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ARTICLES

Photoseparation of Ion Radicals following Exciplex Formation and Spin Conversion

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Assuming that exciplexes are formed from solvent-separated ion pairs that are subjected to singlet−triplet conversion, we calculated the exciplex fluorescence and ion−radical separation quantum yields. Analytical expressions for both were obtained within the contact approximation for ion recombination to the excited triplet state. The spin conversion affects the competition between exciplex formation and charge recombination if their rates are not equal. The effect significantly depends on the initial separation of photochemically generated ion pairs and the rate of spin conversion that can be changed with the external magnetic field.

I. Introduction

Exciplex formation in the course of bimolecular ionization was recognized long ago[1] and is now a commonly accepted idea that explains some peculiarities of subsequent fluorescence and charge recombination. Two alternative kinetic schemes of exciplex formation were discussed in the literature before one of them was given a preference. "Scheme 1" proposed by Weller et al.[2,3] assumed that the exciplexes $^1[D^+A^-]$ are primary products of ionization during encounters of excited reactants, $D^* + A$ (or $D + A^*$). Then, they irreversibly dissociate to a solvent-separated ion pair in the singlet state $^1[D^+...A^-]$. It was well-established experimentally that the singlet pair reversibly converts into the triplet state[4,5]

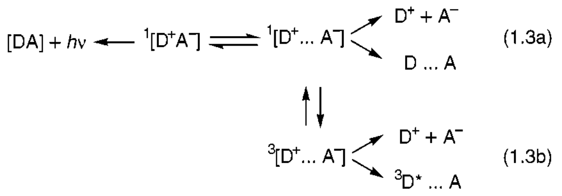
$$D^* + A \rightarrow {}^1[D^+A^-] \rightarrow {}^1[D^+...A^-] \rightleftharpoons {}^3[D^+...A^-] \qquad (1.1)$$

The singlet pair is subjected to subsequent geminate recombination competing with diffusional separation of ions in any spin state.[6] In principle, "Scheme 1" admits that the exciplexes and solvent-separated ion pairs are created in parallel[2] and the reversible reaction between them was finally assumed to be possible (see ref 7 and references herein).

However, there was some experimental evidence that "in polar solvents fluorescence quenching can occur through electron transfer without excited and quencher molecules forming a sandwich type charge-transfer complex. Consequently, a solvent-shared ion pair, $[D^+...A^-]$, in which the radical ions are partially solvated has been postulated as primary intermediate in this process".[8] This is the Scheme 2 also proposed by Weller.[9] In ref 10 Scheme 1 was proved to be reasonable for bound species (for intermolecular exciplex formation), while for intramolecular electron transfer an alternative Scheme 2 was used. In this scheme the primary product of ionization is a solvent-separated ion pair in the singlet state undergoing the reversible conversion to the triplet state

$$D^* + A \rightarrow {}^1[D^+...A^-] \rightleftharpoons {}^3[D^+...A^-] \qquad (1.2)$$

Both singlet and triplet ion pairs are subjected to further geminate recombination and separation, but only the singlet pair undergoes reversible transformation to the exciplex providing specific fluorescence at red-shifted frequency ν



In this article we will restrict ourself to Scheme 2, which to our knowledge is now generally accepted.[11−14]

An essential stage of the scheme is the singlet−triplet conversion in the ion pair, which opens an additional channel for ion recombination via the excited triplet state of the neutral product.[4] For normal ionization the triplet channel is much more efficient than the singlet pair recombination to the ground state.[4,15] Since the latter lays deep in the inverted region, it should be much slower than exciplex formation and will be ignored hereafter. Owing to this simplification only two competing channels of recombination remain to be considered: via exciplex and excited triplet state. The latter is carried out by electron transfer in the normal region, if the recombination free energies are smaller than the reorganization energy of the surroundings. Under this condition the recombination rate is sharp quasi-exponential functions of inter-ion distance[16,17] that allows us to use the *contact approximation*,[18,19] which works equally well for an analytical calculation of both exciplex and charge separation quantum yields. In fact, this approximation

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will be significantly extended to build up the spin-conversion stage into a recombination scheme. This has been done already for recombination following the ionization of the triplet state.[20] Here we will do the same for singlet state ionization followed by exciplex formation. In this case the singlet–triplet conversion in the ion pair affects the exciplex fluorescence as well as charge separation quantum yield. We will study both of them as functions of the spin conversion rate that can be changed with the external magnetic field. It is well-established experimentally that that kind of magnetic field effects indicate that the spin conversion is the limiting stage of the whole process.[21–23]

II. Geminate Recombination of the Solvent-Separated Ion Pair

Under certain conditions one can introduce the rate constants $3k_0$ for singlet to triplet transitions and k_0 for triplet to singlet transition (see Appendix). This is the simplest way to account for the spin conversion.[24–28] We have also employed this approximation in our previous work[20] and continue to use it here by writing equations for the populations of singlet and triplet states, p_S and p_T

$$\frac{\partial}{\partial t}p_S = k_0 p_T - 3k_0 p_S + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}p_S \tag{2.1a}$$

$$\frac{\partial}{\partial t}p_T = k_0 p_T + 3k_0 p_S + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}p_T \tag{2.1b}$$

Here $\tilde{D}$ is the coefficient of mutual diffusion of ions, $r_c = e^2/\epsilon k_B T$ is the Onsager radius of their Coulomb interaction, and $W_R(r)$ is the position-dependent rate of triplet pair recombination to the triplet state of the products. The recombination to their ground state from the singlet ion pair is ignored.

The initial separation of ion pairs is described by their normalized distribution function, $f_0(r_0)$, resulting from precursor irreversible ionization of the excited reactants.[29–31] In general, the solution obtained with initial conditions

$$p_S(r, r_0, 0) = \frac{\delta(r - r_0)}{4\pi r^2}, \quad p_T(0) = 0 \tag{2.2}$$

has to be averaged over $f_0(r_0)$. However, for the important particular case of contact born ions one can simply set $r_0 = \sigma$ to get the final result.

