Noncontact Bimolecular Photoionization Followed by Radical-Ions Separation and Their Geminate Recombination Assisted by Coherent HFI Induced Spin-Conversion

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The Hamiltonian description of the spin-conversion induced by a hyperfine interaction (HFI) in photogenerated radical−ion pairs is substituted for the rate (incoherent) description of the same conversion provided by the widely used earlier elementary spin model. The quantum yields of the free ions as well as the singlet and triplet products of geminate recombination are calculated using distant dependent ionization and recombination rates, instead of their contact analogs. Invoking the simplest models of these rates, we demonstrate with the example of a spin-less system that the diffusional acceleration of radical−ion pair recombination at lower viscosity gives way to its diffusional deceleration (Angulo effect), accomplished with a kinetic plateau inherent with the primitive exponential model. Qualitatively the same behavior is found in real systems, assuming both ionization and recombination is carried out by the Marcus electron-transfer rates. Neglecting the Coulomb interaction between solvated ions, the efficiencies of radical−ion pair recombination to the singlet and triplet products are well fitted to the available experimental data. The magnetic field dependence of these yields is specified.

I. Introduction

The radical−ion pair (RIP) created in its singlet state becomes a triplet with time and recombines in either the singlet or triplet states of the neutral products, though with different rates, W_S and W_T. In particular, this scenario is realized after the excited perylene (Per*) molecules are quenched in the encounters with *N*,*N′*-dimethylaniline (DMA) molecules which are the electron donors

$$\begin{array}{llll} Per^{*}\ +DMA \xrightarrow{W_I} {}^{1}[Per^{-}\cdots DMA^{+}] & \rightleftharpoons {}^{3}[Per^{-}\cdots DMA^{+}] & \xrightarrow[D]{\bar{\varphi}} & {}^{2}Per^{-} + {}^{2}DMA^{+} \\ \downarrow\tau \qquad\qquad \downarrow_{W_S} & \qquad \downarrow_{W_T} & & \\ Per\ \ +DMA \qquad [Per\cdots DMA] & [{}^{3}Per^{*}\cdots DMA] & \xrightarrow{\varphi_T} & {}^{3}Per^{*}+DMA \end{array} \tag{1.1}$$

Here the singlet, doublet, and triplet states are indicated by left-hand superscripts 1, 2, and 3, respectively. $\bar{\varphi}$ is the quantum yield of RIP separation, whereas φ_T is the yield of the excited triplet product of their recombination. The quantum yield of the free ions, Per$^-$ and DMA$^+$, is $\phi = (1 - \eta)\bar{\varphi}$, where η is the yield of Per* fluorescence. Reaction 1.1 has been studied for a wide variation of the viscosity of dimethyl sulfoxide-glycerol mixtures, keeping all solvent parameters constant, except for the encounter diffusion coefficient *D*.[1−3]

The triplet products of the geminate recombination of singlet born RIPs were detected and/or discussed in a number of previous papers.[4−10] It is always presumed that there is a singlet−triplet spin conversion in RIPs accompanying their recombination. However, in a number of papers, the spin-conversion which opens the triplet channel of charge recombination was considered as an incoherent transition proceeding from the singlet to triplet state with a phenomenological rate $3k_s$ and backward with a rate k_s.[11−13] These investigations have shown that the experimental data for recombination and ionization can be satisfactory fitted only with the noncontact initial distribution, provided that the recombination is also noncontact and even more distant than ionization.[13] The rate model of incoherent spin conversion is known to be appropriate at the zero magnetic field only.[11,12] Here we substitute the rough rate model of spin conversion with a true HFI mechanism of coherent spin conversion, assisting the double channel RIP recombination.

For geminate recombination assisted by coherent (HFI induced) spin conversion for a zero magnetic field, the exact analytical solution of the problem was recently obtained.[14] However, it was assumed also that the electron transfer occurs only at the contact distance. The numerical methods we are using here allow us to be free in choosing the space dependence of the ionization rate $W_I(r)$ as well as both the recombination rates $W_S(r)$ and $W_T(r)$. For the fitting of the real experimental data the most fundamental Marcus formulas for $W(r)$ are used with the appropriate free and reorganization energies and reasonable values of electron coupling and tunneling length. Even their plausible models (exponential or rectangular) represent the electron transfer as a distant (remote) process, not a contact one.

These models as well as the simplest spin-less theory will be used only in the next section for the demonstration of the main features of the phenomenon. For such a simplified example we will demonstrate that the recombination efficiency is a function of the diffusion coefficient varying with the solvent viscosity. The origin of the non-monotonous viscosity dependence of the recombination efficiency (Angulo effect) will be

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disclosed and related to the strength of the forward and backward charge transfer.

Qualitatively the same takes place in the real RIPs subjected to a double channel recombination assisted by the spin-conversion. In a zero magnetic field, there are a few different mechanisms for such a conversion: the paramagnetic relaxation of the electronic spins, the intersystem crossing in the intermediate complex state, the hyper-fine interaction (HFI) of the electron spins of the radical-ions with magnetic nuclei, and the bulk recombination.[9,10,15] To study the recombination of our particular RIP, we have to specify it.

First of all, dealing with only geminate recombination of organic RIPs, one can ignore the bulk processes. The intersystem crossing in perylene is known to be negligible. The main role in this system is played by the HFI mechanism of singlet−triplet mixing which is much more effective than that of paramagnetic relaxation in organic radical-ions.[15] For instance, in the system consisting of pyrene and derivatives of aniline, the magnetic field strength, $B_{1/2}$ (at which the magnetic field effect takes half the saturation value) was shown to be determined by the equation[15,16]

$$B_{1/2} = \frac{2(B_1{}^2 + B_2{}^2)}{B_1 + B_2}, \quad \text{where } B_i = [\sum_j a_{ij}{}^2 I_{ij}(I_{ij} + 1)]^{1/2} \tag{1.2}$$

Here a_{ij} are the hyperfine coupling constants of the jth nucleus in the ith radical-ion and I_{ij} are the spins of the respective nuclei. Hence, this is the hyperfine coupling mechanism 1.2 which is responsible for the singlet−triplet transitions in the system which is very much similar to ours.

