816 *J. Phys. Chem. A* **1998,** *102,* 816−824

Photochemical Charge Separation Suppressed by Spin Conversion

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Received: July 24, 1997; In Final Form: November 10, 1997

We present the unified theory of binary triplet state ionization followed by spin conversion to a singlet state of radical ion pair (RIP) and subsequent spin-allowed recombination which hinders the charge separation. An analytical theory of RIPs recombination in contact approximation is developed. At slow diffusion the previous results which ignored the spin states have been confirmed, though the effective recombination constant is weighted with an equilibrium share of singlet state, $^1/_4$. At faster diffusion, the spin conversion becomes a limiting stage if not completed during encounter and/or delivery time (from the initial distance to contact). The analytical and numerical study of charge separation in polar solutions shows that initial interion distance is an important factor in determining the quantum yield dependence on encounter diffusion and spin conversion rates. At distant starts the diffusional control of geminate recombination gives way to kinetic control and/or to spin conversion control as diffusion increases. At any diffusion the quantum yield of RIPs separation decreases with the magnetic field if the latter accelerates the spin conversion.

I. Introduction

A discovery of magnetic field effects in liquid phase chemistry marked the beginning of the active ESR and NMR study of photochemical radical reactions, which has become an independent line of study known as "spin chemistry".[1] Using very sophisticated methods of magnetic spectroscopy to solve the spin part of the problem, most if not all of the authors simplified as much as possible the kinematic aspect of RIPs evolution. This part was usually considered in the frame of the so called "exponential model," which attributes the Poisson distribution to the lifetimes of the radical-ion pairs ignoring their initial distribution on interparticle distances and the diffusional kinematics of the motion.[2]

The exponential model was widely accepted in photochemistry of electron transfer reactions in solutions.[3,4] Using optical registration of excited reactants and/or their charged products, researchers were able to measure the quantum yield of separated ions ignoring their spin states. Assuming that all ions (or radical-ions) (i) are produced at contact distance σ (ii) and recombine only in contact, the exponential model leads to the simplest expression for the charge separation quantum yield

$$\bar{\varphi} = \frac{1}{1 + z/\tilde{D}}$$

where $\tilde{D}$ is an encounter diffusion coefficient and z is proportional to the kinetic constant of charge recombination k_r.

So the primitive approach has been replaced in a few theoretical works by "contact approximation".[5,6] In this approximation the recombination is still considered as a contact reaction, but the initial separation of ions r_0 is left free and is used as a fitting parameter. It turns out that a simple parameter z should be substituted by function Z proportional to z when geminate recombination is under kinetic control but linear in diffusion when the limiting stage of the process is a delivery of ions from starting point to contact.[7,8] Contact approximation was also successfully applied to magnetic field effects in geminate recombination.[9,10] The same was done in a more sophisticated contact theory known as the "Green function method" similar to the "kinematic" or "closure" approximations.[11]

The common demerit of all contact theories of recombination is a crude simplification and an incorrect location of the reaction zone moving aside with increasing exothermicity of recombination.[12,13] Even more important is an arbitrariness in choosing r_0 as the initial condition for the geminate reaction. In fact, the initial distribution over r_0 is created in the course of ionization and nobody is free to choose it voluntarily. Only by considering ionization and the subsequent recombination as a unified process one can eliminate the arbitrariness of the initial distribution of interion distances. Such a "unified theory" of photoionization followed by geminate recombination appeared only recently[14] and was very successful in calculating the real initial distributions[15], the separation quantum yields,[7,16] and even the whole kinetics of the process,[17] taking into account the remote character of electron transfer. Recently the unified theory was justified using a more fundamental and better established convolution formalism of chemical kinetics known as "integral encounter theory".[18]

Here we make an attempt to join the unified theory and spin chemistry using the simplest approach to the latter. Transitions between singlet and triplet states of the RIPs will be considered in balance approximation,[9] using the rate of the singlet−triplet conversion k_0 as a single parameter sensitive to the magnetic field. We will present the general theory for remote forward and backward electron transfer (section II) and its simplified version intended for contact recombination (section III). Both of them will be used to calculate the charge separation quantum yield in polar solutions (section IV). In contact approximation this problem will be solved analytically and allowed to specify

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S1089-5639(97)02414-6 CCC: $15.00 © 1998 American Chemical Society
Published on Web 01/14/1998

an important parameter of the theory, $\kappa = k_0/16\pi\sigma k_r$, which discriminates between spin-controlled and kinetic controlled recombination. Another parameter, $4k_0\sigma^2/\tilde{D}$, determines the diffusional and magnetic field dependence of the quantum yield where recombination is under diffusional control. The difference between contact and remote starts will be analyzed and the results compared with those averaged over the true distribution of interion distances.

II. Photoionization followed by Spin Conversion and Remote Recombination

The irreversible charge transfer from an excited triplet of donor (^{3}D*) to the acceptor of electron (A) is a usual mechanism of energy quenching in liquid solutions:

$$^3\mathrm{D}^* + \mathrm{A} \rightarrow {}^3[\mathrm{D}^*\cdots\mathrm{A}] \Rightarrow {}^3[\mathrm{D}^+\cdots\mathrm{A}^-] \tag{1.1}$$

In the binary approximation the quenching kinetics after δ-pulse excitation is well described by the set of equations of "differential encounter theory":[19−21]

$$\dot{N} = -k_{\mathrm{I}}(t)cN - \frac{1}{\tau_{\mathrm{D}}}N \tag{1.2a}$$

$$k_{\mathrm{I}}(t) = 4\pi\int r^2\,\mathrm{d}r\;W_{\mathrm{I}}(r)n(r,t) \tag{1.2b}$$

$$\frac{\partial}{\partial t}n = -W_{\mathrm{I}}(r)n + \mathrm{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}n \tag{1.2c}$$