To account for the formation of the exciplex, we have to introduce its population $p_e(t)$ and rates of its formation (from singlet pair) and dissociation (to solvent-separated pair), k_{exc} and k_{diss}. Then the boundary conditions are

$$\mathbf{j}p_S = 4\pi\sigma^2\tilde{D}\frac{\partial}{\partial r}e^{-r_c/r}p_S(r, t)|_{r=\sigma} = k_{exc}p_S(\sigma, t) - k_{diss}p_e(t) \tag{2.3a}$$

$$\mathbf{j}p_T = 4\pi\sigma^2\tilde{D}\frac{\partial}{\partial r}e^{-r_c/r}p_T(r, t)|_{r=\sigma} \tag{2.3b}$$

The population of exciplexes obeys the equation

$$\dot{p}_e = k_{exc}p_S(\sigma, t) - \frac{1}{\tau_{exc}}p_e - k_{diss}p_e \tag{2.4}$$

where $p_e(0) = 0$. The inverse exciplex life time, $1/\tau_{exc}$, equals to the sum of the rate constants of emitting (fluorescence) and radiationless transitions.

The quantum yield of the exciplex fluorescence is

$$\varphi_e \frac{1}{\tau_f}\int_0^\infty p_e(t)\, dt = \frac{1}{\tau_f}\tilde{p}_e(0) \tag{2.5}$$

where τ_f is the fluorescence life time and $\tilde{p}_e(s)$ is the Laplace transform of $p_e(t)$. Making the Laplace transformation of eq 2.4, one can easily find that

$$\tilde{p}_e(0) = \frac{k_{exc}}{k_{diss} + 1/\tau_{exc}}\tilde{p}_S(\sigma, 0) \tag{2.6}$$

Using it in eq 2.5, we see that in this approximation the fluorescence quantum yield

$$\varphi_e = k_{exc}\eta_{fl}\tilde{p}_S(\sigma,0) \tag{2.7}$$

is proportional to the concentration of singlet pairs at contact distance and

$$\eta_{fl} = \frac{1}{1 + k_{diss}\tau_{exc}}\cdot\frac{\tau_{exc}}{\tau_f}$$

is the intrinsic quantum yield of the exciplex fluorescence.

On the other hand, by substitution of eq 2.6 into the Laplace transformation of eq 2.3a, we can present the latter in a conventional form of the "absorption boundary condition"

$$\mathbf{j}\tilde{p}_S(\sigma, 0) = K\tilde{p}_S(\sigma, 0) \tag{2.8}$$

where

$$K = \frac{k_{exc}}{1 + k_{diss}\tau_{exc}} \tag{2.9}$$

is the effective kinetic rate constant of the irreversible contact recombination of a singlet ion pair. Hereafter we can solve the problem without use of p_e, which has been excluded from all the equations.

Specifically, the charge separation quantum yield is

$$\varphi = \int [p_S(r, \infty) + p_T(r, \infty)]\, d^3r \tag{2.10}$$

It depends on the initial charge separation r_0 as a parameter. The same is true regarding the quantum yield of exciplex fluorescence $\varphi_e(r_0)$. Both $\phi(r_0)$ and $\varphi_e(r_0)$ are functions of the spin conversion rate k_0. In the contact approximation these functions can be obtained analytically.

III. Contact Approximation

Equation 2.1b with reflecting boundary condition eq 2.3b accounts for the geminate recombination in the triplet ion pair as a remote electron transfer. This is the approach used in ref 32 for examination of the validity limits of the contact approximation. It is well-known that for the endothermic or the moderate exothermic back electron transfer in ion pairs that their recombination may be considered as a contact reaction with the kinetic rate constant

$$k_r = \int W_R(r)\, d^3r \tag{3.1}$$

In the contact approximation the electron transfer at $r > \sigma$ is ignored by setting $W_R = 0$, but the boundary condition is changed to account for the recombination with the rate constant of eq 3.1

$$\frac{\partial}{\partial t}p_{\rm T} = -k_0 p_{\rm T} + 3k_0 p_{\rm S} + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 {\rm e}^{r_{\rm c}/r}\frac{\partial}{\partial r}{\rm e}^{-r_{\rm c}/r}p_{\rm T} \quad (3.2a)$$

$$\mathbf{j}p_{\rm T} = k_{\rm r} p_{\rm T}(\sigma, t) \quad (3.2b)$$

With the exception of the quasi-static (slow diffusion) limit, this approach provides a reasonable approximation that opens the way for an analytical solution of the problem. Moreover, this approximation makes no difference whether the triplet ion pair recombines to individual triplet molecules as in scheme 1.3 or transforms to the triplet exciplex, which is subjected to efficient radiationless quenching in the liquid state.[33]

The complete set of kinetic equations 2.1 in the contact approximation thus takes the form

$$\frac{\partial}{\partial t}p_{\rm S} = k_0 p_{\rm T} - 3k_0 p_{\rm S} + \mathbf{L}p_{\rm S} \qquad \mathbf{j}p_{\rm S} = Kp_{\rm S}(\sigma, t) \quad (3.3a)$$

$$\frac{\partial}{\partial t}p_{\rm T} = k_0 p_{\rm T} + 3k_0 p_{\rm S} + \mathbf{L}p_{\rm T} \qquad \mathbf{j}p_{\rm T} = k_{\rm r} p_{\rm T}(\sigma, t) \quad (3.3b)$$

where ***L*** is the operator of encounter diffusion. Using the total ion pair population $p = p_{\rm S} + p_{\rm T}$ we can represent eqs 3.3a, 3.3b in an alternative form

$$\frac{\partial}{\partial t}p = \mathbf{L}p \qquad \mathbf{j}p = Kp(\sigma, t) + \kappa p_{\rm T}(\sigma, t) \quad (3.4a)$$

$$\frac{\partial}{\partial t}p + 4k_0 p_{\rm T} = \mathbf{L}p_{\rm T} + 3k_0 p \qquad \mathbf{j}p_{\rm T} = k_{\rm r} p_{\rm T}(\sigma, t) \quad (3.4b)$$

where $\kappa = k_{\rm r} - K$.

