

Magnetic field effect on the hyperfine-induced electron spin motion in radicals undergoing diamagnetic-paramagnetic exchange

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A semiclassical description of the hyperfine-induced spin motion of radical pairs suggested recently [K. Schulten and P. G. Wolynes, *J. Chem. Phys.* **68**, 3292 (1978)] has been generalized to arbitrary magnetic field situations. Analytical expressions for the elements of the electron spin correlation tensor $\langle S(o) S(t) \rangle$ averaged over all nuclear spin configurations are derived and applied to calculate the time evolution of the electron spin state of radical pairs initially prepared in a singlet state. The treatment includes the possibility that the radicals undergo a diamagnetic-paramagnetic exchange reaction. The effect of such exchange on the magnetic field dependence of the radical pair (triplet) recombination is predicted.

I. INTRODUCTION

The unpaired electrons in radicals undergo a spin motion induced by the hyperfine interaction with the nuclear spins. In connection with spin-dependent reaction processes, this motion gives rise to the well-known chemically induced dynamic polarization.¹ If radical pairs are generated by photoinduced electron transfer in a pure singlet state, the initial spin alignment of the two unpaired electron spins is changed by the hyperfine interaction and after a few nanoseconds the radical pair assumes triplet character. Recombination of the radical pairs then leads to triplet products. External magnetic fields can alter the spin motion and give rise to a magnetic field modulation of the triplet products. This effect provides an experimental method for exploring the nanosecond dynamics of radical processes by magnetic fields² and has been observed for electron transfer in solution,³ at crystal surfaces,⁴ and in photosynthetic reaction centers.⁵

An analysis of the magnetic field effect requires accurate knowledge of the hyperfine-induced electron spin motion. The large number of electron and nuclear spin degrees of freedom makes a detailed quantum mechanical calculation a difficult, and in many cases impossible, task. We have therefore recently suggested a semiclassical description which treats the nuclear degrees of freedom in a statistical manner and applies in the limit of large numbers of nuclear spins.⁶ The approximation yields simple analytical expressions for the electron spin probability at zero and high magnetic field and was found to be in good agreement with the exact quantum mechanical results for the case of the pyrene (Py)/*N*, *N*-dimethylaniline (DMA) radical pairs. In this paper we want to apply the semiclassical description of Ref. 6 to arbitrary magnetic fields. The corresponding triplet probabilities acquire analytical formulas, albeit more complicated than those in the limits of zero and high field.

The semiclassical description of the hyperfine-in-

duced spin motion allows one to account for the effect of a diamagnetic-paramagnetic exchange reaction (electron hopping)



which plays a role in the case of electron transfer at crystal interfaces⁷ as well as in solution.⁸ A corresponding description had been proposed and applied to zero and high magnetic field situations in Ref. 6. In this paper we also generalize this description to arbitrary fields. The calculations yield the magnetic field dependence of the triplet recombination yield of radical pairs undergoing the exchange process (1), a quantity amenable to experimental observation.³

II. SEMICLASSICAL DESCRIPTION OF THE HYPERFINE-INDUCED SPIN MOTION

In the semiclassical description of the hyperfine-induced spin motion presented in Ref. 6, the electron spin S_k in each of the radicals $k = 1, 2$ precesses around the vector

$$\omega_k = \omega_L + I_k \quad (2)$$

with frequency ω_k . The first term accounts for the Zeeman-induced spin motion

$$\omega_L = \mu g B / \hbar \quad (3)$$

(for the sake of simplicity we will assume identical g values for both radicals)⁹ and the second term for the hyperfine coupling to the n_k nuclear spins I_{kI} on radical k

$$I_k = \sum_{i=1}^{n_k} a_{ki} I_{ki} \quad (4)$$

The semiclassical approximation assumes I_k to be constant in time, an assumption which holds for large n_k and small scatter in the values of the (isotropic) hyperfine coupling constants.

The time evolution of the operator $S_k(t)$ of an electron spin precessing about the vector ω_k is governed by

$$\frac{d}{dt} S_k(t) = \omega_k \times S_k(t)$$

and can be cast into the Heisenberg representation⁶

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$$S_k(t) = U_k(t) S_k(0) U_k^\dagger(t), \quad (5)$$

$$U_k(t) = \begin{pmatrix} v_k & iw_k x_k \\ iw_k \bar{x}_k & \bar{v}_k \end{pmatrix}, \quad (6)$$

where

$$v_k = \cos^2(\theta_k/2) \exp(i\omega_k t/2) + \sin^2(\theta_k/2) \exp(-i\omega_k t/2), \quad (7)$$

$$w_k = -\sin\theta_k \sin(\omega_k t/2), \quad (8)$$

$$x_k = \exp(i\phi_k). \quad (9)$$

The angles θ_k and ϕ_k define the orientation of ω_k with respect to ω_L .