The aims of this paper is to fit the diffusional dependence of the quantum yields of charge separation and triplet production exploring (i) the noncontact (Marcus) ionization and recombination rates and (ii) the coherent (HFI) mechanism of spin conversion.

II. Spin-Less Unified Theory of Bimolecular Ionization Followed by Geminate Recombination

The original unified theory[17,18] proposed for irreversible ionization followed by ion recombination and separation considers the spin-less reaction scheme

$$\begin{array}{lllll} & & \psi & & \bar{\varphi} \\ Per^* + DMA & \xrightarrow[D]{W_I} & [Per^- \cdots DMA^+] & \xrightarrow[D]{} & Per^- + DMA^+ \\ \downarrow \tau & & \downarrow W_R & & \end{array} \qquad \phi = \psi\bar{\varphi} \tag{2.1}$$

In eq 2.1 ψ is the yield of ions produced by the forward electron transfer (with a rateW_I) and $\bar{\varphi}$ is the charge separation quantum yield. The latter is the fraction of ions avoided geminate recombination (with the rateW_R) and averaged over their initial separation. It contributes to the free ion quantum yield $\phi = \psi\bar{\varphi}$ in line with $\psi = 1 - \eta$, where η is the fluorescence quantum yield.[11,12]

The input parameters of the theory are the forward and backward transfer rates, W_I and W_R. In the case of weak tunneling, the rates are given by the simplest Golden Rule formula

$$W(r) = V^2(r)\sqrt{\frac{\pi}{\lambda(r)T}}\exp\left\{-\frac{[\Delta G(r) + \lambda(r)]^2}{4\lambda(r)T}\right\} \tag{2.2}$$

The electronic coupling $V(r) = V_\mathrm{c}\exp(-(r - \sigma)/L)$, where L is the length of electron tunneling, σ is the closest approach distance, T is the absolute temperature measured in units of energy (the Boltzmann constant $k_\mathrm{B} = 1$), and $\lambda(r)$ is the distance dependent reorganization energy. Usually the ionization proceeds in the normal Marcus region where $|\Delta G_\mathrm{I}(\sigma)| < \lambda(\sigma)$ while recombination is more exergonic and occurs in the Marcus inverted region, $|\Delta G_\mathrm{R}(\sigma)| > \lambda(\sigma)$, as shown in Figure 1. Two different models, exponential and rectangular, are commonly used to account approximately for their space dependence (Figure 1).[11,12] They are explored only in this section for the approximate calculation of the charge separation and recombination yields and explanation of unusual non-monotonous viscosity dependence of the recombination efficiency given in refs 1 and 19. Thereafter this dependence as well as that of the triplet product yield will be studied more accurately taking into account the spin conversion in RIPs, subjected to double channel recombination with the Marcus rates.

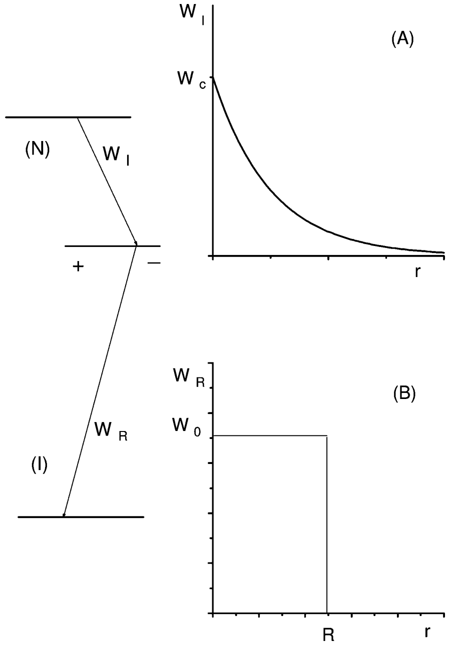

Figure 1. Exponential (A) and rectangular (B) models for the space dependencies of ionization and recombination in normal (N) and inverted (I) regions, respectively.

A. Angulo Effect. The total charge separation yield is actually an average of the partial quantum yields from a given initial separation, $\varphi = \varphi(r,\tilde{D})$, over the initial distribution of inter-radical distances prepared by the precursor bimolecular ionization, $f_0 = f_0(r,D)$[11,12]

$$\bar{\varphi} = \int \varphi(r,\tilde{D}) f_0(r,D) d^3r = \frac{1}{1 + Z(D,\tilde{D})/\tilde{D}} \tag{2.3}$$

where $Z(D,\tilde{D})$ is the recombination efficiency.[11] The partial yield and the initial distribution depend on the encounter diffusion coefficient of the radical-ions, $\tilde{D}$, and neutral reactants, D, correspondingly. In general, these coefficients are different. The difference is caused by the solvation of the ions in polar solvents resulting in a larger effective ion radius than that of the neutral precursors. A consistent theory should explicitly describe the solvation of the created ions. Until now there has been no such theory. This is the reason why in what follows we set $D = \tilde{D}$.

To simplify the problem let us consider a single RIP separating from the distance r_0 which is set equal to the average separation[11,12]

$$r_0 \approx \int r f_0(r) d^3r = \bar{r}(D) \tag{2.4}$$

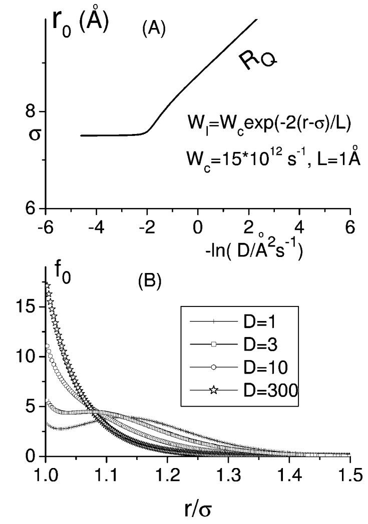

Figure 2. (A) Reduction of the average separation $\bar{r}$ with D and (B) initial distributions of charge separations at different diffusion coefficients for exponential $W_I(r)$. Diffusion coefficient D is given in Å^2/ns.