Our main goal is to calculate the charge separation quantum yield

$$\varphi(r_0) = \int p(r, r_0, \infty)\, {\rm d}^3 r = \lim_{s\to 0} s\langle\tilde{p}(s)\rangle \quad (3.5)$$

and the exciplex fluorescence quantum yield

$$\varphi_{\rm e}(r_0) = K\eta_0[\tilde{p}(\sigma, r_0, 0) - \tilde{p}_{\rm T}(\sigma, r_0, 0)] \quad (3.6)$$

where $\eta_0 = \tau_{\rm exc}/\tau_{\rm f}$ is the fluorescence quantum yield of the "stable" exciplex (as if it were not subjected to dissociation), $\tilde{p}(s) = \int_0^\infty p(t){\rm e}^{-st}\,{\rm d}t$ is the Laplace transform of the time-dependent population, and $\langle ... \rangle$ means averaging over space.

IV. General Solution in Contact Approximation

Let us express all the results via the unperturbed Green function $G_0(r, r_0, t)$, which yields the free diffusion equation with reflecting boundary conditions:

$$\frac{\partial}{\partial t}G_0 = \mathbf{L}G_0 \qquad \mathbf{j}G_0 = 0$$

where $G_0(r, r_0, 0) = [\delta(r - r_0)]/(4\pi r^2)$. Using this Green function we can represent the Laplace transform of the solution to eq 3.4a in the following form

$$\tilde{p}(r, r_0, s) = \tilde{G}_0(r, r_0, s) - K\tilde{G}_0(r, \sigma, s)\tilde{p}(\sigma, r_0, s) - \kappa\tilde{G}_0(r, \sigma, s)\,\tilde{p}_{\rm T}(\sigma, r_0, s) \quad (4.1)$$

After averaging over r, eq 4.1 gives

$$\langle\tilde{p}(s)\rangle = \frac{1}{s}[1 - K\tilde{p}(\sigma, r_0, s) - \kappa\tilde{p}_{\rm T}(\sigma, r_0, s)] \quad (4.2)$$

Substituting this result into eq 3.5, we obtain

$$\varphi(r_0) = 1 - K\tilde{p}(\sigma, r_0, 0) - \kappa\tilde{p}_{\rm T}(\sigma, r_0, 0) \quad (4.3)$$

The formal solution to eq 3.4b may now be represented as follows

$$\tilde{p}_{\rm T}(r, r_0, s) = 3k_0\int\tilde{G}(r, r', s + 4k_0)\,\tilde{p}(r', r_0, s)\,{\rm d}^3 r' \quad (4.4)$$

where the Green function $G(r, r_0, t)$ yields an equation similar to eq 3.4a

$$\frac{\partial}{\partial t}G = \mathbf{L}G \qquad \mathbf{j}G = k_{\rm r}G(\sigma, t) \quad (4.5)$$

solution to which may be also expressed via the free diffusion Green function $G_0(r, r_0, t)$

$$\tilde{G}(r, r_0, s) = \tilde{G}_0(r, r_0, s) - k_{\rm r}\tilde{G}_0(r, \sigma, s)\,\tilde{G}(\sigma, r_0, s)$$

At $r = \sigma$ this equation may be solved for $\tilde{G}(\sigma, r_0, s)$

$$\tilde{G}(\sigma, r_0, s) = \frac{\tilde{G}_0(\sigma, r_0, s)}{1 + k_{\rm r}\tilde{G}_0(\sigma, \sigma, s)} \quad (4.6)$$

Setting now $r = \sigma$ in eq 4.1, we can solve it for $\tilde{p}(\sigma, r_0, s)$ and find the following expression for the density of ion pairs on the contact

$$\tilde{p}(\sigma, r_0, s) = \frac{\tilde{G}_0(\sigma, r_0, s) - \kappa\tilde{G}_0(\sigma, \sigma, s)\,\tilde{p}_{\rm T}(\sigma, r_0, s)}{1 + K\tilde{G}_0(\sigma, \sigma, s)} \quad (4.7)$$

After substituting this result into eq 4.1 we obtain

$$\tilde{p}(r, r_0, s) = \tilde{G}_0(r, r_0, s) - \tilde{G}_0(r, \sigma, s)\frac{K\tilde{G}_0(\sigma, r_0, s) - \kappa\tilde{p}_{\rm T}(\sigma, r_0, s)}{1 + K\tilde{G}_0(\sigma, \sigma, s)} \quad (4.8)$$

Using this result in the right-hand side (rhs) of eq 4.4, the closed equation for triplet pair density may be found

$$\tilde{p}_{\rm T}(r, r_0, s) = 3k_0 J_0(r, s) - 3k_0 J_\sigma(r, s)\frac{K\tilde{G}_0(\sigma, r_0, s) - \kappa\tilde{p}_{\rm T}(\sigma, r_0, s)}{1 + K\tilde{G}_0(\sigma, \sigma, s)} \quad (4.9)$$

where

$$J_0(r, s) = \int\tilde{G}(r, r', s + 4k_0)\tilde{G}_0(r', r_0, s)\,{\rm d}^3 r', \qquad J_0(\sigma, s) = \frac{\tilde{G}_0(\sigma, r_0, s) - \tilde{G}_0(\sigma, r_0, s + 4k_0)}{4k_0[1 + k_{\rm r}\tilde{G}_0(\sigma, \sigma, s + 4k_0)]}$$

$$J_\sigma(r, s) = \tilde{G}(r, r', s + 4k_0)\tilde{G}_0(r', \sigma, s)\,{\rm d}^3 r', \qquad J_\sigma(\sigma, s) = \frac{\tilde{G}_0(\sigma, \sigma, s) - \tilde{G}_0(\sigma, \sigma, s + 4k_0)}{4k_0\,[1 + k_{\rm r}\tilde{G}_0(\sigma, \sigma, s + 4k_0)]} \quad (4.10)$$