We are interested in the electron spin motion for an ensemble of radical pairs with all nuclear spin configurations being equally likely. For large n_k the corresponding statistical distribution of I_k in the volume element $I_k + dI_k$ is given by the continuous function⁶

$$f^{(k)}(I_k) = \left(\frac{\tau_k^2}{4\pi}\right)^{3/2} \exp(-\frac{1}{4} I_k^2 \tau_k^2), \quad (10)$$

where¹⁰

$$\tau_k^{-2} = \frac{1}{6} \sum_{l=1}^{n_k} a_{kl}^2 I_{kl} (I_{kl} + 1). \quad (11)$$

The average over the nuclear spin distribution of radical k defined by $\langle \rangle_k$ is best carried out in polar coordinates, i.e.,

$$\langle q \rangle_k = (\tau_k^2/4\pi)^{3/2} \int_0^{2\pi} d\phi_k \int_{-1}^{+1} dy_k \int_0^\infty d\omega_k \omega_k^2 \times \exp(-\frac{1}{4} I_k^2 \tau_k^2) q(\omega_k, y_k, \phi_k), \quad (12)$$

with

$$I_k^2 = \omega_k^2 + \omega_L^2 - 2\omega_k \omega_L y_k, \quad (13)$$

$$y_k = \cos\theta_k. \quad (14)$$

Since $\langle x_k \rangle_k = 0$, one obtains by virtue of Eqs. (5) and (6)

$$\langle S_k^+(t) \rangle_k = \langle v_k^2 \rangle_k S_k^+(0), \quad (15)$$

$$\langle S_k^-(t) \rangle_k = \langle \bar{v}_k^2 \rangle_k S_k^-(0), \quad (16)$$

$$\langle S_k^z(t) \rangle_k = \langle v_k \bar{v}_k - w_k^2 \rangle_k S_k^z(0), \quad (17)$$

where S_k^+ and S_k^z represent the Pauli matrices in the spin $\frac{1}{2}$ representation, and

$$v_k^2 = \frac{1}{2} (1 + y_k^2) \cos\omega_k t + \frac{1}{2} (1 - y_k^2) + iy_k \sin\omega_k t, \quad (18)$$

$$v_k \bar{v}_k - w_k^2 = (1 - y_k^2) \cos\omega_k t + y_k^2. \quad (19)$$

The quantity of key interest, as pointed out in the Introduction, is the probability $p_T(t)$ to find a radical pair, initially ($t=0$) generated in a singlet state, at time t in a triplet state. Once the time evolution of S_k is established, $p_T(t)$ can be evaluated. According to Ref. 6, the triplet probability is determined by the spin correlation tensors ($k=1, 2$)

$${}_k \mathbf{T}^{(0)}(t) = \text{tr}_k \langle S_k(0) [S_k(t)]^\dagger \rangle_k \quad (20)$$

by virtue of

$$p_T(t) = \frac{3}{4} - {}_1 \mathbf{T}^{(0)}(t) : [{}_2 \mathbf{T}^{(0)}(t)]^\dagger. \quad (21)$$

The trace in (20) is taken over the two electron spin states in radical k . The tensor product in (21) is de-

defined as $(\mathbf{A} \mathbf{B}) : (\mathbf{C} \mathbf{D}) = \mathbf{A} \cdot \mathbf{C} \mathbf{B} \cdot \mathbf{D}$. From Eqs. (15) to (17) and $\text{tr}_k [S_k^+ S_k^z] = \text{tr}_k [S_k^z S_k^-] = \frac{1}{2}$ follows

$${}_k \mathbf{T}^{(0)}(t) = \frac{1}{2} \begin{pmatrix} \langle v_k^2 \rangle_k & 0 & 0 \\ 0 & \langle \bar{v}_k^2 \rangle_k & 0 \\ 0 & 0 & \langle v_k \bar{v}_k - w_k^2 \rangle_k \end{pmatrix} \quad (22)$$

and hence

$$p_T(t) = \frac{3}{4} - \frac{1}{4} [2 \text{Re}(\langle v_1^2 \rangle_1 \langle \bar{v}_2^2 \rangle_2) + \langle v_1 \bar{v}_1 - w_1^2 \rangle_1 \langle v_2 \bar{v}_2 - w_2^2 \rangle_2]. \quad (23)$$

III. EVALUATION OF NUCLEAR SPIN AVERAGES

The averages $\langle v_k^2 \rangle_k$ and $\langle v_k \bar{v}_k - w_k^2 \rangle_k$ needed for the evaluation of the spin correlation tensors ${}_k \mathbf{T}^{(0)}$ and the triplet probability entail integrals of the type

$$\langle p(y) g(\omega t) \rangle = \frac{\tau^3}{8\sqrt{\pi}} \exp(-\alpha^2) \times \int_{-1}^1 dy p(y) \left(-\frac{\partial^2}{\partial t^2}\right) I[g(\omega t)], \quad (24)$$

where $\alpha = \omega_L \tau/2$,

$$I[g(\omega t)] = \int_{-\infty}^{+\infty} d\omega g(\omega t) \exp[-(\omega\tau/2)^2 + y\omega\omega_L \tau^2/2], \quad (25)$$