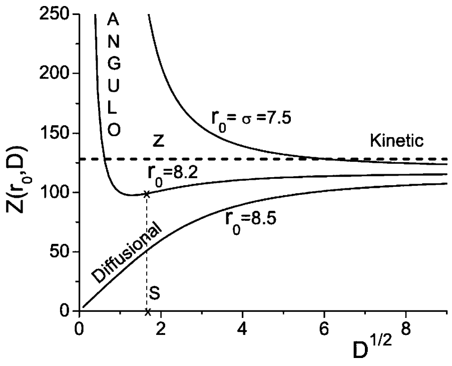

Figure 3. Diffusional dependence $Z(D)$ for a few fixed starts (r_0 = const). The diffusion coefficient D is given in Å^2/ns.

The latter coincides with a distance to the remote maximum of $f_0(r)$ when D is small but reduces to the closest approach distance when diffusion becomes faster (Figure 2B).[17,18] This quantity is close to the effective reaction radius R_Q which is known for the exponential model ($W_I(r) = W_0 \exp[-2(r - \sigma)/L]$)[20]

$$R_Q(D) = \sigma + \frac{L}{2}\left[\ln(\gamma^2\beta) + 2\theta\left(\beta, \frac{2\sigma}{L}\right)\right] \tag{2.5}$$

Here

$$\theta(x,y) = \frac{K_0(2\sqrt{x}) - y\sqrt{x}K_1(2\sqrt{x})}{I_0(2\sqrt{x}) + y\sqrt{x}I_1(2\sqrt{x})}, \beta = \frac{W_cL^2}{4D},$$
$$\gamma = e^C \simeq 1.781 \tag{2.6}$$

where C is the Eiler constant and $K(x)$ and $I(x)$ are the modified Bessel functions. Substituting the average yield by the yield from the average distance we can estimate it approximately as

$$\bar{\varphi} \approx \varphi(\bar{r},D) = \frac{1}{1 + Z(\bar{r},D)/D} \tag{2.7}$$

For the rectangular model of the remote recombination layer the quantity $Z(r_0, D)$ was specified in refs 1 and 21. The near contact layer model used here is a particular case of the remote one having $r_1 = \sigma$ and $r_2 = R$. Setting $r_0 = \bar{r}$, we obtain from Table 1 of ref 1 the following result for it:

$$\frac{Z}{D} = \begin{Bmatrix} \dfrac{\xi\bar{r}[e^{\xi l} - \kappa e^{-\xi l}]}{e^{\xi(\bar{r}-\sigma)} + \kappa e^{-\xi(\bar{r}-\sigma)}} - 1 & \text{at } \bar{r} \le R \\ \dfrac{(\xi R - 1)e^{\xi l} - \kappa(\xi R + 1)e^{-\xi l}}{(\xi(\bar{r} - R) + 1)e^{\xi l} - \kappa((\xi(\bar{r} - R) - 1))e^{-\xi l}} & \text{at } \bar{r} > R \end{Bmatrix} \tag{2.8}$$

where $l = R - \sigma$ is the width of the rectangular reaction layer

$$\xi = \sqrt{\frac{W_0}{D}}, \kappa = \frac{\xi\sigma - 1}{\xi\sigma + 1} \tag{2.9}$$

is the efficiency of the kinetic control recombination.

In the widely used "exponential model",[11,12] $Z \equiv z = W_0 l\sigma$ is independent of diffusion (viscosity). On the contrary, the real efficiency eq 2.8 has an opposite diffusional dependence for RIP started from inside and outside the recombination layer (Figure 3). Since the starting point $\bar{r}$ shifts with diffusion toward the contact (Figure 2), the initial acceleration of recombination gives way to its retardation as soon as $\bar{r}$ reaches σ. As shown in Figure 4, the transition from a distant to a contact start occurs in parallel with an increase in the ionization rate constant

$$k_i = \frac{k_0 k_D}{k_0 + k_D} \tag{2.10}$$

from its diffusional value ($k_D = 4\pi\sigma D$) to the kinetic one (k_0). The fact that Z passing the maximum decreases with diffusion approaching z was first discovered experimentally by Angulo.[1] The position and the height of the maximal Z is determined by the relative values of the rate parameters W_c and W_0. The Angulo effect was first explained in ref 19, but initially its origin was also related to the change in $\lambda(n,\epsilon)$ with solvent composition. This is because the latter varies not only with the viscosity of the solvent but also with the refraction index n and dielectric constant ϵ as well. However, in the particular system studied here and in ref 1, the equality is held, λ = const, and the whole effect originates from $\bar{r}(D)$ reduction.

III. Spin Conversion Assistance of Geminate Recombination

The bimolecular ionization (forward electron transfer) in the framework of differential encounter theory (DET) is described by the equations[11]

$$\dot{N}(t) = -k_I(t)cN(t) - N(t)/\tau \tag{3.1a}$$

$$k_I(t) = \int W_I(r)n(r,t)d^3r \tag{3.1b}$$

where c = [DMA] = const at great excess of electron donors and $N(t)$ is the survival probability of the excited acceptors (Per*), provided that initially $N(0) = 1$. The pair distribution function $n(r,t)$ obeys the auxiliary equation

$$\frac{\partial n(r,t)}{\partial t} = -W_I(r)n(r,t) + \hat{L}n(r,t), n(r,0) = 1 \tag{3.2}$$

Here

$$\hat{L} = \frac{D}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} \tag{3.3}$$

is the operator of encounter diffusion in a free space and τ is the lifetime of the excited acceptor in the absence of quencher.

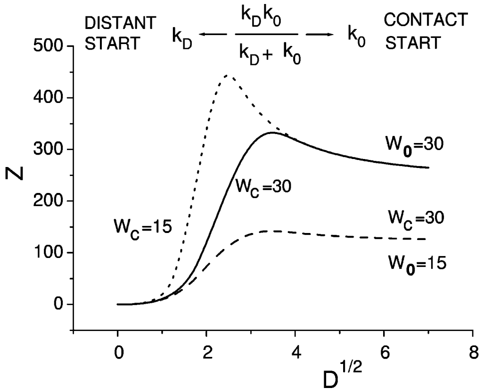

Figure 4. Single channel recombination efficiency as a function of D at different parameters of ionization and recombination rate models. The initial separation distance $\bar{r}(D)$ dependence on diffusion coefficient is determined by eq 2.5. The values of W_0 and W_c are given in ps^{-1}. The diffusion coefficient D is given in Å^2/ns. The remaining parameters are $\sigma = 7.5$ Å, $R = 8.5$ Å, $L = 1$ Å.

