J. Phys. Chem. A **2006,** *110,* 3364−3376

Double-Channel Contact Recombination of Radical Pairs Subjected to Spin Conversion via the Δg Mechanism

V. S. Gladkikh and A. I. Burshtein*

Weizmann Institute of Science, Rehovot 76100, Israel

Received: September 5, 2005; In Final Form: December 21, 2005

The contact recombination from both singlet and triplet states of a radical pair is studied assuming that the spin conversion is carried out by the fast transversal relaxation and Δg mechanism. The alternative HFI mechanism is neglected as being much weaker in rather large magnetic fields. The magnetic-field-dependent quantum yields of the singlet and triplet recombination products, as well as of the free radical production, are calculated for any initial spin state and arbitrary separation of radicals in a pair. The magnetic field effect is traced and its diffusional (viscosity) dependence is specified.

1. Introduction

The most general diffusional theory of contact but spinless geminate recombination of an ion pair was developed by Hong and Noolandi.[1] Later on, the theory was developed further in a few works[2,3] and extended for the noncontact recombination from any starting distance between reactants[4,5] (see also section VIIB in the review[6]).

However, as was recognized long ago, in pairs of radicals or ion radicals the recombination is affected by spin conversion between initially populated and other spin states. Such a conversion is carried out by the spin relaxation and/or some mechanisms acting in a magnetic field. These are the Δg mechanism of spin conversion in pairs of radicals having different g factors and the mechanism of the hyperfine interaction (HFI) between the electron and nuclear spins if any. The HFI mechanism alone was studied a number of times assuming that the radical recombination proceeds via a single channel (either singlet or triplet).[7] This is a situation typical for the radical pairs with such long spin relaxation times T_2 and T_1 that the corresponding rates $1/T_2$ and $1/T_1$ are negligible in comparison with a rather large HFI constant A. Just recently, HFI theory was extended for the double-channel recombination which proceeds into both singlet and triplet products though in a zero magnetic field.[8] Here, we are going to do quite the opposite: neglecting HFI in comparison with the fast transversal spin relaxation $1/T_2$, we will study the magnetic field effect (MFE) produced by the Δg mechanism of spin conversion. The spin relaxation really dominates over HFI in transition metal complexes with strong spin−orbital coupling.[9−11] The exact solution of this problem will be obtained analytically assuming that recombination from the singlet and triplet states of the radical pair proceeds only at contact, with the constants k_c^S and k_c^T, respectively. Provided $AT_2 \ll 1$ is really negligible, the theory is valid at arbitrary magnetic fields though it takes into account only the Δg mechanism of spin conversion.

The pair of radicals created in either of its singlet or triplet states can recombine from there in the singlet or triplet products or be separated with the quantum yield φ.

$$\varphi_t \qquad D + {}^3A^* \xleftarrow{k_c^T} {}^3[\dot{D} \ldots \dot{A}] \longrightarrow \dot{D} + \dot{A} \tag{1.1a}$$

$$T_2^{-1} \updownarrow \Omega \qquad\qquad \varphi$$

$$\varphi_s \qquad D + A \xleftarrow[k_c^S]{} {}^1[\dot{D} \ldots \dot{A}] \longrightarrow \dot{D} + \dot{A} \tag{1.1b}$$

Here, T_2 is the transversal relaxation time assumed to be the same in both radicals and

$$\Omega = \frac{1}{2\hbar} \Delta g \beta_0 H \tag{1.2}$$

Here, β_0 is the Bohr magneton, $\Delta g = g_+ - g_-$ where g_+ and g_- are g factors of radical ions in a pair and H is the external magnetic field.

Unlike the majority of our previous works reviewed in refs 6 and 12, here, we do not assume that $\Omega T_2 \ll 1$, allowing the spin conversion to be coherent in a large field. The best analytical solution of this problem valid at any Ω was obtained by Mints and Pukhov[13] but only for a single-channel recombination of a radical pair (RP)—just from its singlet state to the ground state of the product. Unfortunately, the authors did not present the evaluation of their results, and to generalize them for the double-channel recombination, we have to derive everything from the very beginning.

This goal will be reached with a method disclosed in the next section.

II. General Formalism

The density matrix of the radical pair depending on the inter-radical distance r and time t obeys the following evolution equation[15,16]

$$\frac{\partial \rho(r,t)}{\partial t} = \hat{L}\rho(r,t) + \hat{\mathcal{L}}\rho(r,t) - \hat{W}(r)\rho(r,t) \tag{2.1}$$

with a reflective boundary condition at the contact of radicals $r = \sigma$

$$\hat{J}\rho(r,t)|_{r=\sigma} = 0 \tag{2.2}$$

Here, $\hat{L}$ is the operator diagonal in the Liouville space which

---

* To whom correspondence should be addressed. E-mail: anatoly.burshtein@weizmann.ac.il.

10.1021/jp0550107 CCC: $33.50

describes the relative stochastic motion of the radicals, while $\hat{\jmath}$ is a flux operator. As to $\hat{\mathscr{L}}$, this is the Liouville operator which consists of the rates of the paramagnetic relaxation and the spin transitions induced by the magnetic field. The rate operator $\hat{W}(r)$ represents the radical recombination depending on the distance between the radicals, r. The recombination occurs from either the singlet or triplet state of the radical ion pair (RIP) or from both of them.

One can represent the Laplace transformation of the solution of eq 2.1 as

$$\tilde{\rho}(r,r_0,s) = \tilde{\hat{G}}_0(r,r_0,s)\rho_0 - \int \tilde{\hat{G}}_0(r,r',s)\hat{W}(r')\tilde{\rho}(r',r_0,s)\,\mathrm{d}^3r' \tag{2.3}$$

where $\rho_0 = \rho(r,r_0,0)$ and $\hat{G}_0(r,r_0,t)$ is the Green function obeying the following equation

$$\frac{\partial \hat{G}_0(r,r_0,t)}{\partial t} = \hat{L}\hat{G}_0(r,r_0,t) + \hat{\mathscr{L}}\hat{G}_0(r,r_0,t),$$
$$\hat{G}_0(r,r_0,0) = \frac{\delta(r - r_0)}{4\pi r^2}\hat{E} \tag{2.4}$$

where $\hat{E}$ is an identity operator. It is convenient to represent the operator Green function

$$\hat{G}_0(r,r_0,t) = \mathrm{e}^{\hat{\mathscr{L}}t}\phi(r,r_0,t) \tag{2.5}$$

via the scalar analogue $\phi(r,r_0,t)$, which obeys the conventional diffusional equation with evident initial and boundary conditions

$$\frac{\partial \phi(r,r_0,t)}{\partial t} = \hat{L}\phi(r,r_0,t),\ \phi(r,r_0,0) = \frac{\delta(r - r_0)}{4\pi r^2},\ \left.\frac{\partial \phi}{\partial r}\right|_{r=\sigma} = 0 \tag{2.6}$$

The sole restriction of the present theory is the assumption that the recombination takes place only at contact, that is, that the rate operator $\hat{W}(r)$ is

$$\hat{W}(r) = \hat{Q}\,\frac{\delta(r - \sigma)}{4\pi\sigma^2} \tag{2.7}$$

where $\hat{Q}$ depends only on the rate constants k_c^S and k_c^T. Substituting this expression into eq 2.3, we have

$$\tilde{\rho}(r,r_0,s) = \tilde{\hat{G}}_0(r,r_0,s)\rho_0 - \tilde{\hat{G}}_0(r,\sigma,s)\hat{Q}\tilde{\rho}(\sigma,r_0,s) \tag{2.8}$$

This is a closed expression for the contact density matrix, $\tilde{\rho}(\sigma,r_0,s)$. Resolving it we obtain

$$\tilde{\rho}(\sigma,r_0,s) = [\hat{E} + \tilde{\hat{G}}_0(\sigma,\sigma,s)\hat{Q}]^{-1}\tilde{\hat{G}}_0(\sigma,r_0,s)\rho_0 \tag{2.9}$$

This important result was obtained by Purtov and Doktorov[14] and efficiently used in a recent investigation of the spin conversion induced by the HFI mechanism.[8]

The quantum yields of the singlet and triplet products of geminate recombination are defined through the components of the matrix 2.9

$$\varphi_s(r_0) = k_c^S\tilde{\rho}_{SS}(\sigma,r_0,0) \tag{2.10}$$

$$\varphi_t(r_0) = k_c^T[\tilde{\rho}_{T_0T_0}(\sigma,r_0,0) + \tilde{\rho}_{T_-T_-}(\sigma,r_0,0) + \tilde{\rho}_{T_+T_+}(\sigma,r_0,0)] \tag{2.11}$$

In the Liouville space basis (ρ_{SS}, $\rho_{T_0T_0}$, $\mathscr{R}\rho_{ST0}$, $\mathscr{J}\rho_{ST0}$, $\rho_{T_-T_-}$, $\rho_{T_+T_+}$), chosen by Mints and Pukhov,[13] we have

$$\hat{\mathscr{L}} = \begin{pmatrix} -\left(\frac{1}{2T_1} + \frac{1}{T_2}\right) & \frac{1}{T_2} - \frac{1}{2T_1} & 0 & -2\Omega & \frac{1}{2T_1} & \frac{1}{2T_1} \\ \frac{1}{T_2} - \frac{1}{2T_1} & -\left(\frac{1}{2T_1} + \frac{1}{T_2}\right) & 0 & 2\Omega & \frac{1}{2T_1} & \frac{1}{2T_1} \\ 0 & 0 & -\frac{1}{T_1} & 0 & 0 & 0 \\ \Omega & -\Omega & 0 & -\frac{2}{T_2} & 0 & 0 \\ \frac{1}{2T_1} & \frac{1}{2T_1} & 0 & 0 & -\frac{1}{T_1} & 0 \\ \frac{1}{2T_1} & \frac{1}{2T_1} & 0 & 0 & 0 & -\frac{1}{T_1} \end{pmatrix} \tag{2.12}$$

where T_1 and T_2 are the longitudinal and transversal times of paramagnetic relaxation, while the mixing of the S and T_0 states occurs with a frequency Ω from eq 1.2. The recombination operator $\hat{Q}$ in the same basis takes the form

$$\hat{Q} = \begin{pmatrix} k_c^S & 0 & 0 & 0 & 0 & 0 \\ 0 & k_c^T & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{k_c^S + k_c^T}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{k_c^S + k_c^T}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & k_c^T & 0 \\ 0 & 0 & 0 & 0 & 0 & k_c^T \end{pmatrix} \tag{2.13}$$

By finding $\hat{G}_0(r,r_0,t)$ from eqs 2.5 and 2.6 and substituting its Laplace transformation into eq 2.9, one can solve this matrix equation using $\hat{Q}$ from eq 2.13. The elements of the matrix obtained determine not only the partial yields of the recombination products from eqs 2.10 and 2.11 but also the yield of the separated radicals which escape recombination and become free

$$\varphi(r_0) = 1 - \varphi_s(r_0) - \varphi_t(r_0) \tag{2.14}$$

We usually represent all the yields as follows[17,6]

$$\varphi = \frac{D}{D + Z}$$
$$\varphi_t = \frac{Z_t}{D + Z}$$
$$\varphi_s = \frac{Z_s}{D + Z} \tag{2.15}$$

where Z_s and Z_t are the efficiencies of recombination through the singlet and triplet channels, respectively, while

$$Z = Z_s + Z_t$$

is the total efficiency of geminate recombination.