and $p(y)$ and $g(\omega t)$ assume the functional forms

$$p(y) = 1; \quad y; \quad y^2,$$

$$g(\omega t) = 1; \quad \cos\omega t; \quad \sin\omega t,$$

however, only in such combinations that p and g are both either even or odd functions. The integral (25) can be solved analytically (for the derivation see Appendix A):

$$I[g(\omega t)] = (2\sqrt{\pi}/\tau) \exp(-\beta^2/4\alpha^2 + y^2\alpha^2) g(\beta y) \quad (26a)$$

for $g(x) = 1, \cos x, \sin x$, and

$$\alpha = \omega_L \tau/2, \quad \beta = \omega_L t. \quad (26b)$$

The following expressions are then obtained for the averages defined by Eq. (24):

$$\langle p(y) \cos\omega t \rangle = \exp(-\beta^2/4\alpha^2) \int_0^1 dy p(y) \times \exp[\alpha^2(y^2 - 1)] [A(y) \cos\beta y - B(y) \sin\beta y], \quad (27)$$

$$\langle p(y) \sin\omega t \rangle = \exp(-\beta^2/4\alpha^2) \int_0^1 dy p(y) \times \exp[\alpha^2(y^2 - 1)] [A(y) \sin\beta y + B(y) \cos\beta y], \quad (28)$$

where

$$A(y) = 2\alpha^2 y^2 + 1 - \beta^2/2\alpha^2, \quad (29)$$

$$B(y) = 2\beta y.$$

The following functions will be needed:

$$C_n(\alpha, \beta) = \int_0^1 dy y^{2n} \exp[\alpha^2(y^2 - 1)] \cos\beta y, \quad (30)$$

$$S_n(\alpha, \beta) = \int_0^1 dy y^{2n+1} \exp[\alpha^2(y^2 - 1)] \sin\beta y, \quad (31)$$

$$I_n(\alpha) = \int_0^1 dy y^{2n} \exp[\alpha^2(y^2 - 1)]. \quad (32)$$

By virtue of Eqs. (18) and (19) and (27)–(29) and the equations listed in Appendix B, one obtains

$$\langle v_k^2 \rangle_k = (1/2 \alpha_k^2) \{ \exp(-\beta^2/4\alpha_k^2) [C_0(\alpha_k, \beta) + \exp(i\beta)(2\alpha_k^2 - 1 + i\beta)] + 1 - I_0(\alpha_k) \}, \quad (33)$$

$$\langle v_k \bar{v}_k - w_k^2 \rangle_k = \alpha_k^{-2} \{ \exp(-\beta^2/4\alpha_k^2) [\cos\beta - C_0(\alpha_k, \beta)] + \alpha_k^2 + I_0(\alpha_k) - 1 \}. \quad (34)$$

In the limit of large magnetic fields one observes the asymptotic behavior $\langle v_k^2 \rangle_k \rightarrow \exp(i\omega_L t - t^2/\tau_k^2)$ and $\langle v_k \bar{v}_k - w_k^2 \rangle_k \rightarrow 1$ and, hence, agreement with Ref. 6. For the case of zero field the results of Ref. 6 are recovered by virtue of $I_0(t) \rightarrow 1 - \frac{2}{3} \alpha^2 (\alpha^2 \ll 1)$ and $\langle v_k^2 \rangle_k = \langle v_k \bar{v}_k - w_k^2 \rangle_k = \frac{1}{3} [1 + 2(1 - 2t^2/\tau_k^2) \exp(-t^2/\tau_k^2)]$.

The components (33) and (34) require knowledge of the integrals $C_0(\alpha, \beta)$ and $I_0(\alpha)$ defined by Eqs. (30) and (32), respectively. I_0 is related to the error integral with imaginary argument

$$I_0(\alpha) = \exp(-\alpha^2) \sqrt{\pi} \operatorname{erf}(i\alpha) / 2i\alpha \quad (35)$$

and can be calculated by means of the expansions¹¹

$$I_0(\alpha) = \sum_{n=0}^{\infty} (-)^n \frac{(2\alpha^2)^n}{1 \cdot 3 \cdots (2n+1)} \quad |\alpha| < 1.5$$

$$I_0(\alpha) = \frac{\exp(-\alpha^2)}{2\sqrt{\pi}} \times \left(1 + \frac{2}{\alpha} \sum_{n=1}^{\infty} \frac{\exp[-(n/2)^2]}{n} \sinh(n\alpha) \right) \quad 1.5 < |\alpha| < 3.5$$

$$I_0(\alpha) = \frac{1}{2\alpha^2} \left[1 + \sum_{n=1}^{n \leq 12} \frac{1 \cdot 3 \cdots (2n-1)}{(2\alpha^2)^n} \right] \quad |\alpha| > 3.5. \quad (36)$$

The last expansion in (36) is an asymptotic series which yields an accuracy of more than five significant digits.