The charged products of ionization constitute the RIP in the same spin state as its precursor.

For Per/DMA created in a singlet state the charge recombination is allowed to either the singlet ground state DMA + Per or to the triplet excited state DMA + ^{3}Per*, provided that the spin conversion is accomplished during the life time of the RIP. Which of the two possible routes is realized depends also on the relative rates for the singlet and triplet recombination channels.

The coherent evolution of an ensemble of RIPs with respect to spin and space degrees of freedom is described in terms of the distance-dependent spin density matrix $\hat{m}(r,t)$[11]

$$\frac{\partial \hat{m}(r,t)}{\partial t} = \hat{L}\hat{m}(r,t) - i[\hat{H},\hat{m}(r,t)]_- - \frac{1}{2}[\hat{W}(r),\hat{m}(r,t)]_+ + \hat{f}(r,t) \tag{3.4}$$

where $f(r,t)$ is the pumping term originated by ionization, $\hat{H}$ is the spin Hamiltonian of the RIP and $\hat{W}$ is the reaction operator of the backward electron transfer (recombination). The notations of the commutator and anticommutator $[a, b]_\pm = ab \pm ba$ are used.

The spin Hamiltonian includes the interaction of the RIP with an external magnetic field, the singlet−triplet splitting, and the hyperfine interaction. It has the form

$$H = H_{el} + H_{hfi} \tag{3.5}$$

where

$$H_{el} = \omega_D S_{Dz} + \omega_A S_{Az} + J(r)\left(\frac{1}{2} + 2\mathbf{S}_D\mathbf{S}_A\right) \tag{3.6}$$

$$H_{hfi} = A\mathbf{I}\mathbf{S}_D \tag{3.7}$$

$S_A = 1/2$, $\omega_A = g_A\beta_e B$ and $S_D = 1/2$, $\omega_D = g_D\beta_e B$ are the spins and the Larmor frequencies of radical-ions ^{2}Per$^-$ and ^{2}DMA$^+$ in the magnetic field B; g_A and g_D are their g-factors; β_e is Bohr's magneton; $2J(r)$ is the singlet−triplet splitting; A is the HFI constant and $I = 1/2$ is the spin of a nuclei. In this paper the electron spin interaction with a number of nuclear spins is modeled by an interaction with a single nuclear spin with an effective HFI constant.[22] In the system considered, Per/DMA, for both the anion-radical and cation-radical all HFI constants are known.[23,24] Estimations have shown the effective HFI constant of the radical-cation DMA to be four times as great as that of the Per radical-anion, therefore the effective HFI constant of the RIP is mainly determined by the DMA radical.

The reaction operator $\hat{W}(r)$ allows back electron transfer to the singlet ground state and excited triplet state with the rate constants $W_S(r)$ and $W_T(r)$, correspondingly. The total recombination operator can be specified in the form

$$\hat{W}(r) = W_S(r)\hat{P}_S + W_T(r)\hat{P}_T \tag{3.8}$$

where $\hat{P}_S$ and $\hat{P}_T$ are the projection operators in the singlet and triplet states of the RIP, respectively. They can be represented as follows:

$$\hat{P}_S = \frac{\hat{E}}{4} - \mathbf{S}_D\mathbf{S}_A \tag{3.9}$$

$$\hat{P}_T = \frac{3\hat{E}}{4} + \mathbf{S}_D\mathbf{S}_A \tag{3.10}$$

where $\hat{E}$ is the unity operator.

The Unified Theory specifies the pumping term $f(r,t)$ which is actually the flux of the particles converting from the neutral to the charged ones[11]

$$\hat{f}(r,t) = W_I(r)n(r,t)N(t)\hat{P}_S \tag{3.11}$$

According to this formula, the ions appear in the singlet state and in the same very points where their neutral precursors were before electron transfer. As long as the contact distance for n and m is the same, there are the same reflective boundary conditions for n and m and no other sources of ions except the space distributed flux (3.11). Equation 3.4 should be solved with the initial conditions $\hat{m}(r,0) = 0$.

Integrating out eq 3.4 over time, from zero to infinity, we obtain[11]

$$\hat{L}\hat{m}(r) - i[\hat{H},\hat{m}(r)]_- - \frac{1}{2}[\hat{W},\hat{m}(r)]_+ = -\hat{f}_0(r) \tag{3.12}$$

where

$$\hat{m}(r) = \int_0^\infty \hat{m}(r,t)\,\mathrm{d}t \tag{3.13}$$

$$\hat{f}_0(r) = \int_0^\infty \hat{f}(r,t)\,\mathrm{d}t \tag{3.14}$$

Having solved this equation, one can find the quantum yields of free ions as well as the triplet and singlet neutral products as follows:[11]

$$\psi\varphi_S = \frac{1}{2}\int Tr[W_S(r)\hat{P}_S, \hat{m}(r)]_+\,\mathrm{d}^3r \tag{3.15}$$

$$\psi\varphi_T = \frac{1}{2}\int Tr[W_T(r)\hat{P}_T, \hat{m}(r)]_+\,\mathrm{d}^3r \tag{3.16}$$

where

$$\psi = c\int Tr\hat{f}_0(r)\,\mathrm{d}^3r \tag{3.17}$$

is the quantum yield of the primary RIPs and $1 - \psi = \eta$ is the quantum yield of fluorescence; φ_S and φ_T are the quantum yields of the geminate recombination to the singlet and the triplet states of the neutral products, while

$$\varphi = 1 - \varphi_S - \varphi_T \tag{3.18}$$

is the probability of diffusional separation of the RIP. The quantum yield of free ions is

$$\phi = \psi\varphi \tag{3.19}$$

Instead of quantum yields, their efficiency, Z, is often used[3,12]

$$\varphi = \frac{1}{1 + Z/D}, \quad \varphi_S = \frac{Z_S/D}{1 + Z/D}, \quad \varphi_T = \frac{Z_T/D}{1 + Z/D} \tag{3.20}$$

where the total efficiency of the recombination is

$$Z = Z_S + Z_T \tag{3.21}$$

The ionization and triplet recombination rates have the Marcus' form eq 2.2 with the distance dependent reorganization energy:

$$\lambda(r) = \lambda_i + \lambda_m\left(2 - \frac{\sigma}{r}\right) \tag{3.22}$$

consisting of the intramolecular low-frequency contribution, λ_i, and the medium part λ_m.