III. Exact Solution of the Problem

In our previous article, we solved the double-channel problem of geminate recombination assuming that the spin conversion is incoherent which is the case at $\Omega T_2 \ll 1$.[18] This limitation was obviated by Mints and Pukhov,[13] who solved the problem exactly (i.e., generally, for coherent spin conversion) but for a single (singlet) recombination channel, when $Z_t = 0$ while $Z_s = Z \neq 0$. Here, we have to do the same but for the double-channel recombination when both Z_t and Z_s are not zero.

As the first step, one has to specify the exponent operator $e^{\hat{\mathcal{L}}t}$ in eq 2.5 that was found to be the following

$$e^{\hat{\mathcal{L}}t} = \begin{pmatrix} A_+ & A_- & 0 & -\sin(2\Omega t)e^{-2t/T_2} & B & B \\ A_- & A_+ & 0 & \sin(2\Omega t)e^{-2t/T_2} & B & B \\ 0 & 0 & e^{-t/T_1} & 0 & 0 & 0 \\ \frac{\sin(2\Omega t)}{2}e^{-2t/T_2} & -\frac{\sin(2\Omega t)}{2}e^{-2t/T_2} & 0 & \cos(2\Omega t)e^{-2t/T_2} & 0 & 0 \\ B & B & 0 & 0 & C_+ & C_- \\ B & B & 0 & 0 & C_- & C_+ \end{pmatrix} \tag{3.1}$$

where

$$A_\pm = \frac{1}{4} + \frac{1}{4}e^{-2t/T_1} \pm \frac{\cos(2\Omega t)}{2}e^{-2t/T_2}$$

$$B = \frac{1}{4} - \frac{1}{4}e^{-2t/T_1}$$

$$C_\pm = \frac{1}{4} + \frac{1}{4}e^{-2t/T_1} \pm \frac{1}{2}e^{-t/T_1}$$

In the particular case $T_2 \ll T_1 = \infty$, we have $B = C_\pm = 0$ and the rank of the problem reduces to 4×4 and becomes formally identical to the case of spin conversion via the HFI mechanism at the highest fields,[19] provided the exchange splitting of the singlet and triplet is negligible. For the particular case of incoherent spin conversion, the same problem was solved recently in refs 20 and 21.

Solving eq 2.6 and using the result in eq 2.5, we calculated exactly the Laplace transformation of the Green operator

$$\tilde{\hat{G}}_0(\sigma,r_0,0) = \begin{pmatrix} \frac{F}{4}+\frac{P_2}{4}+\frac{Q_1}{4} & \frac{F}{4}+\frac{P_2}{4}-\frac{Q_1}{4} & 0 & -\frac{Q_2}{2} & \frac{F}{4}-\frac{P_2}{4} & \frac{F}{4}-\frac{P_2}{4} \\ \frac{F}{4}+\frac{P_2}{4}-\frac{Q_1}{4} & \frac{F}{4}+\frac{P_2}{4}+\frac{Q_1}{4} & 0 & \frac{Q_2}{2} & \frac{F}{4}-\frac{P_2}{4} & \frac{F}{4}-\frac{P_2}{4} \\ 0 & 0 & P_1 & 0 & 0 & 0 \\ \frac{Q_2}{4} & -\frac{Q_2}{4} & 0 & \frac{Q_1}{2} & 0 & 0 \\ \frac{F}{4}-\frac{P_2}{4} & \frac{F}{4}-\frac{P_2}{4} & 0 & 0 & \frac{F}{4}+\frac{P_2}{4}+\frac{P_1}{2} & \frac{F}{4}+\frac{P_2}{4}-\frac{P_1}{2} \\ \frac{F}{4}-\frac{P_2}{4} & \frac{F}{4}-\frac{P_2}{4} & 0 & 0 & \frac{F}{4}+\frac{P_2}{4}-\frac{P_1}{2} & \frac{F}{4}+\frac{P_2}{4}+\frac{P_1}{2} \end{pmatrix} \tag{3.2}$$

where

$$F = \tilde{\phi}(\sigma,r_0,0)$$

$$P_n = \tilde{\phi}(\sigma,r_0,n/T_1) \quad n = 1, 2 \tag{3.3}$$

and

$$Q_1 = 2\int_0^\infty e^{-2t/T_2}\cos(2\Omega t)\phi(\sigma,r_0,t)\,dt$$

$$Q_2 = 2\int_0^\infty e^{-2t/T_2}\sin(2\Omega t)\phi(\sigma,r_0,t)\,dt \tag{3.4}$$

IV. Highly Polar Solvents

In solvents with a large dielectric constant ϵ, one can neglect the Coulombic interactions between the counterions, setting the Onsager radius $r_c = 0$. For this particular case, $\tilde{\phi}(\sigma,r_0,s)$ is known to be

$$\tilde{\phi}(\sigma,r_0,s) = \frac{1}{4\pi r_0 D}\frac{\exp\{-(r_0-\sigma)\sqrt{s/D}\}}{1+\sigma\sqrt{s/D}} \tag{4.1}$$

so that the expressions in eq 3.3 become

$$F = \frac{1}{4\pi r_0 D}$$

$$P_n = \frac{\sigma}{r_0}\frac{e^{(1-r_0/\sigma)\sqrt{(n\tau_d/T_1)}}}{k_D(1+\sqrt{n\tau_d/T_1})} \quad n = 1, 2 \tag{4.2}$$

where $k_D = 4\pi\sigma D$ is the diffusional rate constant, while $\tau_d = \sigma^2/D$ is the so-called encounter time.

Taking the integrals in eq 3.4, one finds that the results can be expressed via $\tilde{\phi}(\sigma,r_0,s)$ given in eq 4.1. Using the latter, we obtain for highly polar solvents

$$Q_1 = \frac{2\sigma e^{(1-r_0/\sigma)\alpha_R}}{k_D r_0}\frac{(1+\alpha_R)\cos[\alpha_I(r_0/\sigma-1)] - \alpha_I\sin[\alpha_I(r_0/\sigma-1)]}{(1+\alpha_R)^2+\alpha_I^2} \tag{4.3a}$$

$$Q_2 = \frac{2\sigma e^{(1-r_0/\sigma)\alpha_R}}{k_D r_0}\frac{(1+\alpha_R)\sin[\alpha_I(r_0/\sigma-1)] + \alpha_I\cos[\alpha_I(r_0/\sigma-1)]}{(1+\alpha_R)^2+\alpha_I^2} \tag{4.3b}$$

where

$$\alpha_R = \sqrt{\frac{\tau_d}{T_2}}\sqrt{\sqrt{\Omega^2 {T_2}^2+1}+1}$$

$$\alpha_I = \sqrt{\frac{\tau_d}{T_2}}\sqrt{\sqrt{\Omega^2 {T_2}^2+1}-1} \tag{4.4}$$

are the most important parameters responsible for the spin conversion due to transversal relaxation ($1/T_2$) and field-induced coherent transitions with a frequency Ω.

In the limit of the low field, $\Omega^2 T_2^2 \ll 1$, the expressions in eq 4.4 reduce to the following

$$\text{At } \Omega \to 0$$

$$\alpha_R \to \sqrt{\frac{2\tau_d}{T_2}} = \gamma \quad \alpha_I \to 0 \tag{4.5}$$

Most of the experimental works studying electron-transfer reactions by optical and electrochemical methods are performed in the natural magnetic field of the Earth which is rather low. This is why this particular case is of exceptional importance.

V. Recombination only through the Singlet Channel

To illustrate the general theory, let us start from the simplest example of the triplet RIP irreversibly created by electron transfer from a triplet precursor.[9−11] Such a triplet RIP has to recombine through the singlet channel to the ground state because recombination from this triplet state is prohibited, $k_c^T = 0$, that is

$$Z_t = 0, \quad Z \equiv Z_s \tag{5.1}$$

Cumbersome but straightforward calculations show that the result depends on what spin level of a pair was initially populated. If this is S, T_0, or $T_\pm$, then

$$
{}^{\mathrm{S}}\varphi_{\mathrm{s}} = \frac{{}^{\mathrm{S}}Z_{\mathrm{s}}}{D + {}^{\mathrm{S}}Z_{\mathrm{s}}}
$$

$$
{}^{\mathrm{T}_0}\varphi_{\mathrm{s}} = \frac{{}^{\mathrm{T}_0}Z_{\mathrm{s}}}{D + {}^{\mathrm{T}_0}Z_{\mathrm{s}}}
$$

$$
{}^{\mathrm{T}_\pm}\varphi_{\mathrm{s}} = \frac{{}^{\mathrm{T}_\pm}Z_{\mathrm{s}}}{D + {}^{\mathrm{T}_\pm}Z_{\mathrm{s}}} \tag{5.2}
$$

where the corresponding recombination efficiencies are

$$
\frac{{}^{\mathrm{S}}Z_{\mathrm{s}}}{D} = \frac{k_{\mathrm{c}}^{\mathrm{S}}((4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(F + P_2 + Q_1) + k_{\mathrm{c}}^{\mathrm{S}}q_2Q_2)}{16 + k_{\mathrm{c}}^{\mathrm{S}}((4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(f - F + p_2 - P_2 + q_1 - Q_1) + 4q_1 + k_{\mathrm{c}}^{\mathrm{S}}q_2(q_2 - Q_2))} \tag{5.3}
$$

$$
\frac{{}^{\mathrm{T}_0}Z_{\mathrm{s}}}{D} = \frac{k_{\mathrm{c}}^{\mathrm{S}}((4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(F + P_2 - Q_1) - k_{\mathrm{c}}^{\mathrm{S}}q_2Q_2)}{16 + k_{\mathrm{c}}^{\mathrm{S}}((4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(f - F + p_2 - P_2 + q_1 + Q_1) + 4q_1 + k_{\mathrm{c}}^{\mathrm{S}}q_2(q_2 + Q_2))} \tag{5.4}
$$

$$
\frac{{}^{\mathrm{T}_\pm}Z_{\mathrm{s}}}{D} = \frac{k_{\mathrm{c}}^{\mathrm{S}}(4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(F - P_2)}{(4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(4 + k_{\mathrm{c}}^{\mathrm{S}}(f - F + p_2 + P_2 + q_1)) + (k_{\mathrm{c}}^{\mathrm{S}}q_2)^2} \tag{5.5}
$$

where

$$
p_2 = P_2(r_0 = \sigma)
$$

$$
q_{\mathrm{i}} = Q_{\mathrm{i}}(r_0 = \sigma)
$$

$$
f = F(r_0 = \sigma) = 1/k_{\mathrm{D}}
$$

are the contact values of the corresponding r_0-dependent quantities. For the particular case of contact start ($r_0 = \sigma$), all these results are identical to those obtained earlier by Mints and Pukhov.[13]

However, the most reasonable situation, presumed in the majority of earlier works, is the start from the equilibrated triplet state (T-pair) whose sublevels, T_0, T_+, T_-, are equally populated with the weights ($^1/_3$,$^1/_3$,$^1/_3$).