Here $N(t)$ is a share of the excitations survived at time t, although they decay with a lifetime τ_{D} and are quenched by acceptors given in concentration c with a "rate constant" $k_{\mathrm{I}}(t)$. The latter is expressed via the donor distribution around acceptor $n(r,t)$ that changes with time due to ionization with the position dependent rate $W_{\mathrm{I}}(r)$ and encounter diffusion of reactants with a coefficient D. The pair distribution should satisfy the following initial and boundary conditions:

$$n(r,0) = 1,\quad \frac{\partial}{\partial r}n(r,t)|_{r=\sigma} = 0 \tag{1.3}$$

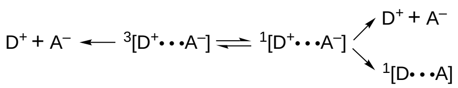
If nothing happens to the charged products of the reaction after ionization, as if they were immobile and chemically inactive, then their pair distribution in space is given by the equation:[14−16,7]

$$m_0(r) = W_{\mathrm{I}}(r)\int_0^{\infty} n(r,t)N(t)dt \tag{1.4}$$

and the total ionization quantum yield is

$$\psi = c\int_{\sigma}^{\infty} m_0(r)4\pi r^2 dr \tag{1.5}$$

In fact, the ion pair may be separated by diffusion if it escapes geminate recombination to the ground state allowed from the singlet state and forbidden from the triplet one. Therefore, the triplet−singlet conversion in RIPs with a rate k_0 is a necessary step that makes recombination possible and leads to an essential decrease in the quantum yield of separated (survived) ions. The process proceeds according to the kinetic scheme proposed in ref 22 for the reaction of photoexcited Ru−trisbipyrigine (D) with methylviologen (A) (Figure 1):



(1.6)

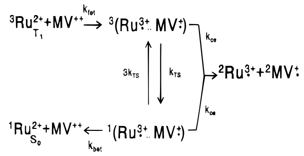


Figure 1. The reaction scheme for the forward and backward electron transfer (with contact rates k_{fet} and $k_{\mathrm{bet}} \equiv k_r$, correspondingly) assisted by the spin conversion with a rate $k_{\mathrm{TS}} \equiv k_0$ that suppresses the ion pair separation in either the triplet or singlet state.

Previously the charge separation was studied in systems where recombination is not spin forbidden because ionization proceeds from the excited singlet state.[4] Therefore, in the original *unified theory*, we operated with only the pair distribution function of ions, $m(r,t)$, which describes their accumulation, resulting from ionization, and recombination with a rate $W_{\mathrm{R}}(r)$.[7,14−16] Here we should use instead of a single distribution at least two of them: one for triplet RIPs, $m(r,t)$, and another for a singlet one, $s(r,t)$. The former is pumped by ionization while recombination is possible only in the latter. Taking into account the spin conversion with the position independent rate k_0, we can write a system of differential equations for the RIP distribution functions:

$$\frac{\partial}{\partial t}m = -k_0 m + 3k_0 s + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 \mathrm{e}^{r_c/r}\frac{\partial}{\partial r}\mathrm{e}^{-r_c/r}m + W_{\mathrm{I}}(r)nN(t) \tag{1.7a}$$

$$\frac{\partial}{\partial t}s = k_0 m - 3k_0 s + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 \mathrm{e}^{r_c/r}\frac{\partial}{\partial r}\mathrm{e}^{-r_c/r}s - W_{\mathrm{R}}(r)s \tag{1.7b}$$

where $\tilde{D}$ is an encounter diffusion coefficients for RIPs, different from that for reactants (D), and $r_c = \mathrm{e}^2/\epsilon k_{\mathrm{B}}T$ is the Onsager radius of the Coulomb well. The initial and boundary conditions for both distributions are the same:

$$m(r,0) = s(r,0) = 0,$$
$$\frac{\partial}{\partial r}\mathrm{e}^{-r_c/r}m(r,t)|_{r=\sigma} = \frac{\partial}{\partial r}\mathrm{e}^{-r_c/r}s(r,t)|_{r=\sigma} = 0 \tag{1.8}$$

The total survival probability of the ionized products is

$$P(t) = c\int_{\sigma}^{\infty}[m(r,t) + s(r,t)]4\pi r^2\,\mathrm{d}r \tag{1.9}$$

The solution of eqs 1.7 may be obtained in the following form:

$$\begin{pmatrix} m(r,t) \\ s(r,t) \end{pmatrix} = \int_0^t \mathrm{d}t'\int \mathrm{d}^3r' \begin{pmatrix} p_{\mathrm{T}}(r,r',t-t') & p'_{\mathrm{S}}(r,r',t') \\ p_{\mathrm{S}}(r,r',t-t') & p'_{\mathrm{T}}(r,r',t') \end{pmatrix} \begin{pmatrix} W_{\mathrm{I}}(r')n(r',t')N(t') \\ 0 \end{pmatrix} \tag{1.10}$$

We need only p_{T} and p_{S} which are the Green functions for triplet and singlet RIPs originating from an initially excited triplet state because another pair, p'_{T} and p'_{S}, are the similar functions but for RIPs produced from a singlet excitation. From eqs 1.9 and 1.10 one can easily obtain

$$P(t) = c\int \mathrm{d}^3r\int \mathrm{d}^3r' W_{\mathrm{I}}(r')\int_0^t p(r,r',t')n(r',t')N(t')\,dt' \tag{1.11}$$

Here the total charge distribution in RIP,

$$p(r,r',t-t') = p_{\mathrm{T}}(r,r',t-t') + p_{\mathrm{S}}(r,r',t-t') \tag{1.12}$$

is composed of triplet and singlet components which yield the homogeneous differential equations

$$\frac{\partial}{\partial t}p_T = -k_0p_T + 3k_0p_S + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}p_T \quad (1.13a)$$

$$\frac{\partial}{\partial t}p_S = k_0p_T - 3k_0p_S + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}p_S - W_R(r)p_S \quad (1.13b)$$

with the corresponding initial and reflecting boundary conditions:

$$p_T(r,r',0) = \frac{\delta(r-r')}{4\pi r^2}, \quad p_S(0) = 0,$$
$$\frac{\partial}{\partial r}e^{-r_c/r}p_T(r,t)|_{r=\sigma} = \frac{\partial}{\partial r}e^{-r_c/r}p_S(r,t)|_{r=\sigma} = 0 \quad (1.14)$$

The charge photoseparation quantum yield $\phi = P(\infty)$ resulting from eqs 1.11 and 1.4

$$\phi = c\int d^3r\int d^3r'\, p(r,r',\infty)m_0(r') = \psi\bar{\varphi} \quad (1.15)$$

is actually a product of the total ionization quantum yield ψ given in eq 1.5 and the charge separation quantum yield $\varphi(r)$ averaged over initial distribution of ions, $f_0(r)$:

$$\bar{\varphi} = \int \varphi(r')f_0(r')\, d^3r' \quad (1.16)$$

where

$$\varphi(r') = \int_\sigma^\infty p(r,r',\infty)4\pi r^2\, dr \quad (1.17)$$

is the charge separation quantum yield of ions initially separated by distance r' and

$$f_0(r') = \frac{m_0(r')}{\int_\sigma^\infty m_0(r)4\pi r^2\, dr} \quad (1.18)$$

is a normalized distribution of these distances in RIPs created by binary photoionization.