For the system consisting of Per and DMA the recombination to the singlet ground state proceeds in the deep Marcus inverted region. In this case the intramolecular quantum modes have to be taken into consideration. For the model with a single quantum mode, the rate is determined by the equation

$$W_S(r) = V_S^{\,2}(r)\sqrt{\frac{\pi}{\lambda(r)T}}\sum_0^{\infty}\frac{S^n e^{-S}}{n!}\exp\left\{-\frac{[\Delta G_S + \lambda(r) + \Omega n]^2}{4\lambda(r)T}\right\} \tag{3.23}$$

where $S = \lambda_q/\Omega$ is the Hyang-Rhys factor,[25] λ_q is the reorganization energy of the quantum intramolecular mode with the frequency, Ω (the Planck constant $\hbar = 1$ and the frequency is measured in units of energy).

IV. Theories of Contact Ionization and Recombination Versus Experiment

A. Coherent Contact Ionization and Recombination. The problem under consideration is characterized by a considerable number of independent parameters. To get an idea how these parameters affect the quantum yields and which of them are determinative, it is instructive to analyze a more simple problem having an analytical solution. To do this, we refer to ref 14 where the analytical expressions for the geminate recombination efficiencies were obtained for contact recombination in a zero external magnetic field. The results are also valid for the model considered here, when the ionization also being contact guarantees the contact start of RIPs. In high polarity solvents, the Coulomb interaction between ions is negligible and the recombination efficiency is given by the equations[14]

$$Z/D = k_s + [3(k_t - k_s)(2 + k_s + k_t)\theta(2 + k_s + k_t + 4\theta)]/\Delta \tag{4.1}$$

$$Z_T/D = [3k_t(2 + k_s + k_t)\theta(2 + k_s + k_t + 4\theta)]/\Delta \tag{4.2}$$

where

$$\Delta = 8(1 + k_t)(2 + k_s + k_t)^2 + 2(2 + k_s + k_t)(16 + 3k_s + 13k_t)\theta + 8(8 + 3k_s + 5k_t)\theta^2 \tag{4.3}$$

$$k_s = \frac{k_c^S}{k_D}, \quad k_t = \frac{k_c^T}{k_D}, \quad k_D = 4\pi\sigma D, \quad \theta = \sqrt{\frac{A\sigma^2}{2D}} \tag{4.4}$$

$$k_c^S = 4\pi\int_0^{\infty} dr\, r^2\, W_S(r) \tag{4.5}$$

$$k_c^T = 4\pi\int_0^{\infty} dr\, r^2\, W_T(r) \tag{4.6}$$

Let us consider the triplet quantum yield in the limit of slow diffusion $D \rightarrow 0$, when it is under diffusional control. Substituting eqs 4.1 and 4.2 into eq 3.20, we obtain

$$\varphi_T \simeq \frac{3\theta}{8k_s} \sim D^{1/2} \tag{4.7}$$

In the opposite limit $D \rightarrow \infty$, it follows that the yield is hindered by the fast ion separation not allowing the time for spin conversion

$$\varphi_T \simeq \frac{3\theta k_t}{8} \sim D^{-3/2} \tag{4.8}$$

Thus, in both limits, φ_T vanishes and therefore a maximum of this function in a region intermediate between these limits should be expected. For a more detailed analysis see ref 13.

Simple equations determining the characteristics of the maximum, can be obtained for the case of a large recombination rate to the triplet state, $k_t \gg k_s$, θ, 1. This region of the parameters is of special interest for the system considered here, because for reasonable values of the effective HFI constant, the calculated triplet quantum yield approaches the experimental values only in this limit. Making use of eqs 4.1 and 4.2, we get

$$\varphi_T = \frac{3\theta/8}{1 + k_s + 3\theta/8} \tag{4.9a}$$

$$\varphi_S = \frac{k_s}{1 + k_s + 3\theta/8} \tag{4.9b}$$

$$\varphi = \frac{1}{1 + k_s + 3\theta/8} \tag{4.9c}$$

It should be emphasized that in this limit the quantum yields do not depend on the triplet recombination rate because saturation has been achieved, that is, all triplet RIPs recombine as soon as they reach the closest approach distance, σ. This equation provides a good approximation everywhere over the region of the D values, except for the fast diffusion wing where k_t becomes less than unity.

The quantum yields are determined by two independent dimensionless parameters, k_s and θ. Both of them can be readily extracted from the measured values of the quantum yields. Indeed, it is follows from eq 4.9

$$\frac{\varphi_T}{\varphi} = 3\theta/8 \tag{4.10a}$$

$$\frac{\varphi_S}{\varphi} = k_s \tag{4.10b}$$

These equations predict a very simple diffusion dependence of the quantum yields ratios. Hence, experimental investigations of the viscosity dependence of the quantum yields could provide us with very valuable data which would allow direct determination of the intrinsical parameters of the process.

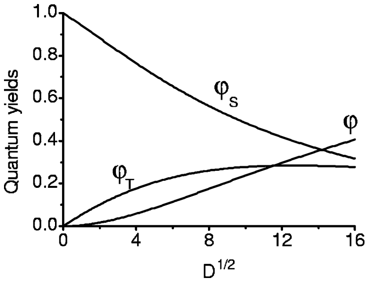

Figure 5. Diffusional dependencies of the free ions as well as singlet and triplet recombination quantum yields calculated in the framework of the contact model eqs 4.1 and 4.2. The diffusion coefficient D is given in Å^2/ns. The parameters are $\sigma = 7.5$ Å, $A = 34$ ns^{-1}, $k_c^S = 20$ Å^3/ps, $k_c^T = 290$ Å^3/ps. See also Figure 6 in ref 14.