In order to find $J_0(\sigma)$ and $J_\sigma(\sigma)$, we used the relationship 4.6 and the following identity

$$\int \tilde{G}_0(\sigma, r, s + 4k_0)\, \tilde{G}_0(r, \sigma, s)\, \mathrm{d}^3r = \int \mathrm{d}^3r \int_0^\infty \mathrm{e}^{-st}\, \mathrm{d}t \times \int_0^t G(\sigma, r, t - t')\mathrm{e}^{-4k_0(t-t')} G_0(r, \sigma, t')\, \mathrm{d}t' = \int_0^\infty G_0(\sigma, \sigma, t)\mathrm{e}^{-st}\, \mathrm{d}t \int_0^t \mathrm{e}^{-4k_0(t-t')}\, \mathrm{d}t' = \frac{\tilde{G}_0(\sigma, \sigma, s) - \tilde{G}_0(\sigma, \sigma, s + 4k_0)}{4k_0} \qquad (4.11)$$

At $r = \sigma$ eq 4.9 may be resolved for triplet density on the contact

$$\tilde{p}_\mathrm{T}(\sigma, r_0, s) = 3k_0 \frac{J_0(\sigma, s)[1 + K\tilde{G}_0(\sigma, \sigma, s)] - J_\sigma(\sigma, s)K\tilde{G}_0(\sigma, r_0, s)}{1 + 3k_0k_\mathrm{r}J_\sigma(\sigma, s) + K[\tilde{G}_0(\sigma, \sigma, s) - 3k_0J_\sigma(\sigma, s)]} \qquad (4.12)$$

which determines also the total contact density given in eq 4.7. Using these densities at $s = 0$ in eqs 3.6 and 4.3, we obtain quantum yields for both charge separation and exciplex fluorescence.

V. Quantum Yields

The quantum yield for ion pairs with initial separation r_0 is given by the following general formula

$$\varphi(r_0) = 1 - \frac{K\tilde{G}_0(\sigma, r_0, 0)}{1 + K\tilde{G}_0(\sigma, \sigma, 0)} - \frac{3k_0\kappa\, [J_0(\sigma, 0)\, (1 + K\tilde{G}_0(\sigma, \sigma, 0)) - J_\sigma(\sigma, 0)\, K\tilde{G}_0(\sigma, r_0, 0)]}{(1 + K\tilde{G}_0(\sigma, \sigma, 0))\, [1 + 3k_0k_\mathrm{r}J_\sigma(\sigma, 0) + K\, (\tilde{G}_0(\sigma, \sigma, 0) - 3k_0J_\sigma(\sigma, 0))]} \qquad (5.1)$$

while the quantum yield of the exciplex fluorescence is

$$\varphi_\mathrm{e}(r_0)/\eta_0 = \frac{K\tilde{G}_0(\sigma, r_0, 0)}{1 + K\tilde{G}_0(\sigma, \sigma, 0)} - K\tilde{p}_\mathrm{T}(\sigma, r_0, 0) \left[1 + \frac{\kappa\tilde{G}_0(\sigma, \sigma, 0)}{1 + K\tilde{G}_0(\sigma, \sigma, 0)}\right] \qquad (5.2)$$

where $\tilde{p}_\mathrm{T}(\sigma, r_0, 0)$, defined in eq 4.12, depends on the spin conversion rate constant k_0. If k_0 is zero, the last terms in eqs 5.1 and 5.2 vanish and the remainder gives the same result as that obtained within the spinless reaction scheme. In such a trivial case $\varphi_\mathrm{e} = \eta_0(1 - \varphi)$.

A few important particular cases follow from eqs 5.1 and 5.2 at particular values of κ:

1. $\kappa = -K$, that is, $k_\mathrm{r} = 0$. The recombination of ion pairs is possible from only the singlet state (to exciplex). The charge separation quantum yield should increase with increasing the rate of the spin conversion to the triplet state.

2. $\kappa = 0$, that is, the rate constant of recombination is the same for the singlet and the triplet ion pairs ($k_\mathrm{r} = K$). The quantum yields do not depend on spin conversion, as well as in the case $k = 0$.

3. $\kappa = k_\mathrm{r}$, that is, either $k_\mathrm{r} \rightarrow \infty$ or $K = 0$. The triplet recombination is much faster than the singlet one. Therefore, the quantum yield of charge separation decreases with increasing the singlet−triplet conversion rate constant.

To make further progress in the analytical calculations, we have to restrict our consideration to highly polar liquids, assuming $r_\mathrm{c} = 0$. In this case the only Green function we need is well-known:[20,34]

$$\tilde{G}_0(\sigma, r_0, s) = \tilde{G}_0(\sigma, r_0, 0)\frac{\mathrm{e}^{-(r_0-\sigma)\sqrt{s/\tilde{D}}}}{1 + \sigma\sqrt{s/\tilde{D}}} \qquad (5.3)$$

where

$$\tilde{G}_0(\sigma, r_0, 0) = 1/4\pi r_0\tilde{D}$$

This information is sufficient to obtain the quantum yields, as well as the kinetics of charge survival, given by its Laplace transformation 4.2 and auxiliary eqs 4.7 and 4.12.

Let us start from the particular case 3 when no exciplex formation occurs ($K = 0$, $\kappa = k_\mathrm{r}$). Then $\varphi_\mathrm{e} = 0$ while

$$\varphi(r_0) = \frac{4\, [1 + k_\mathrm{r}\tilde{G}_0(\sigma, r_0, 4k_0)]}{4\, [1 + k_\mathrm{r}\tilde{G}_0(\sigma, r_0, 4k_0)] + 3k_\mathrm{r}\, [\tilde{G}_0(\sigma, r_0, 0) - \tilde{G}_0(\sigma, r_0, 4k_0)]} \qquad (5.4)$$

If the ion pairs were born at contact the result is even simpler

$$\varphi(\sigma) = \frac{1 + \alpha + (k_\mathrm{r}/k_\mathrm{D})}{1 + \alpha + (k_\mathrm{r}/k_\mathrm{D})(1 + {}^3/_4\alpha)} \qquad (5.5)$$

where $k_\mathrm{D} = 4\pi\sigma\tilde{D}$ is the diffusional rate constant and

$$\alpha = \sqrt{4k_0\sigma^2/\tilde{D}}$$

is the dimensionless rate of spin conversion. As was expected for this case, the charge separation quantum yield shows monotonous decrease with this parameter approaching the constant value

$$\varphi_\infty = \lim_{\alpha \rightarrow \infty} = \frac{1}{1 + (3k_\mathrm{r}/4k_\mathrm{D})}$$

In Figure 1 the transition from $\varphi = 1$ to φ_∞ is shown for contact born ion pairs. The higher the ratio $k_\mathrm{r}/k_\mathrm{D}$ the faster and deeper is this transition.