The integral $C_0(\alpha, \beta)$ can also be expressed by means of the complex error function

$$C_0(\alpha, \beta) = (\sqrt{\pi}/2\alpha) \exp[(\beta^2/4\alpha^2) - \alpha^2] \operatorname{Im}[\operatorname{erf}[(\beta/2\alpha) + i\alpha]]. \quad (37)$$

For $\beta=0$ this expression reduces to $I_0(\alpha)$ as required by a comparison of Eqs. (30) and (32) [note: $\operatorname{Im}[\operatorname{erf}(i\alpha)] = -i \operatorname{erf}(i\alpha)$].

For the sake of numerical convenience, we rewrite Eq. (37) to yield

$$C_0(\alpha, \beta) = -(1/2\alpha) \operatorname{Im}\{[(\beta/2\alpha) + i\alpha]^{-1} \times \exp(-i\beta) F[(\beta/2\alpha) + i\alpha]\}, \quad (38)$$

where

$$F(z) = \sqrt{\pi} z \exp(z^2) \operatorname{erfc}(z). \quad (39)$$

An efficient algorithm for $F(z)$ had been pointed out in Ref. 12.

IV. HYPERFINE-INDUCED TRIPLET PROBABILITY

Figure 1 compares the semiclassical triplet probability at magnetic fields 10, 40, 60, and 150 G as evaluated by the method described in this paper and as predicted from an exact quantum mechanical analysis for a ${}^2\text{Py}^- + {}^2\text{DMA}^+$ radical pair generated in a singlet state. One finds good agreement between the quantum mechanical

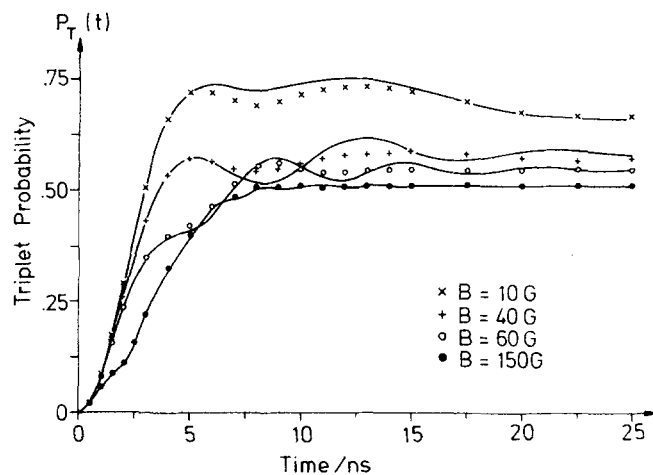


FIG. 1. Comparison of the triplet probability of the unpaired electron spins of ${}^2\text{Py}^- + {}^2\text{DMA}^+$ predicted by the semiclassical approach [—] and evaluated from an exact quantum mechanical analysis (Ref. 15) at four magnetic fields: 10 G [x], 40 G [+], 60 G [o], and 150 G [•]. The hyperfine coupling constants assumed are¹³ Py: $4 \times (a_{\text{H}} = 2.3 \text{ G})$, $4 \times (a_{\text{H}} = 5.2 \text{ G})$; DMA: $6 \times (a_{\text{CH}_3} = 12.0 \text{ G})$, $1 \times (a_{\text{N}} = 12.0 \text{ G})$, $3 \times (a_{\text{H}} = 6.25 \text{ G})$.

results (which involve great numerical effort) and the semiclassical description, especially for short times ($t \leq 5$ ns) and large magnetic fields ($B=60, 150$ G).

The small error ($\leq 7\%$) in the triplet probability can be traced to the contributions of small nuclear spin $\sum_i I_{ki}$ to the electron spin motion of radical pair ensembles. For small $\sum_i I_{ki}$ and at small magnetic fields, the time variation of I_k [Eq. (4)] cannot be neglected. However, small $\sum_i I_{ki}$ implies small I_k (as long as the a_{ki} values do not scatter too much) and hence slow electron spin precession, i.e., the error corresponding to the time variation of I_k surfaces only at later times. At large fields only the z component of I_k , which remains invariant in time, induces the electron spin motion. In this case a very small error is to be expected for all times.