The main difficulties encountered in solving these equations result from the complex space dependence of the recombination rate $W_R(r)$. Even in the simplest case of a single-channel reaction the forward and backward electron transfer rates are given by the famous Marcus formulas:

$$W_I(r) = V_I^2\sqrt{\frac{\pi}{\lambda k_BT}}\exp\left[-\frac{(\Delta G_I + \lambda)^2}{4\lambda k_BT}\right]$$
$$W_R(r) = V_R^2\sqrt{\frac{\pi}{\lambda k_BT}}\exp\left[-\frac{(\Delta G_R + \lambda)^2}{4\lambda k_BT}\right] \quad (1.19)$$

where $\Delta G_I(r)$ and $\Delta G_R(r)$ are the free energies for ionization and recombination, $\lambda(r)$ is the reorganization energy of a classical (low-frequency) assisting mode. In reality, there may be one or more quantum modes that should be also taken into account.[23,24] Their influence on the shape of the rates and the charge-separation quantum yields was recently studied in ref 25, but here we have restricted ourselves to the simplest case. For the sake of simplicity we have already assumed that the interparticle interaction is spherically isotropic. This is not always the case,[26] but in low-viscosity solvents the chemical anisotropy is very efficiently averaged by rotation and numerous recontacts,[27] so one may take

$$V_I(r) = V_i e^{-(r-\sigma)/L} \quad \text{and} \quad V_R(r) = V_r e^{-(r-\sigma)/l} \quad (1.20)$$

as exchange interaction matrix elements for the forward and backward charge transfer.

Equation 1.16 separates the whole problem into two independent parts: calculation of the initial distribution $f_0(r)$ by means of encounter theory with a given $W_I(r)$ and calculation of the charge separation yield from a particular initial distance, $\varphi(r)$, at the given recombination rate $W_R(r)$. The former part is essentially non-contact while the latter may be significantly simplified if $W_R \neq 0$ only at $r - \sigma \ll \sigma$, that is, in a thin layer adjacent to the contact.

III. Recombination in the Contact Approximation

If the back electron transfer occurs in the normal region, where $|\Delta G_R| < \lambda$, then the distance dependence of the recombination rate may be considered as exponential and sharp:[12,13]

$$W_R(r) = W_r \exp[-2(r-\sigma)/l] \quad (2.1)$$

At higher exothermicity the contact transfer becomes inverted and the recombination layer takes a bell shape and moves out of contact.[12,13] However, the shift of the reaction layer from the contact is smaller if the ionization is a multichannel transfer assisted by the high-frequency quantum mode.[28] Thus, for low exothermal and/or multichannel back electron transfer the recombination may be considered as contact and characterized by a single parameter

$$k_r = \int_\sigma^\infty W_R(r)4\pi r^2\, dr$$

which is actually a kinetic rate constant. Using this parameter one can omit the last term in eq 1.13b, but account for recombination through the radiation boundary condition different from that given in eq 1.14:

$$p_S(0) = 0, \quad 4\pi\tilde{D}\sigma^2\left(\frac{\partial p_S}{\partial r} + \frac{r_c}{r^2}p_S\right)|_{r=\sigma} = k_rp_S(\sigma,t) \quad (2.2)$$

Equations 1.13 may be now rewritten for functions p_s and p as follows:

$$\frac{\partial}{\partial t}p_S + 4k_0p_S = \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}p_S + k_0p \quad (2.3a)$$

$$\frac{\partial}{\partial t}p = \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}p \quad (2.3b)$$

with the following initial and boundary conditions for p,

$$p(0) = \frac{\delta(r-r')}{4\pi r^2}, \quad 4\pi\tilde{D}\sigma^2\left(\frac{\partial p}{\partial r} + \frac{r_c}{r^2}p\right)|_{r=\sigma} = k_rp_S(\sigma,t) \quad (2.4)$$

The solution of eq 2.3a may be presented in the following form:

$$p_S(r,r_0,t) = k_0\int d^3r'\int_0^t G(r,r',t-t')e^{-4k_0(t-t')}p(r',r_0,t')\, dt' \quad (2.5)$$

where the Green function yields the free diffusion equation

$$\frac{\partial}{\partial t}G = \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}G \quad (2.6)$$

with the same boundary conditions as in eq 2.2 but with a different initial one,

$$G(0) = \frac{\delta(r - r')}{4\pi r^2}, \quad 4\pi\tilde{D}\sigma^2\left(\frac{\partial G}{\partial r} + \frac{r_c}{r^2}G\right)\Big|_{r=\sigma} = k_r G(\sigma,t)$$

Making the Laplace transformation of eq 2.5 we have

$$\tilde{p}_S(r,r_0,s) = k_0\int \tilde{G}(r,r',s + 4k_0)\tilde{p}(r',r_0,s)\ \mathrm{d}^3r' \tag{2.7}$$

In contact approximation eq 2.3b has a well-known solution[6] whose the Laplace transform may be presented as follows:

$$\tilde{p}(r,r_0,s) = \tilde{G}_0(r,r_0,s) - k_r\tilde{G}_0(r,\sigma,s)\tilde{p}_S(\sigma,r_0,s) \tag{2.8}$$

where G_0 also yields the free diffusion eq 2.6 but with reflecting boundary condition,

$$G_0(r,r_0,0) = \frac{\delta(r - r_0)}{4\pi r^2}, \quad \left(\frac{\partial G_0}{\partial r} + \frac{r_c}{r^2}G_0\right)\Big|_{r=\sigma} = 0 \tag{2.9}$$

After integration over r we obtain from eq 2.8

$$\tilde{p}(r_0,s) = \int \tilde{p}(r,r_0,s)d^3r = \frac{1}{s} - \frac{k_r}{s}\tilde{p}_S(\sigma,r_0,s) \tag{2.10}$$

and

$$\varphi(r_0) = \lim_{s\to 0} s\tilde{p}(r_0,s) = 1 - k_r\tilde{p}_S(\sigma,r_0,0) \tag{2.11}$$

After substitution of eq 2.8 into eq 2.7 the latter becomes an algebraic equation for $\tilde{p}_S(\sigma,r_0,s)$ at $r = \sigma$. The solution of the equation is the following:

$$\tilde{p}_S(\sigma,r_0,s) = \frac{k_0\int \tilde{G}(\sigma,r',s + 4k_0)\tilde{G}_0(r',r_0,s)\ \mathrm{d}^3r'}{1 + k_0k_r\int \tilde{G}(\sigma,r',s + 4k_0)\tilde{G}_0(r',\sigma,s)\ \mathrm{d}^3r'}$$