A similar decrease in quantum yield is seen for the noncontact ion pair (Figure 2), but here the effect is smaller the farther apart the ions are in the beginning. We considered the situation when geminate recombination is under diffusional control ($k_\mathrm{r} \gg k_\mathrm{D}$). No qualitative changes are expected in the kinetic control limit ($k_\mathrm{r} \ll k_\mathrm{D}$) except that the difference $1 - \varphi_\infty$ should be smaller.

Now let us turn to the general case when both reaction channels are open and recombination to the exciplex competes with recombination into the triplet product. In Figure 3 we plot the charge separation and fluorescence quantum yields for contact born pairs as functions of the spin conversion rate constant. At chosen ratio $K/k_\mathrm{D} = 1$ and $k_0 = 0$ we have $\varphi = \varphi_\mathrm{e}/\eta_0 = 1/2$. In accordance with the qualitative classification given above, the charge separation quantum yield does not depend on the spin conversion in case 2 (horizontal line 4), when the rate constants of recombination through both reaction channels (the exciplex and the triplet state) are the same ($K = k_\mathrm{r}$). If exciplex formation is more efficient than triplet recombination ($K > k_\mathrm{r}$), the spin conversion increases the charge separation quantum yield (approaching case 1). If triplet recombination dominates over formation of the exciplex ($K < k_\mathrm{r}$), the charge separation quantum yield decreases approaching the limit $K/k_\mathrm{r} = 0$ described above (case 3).

Contact generation of ion pairs is the most favorable condition for exciplex formation but exciplex fluorescence is es-

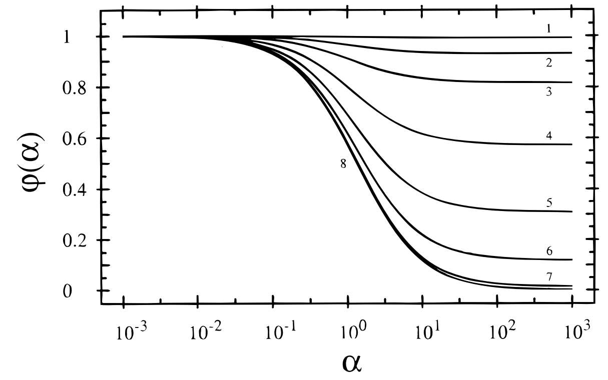

Figure 1. Spin conversion hindering of the separation of contact pairs which do not form exciplexes (at k_r/k_D = (1) 0.01; (2) 0.1; (3) 0.3; (4) 1; (5) 3; (6) 10; (7) 100; (8) 10^3.

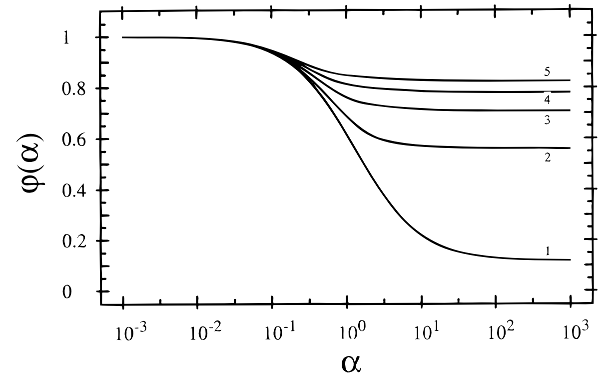

Figure 2. Same as in Figure 1 but for ions initially separated by distance $r_0 = \sigma$ (1), 2σ (2), 3σ (3), 4σ (4), 5σ (5) at $k_r/k_D = 10$.

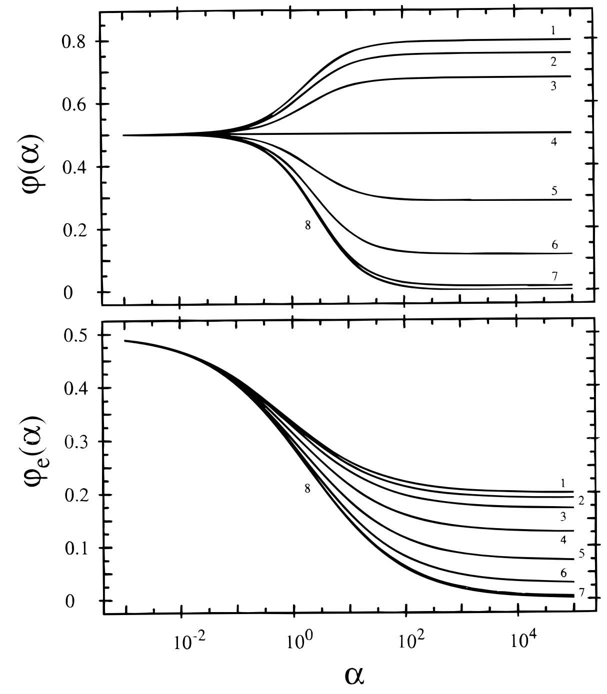

Figure 3. Quantum yields of exciplex fluorescence (at $\eta_0 = 1$) and separation of contact born ions as functions of the spin conversion rate k_0 at $K/k_D = 1$ and k_r/k_D = (1) 0.01; (2) 0.1; (3) 0.3; (4) 1; (5) 3; (6) 10; (7) 100; (8) 10^3; (9) 10^4; (10) 10^5.