V. EFFECT OF DIAMAGNETIC-PARAMAGNETIC EXCHANGE

We consider now the situation where the unpaired electron spin does not reside permanently on one molecule but rather exchanges between like molecules according to Reaction (1). The correlation tensor $\mathbf{T}^{(0)}(t)$ in the absence of any electron exchange on a time scale relevant for the hyperfine-induced spin motion has been determined in Secs. II and III by averaging over all nuclear spin configurations of an ensemble of radicals. When exchange occurs, the unpaired electron spin finds a new, random nuclear spin configuration, a situation illustrated in Fig. 2 for the ${}^1\text{DMA} + {}^2\text{DMA}^+ \rightarrow {}^2\text{DMA}^+ + {}^1\text{DMA}$ exchange. The electron spin transfer may then be described as a random change of I_k inducing a concomitant change of electron spin precession. As the situation is reminiscent of rotational diffusion, the treatment of the diamagnetic-paramagnetic exchange by electron transfer, presented in Ref. 6, had been based on the theory developed for the correlation function of rotating molecules.^{13,14}

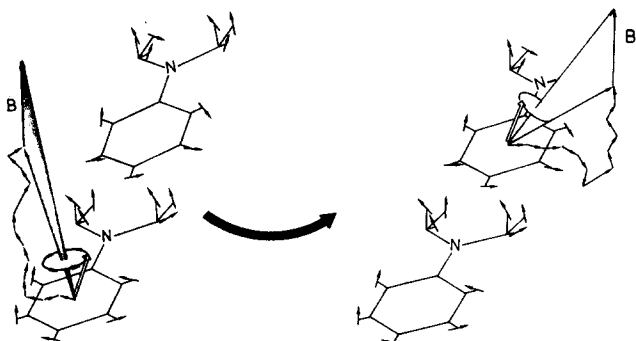


FIG. 2. Schematic illustration of the electron spin precession in the N,N -dimethylaniline (${}^2\text{DMA}^+$) radical undergoing diamagnetic-paramagnetic exchange, i. e., ${}^2\text{DMA}^+ + {}^1\text{DMA} \rightarrow {}^1\text{DMA} + {}^2\text{DMA}^+$.

To account for the exchange process (1) one must average the electron spin correlation tensor over all possible sequences of exchange events. Let us denote by ${}_h\mathbf{T}^{(n)}(t)$ the contribution to ${}_h\mathbf{T}(t)$ due to electron spins which have undergone $n - 1$ exchanges up to time t so that

$${}_h\mathbf{T}(t) = \sum_{n=1}^{\infty} {}_h\mathbf{T}^{(n)}(t). \quad (40)$$

The exchanges are assumed to be independent and to occur by first order kinetics. For a mean residence time τ_0 of the electron spin at a single molecule the probability of no exchange in the time interval $[0, t]$ is $\exp(-t/\tau_0)$. The contribution of spin precession without exchange to the sum of Eq. (40) is then

$${}_h\mathbf{T}^{(1)}(t) = \exp(-t/\tau_0) {}_h\mathbf{T}^{(0)}(t), \quad (41)$$

where ${}_h\mathbf{T}^{(0)}(t)$ has been defined by Eq. (20). When the exchange events are independent the further contributions to (40) are related by the recursion equation

$${}_h\mathbf{T}^{(n)}(t) = \tau_0^{-1} \int_0^t dt' {}_h\mathbf{T}^{(1)}(t-t') {}_h\mathbf{T}^{(n-1)}(t'). \quad (42)$$

Summing over all n yields

$${}_h\mathbf{T}(t) = {}_h\mathbf{T}^{(1)}(t) + \tau_0^{-1} \int_0^t dt' {}_h\mathbf{T}^{(1)}(t-t') {}_h\mathbf{T}(t'). \quad (43)$$

This equation, a Volterra integral equation of the first kind, can be solved separately for each component of the diagonal spin correlation tensor.

The solution of (43) in the limit of very slow exchange, i. e., $\tau_0 \rightarrow \infty$, is ${}_h\mathbf{T}(t) = {}_h\mathbf{T}^{(0)}(t)$. In the limit of very rapid exchange, i. e., $\tau_0 \rightarrow 0$, one can derive (see Appendix C).

$${}_h\mathbf{T}(t) \rightarrow \begin{pmatrix} \exp(i\omega_L t) & 0 & 0 \\ 0 & \exp(-i\omega_L t) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (44)$$

This correlation tensor corresponds to spin motion with vanishing hyperfine coupling.

Figure 3 presents the triplet probability for the ${}^2\text{Py}^- + {}^2\text{DMA}^+$ radical pair in an external magnetic field of 40 G when DMA undergoes diamagnetic-paramagnetic exchange processes (1). Varying the exchange rate τ_0^{-1}

from zero (no exchange) to infinite (very rapid exchange), one observes a drastic slowdown of the singlet \rightarrow triplet transition. This behavior can be rationalized as follows: When exchange weakens the ${}^2\text{DMA}^+$ hyperfine coupling, only the ${}^2\text{Py}^-$ coupling remains, which amounts to $\langle |I_{\text{Py}}| \rangle_{\text{Py}} = (8/\sqrt{\pi}) \tau_{\text{Py}}^{-1} = 18$ G. The slow increase of the triplet probability for fast electron exchange reflects this small value (18 G) of the mean hyperfine coupling strength of the ${}^2\text{Py}^-$ radical alone. There is also a transition from high field behavior to low field behavior (cf. Fig. 1) discernable for the triplet probability in Fig. 3 in going from slow to fast electron exchange. This is because 40 G is a rather weak magnetic field compared to the mean hyperfine interaction of ${}^2\text{Py}^- + {}^2\text{DMA}^+$, which under exchange-free conditions amounts to $\sum_{h=1}^2 \langle |I_h| \rangle_h = (8/\sqrt{\pi}) (\tau_1^{-1} + \tau_2^{-1}) = 77$ G. In the case of rapid exchange with an effective (${}^2\text{Py}^-$) hyperfine coupling of only 18 G, the 40 G field elicits rather a high field behavior of the triplet probability.