Summing the above efficiencies with these weights, we obtain for this case

$$
{}^{\mathrm{T}}\varphi_{\mathrm{s}} = \frac{1}{3}\,{}^{\mathrm{T}_0}\varphi_{\mathrm{s}} + \frac{2}{3}\,{}^{\mathrm{T}_\pm}\varphi_{\mathrm{s}} = \frac{{}^{\mathrm{T}}Z_{\mathrm{s}}}{D + {}^{\mathrm{T}}Z_{\mathrm{s}}} \tag{5.6}
$$

where

$$
\frac{{}^{\mathrm{T}}Z_{\mathrm{s}}}{D} = \frac{k_{\mathrm{c}}^{\mathrm{S}}[(4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(3F - P_2 - Q_1) - k_{\mathrm{c}}^{\mathrm{S}}q_2Q_2]}{48 + k_{\mathrm{c}}^{\mathrm{S}}[(4 + k_{\mathrm{c}}^{\mathrm{S}}q_1)(3f - 3F + 3p_2 + P_2 + 3q_1 + Q_1) + 12q_1 + k_{\mathrm{c}}^{\mathrm{S}}q_2(3q_2 + Q_2)]} \tag{5.7}
$$

is the efficiency of a singlet recombination from the initially equilibrated triplet indicated as T.

A. Recombination of a Contact Born Pair. At contact start, $r_0 = \sigma$ and therefore it follows from eqs 4.3 and 4.2 that

$$
Q_1 = \frac{2}{k_{\mathrm{D}}}\frac{1 + \alpha_{\mathrm{R}}}{(1 + \alpha_{\mathrm{R}})^2 + \alpha_{\mathrm{I}}^2} = q_1 \tag{5.8a}
$$

$$
Q_2 = \frac{2}{k_{\mathrm{D}}}\frac{\alpha_{\mathrm{I}}}{(1 + \alpha_{\mathrm{R}})^2 + \alpha_{\mathrm{I}}^2} = q_2 \tag{5.8b}
$$

$$
P_2 = \frac{1}{k_{\mathrm{D}}(1 + \beta)} = p_2 \tag{5.8c}
$$

while α_{R} and α_{I} are defined in eq 4.4 and

$$
\beta = \sqrt{\frac{2\tau_{\mathrm{d}}}{T_1}} \tag{5.9}
$$

1. Recombination of the S-Pair. Using the results in eq 5.3, we obtain from there the recombination efficiency of the contact born radical pair initially created in the singlet state (S-pair)

$$
\frac{{}^{\mathrm{S}}Z_{\mathrm{s}}}{D} = \frac{k_{\mathrm{c}}^{\mathrm{S}}}{16 + 4k_{\mathrm{c}}^{\mathrm{S}}q_1}\left[\frac{4 + k_{\mathrm{c}}^{\mathrm{S}}q_1}{k_{\mathrm{D}}}\left(\frac{2 + \beta}{1 + \beta} + k_{\mathrm{D}}q_1\right) + k_{\mathrm{c}}^{\mathrm{S}}{q_2}^2\right] \tag{5.10}
$$

Such a complex result expressed via $q_{\mathrm{i}}(\alpha_{\mathrm{R}},\alpha_{\mathrm{I}})$ from eq 5.8 is identical to that found by Mints and Pukhov.[13] Fortunately, it can be represented in a much more simple and transparent form found in ref 20

$$
\frac{{}^{\mathrm{S}}Z_{\mathrm{s}}}{D} = \frac{k_{\mathrm{c}}^{\mathrm{S}}}{2k_{\mathrm{D}}}\left[\frac{\alpha + 2}{\alpha + 1} - \frac{\beta}{2(\beta + 1)}\right] \tag{5.11}
$$

where

$$
\alpha = \alpha_{\mathrm{R}} + \frac{{\alpha_{\mathrm{I}}}^2}{1 + \alpha_{\mathrm{R}} + k_{\mathrm{c}}^{\mathrm{S}}/2k_{\mathrm{D}}} \tag{5.12}
$$

is the only conversion-dependent parameter.

2. Recombination of the T-Pair. The same simplification is presented here for the efficiency of the singlet recombination from the equilibrated triplet state

$$
{}^{\mathrm{T}}Z_{\mathrm{s}}/D = \frac{k_{\mathrm{c}}^{\mathrm{S}}}{2k_{\mathrm{D}}}\,\frac{2\alpha + \beta(1 + 3\alpha)}{2\left[3(1 + \beta)(1 + \alpha) + (3 + 2\beta + \alpha)\dfrac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}}}\right]} \tag{5.13}
$$

In the limits of kinetic and diffusional recombination, it takes the alternative forms

$$
{}^{\mathrm{T}}Z_{\mathrm{s}}/D = \begin{cases} \dfrac{k_{\mathrm{c}}^{\mathrm{S}}}{2k_{\mathrm{D}}}\left[\dfrac{\alpha}{3(1 + \alpha)} + \dfrac{\beta}{6(1 + \beta)}\right] & \text{at } \dfrac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}}} \ll 1 \text{ kinetic} \\ \dfrac{2\alpha + \beta(1 + 3\alpha)}{4(3 + 2\beta + \alpha)} & \text{at } \dfrac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}}} \gg 1 \text{ kinetic} \end{cases} \tag{5.14}
$$

It must be noted that the general relationship between ${}^{\mathrm{S}}\varphi_{\mathrm{s}}$ and ${}^{\mathrm{T}}\varphi_{\mathrm{s}}$ reported in section 3.2.1 of ref 7 holds true. The product yields of the S-pair and T-pair recombination relate to each other as follows

$$
{}^{\mathrm{S}}\varphi_{\mathrm{s}} = \lambda - 3(1 - \lambda){}^{\mathrm{T}}\varphi_{\mathrm{s}}, \quad \text{where } \lambda = \frac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}} + k_{\mathrm{c}}^{\mathrm{S}}}
$$

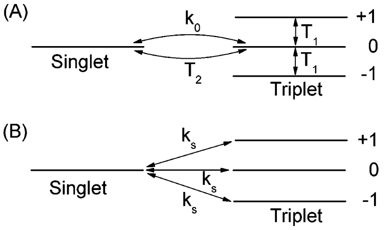

Figure 1. Scheme of spin transitions in the radical pair induced by transversal and longitudinal relaxation as well as by a Δg mechanism of incoherent spin conversion (A) and the elementary spin model of the same at equal relaxation times (B).

It is the straightforward consequence of the detailed balance principle and can be easily verified here using ${}^{S}\varphi_s$ from eq 5.2 and ${}^{T}\varphi_s$ from eq 5.6.

VI. Incoherent Spin-Conversion

In a rather low field (at $\Omega T_2 \ll 1$)

$$\alpha_R \approx \sqrt{\frac{2\tau_d}{T_2}\left(1+\frac{\Omega^2 T_2^{\,2}}{4}\right)} \qquad \alpha_I \approx \Omega\sqrt{\tau_d T_2/2} \tag{6.1}$$

Obviously that in such a case the conversion proceeds with the rate $\Omega^2 T_2$ which is a parameter of the incoherent process. Using the results of eq 6.1 in the formulas in eq 5.12, we obtain the value of α for the incoherent spin conversion

$$\alpha = \sqrt{\frac{2\tau_d}{T_2}\left(1+\frac{\Omega^2 T_2^{\,2}}{4}\right)} + \frac{1}{2}\frac{\Omega^2 \tau_d T_2}{1+\frac{k_c^S}{2k_D}+\sqrt{\frac{2\tau_d}{T_2}\left(1+\frac{\Omega^2 T_2^{\,2}}{4}\right)}} \tag{6.2}$$

This parameter depends on recombination only through the ratio $k_c^S/2k_D$, that is, small in the kinetic limit and large in the diffusional one. Correspondingly, we obtain in these limits

$$\alpha = \begin{cases} \sqrt{\frac{2\tau_d}{T_2}\left(1+\frac{3\Omega^2 T_2^{\,2}}{4}\right)} & \text{at } \frac{k_c^S}{2k_D} \le 1 \ll \sqrt{\frac{\tau_d}{T_2}} \\ \sqrt{\frac{2\tau_d}{T_2}\left(1+\frac{\Omega^2 T_2^{\,2}}{4}\right)} & \text{at } \frac{k_c^S}{2k_D} \gg 1, \sqrt{\frac{\tau_d}{T_2}} \end{cases} \tag{6.3}$$

These are exactly the same results that were found in appendix B of ref 20.

In the case of a low field

$$\alpha = \gamma = \sigma\sqrt{\frac{2}{DT_2}} \qquad \Omega^2 T_2^{\,2} \ll 1 \tag{6.4}$$

depends on a single variable parameter, encounter diffusion, changing with viscosity.

A. Rate Models. In a number of our and other works, the spin conversion was presumed to be incoherent and was considered from the beginning as a stochastic process occurring with some rate, k_0.[6,9,12,22−25] In general, when the nonreacting radical pair is immobile, its density matrix obeys the equation following from eq 2.1

$$\dot{\rho} = \hat{\mathscr{L}}\rho \tag{6.5}$$

However, under the condition of incoherent conversion, $\Omega T_2 \ll 1$, the latter can be conventionally reduced to a set of four master equations for only diagonal elements of the density matrix, that is, populations of a singlet level, $\rho_S \equiv p_S$, and three sublevels of the triplet state, ρ_-, ρ_0, and ρ_+ (see Figure 1A)[12,20]

$$\dot{\rho}_S = \left(k_0+\frac{1}{T_2}-\frac{1}{2T_1}\right)\rho_0 - \left(k_0+\frac{1}{T_2}-\frac{1}{2T_1}\right)\rho_S + \frac{\rho_+ + \rho_-}{2T_1} \tag{6.6a}$$

$$\dot{\rho}_0 = \left(k_0+\frac{1}{T_2}-\frac{1}{2T_1}\right)\rho_S - \left(k_0+\frac{1}{T_2}+\frac{1}{2T_1}\right)\rho_0 + \frac{\rho_+ + \rho_-}{2T_1} \tag{6.6b}$$

$$\dot{\rho}_+ = \frac{\rho_+ + \rho_-}{2T_1} - \frac{\rho_+}{T_1}$$

and

$$\dot{\rho}_- = \frac{\rho_+ + \rho_0}{2T_1} - \frac{\rho_-}{T_1} \tag{6.6c}$$

Here

$$k_0 = \Omega^2 T_2 \tag{6.7}$$

is the rate of incoherent spin conversion in a stable radical pair proceeding via a Δg mechanism.

1. Two-Level Model. For the extreme case $T_1 = \infty$ ($\beta = 0$), only two levels out of four are involved in the spin conversion and the set (eq 6.6) is reduced to the following

$$\dot{\rho}_S = k_s(\rho_0 - \rho_S) \tag{6.8a}$$

$$\dot{\rho}_0 = k_s(\rho_S - \rho_0) \tag{6.8b}$$

while $\rho_+(t) = \rho_+(0)$, $\rho_-(t) = \rho_-(0)$ and

$$k_s = k_0 + \frac{1}{T_2} \tag{6.9}$$

The single-channel contact recombination assisted by the incoherent spin conversion in the two-level system was the subject of a separate exhaustive investigation in ref 20.