Equation 4.9 shows that, if k_c^S and A are not zero, the variation of the diffusion coefficient in a sufficiently wide range should inevitably lead to intersections of the curves φ_T and φ_S with φ (see Figure 5). From the equation $\varphi_T = \varphi$, we obtain

$$D_T = \frac{9A\sigma^2}{128} \tag{4.11}$$

This equation determines the value of the diffusion coefficient, D_T, at which the two curves, φ_T and φ, intersect. If the crossing point, D_T, lies in the experimentally achievable region, as it does for the system considered,[3] eq 4.11 fixes the product $A\sigma^2$, and as long as the value of σ is well defined, eq 41 satisfactorily determines the value of the effective HFI constant.

Analogously, we obtain the point D_S where the curves, φ_S and φ, intersect

$$D_S = \frac{k_c^S}{4\pi\sigma} \tag{4.12}$$

This point allows obtaining the singlet recombination constant k_c^S. Unfortunately, this point in the system considered lies out of the region of experimental observation.

Equation 4.9 predicts a bell-shaped dependence of φ_T on the diffusion coefficient. The maximum is reached at the point $D = D_{max}$ determined by the equation

$$D_{max} = \frac{k_c^S}{4\pi\sigma} \tag{4.13}$$

and the maximum value of φ_T is equal to

$$\varphi_T^{max} = \frac{\gamma}{2 + \gamma} \tag{4.14}$$

where

$$\gamma = \frac{3}{8}\sqrt{\frac{2\pi A\sigma^3}{k_c^S}} \tag{4.15}$$

Two other quantum yields are equal at the point $D = D_{max}$ to $1/(2 + \gamma)$ both being less than a half. This is a very natural result because $k_s = 1$ at the point $D = D_{max}$ (see eqs 4.13 and 4.9).

Experimental data demonstrate a monotonous increase of φ_T in the whole region investigated,[3] 1 Å^2/ns $< D <$ 136 Å^2/ns. This implies that the maximum has not been reached, and from eq 4.13, we obtain an estimation $k_c^S > 4\pi\sigma 136 = 12800$ Å^3/ns.

B. Coherent vs Incoherent Singlet−Triplet Evolution. It is worthy to note that in the case of a zero magnetic field the incoherent model of singlet−triplet evolution leads to exactly the same results as the coherent one in either the slow or fast diffusion limits.[3,11] The incoherent spin conversion is described by the rate equations for the spin state populations[11]

$$\dot{m}_S = -3K_S m_S + K_S m_T \tag{4.16a}$$

$$\dot{m}_T = 3K_S m_S - K_S m_T \tag{4.16b}$$

where $m_S = m_{SS}$ and $m_T = m_{T_0T_0} + m_{T_+T_+} + m_{T_-T_-}$ are the populations of the RIP's singlet and triplet states, respectively.

The recombination efficiencies for this model are[3]

$$\frac{Z_T}{D} = \frac{3\alpha k_t/4}{1 + k_t + \alpha} \tag{4.17}$$

$$\frac{Z_S}{D} = k_s - \frac{3\alpha k_s/4}{1 + k_t + \alpha} \tag{4.18}$$

where $\alpha = (4K_S\sigma^2/D)^{1/2}$.

In the whole region $k_t \gg k_s$, α, 1, the corresponding quantum yields are

$$\varphi_T = \frac{3\alpha/4}{1 + k_s + 3\alpha/4} \tag{4.19a}$$

$$\varphi_S = \frac{k_s}{1 + k_s + 3\alpha/4} \tag{4.19b}$$

$$\varphi = \frac{1}{1 + k_s + 3\alpha/4} \tag{4.19c}$$

They are identical to eq 4.9 provided that $\theta = 2\alpha$, that is

$$A/2 = 16K_S \tag{4.20}$$

We see that the predictions for the coherent and incoherent models coincide if eq 4.20 holds. These results indicate unequivocally that the quantum yields of the geminate recombination and free ion formation are weakly sensitive to the mechanism of the spin conversion and the determinative quantity is an effective rate of the spin transitions. This consequence allows us also to suppose that the electronic spin interaction with many nuclear spins may be approximated well by an interaction with a single nuclear spin characterized by an effective HFI constant.

C. Contact Theory vs Experimental Data. We first of all compare the theoretical dependencies of the quantum yields on the diffusion coefficient with those obtained in the experimental explorations of the Per/DMA system in sulfoxide-glycerol mixtures and published in ref 3. In Figure 6 A, the experimental values of the ratio φ/φ_T versus $D^{1/2}$ are depicted. They show that in the region of slow diffusion there is a considerable deviation of the experimental results from the theoretical linear dependence following from eq 4.10a. The linear best fit gives a straight line the slope of which should be equal to $(8/3)[2/(A\sigma^2)]^{1/2}$. This leads to the effective HFI constant $A = 36$ ns^{-1}.

The experimental data allows one to determine also the point of intersection of the φ and φ_T curves. Figure 11 in ref 3 shows that the intersection lies in the vicinity of the experimental point corresponding to the largest value of the diffusion coefficient $D = 136$ Å^2/ns. Using eq 4.11, we get $A = 34$ ns^{-1} which is rather close to that found above from the best fit. Both of them are at least 1 order of magnitude larger than that estimated from

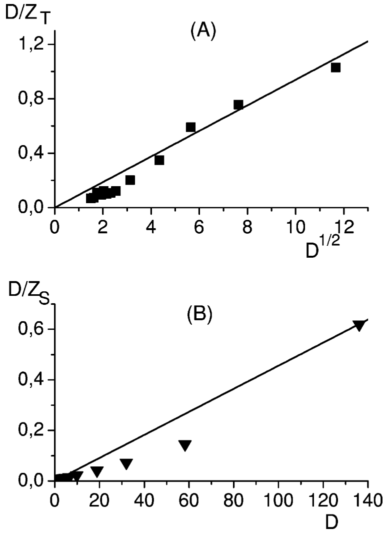

Figure 6. (A) Ratio $\varphi/\varphi_T = D/Z_T$ versus $D^{1/2}$. The straight line is a prediction of the contact theory. (B) The ratio $\varphi/\varphi_S = D/Z_S$ versus D. The straight line is a prediction of the contact theory. The symbols are experimental data.[3]

the well-known values of HFI constants between electronic spins of Per and DMA ion-radicals and each nuclear spin (see next section).