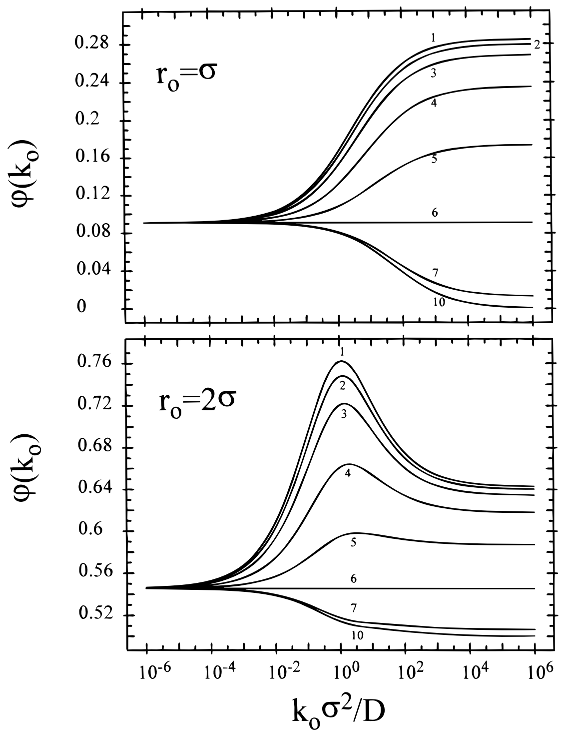

Figure 4. Separation quantum yield as a function of the spin conversion rate for contact ($r_0 = \sigma$) and noncontact ($r_0 = 2\sigma$) ion pairs at $K = 10k_D$ and k_r/k_D = (1) 0.01; (2) 0.1; (3) 0.3; (4) 1; (5) 3; (6) 10; (7) 100; (10) 10^5.

sentially depleted by spin conversion, opening competing channels for ion recombination and/or their separation. Even when triplet recombination is prohibited ($k_r = 0$), the decrease in fluorescence with the increasing spin conversion rate is minimal but nonzero. In this particular case one can obtain from eq 5.2

$$\varphi_e(r_0)/\eta_0 = K\frac{\tilde{G}_0(\sigma, r_0, 0) - \tilde{p}_T(\sigma, r_0, 0)}{1 + K\tilde{G}_0(\sigma, \sigma, 0)} \tag{5.6}$$

For ions created at contact distance $r_0 = \sigma$ this expression allows for further simplification:

$$\varphi_e(r_0)/\eta_0 = \frac{K}{K + k_D}\left\{1 - \frac{3}{4}\frac{\sigma\sqrt{4k_0/\tilde{D}}}{(1 + \sigma\sqrt{4k_0/\tilde{D}})(1 + K/4k_D) + 3K/4k_D}\right\} \tag{5.7}$$

This is the equation for the upper limit for the curve family shown in Figure 3. It describes the gradual decrease of φ_e/η_0, with k_0 from 1/2 to 1/5 at $K/k_D = 1$.

There is an essential difference in the separation quantum yields of contact born ion pairs and those created out of contact ($r_0 > \sigma$). As shown in Figure 4, in case 1 (when $K > k_r$), the separation quantum yield of the distant ion pair changes with the rate constant of spin conversion no-monotonously: it increases at low k_0 and decreases at high k_0. If the spin conversion is slow and can only partially depopulate the initial singlet state, during the pair life time $\tau_e = \sigma^2/\tilde{D}$, then the more ion pairs convert into the triplet state (which is practically stable), the higher are their chances to survive and be separated. However, if the fast spin conversion can equalize populations of both spin states before ions come in contact, then the back conversion from triplet to singlet state stimulates the contact recombination to exciplex, thus reducing the fraction of survived ions. This effect is most pronounced at $k_r = 0$. The curves 1 in Figure 4 are the closest to this limit that can be easily obtained from the general eq 5.1 at $k_r = 0$

$$\lim_{k_r\to 0}\varphi(r_0) = 1 - \frac{(\sigma/r_0)\,(1+\alpha+3\exp\{-\alpha(r_0/\sigma-1)\})}{(1+4k_D/K)\,(1+\alpha)+3} \qquad (5.8)$$

This curve has a maximum at finite α, at any $r > \sigma$.

The total effect of spin conversion may be characterized by the relative difference in the quantum yield at the infinitely fast conversion, $\lim_{k_0\to\infty}\varphi(r_0, k_0) = \varphi(r_0, \infty)$, and the spinless (or conversion-free) value $\varphi_0 = \varphi(r_0, 0)$

$$M = \frac{\varphi(r_0,\infty)-\varphi(r_0,0)}{\varphi(r_0,0)} \qquad M_e = \frac{\varphi_e(r_0,\infty)-\varphi_e(r_0,0)}{\varphi_e(r_0,0)} \qquad (5.9)$$

These definitions are analogous to those used for estimating the magnetic field effect on the charge separation quantum yield and exciplex fluorescence.[35] As seen from Figure 5, parameter M does not necessarily coincide with a maximal spin conversion effect but merely characterizes the scale of it.

Consider for example the simplest case of contact born ion pairs when the general expression 5.1 reduces to the following

$$\varphi(\sigma) = \varphi_0(\sigma)\left[1 - \frac{A}{1+A}\right] \qquad (5.10)$$

where $\sigma_0 = [1 + K\tilde{G}_0(\sigma, \sigma, 0)]^{-1}$ and

$$A(k_0) = 3k_0\kappa J_\sigma(\sigma)\varphi_0 = \frac{3(k_r-K)\alpha\varphi_0}{4k_D(1+\alpha)+4k_r} \qquad (5.11)$$

From eqs 5.9−5.11 we obtain

$$M(\sigma) = -\frac{A(\infty)}{1+A(\infty)} = \frac{3(K-k_r)}{K+4k_D+3k_r} \qquad (5.12)$$

In the absence of exciplex formation ($K = 0$), then the spin conversion effect is negative and changes from 0 to −1 with k_r. The effect is 0 at $k_r = 0$ because there is no recombination at all and the quantum yield is 1 at any k_0. In contrast, at $k_r = \infty$ and $k_0 = \infty$ all triplets immediately recombine, so that after instantaneous conversion there are no ions to separate: $\varphi(\sigma, k_0 = \infty) = 0$ and $M = -1$. The exciplex formation makes M increase up to the upper limit, which equals 3, because at spin conversion being infinitely fast the quantum yield is four times higher than φ_0.

