known that UT is “half-integral” theory: preserving the rate description Eq. (2) for irreversible exciplex creation it considers the further exciplex evolution beyond the rate concept.

Making the Laplace transformation of Eq. (61) taking into account Eqs. (59) and (56) one can easily get:

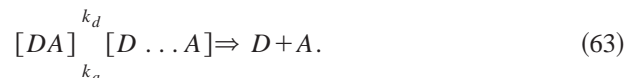
$$\tilde{P}_e(s) = \left[ s + \frac{1}{\tau_{\text{exc}}} + k_d \frac{1 + k_r^S \tilde{G}_0(\sigma, s)}{1 + (k_a + k_r^S) \tilde{G}_0(\sigma, s)} \right]^{-1}. \quad (62)$$

This result is identical to Eq. (2.10b) obtained in the work of Gopich and Agmon<sup>33</sup> with a different method. In the absence of an interaction between the ions (as in highly polar solvents) the authors took its inverse Laplace transform and subjected it to the exhaustive analysis that is of no sense to report here. It should be only mentioned that the decay of the dissociation product was also incorporated in their theory by a simple generalization of  $\tilde{G}_0(\sigma, s)$ . In our system it can result from a discharge of anion or cation by the strange scavengers if they are present in the solution.

The asymptotic behavior of exciplex decay was analyzed even in the presence of ion interaction.<sup>34</sup> It experiences the transition from the power law time dependence for stable dissociation products (“the A regime”) to an exponential decay for highly unstable products (“the AB regime”). Here we deal with a former case, but the generalization is obvious.

### C. Dissociation of complex

If instead of an exciplex a stable complex is considered, then  $\tau_{\text{exc}} = \infty$  and  $k_r^S = 0$ . The reaction scheme of such a reversible dissociation is subjected to further simplification:



For such an elementary reaction we have to set  $1/\tau_E \equiv k_d$ , reducing Eq. (54) to Eq. (5.1) of the classical Berg work:<sup>15</sup>

$$\dot{P}_e = -k_d P_e + k_d \int_0^t \mathcal{F}(t-\tau) P_e(\tau) d\tau. \quad (64)$$

Hence, the analysis of this equation made in Ref. 15 remains valid including an establishment of the asymptotic power law for dissociation:

$$P_e(t) \propto K(4\pi\tilde{D}t)^{-3/2} \text{ at } t \rightarrow \infty. \quad (65)$$

Almost simultaneously this law was derived in another work,<sup>35</sup> confirmed experimentally,<sup>36</sup> and reproduced a few times later.<sup>37,38</sup>

In fact, all subsequent derivations are equivalent to that of Berg. For instance, in the theory of “Reversible Diffusion Influenced Reactions” of Agmon and Szabo,<sup>37</sup> the authors started from their original integral equation (3.1a) which in our notations presents itself as

$$1 - P_e(t) = k_d \int_0^t S_{\text{rad}}(t-t'|\sigma) P_e(t') dt'. \quad (66)$$

According to Eq. (2.4) of their work, there are the following relationships:

$$S_{\text{rad}}(t|\sigma) = \int p(r, t|\sigma) d^3r, S_{\text{rad}}(0|\sigma) = 1, \quad (67)$$

where the Green function  $p(r, t|\sigma) \equiv G(r, t)$  in our notations. According to Eqs. (2.1) and (2.2) of the same work there is an identity:

$$\begin{aligned} S_{\text{rad}}(t|\sigma) &= \int \dot{p}(r, t|\sigma) d^3r \\ &= \int \mathcal{L}_r p(r, t|\sigma) d^3r \\ &= 4\pi\sigma^2 \tilde{D} \left. \frac{\partial p(r, t|\sigma)}{\partial r} \right|_{r=\sigma} = k_a p(\sigma, t|\sigma). \end{aligned} \quad (68)$$

The differentiation of Eq. (66) taking into account Eq. (68) reduces it to the integro-differential one,

$$\begin{aligned} \dot{P}_e &= -k_d P_e(t) + k_d \int_0^t k_a p(\sigma, t-t'|\sigma) P_e(t') dt' \\ &= -k_d \int_0^t F(t-t') P_e(t') dt', \end{aligned} \quad (69)$$

which is exactly the Berg equation (64) with  $\mathcal{F}(t) = k_a p(\sigma, t|\sigma)$  or IET equation (61) at  $\tau_{\text{exc}} = \infty$ .

### D. Delayed fluorescence

Not only the power law Eq. (65) is widely recognized, but it is also extended to the exciplex dissociation.<sup>33,34,39,40</sup> Since our products of reversible dissociation are stable we are in pure “A regime” according to classification given in Refs. 33 and 34. In this case the lifetime of exciplex affects only the prefactor of the same power law<sup>34</sup>

$$P_e(t) \propto Z^2 K(4\pi\tilde{D}t)^{-3/2} \text{ at } t \rightarrow \infty, \quad (70)$$

where

$$Z = \frac{k_D k_d \tau_{\text{exc}}}{k_a + k_D [1 + k_d \tau_{\text{exc}}]}.$$

At the beginning the dissociation enhances the exciplex decay making its rate equal to  $1/\tau_E = 1/\tau_{\text{exc}} + k_d$ , but at the very end the survival probability  $P_e(t)$  vanishes much slower following the power law Eq. 70. This is caused by geminate recombination that lasts much longer and backs the delayed fluorescence. In log–log coordinates of Fig. 2(a) the power