In Figure 6B, the experimental data[3] for φ/φ_S versus the diffusion coefficient D are plotted. Contrary to eq 4.10b, the experiment shows a pronounced nonlinear dependence. This discrepancy and the too large magnitude of the HFI constant A obtained from the fitting lead us to conclude that the theory of contact photoionization and geminate recombination in the Per/DMA pairs, does not provide an adequate description of the quantum yield dependence on the diffusion coefficient.

V. Fitting a Model of Remote Ionization and Recombination

To investigate the quantum yield dependence on the solvent viscosity for the remote ionization and recombination the problem was solved numerically. The code was first tested on the contact model with a known solution.[14]

The following fixed parameters were used:[1−3] $\Delta G_I = -0.56$ eV, $\Delta G_T = -0.72$ eV, $\Delta G_S = -2.27$ eV, $\tau = 4.3$ ns, $\sigma = 7.5$ Å, $c = 0.033$ M, $T = 300$ K, $\Omega = 0.15$ eV, the singlet−triplet splitting in RIPs has been set to $J = 0$.[10] The parameters of the classical reorganization energy, λ_i and λ_m, were accepted the same for the ionization and both recombination channels. The best fit parameters are as follows: the ionization electronic coupling $V_I = 0.00607$ eV, the triplet and singlet recombination electronic couplings $V_T = 0.02$ eV, $V_S = 0.00488$ eV, the tunneling length $L = 1.24$ Å, the effective HFI constant $A = 9$ ns^{-1}, $\lambda_i = 0.13$ eV, $\lambda_m = 0.885$ eV and the Huang−Rhys parameter $S = 4$.

The results of the fitting are presented in Figure 7. It is seen that all theoretical points excellently fit the experimental values, except for the last point at the largest diffusion coefficient. In the framework of the present theory, it is impossible to avoid this discrepancy.

We would like to stress that all fitting parameters are very reasonable, except for the HFI constant A. The last inconsistency is discussed in the next section.

VI. Magnetic Field Effect

There are two magnetic field sensitive quantities, which can be experimentally measured: the quantum yields of free ions and triplet products. The magnetic field effects (MFEs) are determined as follows:

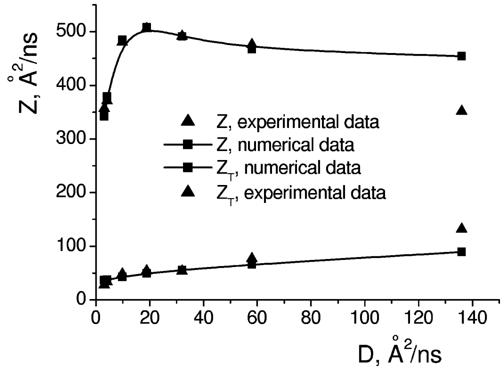

Figure 7. Best fit to the experimental diffusional dependence of the efficiencies. The values of the fitting parameters are given in the text.

$$R(B) = \frac{\varphi(B) - \varphi(0)}{\varphi(0)} \tag{6.1}$$

and

$$R_T(B) = \frac{\varphi_T(B) - \varphi_T(0)}{\varphi_T(0)} \tag{6.2}$$

Using the parameters obtained in the previous section, the MFEs of the free ions and triplet production have been calculated within the model of coherent spin-conversion used in section III. Because the g-factors of Per radical anion and DMA radical cation are very close to each other, the inequality $|\Delta\omega| = |\omega_A - \omega_D| \ll A$ is held in the magnetic fields considered. Therefore the Δg mechanism of spin conversion is not taken into account. The results are plotted in Figure 8. They show that the magnitude of the MFE for triplet recombination may be as large as 15%, whereas it does not exceed 3−4% for the free ion yield.

A distinguishing feature of these field dependencies is their nonmonotonous character. In particular, the quantity $R_T(B)$ has a rather high positive maximum in the region of weak fields (Figure 8A). Such a behavior is well-known.[26] Indeed in the fields $B \sim A$ the singlet level intersects one of the triplet levels of the RIP. This intersection enhances singlet−triplet transitions, sharply increasing the quantum yield of the triplet Per. Such an increase is not obvious because in the zero field the transitions into all triplet states are allowed. To appreciate this tendency, one should account for an interference of the transitions to three different triplet states that manifests itself in the non-additivity of these transitions.[26] Combination of the level intersection and interference of the transitions leads to a positive MFE for the triplet quantum yield in weak magnetic fields. In stronger fields, the Zeeman interaction lifts the degeneracy between the S, T_0, and $T_\pm$ states and the singlet−triplet transition probability is reduced. This results in a lowering of the singlet−triplet transition probability and, hence, in negative $R_T(B)$. So, one may expect that the quantity $R_T(B)$ has a maximum in the fields $B \sim A$.[26] Unfortunately, the MFE in Per$^-$/DMA$^+$ has not been detected yet, whereas in a similar system, containing pyrene and DMA, it has been known for a long time.[10] However, the extremum in small fields was not reached in this system, since rather large $B > 6 \times 10^{-4}$ T only were used. The maximal MFE was estimated by the extrapolation of the descending branch to the zero field.[27]

Figure 8 shows also that the changes of $R_T(B)$ and $R(B)$ are oppositely directed. This is an immediate consequence of the