The comparison of the incoherent and coherent spin conversion assisting a single-channel contact recombination in a two-level system was continued in ref 21. It was confined only to the RIP starting from contact ($r_0 = \sigma$) when all the results are much simpler. If, in addition, $\beta = 0$, then the recombination efficiencies in eqs 5.11 and 5.13 gain the following form

$$ {}^{S}Z_s = \frac{z_s}{2}\left[\frac{\alpha+2}{\alpha+1}\right]$$

$$ {}^{T}Z_s = \frac{z_s}{2}\frac{\alpha}{3(1+\alpha)+(3+\alpha)\frac{z_s}{D}} \tag{6.10}$$

Here, $z_s = k_c^S/4\pi\sigma$ is the usual constant of the conventional (spinless) "exponential model".[12,6] Exactly the same result has been obtained in ref 20 solving the rate equations for the two-level problem, eq 6.8, except that

$$\alpha = \sqrt{2\frac{\tau_d}{T_2}(1 + \Omega^2 T_2^{\,2})} \qquad (6.11)$$

does not depend on k_c^S at all, unlike its coherent analogue 6.2. Moreover, α from eq 6.11 does not coincide with either of the expressions in eq 6.3.

This is because the rate eqs 6.6 were obtained from their coherent analogue, eq 6.5, when the motion of radicals was switched off, together with the boundary conditions accounting for the recombination. When the motion of radicals is accounted for afterward, their recombination is affected by the spin conversion but the recombination itself no longer affects the spin conversion. This is a main weakness of rate theories first reducing the coherent spin conversion to incoherent and only then accounting for the encounter diffusion and recombination of radicals. Here, in section III, we did quite the opposite: we first solved the problem by simultaneously taking into account the relative motion and conversion and only then turned to the particular case (eq 6.1) where the latter is incoherent. Therefore, our α for coherent spin conversion is given by eq 5.12 and for the incoherent limit by eq 6.2, but the rate estimate (eq 6.11) does not follow from either of them.[20]

However, there is an exceptional case of zero field ($\Omega = 0$) when the transfer is carried out by only spin relaxation. This stochastic process, incoherent by its nature, is executed with the rate $k_s = 1/T_2$. Hence, the results (eq 6.10) with $\alpha = \gamma$ are exact for the zero field.

According to eq 6.4, γ increases with viscosity. On the other hand, the ratio ${}^SZ_s/z_s$ monotonically decreases with $(1/D)^{1/2}$ from 1 to $^1/_2$ (upper dashed line in Figure 2(A) At fast diffusion, the spin conversion does not have time to affect the recombination and ${}^SZ_s/z_s = 1$. On the contrary, for small values of D, the equipartition between S and T_0 is completed during the encounter time, reducing the recombination efficiency by one-half.

As for ${}^TZ_s$, it is zero at fast and slow diffusion passing through a maximum between (lower dashed line in Figure 2A). At fast diffusion, it is zero because no transition from T_0 to the reacting S state occurs before separation of the radicals. On the contrary, at slow diffusion, the encounter time is long enough for transfer to be completed

$$\left.\frac{{}^TZ_s}{D}\right|_{D\ll z_s} = \frac{1}{2}\,\frac{\alpha}{3+\alpha} \to \frac{1}{2} \quad \text{at } \alpha \gg 1$$

so that

$$\lim_{D\to 0} {}^T\varphi_s = \frac{{}^TZ_s/D}{1 + {}^TZ_s/D} = \frac{1}{3} \qquad (6.12)$$

After T_0 is completely exhausted, the share of triplets that have reacted is only $^1/_3$ of the initial triplet population. The remaining $^2/_3$ that were in the other triplet states, $T_\pm$, were not involved in the reaction.

A similar picture develops when the system recombines only through the triplet channel except that ${}^SZ$ and ${}^TZ$ are interchanged (dashed lines in Figure 2B). The former passes through a maximum, while the latter monotonically decreases to another value, $^3/_4$, which needs a special explanation. In fact, the efficiency of recombination from T_0 reduces by one-half when $D \to 0$ while that from $T_\pm$ remains $z_t = k_c^T/4\pi\sigma$ at any D value. Therefore, eq 5.6 at slow D takes the following form

$${}^T\varphi_t = \frac{1}{3}\,\frac{z_t/2}{D + z_t/2} + \frac{2}{3}\,\frac{z_t}{D + z_t} = \frac{{}^TZ_t}{D + {}^TZ_t} \qquad (6.13)$$

where

$$\text{At } D \to 0$$

$${}^TZ_t = \frac{5z_tD + 3z_t^{\,2}}{6D + 4z_t} \to \frac{3}{4}z_t$$

This is the very same limit for ${}^TZ_t$ as in the case $T_1 = T_2$ considered below and represented by solid lines in Figure 2.

2. Equal Spin Relaxation Times. If T_1 is finite, then all four states in eq 6.6 are involved in the reaction but the result (eq 5.11) first obtained for the incoherent spin conversion in ref 18 holds true provided that the parameter α is given by the expression 6.11. For the particular case of equal times

$$\alpha = \gamma\sqrt{(1 + k_0T)} \qquad (6.14)$$

where $T = T_1 = T_2$

$$\gamma = \sqrt{2\tau_d/T} = \sqrt{x/D}$$

and

$$x = 2\sigma^2/T \qquad (6.15)$$

In this case, it follows from eq 5.11 that

$$\frac{{}^SZ_s}{D} = \frac{k_c^S}{2k_D}\left[\frac{\gamma\sqrt{1 + k_0T} + 2}{\gamma\sqrt{1 + k_0T} + 1} - \frac{\gamma}{2(\gamma + 1)}\right] \qquad (6.16)$$

Similarly, from eq 5.13, one gets

$$\frac{{}^TZ_s}{D} = \frac{k_c^S}{4k_D} \times \frac{\gamma[1 + (2 + 3\gamma)\sqrt{1 + k_0T}]}{3(1 + \gamma)(1 + \gamma\sqrt{1 + k_0T}) + (3 + 2\gamma + \gamma\sqrt{1 + k_0T})\dfrac{k_c^S}{k_D}} \qquad (6.17)$$

When the magnetic field is zero ($k_0 = \Omega = 0$), we obtain from eqs 6.16 and 6.17

$${}^SZ_s = \frac{z_s}{4}\,\frac{\gamma + 4}{\gamma + 1}$$

$${}^TZ_s = \frac{z_s}{4}\,\frac{\gamma}{1 + \gamma + \dfrac{k_c^S}{k_D}} \qquad (6.18)$$

At very fast diffusion when $\tau_d = \sigma^2/D \to 0$, the spin conversion has no time to occur and $\gamma = 0$. In this limit, ${}^SZ_s$ reaches its maximal value, z_s, which is the efficiency of the singlet recombination in the absence of the spin conversion. As soon as the spin conversion is switched on, ${}^SZ_s$ falls down with decreasing diffusion and reaches the minimal value $z_s/4$ at $D = 0$. In this limit, all spin states are equally populated and the share of the singlet one is $^1/_4$.

Although the diffusional dependence of the singlet recombination from the equilibrated triplet state (the lower solid line

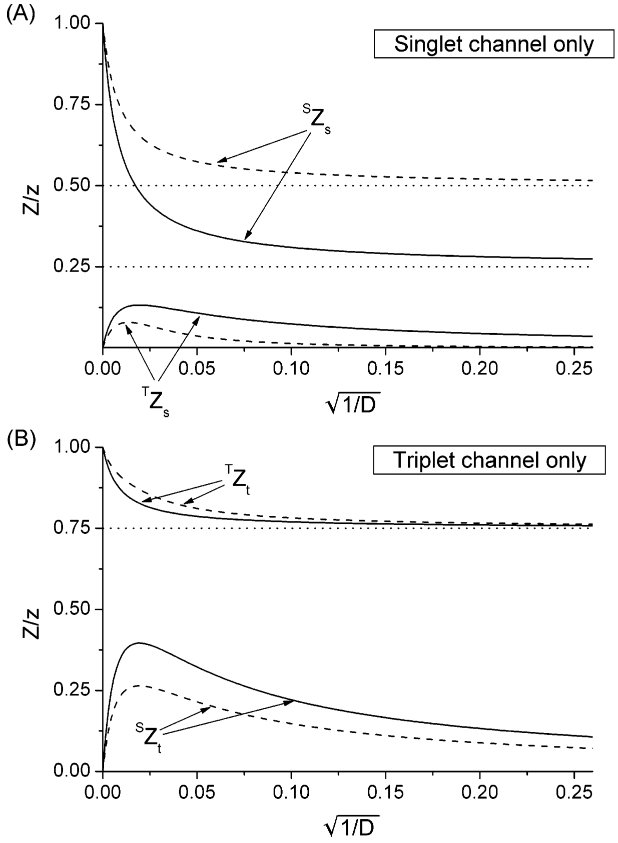

Figure 2. Zero field recombination efficiencies for a single-channel recombination through either singlet (A) or triplet (B) channels (z_s and z_t were taken equal, $z = 2.63 \times 10^{-4}$ cm^2/s). Dashed and solid lines relate to the cases $T_1 = \infty$ and $T_1 = T_2 = 15$ ps, respectively. The upper curves in (A) and (B) are for the efficiencies of allowed recombination from initially populated states, while the lower ones are for the recombination initially forbidden but switched on by spin conversion to the reacting state. The contact distance is $\sigma = 10$ Å everywhere.

in Figure 2A) is qualitatively the same as for the two-level model, the result appearing in the slow diffusion limit is different

$$\lim_{D\to 0} {}^{T}Z_s = \frac{z_s}{4}$$

so that

$$\lim_{D\to 0} {}^{T}\varphi_s = \frac{z_s/4D}{1 + z_s/4D} = 1 \qquad (6.19)$$

In contrast to eq 6.12, in this case, the whole triplet is completely exhausted due to the longitudinal relaxation between its sublevels (see Figure 1A) which is as fast as the transversal one.

B. Elementary Spin Model (ESM). The simplest, but most widely used and rather successful, rate model follows from the set (eq 6.6) phenomenologically reduced to only two equations at $T_1 = T_2 = T$. These equations relate to each other the population of the singlet, $m_S \equiv \rho_S$, and the total population of the triplet, $m_T = \rho_0 + \rho_+ + \rho_-$. How these equations were obtained one can see in section VIIIA of ref 12. For the case of equal relaxation times, we have

$$\dot{m}_S = -3k_s m_S + k_s m_T \qquad (6.20a)$$

$$\dot{m}_T = 3k_s m_S - k_s m_T \qquad (6.20b)$$

with a microscopically defined spin conversion rate

$$k_s = \frac{1}{2T} + \frac{\Omega^2 T}{3} \qquad (6.21)$$

As seen from Figure 1B, the conversion rate is $3k_s$ for the transition from singlet to triplet, while from any triplet substate as well as from all of them this is only k_s. Due to the spin conversion, the population of the singlet and triplet at $t \gg k_s^{-1}$ relate to each other as $^1/_4$:$^3/_4$, whatever was the initial state.

