The effect of intramolecular paramagnetic–diamagnetic exchange on the magnetic field effect of radical pair recombination

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Diamagnetic–paramagnetic exchange has a profound influence on the magnetic field dependence of the geminate recombination between the partners of a radical pair generated in a pure spin state. We consider the situation that the exchange takes place between two groups which are part of one molecule. We outline the proper theory of the spin dynamics, discuss the limits of slow and of fast exchange, and for these two situations provide an estimate of the $B_{1/2}$ value which characterizes the magnetic field dependence at intermediate fields. The theory provides the basis for a novel method of measuring the rates of electron transfer between two molecular sites with a defined geometry.

I. INTRODUCTION

In this paper we consider the recombination process between two doublet molecules (radicals) $^2D_1$ and $^2D_2$. Such a pair can be generated photochemically, e.g., by photoinduced electron transfer,[1,2] and then is initially in a pure singlet $^1(^2D_1 + {}^2D_2)$ or triplet $^3(^2D_1 + {}^2D_2)$ two electron spin state. Since the recombination products also assume a definite singlet (S) or triplet (^3T) spin state, radical recombination is selective with respect to the two spin alignments $^1(^2D_1 + {}^2D_2)$ and $^3(^2D_1 + {}^2D_2)$.

In a typical application[1,2] a radical pair is born in a singlet alignment and is converted into fast (ns) triplet products by means of magnetic interactions[1-5] according to the scheme

$$S \rightarrow {}^1(^2D_1 + {}^2D_2) \xrightarrow{p_T(t)} {}^3(^2D_1 + {}^2D_2) \rightarrow {}^3T. \qquad (1)$$
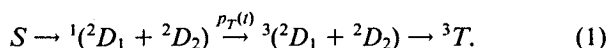
The reaction depends on the probability $p_T(t)$ that the initial singlet pair assumes triplet character after time t before $^2D_1$ and $^2D_2$ recombine. The observation of ^3T furnishes important information on the reaction dynamics of the radical pair $^2D_1 + {}^2D_2$ as reviewed for example in Ref. 5. It has also been realized[5-8] that such observations allow to measure the paramagnetic–diamagnetic exchange of one of the doublet partners, e.g., $^2D_{1a}^+ + {}^1D_{1b} \rightarrow {}^1D_{1a} + {}^2D_{1b}^+$. In Refs. 6, 7, and 8 the exchange considered occurred by random encounters between separable molecules. In the following we want to consider the situation that the exchange takes place between two groups which are part of one molecule. The theory developed for this case should then allow to determine the rates of electron transfer between groups with a defined geometry. For this purpose one needs to observe the magnetic field dependence of the triplet products ^3T of Eq. (1) and compare the data to theoretical predictions.

The dominant magnetic interactions of organic doublet molecules in solution which contribute to the time dependence of $p_T(t)$ in Eq. (1) are the Zeeman and the isotropic hyperfine interactions. These interactions are collected in the following spin Hamiltonian:

$$H = H_1 + H_2, \qquad (2)$$

$$H_i = \sum_k a_{ik}\mathbf{I}_{ki} \cdot \mathbf{S}_i + (g\mu_B/\hbar)\vec{\mathbf{B}} \cdot \mathbf{S}_i. \qquad (3)$$

The sum in Eq. (3) extends over all nuclear spins $\mathbf{I}_{ki}$ of ^2D_i with hyperfine coupling constants a_{ik} and electron spins $\mathbf{S}_i$, g is the relevant gyromagnetic ratio, μ_B the Bohr magneton of the electron, and $\vec{\mathbf{B}}$ the magnetic field. We will assume identical g values for the two doublets. Since most of the time during reencounters of $^2D_1$ and $^2D_2$ the doublet partners are well separated, the contribution of an exchange interaction to Eq. (2) can be neglected.

The triplet probability $p_T(t)$ relevant for reaction (1) can be expressed approximately as[6]

$$p_T(t) = \tfrac{3}{4} - {}_1\mathbf{U} : {}_2\mathbf{U}, \qquad (4)$$

where ($\alpha, \beta = +, -, z$ and $i = 1, 2$),

$$_i\mathbf{U}_{\alpha,\beta} = \langle \text{tr } S_{i\alpha}(0)S_{i\beta}(t) \rangle \qquad (5)$$

are the spin correlation tensors which describe the electron spin motion in each doublet, $S_{i\alpha}(t)$ are the electron spin operators in the Heisenberg representation, and $\langle \ \rangle$ denotes an average over the nuclear spins as specified below. The approximation in deriving Eq. (4) is based on a representation of the nuclear spin operators

$$\mathbf{I}_i = \sum_k a_{ik}\mathbf{I}_{ik} \qquad (6)$$

as continuous classical vectors which are unchanged during the electron spin motion. This approximation is useful and valid in case of large nuclear spin systems.[6,7] Defining

$$\omega_i = \mathbf{I}_i + g\mu_B\vec{\mathbf{B}}/\hbar, \qquad (7)$$

the time development of the electron spins is described by the equation of motion

$$\partial_t\mathbf{S}_i(t) = \omega_i \times \mathbf{S}_i(t). \qquad (8)$$

In the representation of the spin vector operator $\mathbf{S}_i = (S_{i+}, S_{i-}, S_{iz})$ the solution of this equation is

$$S_i(t) = \mathbf{B}(t)S_i(0), \tag{9}$$

where

$$\mathbf{B}(t) = \begin{pmatrix} v^2 & w^2 x^2 & -iwvx \\ w^2 \bar{x}^2 & \bar{v}^2 & iw\bar{v}\bar{x} \\ -2iwv\bar{x} & 2i\bar{w}\bar{x} & v\bar{v} - w^2 \end{pmatrix}, \tag{10}$$

$$v = \cos^2 \theta/2 \; e^{i\omega t/2} + \sin^2 \theta/2 \; e^{-i\omega t/2},$$

$$w = -\sin \theta \sin(\omega t/2),$$

$$x = e^{i\phi}. \tag{11}$$

The angles θ, ϕ describe the orientation of ω_i as given in Eq. (7).