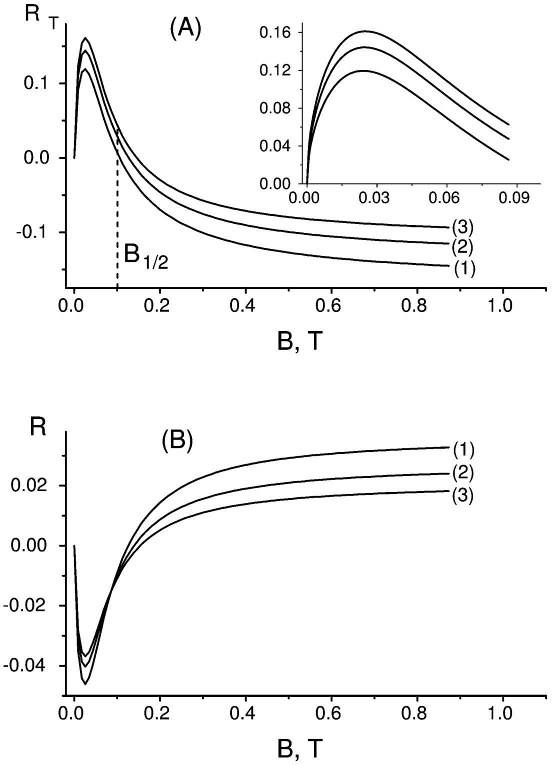

Figure 8. Magnetic field effect on triplet Per production (A) and free ion yield (B). The effect calculated for three values of the diffusion coefficient: (1) $D = 9.8$ Å^2/ns (corresponds to the viscosity coefficient of the solvent[3] $\eta = 31.5$ cP), (2) $D = 18.9$ Å^2/ns (16.3 cP), (3) $D = 32$ Å^2/ns (9.6 cP). The remaining parameters are the same as in Figure 7. Insert: details of MFE, R_T, in weak fields.

fact that the effective rate of the triplet recombination is larger than that of the singlet recombination. Indeed, in this case, singlet−triplet transitions producing triplet RIPs increase the total recombination quantum yield, hence, decreasing the free ion quantum yield.

Using the definition of $B_{1/2}$ as the magnetic field strength at which the MFE is $R_T(B_{1/2}) = (R_T^{\max} - R_T^{\min})/2$, where $R_T^{\max}$ and $R_T^{\min}$ are maximum and minimum values of R_T pictured in Figure 8, we obtain $B_{1/2} = 0.101$ T. It is apparent that this value specified by the above choice of fitting parameters (including A) is too large. Indeed, using eq 3 and the HFI constants,[23,24] we obtain $B_1 = 8.2 \times 10^{-4}$ T for Per$^-$ and $B_2 = 27.0 \times 10^{-4}$ T for DMA$^+$. It results in $B_{1/2} = 45.6 \times 10^{-4}$ T. This theoretical value is 20 times smaller than that obtained from the fitting. The corresponding HFI constant can be estimated from the empirical relationship between A and $B_{1/2}$: $B_{1/2} \simeq 2A$. That is, theoretically we should expect A to be 23×10^{-4} T instead of $A = 9$ ns$^{-1} \simeq 505 \times 10^{-4}$ T, obtained from the fitting to the true kinetic data.

Such a huge overestimation of A obtained from the fitting shows that some important features of the process are not reflected in the model. The clue of how to overcome this drawback may be taken from the contact approximation. Indeed, eqs 4.1−4.6 clearly demonstrate that the triplet quantum yield, φ_T, depends on the value of A only through the dimensionless parameter $\theta^2 = A\tau_d/2$, where $\tau_d = \sigma^2/D$ is the encounter time of the neutral particles. Apparently, the value of φ_T does not change if A reduces but τ_d increases accordingly. The overestimation of A is due to underestimation of τ_d, resulting from neglecting two important factors: the Coulomb attraction between the counter-ions and their solvation making the ions larger and slower than neutral reactants.

It is well-known that the Coulomb interaction increases the lifetime of the geminate radical-ion pair. The encounter time, τ_c, accounting for the Coulomb interaction is[11]

$$\tau_c = \frac{r_c^{\,2}}{D[1 - e^{-r_c/\sigma}]^2}$$

where $r_c = e^2/(\epsilon T)$ is the Onsager radius of the Coulomb attraction and ϵ is the static dielectric permittivity of the solvent. The static dielectric permittivity of dimethyl sulfoxide-glycerol mixtures is $\epsilon \simeq 43$, and $r_c \simeq 12$ Å. So, the Coulomb interaction can increase the encounter time only by a factor of 4.

On the other hand, the ions in polar solvents being solvated can be considered as quasi-particles of larger diameter than their neutral precursors. The solvation reduces also the diffusion coefficient $\tilde{D} < D$ due to the inverse dependence of the diffusion coefficient of particles on their radius. The encounter time can be increased by a factor of 20 or so in total (together with the Coulomb attraction), if one suppose the solvated ions to have the closest approaching distance, $\tilde{\sigma}$, larger than that of the neutral precursors by a factor of 1.7. So we may expect that a theory accounting for the solvation of ions can provide a satisfactory description of the triplet recombination and free ion formation with real effective HFI constant $A = 23 \times 10^{-4}$ T.

VIII. Conclusion Remarks

In this paper, we have shown that (i) contact and noncontact models of geminate recombination predict qualitatively different viscosity dependencies of the free ions quantum yields (Angulo effect); (ii) the fitting of these dependencies with the rate model of spin conversion and the Marcus electron-transfer rates is somewhat successful but only in a zero magnetic field; (iii) the HFI model of spin conversion has to be used instead of the rate one to describe qualitatively and quantitatively the magnetic field effects on the yields of free ions and the triplet products of photoionization.

The fitting of all the yields and their viscosity dependencies is surprisingly good although the real geometry of the reactants and their chemical anisotropy was completely ignored. It appears that a proper account for the transfer rates space dispersion and true conversion mechanism is enough to reach such an impressive success, just using the matrix unified encounter theory of the phenomenon.

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(27) It should be also noted that for a freely diffusing system consisting of pyrene and DMA in acetonitrile, only a negative MFE, $R_T < 0$, was observed.[10] In this case, R_T is a monotonously decreasing function of the magnetic field strength B. The discrepancy between the experimental and theoretical data may have the following origin. In the experiments, the zero value of the external magnetic field strength was not reached. As indicated in ref 4, the smallest value was $B = 6 \times 10^{-4}$ T. Taking into account a very rapid rise of the MFE in a weak magnetic fields, we may suppose that the experimental value of the zero field MFE obtained from the extrapolation is close to its maximum value.