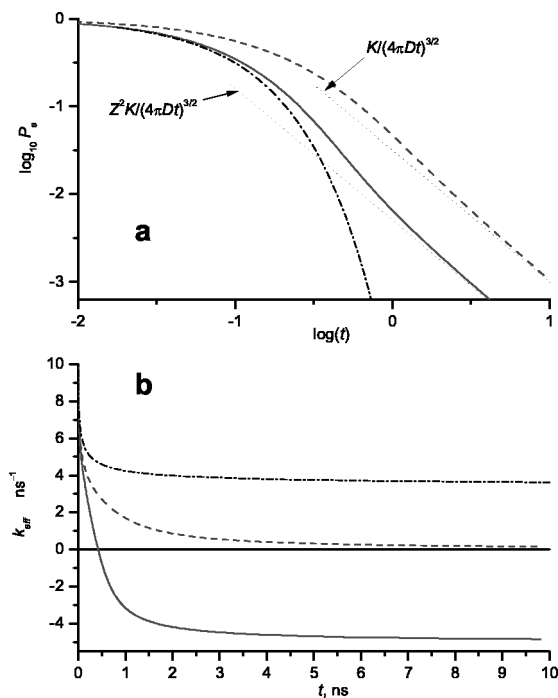


FIG. 2. Dissociation kinetics (a) and the variation of effective rate of transfer (b) for exciplex with a lifetime  $\tau_{\text{exc}}=0,2$  ns (solid lines) and stable complex  $\tau_{\text{exc}}=0$  (dashed lines). The long time asymptotes represented by power law are shown by dotted straight lines in (a). The phenomenological kinetics of exciplex dissociation and corresponding rate constant are shown by dashed-dotted lines in (a) and (b), respectively. The rest of the parameters are the following:  $k_a=10^4$  Å<sup>3</sup>/ns,  $k_D=5 \times 10^3$  Å<sup>3</sup>/ns,  $k_d=10$  ns<sup>-1</sup>, and  $\sigma=5$  Å.

law is represented by the final linear dependence showed by dotted lines. The larger the  $\tau_{\text{exc}}$  the higher it is and the closer to the asymptote of stable complex decay Eq. (65) (dashed line).

Correspondingly, the fluorescence of exciplexes lasts longer than their natural decay and is known as a delayed fluorescence caused by the restoration of exciplexes through geminate recombination of ion pairs. Such a phenomenon cannot be described by the rate equations as well as reversible reactions of intermolecular<sup>41–43</sup> and intramolecular<sup>44</sup> energy transfer. If one uses instead of integral equation (61) the differential one

$$\dot{P}_e = -\frac{P_e}{\tau_{\text{exc}}} - k_{\text{eff}}(t) P_e, \quad (71)$$

then the true solution of the former can be used in the latter to find an exact time dependence of effective dissociation rate  $k_{\text{eff}}(t)$ . At any finite  $\tau_{\text{exc}}$  the latter appears to be the sign-altering quantity because the effective rate becomes negative when electron transfer changes direction from forward to backward [Fig. 2(b)]. Qualitatively, this is the same picture as established for reversible reactions of energy transfer from unstable to more stable reactants.<sup>42,44</sup> The effective transfer rate diverges after changing the sign to negative, thus indicating that the rate description of delayed fluorescence provided by DET is not an appropriate one.<sup>42,44</sup>

However, there is also another way to convert the integral theory to differential, using the so called “modified” or

“phenomenological” rate equations proposed by Lee and Karplus.<sup>45</sup> The same equations were also obtained by Molski and Keizer assuming that the time scale for chemical change is much shorter than an encounter time  $\sigma^2/\bar{D}$ .<sup>46</sup> Although the phenomenological equations are widely used<sup>20,47,48</sup> they provide only the rough interpolation between the initial development of the process and the final state where all the particles are in equilibrium concentrations. The power law is completely lost and the system approaches the equilibrium exponentially [Fig. 2(a)]. As a result, the effective rate  $k_{\text{eff}}(t)$  is always positive accelerating the exciplex decay even at long times [Fig. 2(b)]. That is the delayed fluorescence is also lost. This is a price for the reduction of integral equations to differential ones. The critical comparison of phenomenological and other simplified equations made by Szabo was timely and has not lost its value.<sup>38</sup>

## V. CONCLUSIONS

The bimolecular UT theory of contact exciplex formation followed by their reversible dissociation is reformulated and extended to the case of instantaneous photodissociation of complexes. The relationship of UT to numerous spinless theories of reversible exciplex dissociation is established. It was shown that the kinetics of this process is accurately described by the generalized Berg equation (54) or its IET analog (61). Moreover, these equations can also incorporate the spin conversion in ion pair through the substitution of  $G^{SS}(\sigma, t)$  for  $G(\sigma, t)$  in the definition of their kernels Eq. (59).

As far as we know, our exciplex theory is the only one which incorporates the spin states of ion pairs and allows us to account for their recombination not only to the ground state, but into the triplet one as well. This can be done either in the contact approximation, Eqs. (11), or taking into account the real space dispersion of the reaction rates, Eqs. (9). The rate description of spin conversion employed here is just the simplest model which enables analytical solutions of the problem. It can be easily replaced by the Hamiltonian description of spin dynamics, as we did sometimes when necessary.<sup>49,50</sup> However, to incorporate the free ion recombination in a bulk, one should resort to the general IET<sup>51–53</sup> or similar theories.<sup>18–21</sup>

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