Substituting this result into eq 2.11 we find

$$\varphi(r_0) = 1 - \frac{k_rk_0\int \tilde{G}(\sigma,r',4k_0)\tilde{G}_0(r',r_0,0)\ \mathrm{d}^3r'}{1 + k_0k_r\int \tilde{G}(\sigma,r',4k_0)\tilde{G}_0(r',\sigma,0)\ \mathrm{d}^3r'} \tag{2.12}$$

Now we can again make use of the contact approximation which relates G and G_0 in the same way as $\tilde{p}$ and $\tilde{G}_0$ in eq 2.8:

$$\tilde{G}(r,r',s) = \tilde{G}_0(r,r',s) - k_r\tilde{G}_0(r,\sigma,s)\tilde{G}(\sigma,r',s) \tag{2.13}$$

The solution of this equation at $r = \sigma$ is the following:

$$\tilde{G}(\sigma,r',s) = \frac{\tilde{G}_0(\sigma,r',s)}{1 + k_r\tilde{G}_0(\sigma,\sigma,s)} \tag{2.14}$$

Using this result at $s = 4k_0$ in eq 2.11 we obtain:

$$\varphi(r_0) = 1 - \frac{k_rk_0\int \tilde{G}_0(\sigma,r',4k_0)\tilde{G}_0(r',r_0,0)\ \mathrm{d}^3r'}{1 + k_r\tilde{G}_0(\sigma,\sigma,4k_0) + k_0k_r\int \tilde{G}_0(\sigma,r',4k_0)\tilde{G}_0(r',\sigma,0)\ \mathrm{d}^3r'} \tag{2.15}$$

It is clear that

$$\begin{aligned}\int \tilde{G}_0(\sigma,r',4k_0)\tilde{G}_0(r',r_0,0)\ \mathrm{d}^3r' &= \\ \int_0^\infty \mathrm{d}t \int_0^t \mathrm{d}t' \mathrm{e}^{-4k_0(t-t')}\int G_0(\sigma,r',t - t')G_0(r',r_0,t')\ \mathrm{d}^3r' &= \\ \int_0^\infty G_0(\sigma,r_0,t)\mathrm{e}^{-4k_0t}\ \mathrm{d}t\int_0^t \mathrm{e}^{4k_0t'}\ \mathrm{d}t' &= \frac{\tilde{G}_0(\sigma,r_0,0) - \tilde{G}_0(\sigma,r_0,4k_0)}{4k_0}\end{aligned}$$

as well as

$$\int \tilde{G}_0(\sigma,r',4k_0)\tilde{G}_0(r',\sigma,0)\ \mathrm{d}^3r' = \frac{\tilde{G}_0(\sigma,\sigma,0) - \tilde{G}_0(\sigma,\sigma,4k_0)}{4k_0}$$

Inserting these results into eq 2.15 we obtain finally:

$$\varphi(r_0) = 1 - \frac{(^1/_4)k_r[\tilde{G}_0(\sigma,r_0,0) - \tilde{G}_0(\sigma,r_0,4k_0)]}{1 + (^3/_4)k_r\tilde{G}_0(\sigma,\sigma,4k_0) + (^1/_4)k_r\tilde{G}_0(\sigma,\sigma,0)} \tag{2.16}$$

Let us analyze the limiting case when the mixing of the spin states is so fast that one can expect the restoration of the results that were obtained neglecting the spin states. This is actually true but with minor correction. For large k_0 the quantity

$$\tilde{G}_0(\sigma,r_0,4k_0) = \int_0^\infty \mathrm{e}^{-4k_0t}G_0(\sigma,r_0,t)\ \mathrm{d}t \approx \frac{G_0(\sigma,r_0,0)}{4k_0} = \frac{\delta(\sigma - r_0)}{16\pi k_0r_0^2}$$

may be neglected at any $r_0 > \sigma$. Thus, for an infinitely fast spin conversion we obtain

$$\varphi(r_0) = 1 - \frac{(k_r/4)\tilde{G}_0(\sigma,r_0,0)}{1 + (k_r/4)\tilde{G}_0(\sigma,\sigma,0)} = 1 - R_0(r_0) \tag{2.17}$$

This is the lower limit for the charge separation quantum yield, and the recombination quantum yield,

$$R_0(r_0,x) = \frac{x\tilde{G}_0(\sigma,r_0,0)}{1 + x\tilde{G}_0(\sigma,\sigma,0)} \tag{2.17a}$$

is exactly the same as in the theory ignoring the spin states of RIPs (see eq 5.7 in refs 5 and 6. The only difference is that an effective reaction constant in eqs 2.17, $x = k_r/4$, is one-fourth as much, because of the equilibrium weight of the only reactive (singlet) state in the system.

Let us present the quantum yield as it was done in refs 7 and 8:

$$\varphi(r_0) = \frac{1}{1 + Z/\tilde{D}} \tag{2.18}$$

where

$$Z(r_0) = \frac{qz}{1 + z(1 - q)/\tilde{D}}, \quad q = \frac{1 - \mathrm{e}^{-r_c/r_0}}{1 - \mathrm{e}^{-r_c/\sigma}} \le 1 \tag{2.19}$$

and

$$z = \frac{(k_r/4)[1 - \mathrm{e}^{-r_c/\sigma}]}{4\pi r_c} \tag{2.20}$$

is a single parameter of the problem accounting for the contact recombination. An “exponential model” implies that RIPs are created only at contact,[4] at $r_0 = \sigma$, so that ($q = 1$) and $Z(\sigma) \equiv$

z = const does not depend on diffusion (viscosity of the solvent). In fact, the starting distance may be much larger especially for diffusion controlled or inverted ionization. Therefore

$$Z(r_0) = \begin{cases} \dfrac{q}{1-q}\tilde{D} & \text{at } (1-q)z \gg \tilde{D} \text{ (diffusional recombination)} \\ qz = \text{const} & \text{at } (1-q)z \ll \tilde{D} \text{ (kinetic recombination)} \end{cases} \tag{2.21}$$

does not depend on diffusion only in the low viscosity limit attributed in ref 7 to "kinetic controlled" geminate recombination. At higher viscosities the recombination is controlled by diffusion that delivers ions to the contact and therefore Z is proportional to $\tilde{D}$. In general, Z increases with $\tilde{D}$ approaching the kinetic limit, $Z = qz =$ const, from below.[7] This theoretical prediction was in qualitative agreement with experimental data obtained in ref 22.