VI. MAGNETIC FIELD BEHAVIOR OF THE TRIPLET RECOMBINATION YIELD

We want to demonstrate in this section that the diamagnetic-paramagnetic exchange strongly affects the magnetic field dependence of the geminate triplet recombination yield $\phi_T(B)$, a quantity amenable to experimental observation. In the following we want to assume that the radical pairs undergo free Brownian motion and recombine with equal probability in their respective singlet and triplet electron spin states. These assumptions do not affect the qualitative magnetic field behavior of $\phi_T(B)$ (cf. Refs. 12 and 15). Our simplifying assumptions allow to express the triplet yield by the simple integral¹²

$$\phi_T(B) = \int_0^{\infty} dt \dot{n}(t) p_T(t, B), \quad (45)$$

where $\dot{n}(t)$ represents the recombination rate. For a radical pair (with a relative diffusion constant D) generated initially ($t=0$) at some distance r and recombining

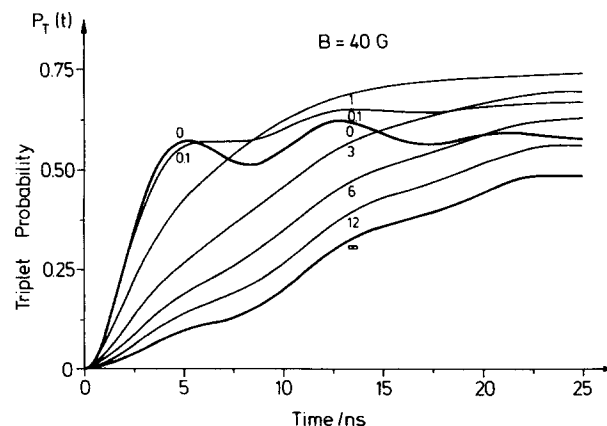


FIG. 3. Triplet probability of the ${}^2\text{Py}^- + {}^2\text{DMA}^+$ radical pair in case of diamagnetic-paramagnetic exchange involving ${}^2\text{DMA}^+$ for exchange rates τ_0^{-1} (in ns^{-1}) 0, 0.1, 1, 3, 6, 12, and ∞ at an intermediate magnetic field $B = 40$ G. The residence time τ_0 of Py is assumed to be infinite (no exchange). Hyperfine coupling constants are given below Fig. 1.

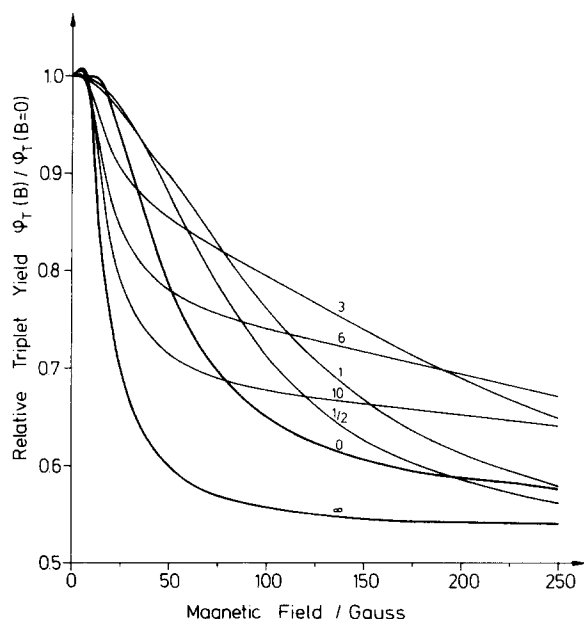


FIG. 4. Magnetic field dependence of the relative triplet recombination yield of the ${}^2\text{Py}^- + {}^2\text{DMA}^+$ radical pair in case of a diamagnetic-paramagnetic exchange involving ${}^2\text{DMA}^+$. Exchange rates τ_0^{-1} assumed are (in ns^{-1}) 0, 0.5, 1, 3, 6, 10, and ∞ . The treatment of diffusion and recombination of the radical pair is described in the text.

ing at the same distance, $\dot{n}(t)$ is determined by the expression¹²

$$\dot{n}(t) = (D/\pi t)^{1/2} [p/r(1-p)] \{1 - F[\sqrt{Dt}/r(1-p)]\}. \quad (46)$$

where $F(x)$ had been defined already by Eq. (39). p denotes the total recombination yield including singlet as well as triplet products. For our calculation of $\phi_T(B)$ we adopted the values $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $r = 6 \text{ \AA}$, and $p = 0.5$. It had been pointed out in Refs. 12 and 15 that the relative triplet yield $\phi_T(B)/\phi_T(B=0)$ does not vary for considerable changes of these constants. We have found the changes of $\phi_T(B)/\phi_T(B=0)$ to be smaller than 2% over the ranges $p \in [0.01, 0.99]$, $D/\text{cm}^2 \text{ s}^{-1} \in [10^{-6}, 5 \times 10^{-5}]$ and $r/\text{\AA} \in [5, 10]$.