Similarly, the fluorescence quantum yield 5.2 in the case of contact born ions reduces to a much simpler expression

$$\varphi_e(\sigma) = \varphi_e^0(\sigma)[1 - \tilde{p}_T(\sigma,\sigma,0)(k_D+k_r)] \qquad (5.13)$$

where $\varphi_e^0(\sigma) = \eta_0 K/(K + k_D)$ is the quantum yield in the absence of spin conversion and

$$\tilde{p}_T(\sigma,\sigma,0) = \frac{3\alpha}{4(K+k_D)(1+k_r/k_D+\alpha)+3\kappa\alpha} \rightarrow \frac{3}{4k_D+3k_r+K} \quad \text{at} \quad \alpha\rightarrow\infty$$

Using this result, we obtain for the spin conversion effect on the fluorescence quantum yield

$$M_e(\sigma) = -\lim_{\alpha\to\infty}\tilde{p}_T(\sigma,\sigma,0)(k_D+k_r) = -\frac{3(k_D+k_r)}{4k_D+3k_r+K} \qquad (5.14)$$

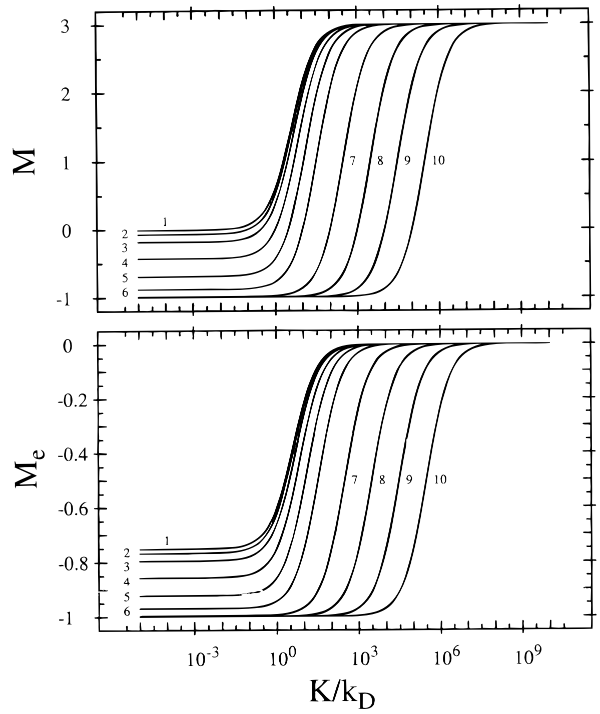

Figure 5. Spin conversion effect in charge separation (M) and exciplex fluorescence (M_e) for the contact born ion pair transforming to an exciplex with the rate K at k_r/k_D = (1) 0.01; (2) 0.1; (3) 1; (4) 3; (5) 10; (6) 100; (7) 10^3; (8) 10^4.

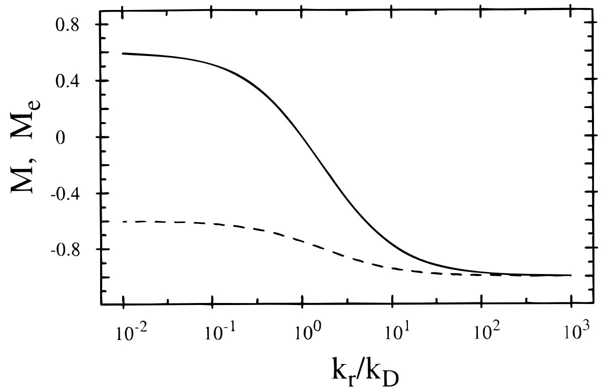

Figure 6. Spin conversion effects for charge separation (solid line) and exciplex fluorescence (dashed line), as functions of the triplet recombination rate at $K/k_D = 1$.

If no exciplex formation occurs ($K = 0$), this parameter varies from −3/4 in the absence of triplet recombination to −1 at infinitely fast recombination. Exciplex formation makes this parameter increase up to 0.

Both M and M_e change rapidly from the minimum to maximum value when the rate of exciplex formation becomes comparable with the separation rate measured by k_D. In the middle of these S-like curves (at $K = k_D$), the effect essentially depends on the triplet recombination rate (Figure 6). This is especially the case with sign alternating M, that turns to zero at $k_r = K$ as usual.

VI. Discussion

Our main goal in this work was to build the exciplex formation in the general scheme of photoionization, followed by spin conversion and recombination in the ion pair. We have shown how this can be done, in principle, within the consistent diffusional theory of the geminate process and obtained an analytical solution for the case when triplet pair recombination may be considered as a contact reaction. The results depend substantially on the initial ion separation and, generally speaking, should be averaged over their initial distribution, which depends on whether ionization is kinetic or diffusion-controlled.[31] This has already been done numerically even for noncontact back-and-forward electron transfer under the spinless approximation.[36,37] Though we have efficient programs to make this also, accounting for the spin conversion,[20] we ignored such an opportunity because this is only a preliminary qualitative investigation of the problem. In some respects it needs further development and generalization before the relevant comparison with the experimental results becomes possible.