IV. Charge Separation in Highly Polar Solutions

If $\epsilon \to \infty$ we may proceed further with the analytical calculations because the important Green function for this particular case is known (see eq 4.11 in ref 29):

$$\tilde{G}_0(\sigma,r_0,s) = \tilde{G}_0(\sigma,r_0,0)\,\frac{e^{-(r_0-\sigma)\sqrt{s/\tilde{D}}}}{1+\sigma\sqrt{s/\tilde{D}}} \tag{3.1}$$

where

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

By substituting eq 3.1 into eq 2.16 we obtain for highly polar solutions:

$$\varphi(r_0) = 1 - \frac{(k_r/4)\tilde{G}_0(\sigma,r_0,0)[1-\exp\{-(r_0-\sigma)\sqrt{4k_0/\tilde{D}}\}/(1+\sigma\sqrt{4k_0/\tilde{D}})]}{1+(k_r/4)\tilde{G}_0(\sigma,\sigma,0)[1+3/(1+\sigma\sqrt{4k_0/\tilde{D}})]} \tag{3.2}$$

In the limiting case of ultrafast conversion, $k_0 \to \infty$, the separation quantum yield eq 2.17 is reproduced as well as it presentation given by eqs 2.18 and 2.19 but with

$$z = k_r/16\pi\sigma \qquad \text{and} \qquad q = \sigma/r_0$$

At finite k_0, we should first concentrate on the case when RIPs are created not far from the contact. If their initial separation $r_0 - \sigma$ is so small that the spin state does not significantly change during delivery time from start to contact, $(r_0 - \sigma)^2/\tilde{D}$, then

$$y = \sqrt{4k_0(r_0-\sigma)^2/\tilde{D}} \ll 1 \tag{3.3}$$

and the exponent in eq 3.2 may be expended in y. In the second-order approximation we obtain:

$$\varphi = \frac{1+(k_r/k_D)+x+y^2(\sigma/2r_0)(k_r/4k_D)}{1+(k_r/k_D)+x[1+(k_r/4k_D)]} \tag{3.4}$$

where

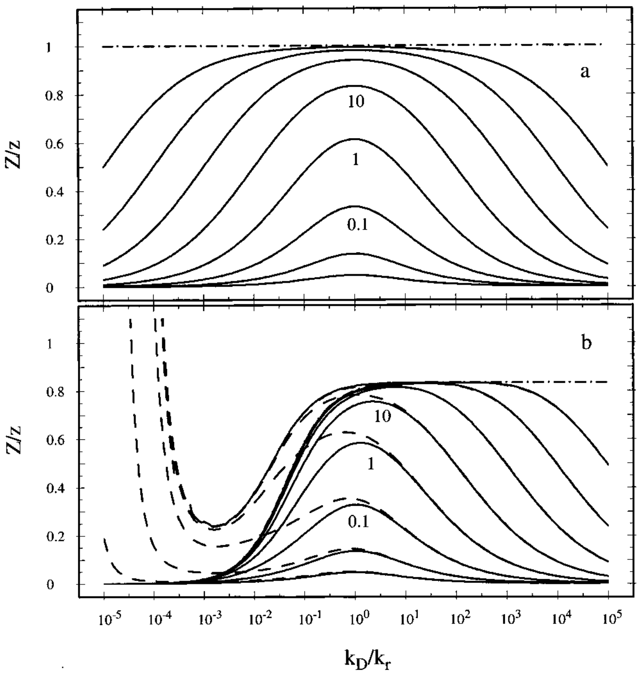


Figure 2. Diffusional dependence of Z for (a) contact, $r_0 = \sigma = 5$ Å, and (b) near-contact RIPs, $r_0 - \sigma = 1$ Å, at different rates of spin conversion characterized by parameter $\kappa = 10^{-3}$, 10^{-2}, 0.1, 1, 10, 10^2, and 10^3. Dashed lines: remote transfer with a rate $W_R(r) = W_r \exp[-2(r - \sigma)/l]$ ($W_r = 5$ ns^{-1}, $l = 0.7$ Å). Solid lines: contact approximation with $k_r = \int W_R(r)\, d^3r = 628$ Å^3/ns.

$$k_D = 4\pi\sigma\tilde{D}, \quad x = \sqrt{4k_0\sigma^2/\tilde{D}} < \text{ or } > 1, \quad y = \frac{r_0-\sigma}{\sigma}x \ll 1 \tag{3.5}$$

If we present this result as in eq 2.18, then neglecting the small correction in y^2 we obtain:

$$Z = z\frac{\sqrt{k_r\kappa k_D}}{k_r + k_D + \sqrt{k_r\kappa k_D}} \tag{3.6}$$

where

$$\kappa = \frac{16\pi\sigma^3 k_0}{k_r}$$

These results do not depend on r_0, though they hold only for the RIPs not too far removed from the contact.

Since the expression 3.6 is invariant with respect to the permutation of k_D and k_r, the diffusional dependence of Z plotted against $\ln(k_D/k_r)$ (Figure 2a) is symmetrical at any κ. When $\kappa \gg 1$ there are three different regions:

$$Z = \begin{cases} z\sqrt{\kappa\left(\dfrac{k_D}{k_r}\right)} = \dfrac{1}{2}\sqrt{k_0\sigma^2\tilde{D}} & \text{at } \sqrt{k_D/k_r} \ll 1/\kappa & \text{(a)} \\ & \text{at } 1/\kappa \ll \sqrt{k_D/k_r} \ll \kappa & \text{(b)} \\ z\sqrt{\kappa\left(\dfrac{k_r}{k_D}\right)} = \dfrac{k_r}{8\pi}\sqrt{k_0/\tilde{D}} & \text{at } \kappa \ll \sqrt{k_D/k_r} & \text{(c)} \end{cases} \tag{3.7}$$

In the intermediate diffusion region b we confirm the existence of the kinetic plateau $Z = z$ predicted in the "exponential model". It is not affected by spin conversion as happens in both side regions where recombination increases with k_0. If the rate of conversion decreases to such an extent that inequality 3.6 is inverted, the side regions are butted together, expelling the kinetic plateau.