The elementary spin model (ESM) used in ref 17 enables us to calculate the efficiency of singlet-channel recombination from the singlet

$${}^{S}Z_s = \frac{z_s}{4}\frac{\alpha + 4}{\alpha + 1} \qquad (6.22)$$

Being very similar to the double-level expression for $^{S}Z_s$ in eq 6.10, it is distinguished by

$$\alpha = \sqrt{4k_s\tau_d} = \sqrt{\frac{2\tau_d}{T}\left(1 + \frac{2\Omega^2T^2}{3}\right)} \qquad (6.23)$$

The latter differs noticeably from eq 6.11 in the weight of Ω^2. Although in this respect the α values from eqs 6.2 and 6.3 are also different at $\Omega = 0$ all of them turn to γ.

VII. Double-Channel Recombination after Contact Start

Let us now turn to the most general case when recombination is possible from either the singlet or triplet state of the pair. The triplet products are excited triplet molecules whose yield can be detected spectroscopically immediately after geminate recombination. Both triplet and singlet yields depend on the initial state of the pair given by $\hat{\rho}_0$. Using the corresponding ρ_0 in eq 2.9 as well as the general $\hat{Q}$ from eq 2.13 and $\hat{G}_0$ from eq 3.2, with parameters from eq 5.8, we calculated from eqs 2.10 and 2.11 the yields $\varphi_s(\sigma)$ and $\varphi_t(\sigma)$. Only from them can one obtain the recombination efficiencies defined in eq 2.15: Z_s, Z_t, and $Z = Z_s + Z_t$, which are discussed below.

A. Start from the Singlet State. If initially only the singlet state is populated, then the efficiency of recombination through the singlet channel is

$${}^{S}Z_s/D = \frac{k_c^S}{2k_D}\left[\frac{\alpha + 2(1 + k_c^T/k_D)}{\alpha + 1 + k_c^T/k_D} - \frac{\beta}{2(\beta + 1 + k_c^T/k_D)}\right] \qquad (7.1)$$

and that for the triplet channel is

$${}^{S}Z_t/D = \frac{k_c^T}{2k_D}\left[\frac{\alpha}{1 + \alpha + k_c^T/k_D} + \frac{\beta}{2(1 + \beta + k_c^T/k_D)}\right] \qquad (7.2)$$

At $k_c^T = 0$, eq 7.1 reduces to eq 5.11 for $^{S}Z_s = {}^{S}Z$, while $^{S}Z_t$ becomes zero as in eq 5.1.

B. Start from the Individual Sublevels of the Triplet State. If initially one populates only the T_0 state, then the results are different

$${}^{T_0}Z_s/D = \frac{k_c^S}{2k_D(1 + \alpha + k_c^S/k_D)}\left[\alpha - \frac{\beta(1 + \alpha + k_c^T/k_D)}{2(1 + \beta + k_c^T/k_D)}\right] \qquad (7.3)$$

$$^{\mathrm{T_0}}Z_{\mathrm{t}}/D = \frac{k_{\mathrm{c}}^{\mathrm{T}}}{2k_{\mathrm{D}}(1 + \alpha + k_{\mathrm{c}}^{\mathrm{S}}/k_{\mathrm{D}})}\left[\alpha + 2\left(1 + \frac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}}}\right) + \frac{\beta(1 + \alpha + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}})}{2(1 + \beta + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}})}\right] \quad (7.4)$$

Equation 7.3 is the contact analogue of eq 5.4 for the double-channel reaction, but it is greatly simplified in the same way as eq 5.11 when compared to eq 5.10.

Subject to similar simplification and generalization, eq 5.5 takes the form

$$^{\mathrm{T_\pm}}Z_{\mathrm{s}}/D = \frac{k_{\mathrm{c}}^{\mathrm{S}}}{2k_{\mathrm{D}}}\,\frac{\beta(1 + \alpha + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}})}{2(1 + \beta)(1 + \alpha) + 2k_{\mathrm{c}}^{\mathrm{S}}k_{\mathrm{c}}^{\mathrm{T}}/{k_{\mathrm{D}}}^{2} + (2 + \beta + \alpha)(k_{\mathrm{c}}^{\mathrm{S}} + k_{\mathrm{c}}^{\mathrm{T}})/k_{\mathrm{D}}} \quad (7.5)$$

and its triplet analogue, which is not zero anymore (since $k_{\mathrm{c}}^{\mathrm{T}} \neq 0$), is equal to

$$^{\mathrm{T_\pm}}Z_{\mathrm{t}}/D = \frac{k_{\mathrm{c}}^{\mathrm{T}}}{2k_{\mathrm{D}}}\left[2 - \frac{\beta(1 + \alpha + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}})}{2(1 + \beta)(1 + \alpha) + 2k_{\mathrm{c}}^{\mathrm{S}}k_{\mathrm{c}}^{\mathrm{T}}/{k_{\mathrm{D}}}^{2} + (2 + \beta + \alpha)(k_{\mathrm{c}}^{\mathrm{S}} + k_{\mathrm{c}}^{\mathrm{T}})/k_{\mathrm{D}}}\right] \quad (7.6)$$

The definition of the spin conversion parameter β remains the same as in eq 5.8c, while for eq 5.12, α should be substituted for the more general one

$$\alpha = \alpha_{\mathrm{R}} + \frac{\alpha_{\mathrm{I}}^{2}}{1 + \alpha_{\mathrm{R}} + (k_{\mathrm{c}}^{\mathrm{S}} + k_{\mathrm{c}}^{\mathrm{T}})/2k_{\mathrm{D}}} \quad (7.7)$$

valid for the double-channel recombination ($k_{\mathrm{c}}^{\mathrm{T}} \neq 0$).

C. Start from the Equipopulated Triplet States. Having all the efficiencies, one can calculate any yield including the total yield of recombination from the equipopulated triplet states, through either the singlet or triplet channels. Analogous to eq 5.6 we have

$$^{\mathrm{T}}\varphi_{\mathrm{s}} = \frac{1}{3}\,{}^{\mathrm{T_0}}\varphi_{\mathrm{s}} + \frac{2}{3}\,{}^{\mathrm{T_\pm}}\varphi_{\mathrm{s}} = \frac{^{\mathrm{T}}Z_{\mathrm{s}}}{D + {}^{\mathrm{T}}Z}$$

$$^{\mathrm{T}}\varphi_{\mathrm{t}} = \frac{1}{3}\,{}^{\mathrm{T_0}}\varphi_{\mathrm{t}} + \frac{2}{3}\,{}^{\mathrm{T_\pm}}\varphi_{\mathrm{t}} = \frac{^{\mathrm{T}}Z_{\mathrm{t}}}{D + {}^{\mathrm{T}}Z} \quad (7.8)$$

where

$$\varphi = 1 - {}^{\mathrm{T}}\varphi_{\mathrm{s}} - {}^{\mathrm{T}}\varphi_{\mathrm{t}} = \frac{D}{D + {}^{\mathrm{T}}Z}$$

and

$$^{\mathrm{T}}Z = {}^{\mathrm{T}}Z_{\mathrm{s}} + {}^{\mathrm{T}}Z_{\mathrm{t}} \quad (7.9)$$

Using, in these formulas, the above obtained results, we get for the efficiencies of the singlet and triplet channels in the case under consideration

$$^{\mathrm{T}}Z_{\mathrm{s}}/D = \frac{k_{\mathrm{c}}^{\mathrm{S}}}{2k_{\mathrm{D}}} \times \frac{2\alpha(1 + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}}) + \beta(1 + 3\alpha + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}})}{2\left(3(1 + \beta)(1 + \alpha) + 3\frac{k_{\mathrm{c}}^{\mathrm{S}}\,k_{\mathrm{c}}^{\mathrm{T}}}{{k_{\mathrm{D}}}^{2}} + \alpha\frac{k_{\mathrm{c}}^{\mathrm{T}}}{k_{\mathrm{D}}} + \beta\frac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}}} + (3 + \beta + \alpha)\frac{k_{\mathrm{c}}^{\mathrm{S}} + k_{\mathrm{c}}^{\mathrm{T}}}{k_{\mathrm{D}}}\right)} \quad (7.10)$$

$$^{\mathrm{T}}Z_{\mathrm{t}}/D = \frac{k_{\mathrm{c}}^{\mathrm{T}}}{2k_{\mathrm{D}}} \times \left[2 - \frac{2\alpha(1 + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}}) + \beta(1 + 3\alpha + k_{\mathrm{c}}^{\mathrm{T}}/k_{\mathrm{D}})}{2\left(3(1 + \beta)(1 + \alpha) + 3\frac{k_{\mathrm{c}}^{\mathrm{S}}\,k_{\mathrm{c}}^{\mathrm{T}}}{{k_{\mathrm{D}}}^{2}} + \alpha\frac{k_{\mathrm{c}}^{\mathrm{T}}}{k_{\mathrm{D}}} + \beta\frac{k_{\mathrm{c}}^{\mathrm{S}}}{k_{\mathrm{D}}} + (3 + \beta + \alpha)\frac{k_{\mathrm{c}}^{\mathrm{S}} + k_{\mathrm{c}}^{\mathrm{T}}}{k_{\mathrm{D}}}\right)}\right] \quad (7.11)$$

D. General Presentation of the Main Results. Later on we will consider only the efficiencies of recombination from either the singlet or equilibrated triplet state, $^{\mathrm{S}}Z$ and $^{\mathrm{T}}Z$. They both can be represented uniformly in a very compact form

$$^{\mathrm{S}}Z_{\mathrm{s}} = z_{\mathrm{s}}(1 - {}^{\mathrm{S}}\Pi) \quad {}^{\mathrm{S}}Z_{\mathrm{t}} = z_{\mathrm{t}}{}^{\mathrm{S}}\Pi \quad (7.12a)$$

$$^{\mathrm{T}}Z_{\mathrm{s}} = z_{\mathrm{s}}{}^{\mathrm{T}}\Pi \quad {}^{\mathrm{T}}Z_{\mathrm{t}} = z_{\mathrm{t}}(1 - {}^{\mathrm{T}}\Pi) \quad (7.12b)$$

where

$$^{\mathrm{S}}\Pi = \frac{\alpha/2}{(1 + \alpha z_{\mathrm{t}}/D)} + \frac{\beta/4}{(1 + \beta + z_{\mathrm{t}}/D)} \quad (7.13a)$$

$$^{\mathrm{T}}\Pi = \frac{(1 + z_{\mathrm{t}}/D)\alpha/2 + (1 + 3\alpha + z_{\mathrm{t}}/D)\beta/4}{3(1 + \alpha)(1 + \beta) + (\alpha z_{\mathrm{t}} + 3z_{\mathrm{s}}z_{\mathrm{t}}/D + \beta z_{\mathrm{s}})/D + (3 + \alpha + \beta)(z_{\mathrm{s}} + z_{\mathrm{t}})/D} \quad (7.13b)$$

E. Double-Channel Recombination in ESM. If the start was made from the singlet, then the efficiencies of the different channels in the ESM are the same as in the exact theory, eq 7.12a, but

$$^{\mathrm{S}}\Pi = \frac{3\alpha}{4(1 + \alpha + z_{\mathrm{t}}/D)} \quad (7.14)$$

where α is given in eq 6.23. At $z_{\mathrm{t}} = 0$, the double-channel expression in eq 7.14 substituted to eq 7.12a reduces $^{\mathrm{S}}Z_{\mathrm{s}}$ to its previously obtained single-channel analogue 6.22.[17]

The start made from the equilibrated triplet, treated the same way, leads to another formula, an alternative to eq 7.13b

$$^{\mathrm{T}}\Pi = \frac{\alpha}{4(1 + \alpha + z_{\mathrm{s}}/D)} \quad (7.15)$$

It is remarkable that the efficiencies at which the recombination is switched on by the spin conversion, $^{\mathrm{S}}Z_{\mathrm{t}}$ and $^{\mathrm{T}}Z_{\mathrm{s}}$, depend on a single recombination parameter, z_{t} or z_{s}, respectively, while two other efficiencies depend on both of them.