Figure 4 presents the magnetic field dependence of the relative triplet yield $\phi_T(B)/\phi_T(B=0)$ for various exchange rates τ_0^{-1} of the ${}^2\text{DMA}^+$ radical. The magnetic field dependence of the triplet yield in the limit of no exchange agrees well with the previous quantum mechanical analysis of Ref. 15. The triplet yield in the limit of very rapid exchange which according to Eq. (44) corresponds to vanishing hyperfine coupling constants of the ${}^2\text{DMA}^+$ radical is also found in agreement with a previous calculation in Ref. 15. The cases of very rapid and very slow exchange both exhibit the typical magnetic field behavior observed previously (cf. Ref. 3), a rather sudden falloff of $\phi_T(B)/\phi_T(B=0)$ down to the saturation value $\phi_T(B \rightarrow \infty)/\phi_T(B=0)$ at the field $B_{1/2}$ defined in Ref. 12. The triplet yield for intermediate exchange rates shows a rather different behavior. The ${}^2\text{Py}^-$ electron spin motion not experiencing any exchange is affected by weak fields and hence contributes a low field decay to the relative triplet yield. The spin motion of ${}^2\text{DMA}^+$, the radical which undergoes the exchange reaction, is dominated by

the short time behavior of its correlation tensor as it can precess only for a short time in a fixed nuclear spin environment. It has been shown, however, that the short time spin precession requires large fields for a modulation of the triplet yield and only gradually reaches the saturation value.^{5c} The resulting overall behavior of the relative triplet yield, a sudden drop at low fields due to ${}^2\text{Py}^-$ and a gradual decrease at high fields due to ${}^2\text{DMA}^+$, is observed in Fig. 4 for τ_0^{-1} values 3 ns^{-1} , 6 ns^{-1} , and 10 ns^{-1} . Slower exchange does not yield the low field falloff, however, it exhibits the high field gradual decline. One should note that an exchange rate as low as 0.5 ns^{-1} induces a significant deviation from the magnetic field behavior without electron exchange. This exchange rate corresponds to a DMA concentration of about 0.1 mol l^{-1} in the experiment of Ref. 3 if one assumes the diamagnetic-paramagnetic exchange to be a diffusion controlled reaction, i. e., $\tau_0^{-1} = 4\pi D r_0$ ($D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $r_0 = 7 \text{ \AA}$).

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APPENDIX A

The identity (26) can be proven by first expanding $\exp(y\omega_L\tau^2/2)$ under the integral (25) in a Taylor series

$$I[g(\omega t)] = \sum_{n=0}^{\infty} \frac{(y\omega_L\tau^2/2)^n}{n!} \hat{I}_n[g(\omega t)], \quad (A1)$$

where

$$\hat{I}_n[g(\omega t)] = \int_{-\infty}^{+\infty} d\omega \omega^n g(\omega t) \exp[-\tau^2\omega^2/4]. \quad (A2)$$

In the case

$$g(\omega t) = \cos(\omega t),$$

one finds¹⁶

$$\hat{I}_n[\cos(\omega t)] = \begin{cases} 0 & \text{if } n \text{ odd} \\ (-)^{n/2} (2\sqrt{\pi}/\tau^{n+1}) \exp(-t^2/\tau^2) H_n(t/\tau) & \text{if } n \text{ even,} \end{cases} \quad (A3)$$

and by virtue of (A1) and (A3),

$$I[\cos(\omega t)] = 2\sqrt{\pi}/\tau \exp(-t^2/\tau^2) \times \sum_{n=0}^{\infty} \frac{(y\omega_L\tau/2)^{2n}}{(2n)!} (-)^n H_{2n}(t/\tau). \quad (A4)$$

Observing that the series in (A4) represents the generating function of Hermite polynomials,¹⁷ we obtain finally

$$I[\cos(\omega t)] = (2\sqrt{\pi}/\tau) \exp[-t^2/\tau^2 + (y\omega_L\tau/2)^2] \cos(\omega_L t). \quad (A5)$$

The same procedure applies to $I[\sin(\omega t)]$.