It is remarkable that diffusion accelerates the process in region a and decelerates it in region c. This effect may be understood if one takes into account that the efficiency of the spin conversion is determined by the product $k_0\bar{t}_e$, where $\bar{t}_e$ is the average "survival time" of a pair before ions either recombine or are separated. For RIPs born in contact this time was shown to increase until $k_D < k_r$ and to decrease at $k_D > k_r$:[6]

$$\bar{t}_e = 1.6\frac{4\pi\sigma^3 k_D}{(k_r + k_D)^2} \tag{3.8}$$

The results given in eq 3.7 for regions a and c may be presented by the common formula,

$$Z = z\sqrt{2.5k_0\bar{t}_e} \tag{3.9}$$

though in region a Z increases while in region c it decreases with diffusion. Since both the ascending and descending branches of $Z(\tilde{D})$ are spin controlled, the quantum yield in regions a and c is rather sensitive to the variation of k_0 but not as much in between, within the kinetic plateau of region b. The latter is wider the higher is κ. Thus we come to the conclusion that k_0 has its greatest impact on the charge recombination if $\kappa \ll 1$.

Moreover, when

$$\kappa \ll 1, \quad \text{that is} \qquad k_r \gg 16\pi\sigma^3 k_0$$

the kinetic region b disappears and the recombination is limited everywhere by the time of the spin conversion. In this case eq 3.9 holds at any speed of diffusion reaching the maximum value

$$Z_{\max} = z\sqrt{\frac{4\pi k_0\sigma^3}{k_r}} = \sqrt{\frac{k_0 k_r \sigma}{64\pi}} \qquad \text{at} \qquad k_D = k_r \tag{3.10}$$

The parabolic dependence 3.8 as well as the symmetrical result 3.6 are peculiar only for RIPs started from the closest approach distance $r_0 = \sigma$. At any nonzero initial ion separation $r_0 - \sigma$, the symmetry of $Z(\tilde{D})$ dependence is lost. The ascending branches of the curves shown in Figure 2b approach each other and even merge, while their descending branches are pushed apart. Even more dramatic changes occur if the theory of remote electron transfer (section II) is used instead of contact approximation developed in section III. For the relatively fast diffusion the contact approximation is well confirmed but the difference increases and becomes qualitative as $\tilde{D} \to 0$.

Returning to contact approximation let us now focus our attention on so distant a start or so slow a diffusion that the inequality 3.3 is inverted. The essentially different result follows from eq 3.4 for $y \gg 1$:

$$\varphi(r_0) = 1 - \frac{k_r}{4k_D}\left(\frac{\sigma}{r_0}\right)\frac{1 + x}{1 + k_r/k_D + x(1 + k_r/4k_D)} = \begin{cases} 1 - R_0(r_0,k_r/4) & \text{at } x \gg 1 \\ 1 - {}^1\!/_4 R_0(r_0,k_r) & \text{at } x \ll 1 \end{cases} \tag{3.11}$$

For the fast spin conversion ($x \gg 1$) we confirm here all the results obtained for infinitely high k_0 in eqs 2.17−2.21. However, when the conversion is slower ($x \ll 1 \ll y$), the equilibration of spin states during the encounter time $\sigma^2/\tilde{D}$ is unattainable though it has been completed during much longer delivery time $(r_0 - \sigma)^2/\tilde{D}$. Therefore the quantum yield of recombination is 4 times smaller then in the case when the spin states were neglected.

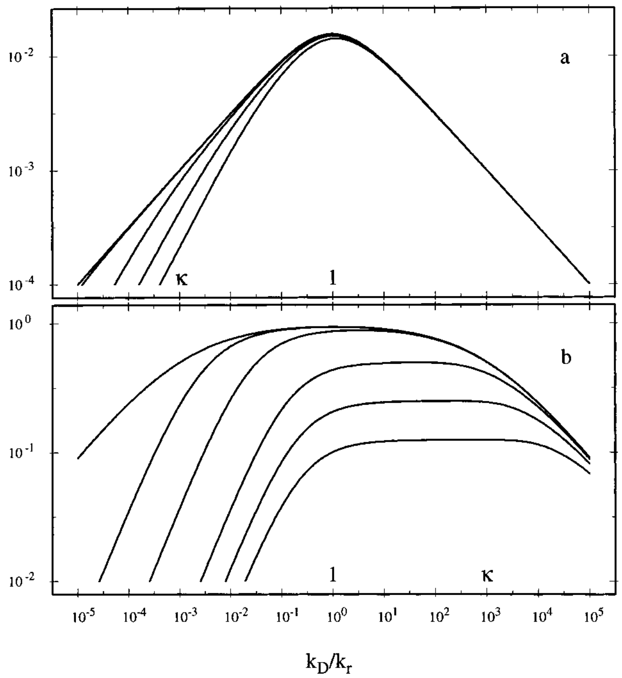


Figure 3. The same as in Figure 2 but for different initial separations (from bottom to top: r_0/σ m= 8, 9, 2, 1.1, 1.01, 1) at (a) slow spin-conversion and (b) fast spin conversion ($\kappa = 10^3$).

This difference can only be seen when the recombination is under diffusional control:

$$\varphi(r_0) \begin{array}{l} \nearrow 1 - \dfrac{\sigma}{r_0}\quad\dfrac{k_r}{4k_D} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{at } k_r \ll k_D \\ \searrow 1 - \dfrac{\sigma}{4r_0}\quad\dfrac{1 + x}{1 + x/4} = \begin{cases} 1 - \dfrac{\sigma}{r_0} & \text{at } x \gg 1 \\ 1 - \dfrac{\sigma}{4r_0} & \text{at } x \ll 1 \end{cases} \quad \text{at } k_r \gg k_D \end{array} \tag{3.12}$$

In the kinetic control limit ($k_r \ll k_D$) the separation quantum yield is not affected by the spin conversion and corresponding

$$Z(r_0) = z\frac{\sigma}{r_0} = \text{const} \tag{3.13}$$

while for diffusion controled recombination ($k_r \gg k_D$) this quantity is approximately linear in the slow and fast conversion limits though the slopes are different:

$$Z(r_0) = \sigma\tilde{D}/\left(r_0\frac{4 + \sqrt{4k_0\sigma^2/\tilde{D}}}{1 + \sqrt{4k_0\sigma^2/\tilde{D}}} - \sigma\right) = \begin{cases} \dfrac{\sigma}{r_0 - \sigma}\tilde{D} & \text{at } \dfrac{4k_0\sigma^2}{\tilde{D}} \gg 1 \\ \dfrac{\sigma}{4r_0 - \sigma}\tilde{D} & \text{at } \dfrac{4k_0\sigma^2}{\tilde{D}} \ll 1 \end{cases} \tag{3.14}$$

The spin effect in diffusional recombination comes to the light as the bend of a quasi-linear $Z(k_D)$ dependence near $k_D/k_r = \kappa$. This region is attainable for distant starts, $r_0 > 2\sigma$, when $\kappa \ll 1$ (Figure 3a), but the smooth bend is not seen in a log−log plot. The slopes of ascending branches of the curves are smaller the larger are initial separations, but at faster diffusion, matching the requirement (eq 3.3), the difference between distant starts and start from contact disappears. In fact, all descending branches of the curves shown on Figure 3 stick together at so fast diffusion. In the case of $\kappa \gg 1$ this happens later and even after the kinetic plateau ($Z = (\sigma/r_0)z$) is over (Figure 3b). Only then (at $k_D/k_r > \kappa \gg 1$) the recombination is coming under conversion control and slows down with diffusion. The transition from diffusion to kinetic control (from ascending branch to plateau) occurs much earlier, at $k_D/k_r = (r_0 - \sigma)/4r_0$.