1. Recombination in a Zero Magnetic Field. In the case of a zero field when $\alpha = \gamma$, the results following from eqs 7.12 after substituting the expressions from eqs 7.14 and 7.15 coincide with those that can be deduced from the exact eqs 7.1, and 7.2 and 7.10 and 7.11, respectively, provided

$$\alpha = \beta = \gamma = \sqrt{x/D} \quad (7.16)$$

that is, $T_1 = T_2 = T$ in addition to $\Omega = 0$. This is because

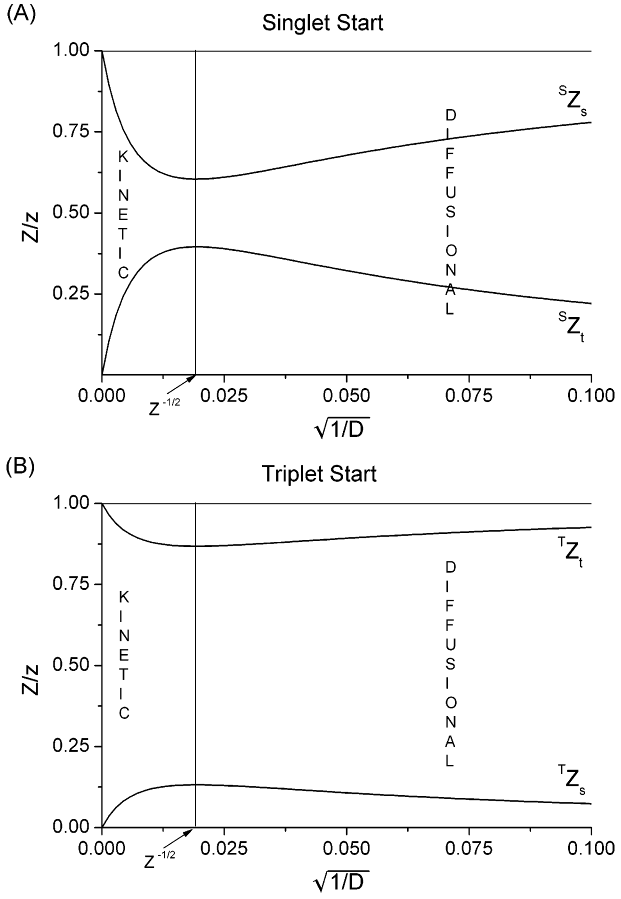

Figure 3. Diffusional dependence of the efficiencies of the zero field double-channel recombination at contact start and equal reaction constants of both channels ($z_s = z_t = z$). Spin conversion efficiency $x = 2\sigma^2/T = 5 \times 10^{-4}$ cm^2/s where $T = T_1 = T_2 = 15$ ps. (A) The start from the singlet state of contact radical pair. (B) The start from the equipopulated triplet states of the pair.

under these conditions the set of eqs 6.6 rigorously reduces to the ESM eqs 6.20 with $k_s = 1/2T$.

Figure 3 shows the viscosity dependence of all the recombination efficiencies at the contact start under condition 7.16. Unlike Figure 2, where they have been shown for the opposite cases of either the singlet channel ($k_c^S \neq 0 = k_c^T$) or triplet channel ($k_c^S = 0 \neq k_c^T$) recombination, here we are dealing with an intermediate case of "spin-independent recombination" first considered in ref 26. This is an exceptional case when the reactions from the singlet and triplet proceed with equal rates: $k_c^S = k_c^T$ ($z_s = z_t = z$). Under such conditions, the spin conversion does not modulate the recombination and cannot affect its total efficiency

$$\text{At } z_s = z_t = z$$

$$Z = Z_S + Z_T = z \tag{7.17}$$

However, Z_S and Z_T change with diffusion as shown in Figure 3. Under conditions 7.16 and 7.17, they obey the simple formulas

$$^SZ_s = z\left[1 - \frac{3\sqrt{x/D}}{4(1 + \sqrt{x/D} + z/D)}\right]$$

$$^TZ_s = z\frac{\sqrt{x/D}}{4(1 + \sqrt{x/D} + z/D)} \tag{7.18a}$$

$$^SZ_t = z\frac{3\sqrt{x/D}}{4(1 + \sqrt{x/D} + z/D)}$$

$$^TZ_t = z\left[1 - \frac{3\sqrt{x/D}}{4(1 + \sqrt{x/D} + z/D)}\right] \tag{7.18b}$$

All of them pass through an extremum at a common point

$$z = D$$

that is at

$$k_c = k_D$$

The vertical line at this point in Figure 3 separates the kinetic control, $D \gg z$, from the regime of diffusion control, $D \ll z$ (left and right branches of the curves).

2. Kinetic/Diffisional Reactions of Radicals Started from Contact. Far to the right, at the slowest diffusion, we obtain from eqs 7.18

$$\text{At } \frac{z}{D} \gg \gamma \gg 1$$

$$^SZ_s = z - \frac{3}{4}\gamma D = z - {}^SZ_t$$

$$\text{and}$$

$$^TZ_t = z - \frac{1}{4}\gamma D = z - {}^TZ_s \tag{7.19}$$

These formulae indicate that the rate constants $4\pi\sigma{}^SZ_t = {}^3/_4\gamma k_D$ and $4\pi\sigma{}^TZ_s = {}^1/_4\gamma k_D$ are proportional to the diffusional constant $k_D = 4\pi\sigma D$, multiplied by the spin conversion factor $\gamma = \sqrt{x/D}$. Therefore, they are proportional to $(D)^{1/2}$. When the radical pair starts from the singlet, the recombination constant is three times larger than in the case of the triplet start.

This is a very interesting peculiarity of a spin-selective theory compared to a spinless one. The latter may be diffusional only in the case of a noncontact start,[12,6] while the former is subdivided into kinetic and diffusional regimes, even if the radicals start to move being in contact. Immediately after the start they become separated; the reaction is switched off and the spin conversion is on. The recombination is now limited by diffusion of radicals from where they find themselves to the contact.

Its rate constant is diffusional when diffusion is slow and the reaction is accomplished at the very first recontact but the singlet and triplet products appear with the weights of these states in the radical pair after spin conversion is accomplished: $^1/_4$ and $^3/_4$.

Under kinetic control, the results are different

$$\text{At } \frac{z}{D} \ll 1 + \gamma$$

$$^SZ_s = \frac{4 + \gamma}{4(1 + \gamma)}z$$

$$^SZ_t = \frac{3\gamma z}{4(1 + \gamma)} = 3{}^TZ_s$$

$$^TZ_t = \frac{4 + 3\gamma}{4(1 + \gamma)}z \tag{7.20}$$

However, as $D \rightarrow \infty$, the spin conversion rate $\gamma \rightarrow 0$ and $^SZ_s =$

${}^{T}Z_t = z$ while ${}^{S}Z_t = {}^{T}Z_s = 0$. The same result follows from eq 7.19 for the opposite diffusional limit, $D \to 0$ ($\gamma \to \infty$).

This means that ${}^{S}Z_s$ and ${}^{T}Z_t$ vary with diffusion from z to z while ${}^{S}Z_t$ and ${}^{T}Z_s$ change from 0 to 0, but between the deviations from the z and 0, horizontal lines are three times larger for the singlet start (A) than for triplet (B). The maximal values of these deviations reached at $z = D$ are

$$\max {}^{S}Z_t = z - {}^{S}Z_s = \frac{3}{4} z \frac{\sqrt{x/z}}{2 + \sqrt{x/z}} \tag{7.21a}$$

$$\max {}^{T}Z_s = z - {}^{T}Z_t = \frac{1}{4} z \frac{\sqrt{x/z}}{2 + \sqrt{x/z}} \tag{7.21b}$$

The efficiency of recombination from the singlet state through the triplet channel is three times larger than the vice versa.

As for the spin conversion, it is either weak or strong depending on whether $x = 2\sigma^2/T$ is less or greater than z. If $x = 1/T = 0$ is zero, then the expressions in eq 7.21 also turn to zero and recombination proceeds only from the initial states: ${}^{S}Z_s = {}^{T}Z_t = z$. In the opposite case ($x \to \infty$), these expressions reach their maximal values which are ${}^{3}/_{4}z$ for the singlet start (A) and ${}^{1}/_{4}z$ for the triplet one (B).

VIII. Magnetic Field Effect

In the present theory, the frequency of spin conversion (eq 1.2) is proportional to the magnetic field H. Affecting conversion, the magnetic field changes the free ion quantum yield, averaged over the distribution of initial separations, $f(r)$

$$\bar{\varphi}(H) = \int \varphi(r,H) f(r)\, \mathrm{d}^3 r = \frac{1}{1 + Z(H)/D} \tag{8.1}$$

The quantitative measure of the magnetic field effect (MFE) is conventionally defined as

$$M = \frac{\bar{\varphi}(H) - \bar{\varphi}(0)}{\bar{\varphi}(0)} = \frac{Z(0) - Z(H)}{D + Z(H)} \tag{8.2}$$

As far as we know, until now, it has been studied experimentally only with systems subjected to a single-channel recombination. In particular, this was done in a wide range of fields with the reaction of photoexcited Ru-trisbipyridine with methyl viologen as an electron acceptor.[27,28] This reaction starts from the equilibrated triplet state of a pair that can recombine only through a singlet channel after the field-dependent spin conversion.

A. Singlet Recombination from the Triplet. In this particular case, $Z \equiv {}^{T}Z_s$. It depends on the starting point r_0 if $f(r) = \delta(r - r_0)/4\pi r^2$. The partial recombination efficiency

$$Z(H) = {}^{T}Z_s(\Omega, r_0) \tag{8.3}$$

is given by expression 5.7, which is too complex for analytic investigations.

1. Contact Start. The situation becomes much simpler if we first focus our attention on the pair starting from contact when

$$Z(H) = {}^{T}Z_s(\Omega, \sigma) \tag{8.4}$$

where the latter is given by expression 5.13 with β and α defined in eqs 5.9 and 5.12, respectively.