The effect of spin conversion shown in Figures 4−6 is only an illustration of the competition between different reaction channels at zero and infinitely fast conversion. In reality the rate of conversion changes in finite limits with the applied magnetic field H. As has been shown in the Appendix, this range is rather restricted in the balance approximation. As follows from eq A.9, $k_0(H) - k_0(0) = \omega^2 T/12 \ll 1/12T < k_0(0)$. Hence, in balance approximation one cannot change significantly the spin conversion rate, which is of the order of $1/2T$. The same is valid for the quantities that characterize the magnetic field effect. For instance

$$m = \frac{\varphi(r_0, k_0(H)) - \varphi(r_0, k_0(0))}{\varphi(r_0, k_0(0))} \approx \frac{\partial \ln \varphi(r_0, k_0)}{\partial k_0}\frac{\mathrm{d}k_0}{\mathrm{d}H} = \frac{\partial \ln \varphi(r_0, k_0)}{\partial k_0}\frac{(g_+ - g_-)^2\beta^2 T}{6\hbar^2}H$$

However, from this linear dependence one can get at least the sign of the derivative $\partial\varphi/\partial k_0$ near $k_0 \approx 1/T_2$. To inspect the $\varphi(k_0)$ dependence in a wider range of k_0 variation, the rate description of spin conversion must be replaced by the dynamic (Hamiltonian) approach, which is free from the limitation A.6. In fact, this limitation can be easily removed by using 16 × 16 rank relaxation matrix accounting for the phase relaxation in line with the interactions of spins with magnetic field. In this case analytical treatment is hardly possible, but the numerical investigation of magnetic field effect is reliable in much wider range. An example of such investigation has been given recently in another work.[38]

Moreover, it has been shown recently that the spin conversion can influence not only the quantum yields but also the kinetics of geminate recombination as well.[15] The effect was obtained in balance approximation neglecting the exciplex formation but taking into account the recombination to the triplet state. This problem is also available for only numerical analysis.

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VII. Appendix

In general, the spin evolution is described by the kinetic equation for the pair density matrix ρ

$$\dot{\rho}(t) = -i[\mathbf{H}, \rho] + \hat{\mathbf{R}}\rho \tag{A1}$$

where $\boldsymbol{H}$ is the spin Hamiltonian and $\hat{\mathbf{R}}$ is the relaxation superoperator accounting for the population and phase relaxation in collective states basis of ion pair ($|T_+>$, $|T_->$, $|T_0>$, and $|S>$). We will concentrate on the simplest example of the Δg mechanism of spin conversion in ion pair at moderate magnetic fields.

The spin Hamiltonian in collective basis takes the form

$$\mathbf{H} = \frac{1}{2}\begin{pmatrix} \omega_+ & 0 & 0 & 0 \\ 0 & -\omega_+ & 0 & 0 \\ 0 & 0 & 0 & \omega_- \\ 0 & 0 & \omega_- & 0 \end{pmatrix} \tag{A2}$$

where

$$\omega_\pm = \frac{(g_+ \pm g_-)\beta}{\hbar}H \tag{A3}$$

β is the Bohr magneton, g_+ and g_- are g-factors of positive and negative ions, and H is the magnetic field. The relaxation superoperator in the Liouville space that has the rank 16 × 16 can be taken from ref 39. We will use it assuming that the longitudinal and transverse times of both radicals are the same (equal to T_1 and T_2).

For moderate magnetic fields, when

$$\omega_- \ll \frac{1}{T_2} \tag{A4}$$

the quasi-stationary solution for off-diagonal elements may be obtained by setting

$$\dot{\rho}_{ij} = 0 \quad \text{for} \quad i \neq j \tag{A5}$$

in general kinetic eqs A1. Then the total set of eqs A1 in the Liouville space reduces to the rate equations for only diagonal elements of density matrix:

$$\dot{\rho}_{\mathrm{SS}} = -\left[\frac{\omega_-^2 T_2}{4} + \frac{1}{T_2} + \frac{1}{2T_1}\right]\rho_{\mathrm{SS}} + \left[\frac{\omega_-^2 T_2}{4} + \frac{1}{T_2} - \frac{1}{2T_1}\right]\rho_{\mathrm{T_0T_0}} + \frac{1}{2T_1}(\rho_{\mathrm{T_+T_+}} + \rho_{\mathrm{T_-T_-}}) \tag{A6a}$$

$$\dot{\rho}_{\mathrm{T_0T_0}} = \left[\frac{\omega_-^2 T_2}{4} + \frac{1}{T_2} - \frac{1}{2T_1}\right]\rho_{\mathrm{SS}} - \left[\frac{\omega_-^2 T_2}{4} + \frac{1}{T_2} + \frac{1}{2T_1}\right]\rho_{\mathrm{T_0T_0}} + \frac{1}{2T_1}(\rho_{\mathrm{T_+T_+}} + \rho_{\mathrm{T_-T_-}}) \tag{A6b}$$

$$\dot{\rho}_{\mathrm{T_+T_+}} = \frac{1}{2T_1}(\rho_{\mathrm{SS}} + \rho_{\mathrm{T_0T_0}}) - \frac{1}{T_1}\rho_{\mathrm{T_+T_+}} \tag{A6c}$$

$$\dot{\rho}_{\mathrm{T_-T_-}} = \frac{1}{2T_1}(\rho_{\mathrm{SS}} + \rho_{\mathrm{T_0T_0}}) - \frac{1}{T_1}\rho_{\mathrm{T_-T_-}} \tag{A6d}$$

At moderate magnetic fields we can assume that

$$T_2 = T_1 = T \tag{A.7}$$

and both of them are field-independent as in the case of rotational relaxation mechanism at $g_\pm\beta H \ll \hbar\tau_\theta$, where τ_θ is the orientational relaxation time.[21] For equal relaxation times the general set of eqs A6 reduces to only two equations for the total population of the triplet state $p_{\mathrm{T}} = \rho_{\mathrm{T_0T_0}} + \rho_{\mathrm{T_-T_-}} + \rho_{\mathrm{T_+T_+}}$ and that of singlet state, $p_{\mathrm{S}} \equiv \rho_{\mathrm{SS}}$

$$\dot{p}_S = -3k_0 p_S + k_0 p_T \tag{A8a}$$

$$\dot{p}_T = 3k_0 p_S - k_0 p_T \tag{A8b}$$

with

$$k_0 = \left[\frac{1}{2T} + \frac{\omega_-^2 T}{12}\right] \tag{A9}$$

According to the inequality A4 the second term in A9 sensitive to magnetic field is a small correction to the first one. Hence, the rate of spin conversion k_0 has an order of inverse relaxation time. It is quadratic in magnetic field, but changes only slightly within balance (rate) approximation A4.

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