Thus, one should look for the case $\kappa \ll 1$ to find the spin effects at slow and moderate diffusion. The corresponding charge separation quantum yield, eq 3.12, depends on the spin conversion only in the case of diffusion-controlled geminate recombination, $k_r \gg k_D$. There is also a strong dependence on the initial charge separation r_0 so that $\varphi(r_0)$ should be averaged over the distribution $f_0(r_0)$ as indicated in eq 1.16. Fortunately, in the diffusion control limit

$$\bar{\varphi} = 1 - \left\langle \frac{\sigma}{4r_0} \right\rangle \frac{1+x}{1+x/4} = \varphi(r_e) \qquad (3.15)$$

where

$$r_e = \left\langle \frac{1}{r_0} \right\rangle^{-1} = \left[\int_0^\infty f_0(r_0) 4\pi r_0 \, dr_0\right]^{-1}$$

At slow diffusion not only recombination but also ionization may be under diffusion control. In this case the distribution of initial distances has a bell shape with the maximum shifted from the contact,[15] so that $r_e > \sigma$. After averaging with this distribution the corresponding $Z = 1/\bar{\varphi} - 1$ may be obtained from eq 3.14 as $Z(r_e)$. Taking $r_e = 15$Å at 12 Å we can hardly see the transition from slow to fast conversion limits in log−log plots (Figure 4a), but in conventional coordinates the curvature of $Z(\tilde{D})$ dependence is clearly seen (Figure 4b). Previously we studied the same dependence ignoring the spin states[7] and came to the conclusion that it should be strictly linear as in eq 2.21. The experimental data taken from ref 22 roughly confirmed this conclusion except that there was a violation of linearity at the lowest diffusion available.[7] This is qualitatively the same curvature that we see now in Figure 4b.

If this is the case then an essential decrease of the ion separation quantum yield $\bar{\varphi}(k_0)$ with k_0 should be seen in the transition region. This is what we see in Figure 5. If the rate of the spin conversion increases with the magnetic field the separation quantum yield must decrease with the field strength B as it was obtained experimentally in refs 30 and 31. For the quantitative description of the magnetic field effect one should know not only the $k_0(B)$ dependence but the distribution of initial interion distances $f_0(r)$ as well. The latter should be used to find the true value of r_e or to average $\varphi(r_0)$ in a general way.

One need more information about reacting system to determine the shape of $f_0(r)$. In polar solutions it depends essentially on two factors which are the shape and location of the ionization layer given by $W_I(r)$ and the speed of diffusion. The latter prescribes the ionization to be either diffusional or kinetic. We may assume that

$$W_I(r) = W_i \exp[-2(r - \sigma)/L] \qquad (3.16)$$

when ionization is normal (at $|\Delta G_I| < \lambda$). Even in this case, which is the more favorable for contact creation of RIPS, $f_0(r) \propto W_I(r)$ is also exponential only in the fast diffusion limit when ionization is under kinetic control. In the limit of slow diffusion, the initial distribution of interion distances is neither exponential nor contactual but has the maximum shifted to ionization radius $R_s > \sigma$ (Figure 6a).[15] In Figure 6b the averaged yields $\bar{\varphi}$ calculated with these distributions (dashed lines) are compared with those, obtained for the contact start $\varphi(\sigma)$ (dashed−dotted lines). In the case of kinetic controlled ionization (K) they coincide practically everywhere. For diffusional ionization, (D)

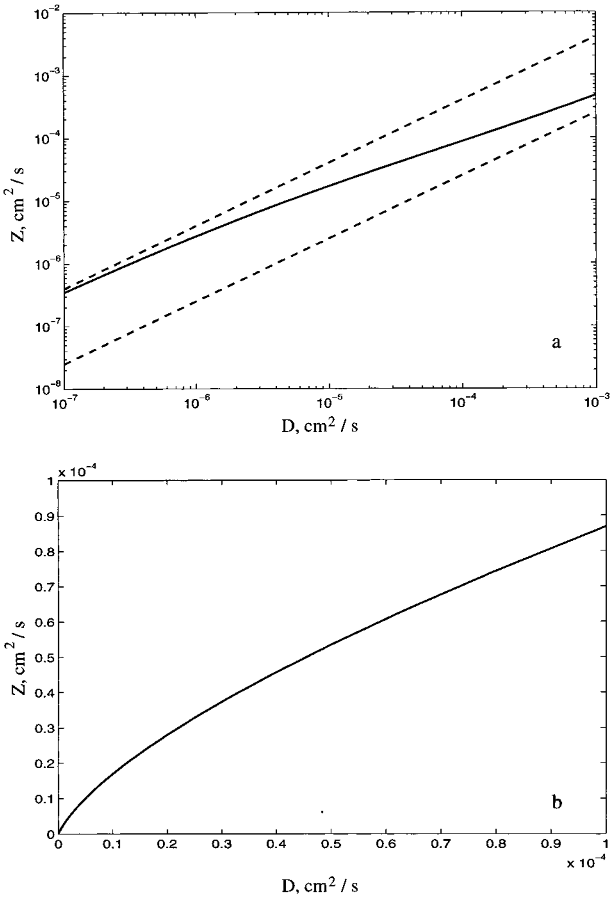


Figure 4. Diffusional dependence of $Z(r_e)$ in logarithmic (a) and usual (b) coordinates at $r_e = 15$ Å, $\sigma = 12$ Å, and $k_0 = 17.4$ ns^{-1}. Upper and lower dashed lines are linear asymptotics corresponding to the opposite limits of the fast and slow spin conversion ($4k_0\sigma^2 \gg \tilde{D}$ and $4k_0\sigma^2 \ll \tilde{D}$).