APPENDIX B

In order to simplify the expressions (27) and (28) to yield (33) and (34), the following properties of $C_n(\alpha, \beta)$ and $S_n(\alpha, \beta)$ given by Eqs. (30) and (31), respectively, were employed:

$$\frac{\partial^2}{\partial \beta^2} C_n(\alpha, \beta) = -C_{n+1}(\alpha, \beta), \quad (\text{B1})$$

$$\frac{\partial^2}{\partial \beta^2} S_n(\alpha, \beta) = -S_{n+1}(\alpha, \beta), \quad (\text{B2})$$

$$\frac{\partial}{\partial \beta} C_n(\alpha, \beta) = -S_n(\alpha, \beta), \quad (\text{B3})$$

$$\frac{\partial}{\partial \beta} C_0(\alpha, \beta) = (\beta/2\alpha^2) C_0(\alpha, \beta) - \sin(\beta/2\alpha^2). \quad (\text{B4})$$

The relations (B1), (B2), and (B3) are obvious. Equation (B4) is derived from Eq. (30) by partial integration.

APPENDIX C

To prove the limit (44), an expansion of $\langle v_k^2 \rangle_k$ [Eq. (33)] and $\langle v_k \bar{v}_k - w_k^2 \rangle_k$ [Eq. (34)] for small times t is required. Employing the expansion (36) for $I_0(\alpha)$ and $C_0(\alpha, \beta) = \sum_{n=0}^{\infty} (-)^n [\beta^{2n}/(2n)!] I_n(\alpha)$, we obtain

$$T_{11}^{(0)} = \bar{T}_{22}^{(0)} = \langle v_k^2 \rangle_k = 1 + i\omega_L t + O(t^2),$$

$$T_{33}^{(0)} = \langle v_k \bar{v}_k - w_k^2 \rangle_k = 1 + O(t^2). \quad (\text{C1})$$

The Volterra equation (43) describing T_{33} can be cast into the form

$$U(t) = 1 + \tau_0^{-1} \int_0^t dt' U(t'), \quad (\text{C2})$$

where

$$U(t) = \exp(t/\tau_0) T_{33}. \quad (\text{C3})$$

Equation (C2) is solved by $T_{33} = 1$. Invoking from (C1)

$$\langle v_k^2 \rangle_k = \exp(i\omega_L t) \quad (\text{C4})$$

for small t , an equation similar to (C2), (C3) is valid for the first two components of the spin correlation tensor T_{11} and T_{22} . By virtue of

$$U(t) = \exp[t/\tau_0 \mp i\omega_L t] T_{11}^{(22)} \quad (\text{C5})$$

one obtains

$$T_{11}^{(22)} = \exp[\pm i\omega_L t]. \quad (\text{C6})$$

- ¹L. T. Muus *et al.* (Eds.) *Chemically Induced Magnetic Polarization* (Reidel, Dordrecht, 1977).
- ²B. Brocklehurst, *J. Chem. Soc. Faraday Trans. 2* **72**, 1869 (1976), and references therein.
- ³(a) K. Schulten, H. Staerk, A. Weller, H.-J. Werner, and B. Nickel, *Z. Phys. Chem. NF* **101**, 371 (1976); (b) H.-J. Werner, H. Staerk, and A. Weller, *J. Chem. Phys.* **68**, 2419 (1978).
- ⁴R. P. Groff, A. Suna, P. Avakian, and R. E. Merrifield, *Phys. Rev. B* **9**, 2655 (1974), and references therein.
- ⁵(a) A. J. Hoff, H. Rademaker, R. van Grondelle, and L. N. M. Duyens, *Biochim. Biophys. Acta* **460**, 547 (1977); (b) R. E. Blankenship, T. J. Schaafsma, and W. W. Parson, *Biochim. Biophys. Acta* **461**, 297 (1977); (c) H. J. Werner, K. Schulten, and A. Weller, *Biochim. Biophys. Acta* **502**, 255 (1978).
- ⁶K. Schulten and P. G. Wolynes, *J. Chem. Phys.* **68**, 3292 (1978).
- ⁷K.-P. Charlè and F. Willig, *Chem. Phys. Lett.* **57**, 253 (1978), and references therein.
- ⁸G. L. Closs and M. S. Czeropski, *J. Am. Chem. Soc.* **99**, 6127 (1977); G. L. Closs and M. S. Czeropski, *Chem. Phys. Lett.* **53**, 321 (1978).
- ⁹The effect of different g values is included in the description given in K. Schulten and I. R. Epstein, *J. Chem. Phys.* (in press).
- ¹⁰A. misprint occurred in the corresponding Eq. (7) of Ref. 6.
- ¹¹M. Abramowitz and I. A. Stegun (Eds.), *Appl. Math. Ser. Natl. Bur. Stand. (US)* **55**, 295 (1970).
- ¹²Z. Schulten and K. Schulten, *J. Chem. Phys.* **66**, 4616 (1977).
- ¹³R. G. Gordon, *J. Chem. Phys.* **44**, 1830 (1966).
- ¹⁴B. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley-Interscience, New York, 1976).
- ¹⁵H.-J. Werner, Z. Schulten, and K. Schulten, *J. Chem. Phys.* **67**, 646 (1977).
- ¹⁶Reference 11, Eq. (22.10.15).
- ¹⁷Reference 11, Eq. (22.9.18).