Low Fields. When the magnetic field is so small that $\Omega^2 T_2^2 \ll 1$, then using the approximate expressions (eq 6.1) in eq 5.12, we obtain in the lowest order approximation with respect to $\Omega^2 T_2^2$

$$\alpha \approx \gamma \left[1 + \frac{\Omega^2 T_2^{\,2}}{8}\left(1 + \frac{2\gamma}{1 + \gamma + z_s/2D}\right)\right] \tag{8.5}$$

Under this condition, the MFE is linear in $\Omega^2 T_2^2$

$${}^{T}M_s \approx -\Phi \frac{\Omega^2 T_2^{\,2}}{8}\left(1 + \frac{2\gamma}{1 + \gamma + z_s/2D}\right) \tag{8.6}$$

where

$$\Phi = (z_s/D)\,\{\gamma(1+\beta)^2(1 + z_s/D)\}/ \left\{\left[3(1+\gamma)(1+\beta) + \frac{z_s}{D}(3 + 2\beta + \gamma)\right]\left[2(1+\gamma)(1+\beta) + \frac{z_s}{D}\left(2 + \frac{3}{2}\beta + \gamma(1 + \beta/2)\right)\right]\right\}$$

The solution of the rate eqs 6.6 leads to a different result

$${}^{T}M_s \approx -\Phi \frac{\Omega^2 T_2^{\,2}}{2} \tag{8.7}$$

because α has to be taken from eq 6.11

$$\alpha = \sqrt{\frac{\tau_d}{T_2} 2(1 + \Omega^2 T_2^{\,2})} \approx \gamma\left[1 + \frac{\Omega^2 T_2^{\,2}}{2}\right] \tag{8.8}$$

As can be seen at slow conversion, ${}^{T}M_s$ is always linear in $\Omega^2 T_2^2$, but the slope of this linearity in the exact formula (eq 8.6) varies from ${}^{1}/_{8}$ at $\gamma \ll 1$ up to ${}^{3}/_{8}$ at $\gamma \gg 1$, $z_s/2D$, while in the analogous rate relationship, eq 8.7, it is always larger, ${}^{1}/_{2}$. Therefore, the parabolic Ω dependence of MFE at slow conversion is much sharper in the approximate rate theory than in the exact one.

This conclusion is also valid for the ESM, where T_1 is equal to T_2 and α is given by eq 6.23. The MFE estimated with ESM obeys exactly the same quadratic dependence (eq 8.7) provided one sets $\gamma = \beta$ in $\Phi(\gamma,\beta)$

$$\Phi_{\mathrm{ESM}} = \Phi|_{\gamma=\beta} = \frac{z_s}{D}\frac{\gamma(1+\gamma)(1 + z_s/D)}{3\left[1 + \gamma + \frac{z_s}{D}\right]\left[2(1+\gamma)^2 + \frac{z_s}{D}\left(2 + \frac{5}{2}\gamma + \gamma^2/2\right)\right]}$$

However, the region where ${}^{T}M_s$ is quadratic in Ω holds in such a narrow strip (see Figure 4) that all the experimental points are usually obtained out of it.

High Magnetic Fields. In high magnetic fields, the MFE decreases with retardation approaching the constant negative value

$$\text{At } \Omega \to \infty$$

$${}^{T}M_s \approx -\Gamma + \frac{\Lambda}{\sqrt{\Omega T_2}} \tag{8.9}$$

where

$$\Gamma = \frac{2 z_s (z_s + D)(1+\beta)^2}{[4(1+\beta)D + z_s(2+\beta)][3(1+\beta)(1+\gamma)D + z_s(3 + 2\beta + \gamma)]}$$

and Λ is also some function of z_s, β, and γ. It is useful to know

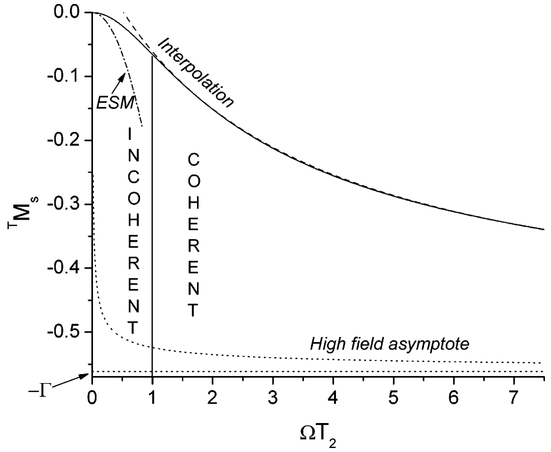

Figure 4. Field dependence of the MFE at contact start in the exact theory (solid line) and in the elementary spin model (dashed−dotted parabolic line). The vertical line separates the low field (incoherent) Ω dependence from the high field MFE, originating from the coherent spin conversion. The latter is well interpolated by the empirical formula 8.10 with $\xi = 0.91$, $\zeta = 3$, and $\Theta = 1.8$ shown as the dashed curve approaching the exact result from above. The highest field asymptotic behavior (eq 8.9) and its limit, $-\Gamma$, are shown by the dotted lines below. The rates of contact recombination, z_s, and other parameters are the same as in the previous figure while $D = 10^{-6}$ cm^2/s.

Γ which is actually an upper limit of the absolute value of MFE: $0 \leq |{}^{T}M_s| \leq \Gamma$. However, the asymptotic dependence (eq 8.9) shown by the dotted line in Figure 4 is not achievable because it holds at too high a magnetic field ($\Omega T_2 \gg 1000$), while the experimentally studied interval is around $\Omega T_2 \sim 1/2$.

Moderate Magnetic Fields. Within this intermediate interval, the descending branch of the solid curve should be better interpolated with the following formula

$$ {}^{T}M_s \approx -\xi\Gamma + \frac{\Theta}{\Omega T_2 + \zeta} \qquad (8.10) $$

With a proper choice of ξ, ζ, and Θ, this interpolation is as good as that shown in Figure 4 by the dashed line. This is the actual observed magnetic field dependence,[27,28,10] while the alternative (incoherent) parabolic dependence (eq 8.6) is hardly detectable and is described by ESM only qualitatively.

In Figure 5, the nonmonotonic diffusional dependence of the MFE is used to compare a few different approaches to the problem. It was exhaustively studied in the frame of “a two-state (S,T$_0$)” model in ref 10, presuming that the system starts from T$_0$ having $\beta = 1/T_1 = 0$. The solution to such a problem at contact recombination and contact start can also be obtained from our theory (dashed line in Figure 5). Nothing changes significantly if we take into account all four spin states, setting $T_1 = T_2$ (lower solid line in Figure 5). But if the start under these conditions is taken from the equilibrated triplet state (upper solid line in Figure 5), then the difference is much more pronounced. This means that the two-level model is too rough for fitting the real experimental data and even more so its incoherent analogue 6.8. On the other hand, it should be noted that the results are rather insensitive to the particular value of T_1 in the whole interval $\infty \geq T_1 \geq T_2$, if the starting state is the same.

2. Noncontact Start. It should be stressed that the results are very sensitive to the starting point especially if it is close to the contact. This peculiarity has been mentioned already in refs 4−6 and 17 where it was shown to result from the contact description of the recombination. In this approximation, the region of too low diffusion is not properly covered especially when the initial particle separation $r_0 - \sigma$ is comparable or less than the tunneling length. However, it is instructive to recognize the general tendency of the MFE to change with r_0.

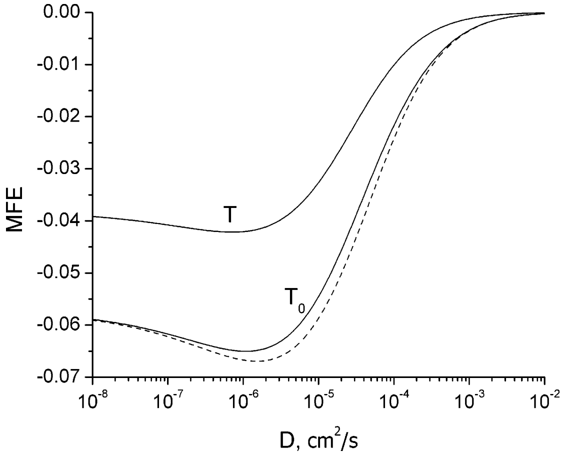

Figure 5. Diffusional dependence of the MFE at $T_1 = \infty$ and start from T$_0$ (dashed line), for $T_1 = T_2 = 15$ ps, and the same start (T$_0$), at equal times but starting from the equilibrated triplet (T). The contact rate constant $k_c^S = 3.31 \times 10^5$ Å^3/ns, $\Omega T_2 = 0.75$.

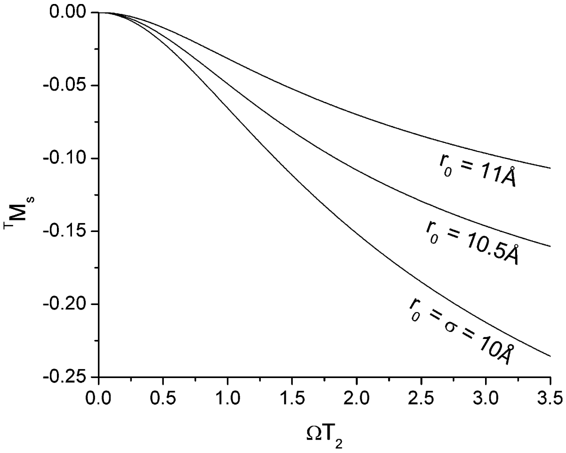

Figure 6. Field dependence of the single-channel MFE at different starting distances. The rest of the parameters are the same as in Figure 4.

As shown in Figure 6, the MFE monotonically decreases with r_0 at any Ω and the sharper the larger it is.

However, the space-dependent recombination rate $W(r)$ is not actually the contact one, as in eq 2.7. Usually it is not narrower than the tunneling length $L \sim 1$ Å, that is, at so close starts, the recombination is for sure not contact. If nevertheless the contact approximation (eq 2.7) is used, then the diffusional dependence of the MFE at the contact start is questionable at slow diffusion (the lowest curve in Figure 7 at $D < 10^{-6}$). However, the curves for large separation are free of this weakness in the fast diffusion region, where the effect is the most pronounced (Figure 7).

Very similar curves with clearly expressed minima were obtained experimentally by Steiner et al.[28] They were fitted in ref 10 within the two-level model with an exponential (noncontact) recombination rate. The calculations include the averaging (eq 8.1) over the realistic distribution $f(r_0)$ which is different for any D values. Unfortunately, all diffusional dependencies were studied by the Steiner group varying D values (viscosity) by changing the solvent composition. This is accompanied by a significant variation of the static and optical dielectric constants changing the outer sphere reorganization energy λ, parallel to diffusion. It was shown later that such a

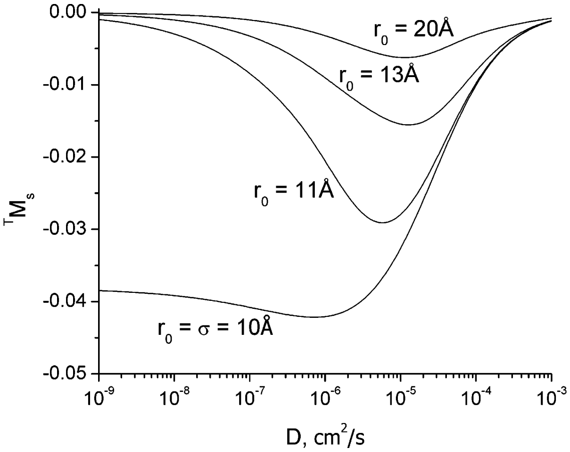

Figure 7. Diffusional dependence of the single-channel MFE at different starting points r_0. All the parameters are the same as in Figure 4..