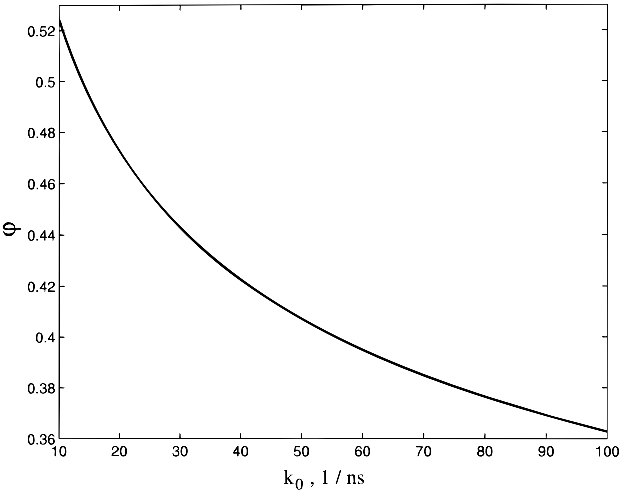


Figure 5. The drop in the averaged charge-separation quantum yield with the rate of spin conversion, accelerated by magnetic field. Parameters r_e and σ are the same as in Figure 4 while $D = 5 \times 10^{-5}$ cm^2/s.

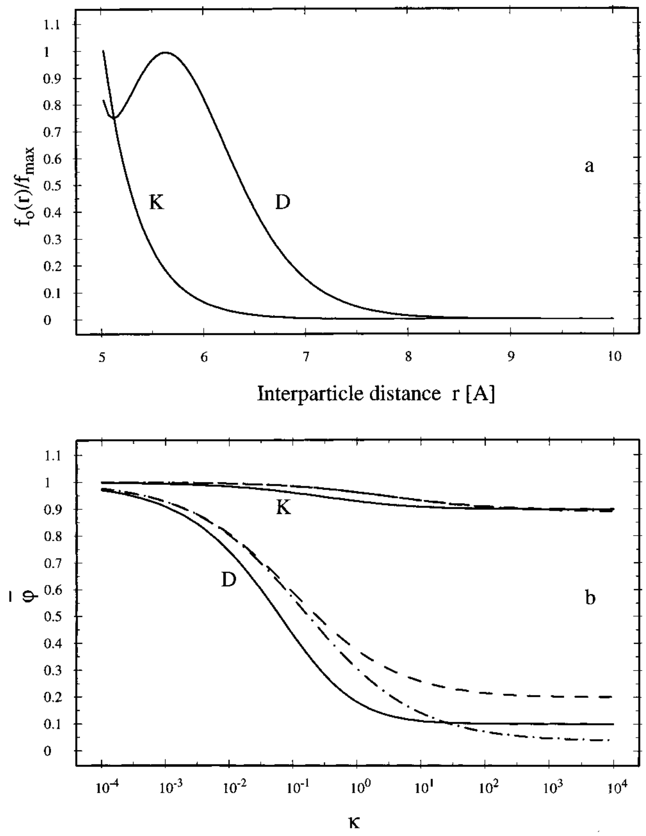


Figure 6. Distributions of initial interion distances (a) and quantum yields of their separation (b) in the case of kinetic ionization (K: $k_r = k_D/2$) and diffusional ionization (D: $k_r = 10^2 k_D$). Dashed−dotted lines: contact creation and contact recombination of RIPs. Dashed lines: contact recombination of RIPs with the given initial distribution of interparticle distances. Solid lines: remote recombination of RIPs with exponential $W_R(r) = W_I(r)$ and the same initial distributions ($D\ \tilde{D} = 10^{-6}$ cm^{2}s, while σ, $W_r = W_i$, and $L = l$ are the same as in Figure 2).

they are the same as long as the spin conversion is slow and takes effect after the difference of initial separations has been washed out by diffusion. At faster conversion the curves differ essentially. Even more essential is the difference between quantum yields calculated with the distant dependent rate of recombination $W_R(r)$ (solid lines) and obtained in the contact approximation. The latter is always higher if the initial distributions are the same, but the recombination of RIPs started from contact is stronger at fast spin conversion and their separation quantum yield is lower than it is in reality.

Such a high sensitivity to a small variation of initial interion distances is a consequence of a very sharp space dependence of the recombination rate $W_R(r)$ determined by electron tunneling. The origin of the effect is actually the same as in scanning tunneling microscopy. Therefore, the contact simplification of the theory is always a rough approximation. Though useful for a qualitative discrimination and semiquantitative description of diffusional and magnetic field effects, it should be replaced by a general theory of remote transfer when applied to any particular experimental data.

V. Discussion

Our last results obtained for the exponential rates of recombination and ionization, eqs 2.1 and 3.16, are related to so called NN case when both transfer processes occur in the normal region: $\Delta G_I \approx \Delta G_R < \lambda$ (see Figure 2 in ref 7). This case is only reliable if the energy of the excited triplet $\epsilon_0 < 2\lambda$. Otherwise one should discriminate between the NI case (normal ionization−inverted recombination) and the IN case (inverted ionization−normal recombination).[7,16] In the former case the spherical reaction layer for ionization is adjacent to the contact but for recombination it is remote, while in the latter case they exchange the positions. At $\epsilon_0 > 2\lambda$ there is also the place for the II case where both reaction layers are remote.[33]

The contact approximation used in sections III and IV is applicable only to the NN and IN cases, assuming that the recombination layer is not only contact but also narrow. If in addition the ionization is under kinetic control, then the initial RIPs distribution is contact and $\bar{\varphi} \approx \varphi(\sigma)$. On the contrary, for diffusional ionization the real averaging over initial separations of ions is inevitable and the shape of such a distribution is of great importance. An increase in the spin conversion rate facilitates recombination unless it is under kinetic control.

In practice the NN and IN cases compatible with the contact approximation of recombination are less common than the opposite NI or II cases. In these cases the radical-ions may be created deeply inside the remote recombination layer. When spin states of these radicals are ignored not their initial location plays the role but only the thickness of the recombination layer and the residence time in there.[8] This result should now be revised numerically or within the rectangular model of the reaction layer used in ref 8. When the spin conversion is necessary for recombination of ions crossing the reaction layer from inside, the number of singlet RIPs produced within the sphere depends on the time spent there.

The main restriction of the present approach is a commonly used assumption that the spin-conversion may be described as stochastic process with a given rate k_0.[9] However, in systems studied in refs 30 and 31 the spin−orbital interaction is so strong that one should consider the dynamical spin conversion assisted by molecular rotation instead of using k_0 estimated with a perturbation theory ("golden rule"). As far as we know such a study has been started already.[34] We also see no difficulties in generalizing the theory in such a way as was done in the contact approximation in refs 10 and 11.

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