TABLE 1

D, cm^2/s	T_2, ps	r_0, Å
6.67×10^{-7}	47.6	11.2
1.16×10^{-6}	40.8	10.8
2.30×10^{-6}	37	10.6

variation of λ affects significantly the space-dependent transfer rate and changes qualitatively the interpretation of the quantum yield diffusional dependence.[4−6] This is not the place to go into the details of fitting the real diffusional dependencies. Instead, it is better to concentrate on fitting the field dependence of the MFE when nothing is changed except Ω.

3. Fitting the Field Dependence of the MFE. The expected field dependence is exhibited in Figure 6. The different starting distances, r_0, represent the difference in diffusion. The faster the latter is the closer to the contact the actual initial distribution, $f(r_0)$, is. Instead of the whole distribution, $f(r_0)$, we take a single r_0, close to its average value, which shifts to contact when diffusion becomes faster. However, not only the starting distance changes with D but also T_2 is subjected to some changes indicated in the original experimental work (Table 1 in ref 28). We used these values to fit the related curves ^TM_s using r_0 as a single variable parameter and borrowing the value for $k_c^S = 3.31 \times 10^5$ Å^3/ns from ref 10 (see the caption to Figure 7 therein).

The results of our fitting are shown in Figure 8 and Table 1. They cannot be expected to be better because the contact approximation for recombination (eq 2.7) is employed instead of the true $W(r)$ and the single starting distance is used instead of $f(r_0)$.

The monotonic decreasing of r_0 with D confirms the nature of the forward electron transfer (ionization) that should be diffusional at such a small D value. The effective radius of the diffusional ionization is known to go down when the diffusion accelerated.[12,6] Of course, the variation of λ simultaneously with diffusion can imitate the same effect as it did already in another respect.[4−6] Nonetheless, the spin conversion responsible for the really observable MFE is an undoubtedly coherent process contrary to what was expected in previous works.[29,30]

B. Double-Channel Recombination. When both reaction channels are switched on, the yield of free radicals (eq 8.1) is also field dependent, though $Z(H) = Z_s + Z_t$ depends on both k_c^S and k_c^T. Until now, there was only one system where Z and Z_t were measured simultaneously.[17] However, the MFE was not detected there. Besides, the spin conversion there was carried out by another (HFI) mechanism that was considered separately.[8]

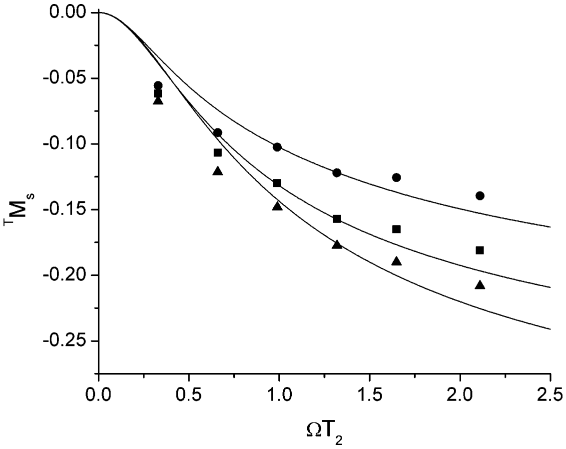

Figure 8. Fitting of the field dependence of MFE at various values of the diffusion coefficient, increasing from top to bottom (Table 1). The points are taken from experimental work.[28]

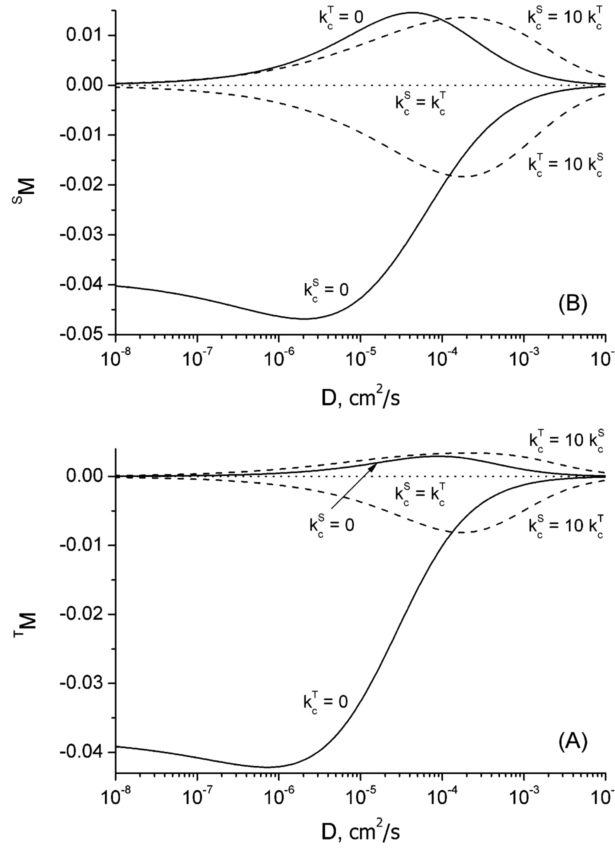

Figure 9. Diffusional dependence of the MFE for triplet (A) and singlet (B) radical pairs, starting from contact. Single-channel recombination is given by solid lines, double-channel recombination by dashed lines, and the spin-independent border case by a dotted one. The relative efficiencies of the singlet and triplet recombination channels are pointed out by the relative k_c^S and k_c^T values.

Therefore, we restrict our attention to only the contact start using $\varphi(\sigma,H)$ in eq 8.2 instead of $\bar{\varphi}(H)$. This is only a demonstration of the qualitatively different diffusional dependence of the MFE, which is very sensitive to the interrelationship between k_c^S and k_c^T at any starting state (Figure 9).

For triplet recombination through the singlet channel, ^TM_s, we have in (A) the lowest curve ($k_c^T = 0$) which is the same as in Figures 7 and 5. An alternative recombination of the same pair, via the triplet channel only, ^TM_t, takes place at $k_c^S = 0$ and has an opposite, positive sign of the MFE. A border case of the double channel but “spin-independent recombination” ($k_c^T = k_c^S$) is a horizontal dotted line ${}^TM = 0$. At comparable but not equal rate constants $k_c^S = 10k_c^T$ and $k_c^T = 10k_c^S$, the signs of the effect are also the opposite as for the single-channel limits.

For recombination from the singlet initial state (B), the picture is qualitatively the same, except that the signs of the MFE when the singlet or triplet channel dominates are interchanged. Since the initial state of the photoinduced pair is usually known, the diffusional dependence of MFE allows one to find easily what channel is more efficient and by how much.

IX. Conclusions

The yields of singlet and triplet products of the double-channel recombination from either of these states and any initial separation of radicals are exactly calculated assuming the spin conversion is due to a Δg mechanism. The results for the recombination through the singlet channel, only obtained previously for the contact start from the singlet, are reproduced and extended for the start from the equipopulated triplet states. In the latter case, the MFE arising from the coherent spin conversion is estimated and well fitted to the available experimental data. The popular model considering the spin conversion as an incoherent rate process is not appropriate in a high field but becomes exact in a zero field, provided the spin relaxation times are equal. In this particular case, the diffusional dependence of all the yields coincides with the exact one and may be used for discrimination between the channels.

The only limitation of the theory is the contact approximation for distant recombination rates. It can be overcome by numerical calculations provided that the distance dependence of the rate is known.

Acknowledgment. The authors are thankful to Professor N. Lukzen for greatly appreciated help.

References and Notes

(1) Hong, K. M.; Noolandi, J. *J. Chem. Phys.* **1978**, *68*, 5163.

(2) Burshtein, A. I.; Zharikov, A. A.; Shokhirev, N. V.; Spirina, O. B.; Krissinel, E. B. *J. Chem. Phys.* **1991**, *95*, 8013.

(3) Zharikov, A. A.; Shokhirev, N. V. *Chem. Phys. Lett.* **1991**, *186*, 253.

(4) Neufeld, A. A.; Burshtein, A. I.; Angulo, G.;. Grampp, G *J. Chem. Phys.* **2002**, *116*, 2472.

(5) Burshtein, A. I.; Neufeld, A. A. *J. Phys. Chem. B* **2001**, *105*, 12364.

(6) Burshtein, A. I. *Adv. Chem. Phys.* **2004**, *129*, 105.

(7) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko A. L. *Spin polarization and magnetic effects in radical reactions*; Molin, Yu., N., Ed.; Elsiever: Amsterdam, The Netherlands, 1984.

(8) Lukzen, N. N.; Pedersen, J. B.; Burshtein, A. I. *J. Phys. Chem. A* **2005**, *109*, 11914.

(9) Steiner, U. E.; Ulrich, Th. *Chem. Rev.* **1989**, *89*, 51.

(10) Krissinel, E. B.; Burshtein, A. I.; Lukzen, N. N.; Steiner, U. E. *Mol. Phys.* **1999**, *96*, 1083.

(11) Burshtein, A. I.; Krissinel, E.; Steiner, U. E. *Phys. Chem. Chem. Phys.* **2001**, *3*, 198.

(12) Burshtein, A. I. *Adv. Chem. Phys.* **2000**, *114*, 419.

(13) Mints, R. G.; Pukhov, A. A. *Chem. Phys.* **1984**, *87*, 467.

(14) Purtov, P. A.; Doktorov, A. B. *Chem. Phys.* **1993**, *178*, 47.

(15) Korst, N. N.; Lazarev, A. V. *Physica* **1969**, *42*, 31.

(16) Pedersen, J. B.; Freed, J. H. *J. Chem. Phys.* **1973**, *58*, 2746.

(17) Gladkikh, V. S.; Burshtein, A. I.; Angulo, G.; Grampp, G. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2581.

(18) Gladkikh, V. S.; Burshtein, A. I. *Chem. Phys.*, in press.

(19) Hansen, M. J.; Neufeld, A. A.; Pedersen, J. B. *Chem. Phys.* **2000**, *260*, 125.

(20) Burshtein, A. I. *Chem. Phys.*, in press.

(21) Burshtein, A. I. *Chem. Phys. Lett.* **2005**, *411*, 66.

(22) Tomkiewicz, M.; Cocivera, M. *Chem. Phys. Lett.* **1971**, *8*, 595.

(23) Bube, W.; Haberkorn, R.; Michel-Beyerle, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 5993.

(24) Sterna, L.; Ronis, D.; Wolfe, S.; Pines, A. *J. Chem. Phys.* **1980**, *73*, 5493.

(25) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 322.

(26) Schulten, Z.; Schulten, K. *J. Chem. Phys.* **1977**, *66*, 4616.

(27) Bürβner, D.; Wolff, H.-J.; Steiner, U. *Z. Phys. Chem. Board* **1993** *182* 297; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1772.

(28) Wolff, H.-J.; Bürβner, D.; Steiner U. *Pure Appl. Chem.* **1995**, *67* (1), 167.

(29) Burshtein, A. I.; Krissinel, E. *J. Phys. Chem. A* **1998**, *102*, 816.

(30) Burshtein, A. I.; Krissinel, E.; Steiner, U. E. *Phys. Chem. Chem. Phys.* **2001**, *3*, 198.