Actual observations involve radicals with a random orientation of nuclear spins $\mathbf{I}_{ki}$ in Eqs. (6) and (7) and, hence, an ensemble average over the nuclear spin orientations is required. At large fields ($B \to \infty$), this average denoted by $\langle \; \rangle$ in Eq. (5) yields the spin correlation tensor[6] ($\omega_0 = g\mu_B B/h$)

$$_i\mathbf{U}_{\alpha,\beta} = \begin{cases} \exp(\pm i\omega_0 t)e_0(t/\tau_i) & \alpha\beta = +-, -+ \\ \frac{1}{2} & \alpha\beta = zz \\ 0 & \text{else} \end{cases}, \tag{12}$$

$$e_0(u) = \exp(-u^2),$$

$$\tau_i^{-2} = \frac{1}{6}B_i^2; \quad B_i^2 = \sum_k a_{ik}^2 I_{ik}(I_{ik} + 1). \tag{13}$$

Here the I_{ik} represent the nuclear spin quantum numbers, e.g., $\frac{1}{2}$ for hydrogen. The tensor describing the spin motion at arbitrary fields can be described as well.[7]

II. TRIPLET YIELD WITHOUT EXCHANGE

The yield of triplet products which are generated by the mechanism (1) assumes its maximum for small fields of a few Gauss and decreases monotonically to a constant asymptotic value at large fields of about 1 kG. The magnetic field dependence of the triplet yield $\phi_T(B)$ can be characterized by the so-called $B_{1/2}$ value. This value measures the magnetic field strength at which half of the asymptotic ($B \to \infty$) decrease of the triplet yield is observed, i.e.,

$$\phi_T(B = 0) - \phi_T(B_{1/2}) = \frac{1}{2}[\phi_T(B = 0) - \phi_T(B \to \infty)]. \tag{14}$$

The $B_{1/2}$ value is defined properly only for situations in which $\phi_T(B)$ does, in fact, reach an asymptotically constant value at fields of about 1 kG, i.e., at the strongest fields applied in an observation.

The $B_{1/2}$ value can be estimated on the basis of the approximation leading to Eqs. (4)–(13). The mean square magnetic moment of a doublet with many hyperfine-coupled nuclei is B_i^2 as given by Eq. (13). If one assumes that the doublets for the second term $\mathbf{I}_i$ in Eq. (7) all take on the absolute value B_i, i.e., $\mathbf{I}_i = B_i \cdot \mathbf{e}_i$, one can determine the average orientation ψ_i of ω_i relative to the field $\vec{B}$ on the basis of an arbitrary orientation of the unit vector $\mathbf{e}_i$. In case $B_i < B$ one obtains for the average over all $\mathbf{e}_i$,

$$\langle \cos \psi_i \rangle = 1 - \frac{1}{3}(B_i/B)^2.$$

The relative orientation ψ between ω_1 and ω_2 is determined

by $\cos \psi = \cos \psi_1 \cos \psi_2 - \sin \psi_1 \sin \psi_2 \cos(\alpha_1 - \alpha_2)$, α_i representing the azimutal angles around $\vec{B}$. The average over the azimutal angles deletes the second term and, hence, the average relative orientation between ω_1 and ω_2 is simply $\langle \cos \psi_1 \rangle \langle \cos \psi_2 \rangle$. One may now characterize the relationship between the Zeeman and the hyperfine interaction at $B = B_{1/2}$ by a certain prescribed value of $\langle \cos \psi \rangle$. At high fields $\langle \cos \psi \rangle$ approaches the value 1, at very low fields holds $\langle \cos \psi_i \rangle = 2B/B_i$ and $\langle \cos \psi \rangle$ approaches zero. We have determined empirically that a value 0.9 for $\langle \cos \psi \rangle$ yields a good characterization of the $B_{1/2}$ value, i.e., the $B_{1/2}$ value can be determined by the relationship

$$[1 - \frac{1}{3}(B_1/B_{1/2})^2][1 - \frac{1}{3}(B_2/B_{1/2})^2] = 0.9. \tag{15}$$

Figure 1 demonstrates for data taken from Ref. 9 that an excellent agreement results between observed and estimated $B_{1/2}$ values. This agreement holds only as long as exchange processes or short lifetimes of the doublet pair $^2D_1 + ^2D_2$ do not alter the asymptotic field dependence of the triplet yield.

III. INTRAMOLECULAR DIAMAGNETIC-PARAMAGNETIC EXCHANGE

Equations (7)–(13) describe the electron spin motion of a doublet molecule as long as the unpaired electron resides only at a single molecular site. We will now consider a molecule in which two identical sites D_a and D_b exist between which the unpaired electron can be exchanged, i.e.,

$$^2D_a^+ - X - {}^1D_b \leftrightarrow {}^1D_a - X - {}^2D_b^+.$$

We will assume that the electron exchanged is the one labeled by $i = 1$ above and we will not specify this index in the following formulas. The group X should hold D_a and D_b preferably in a sterically fixed conformation.[10] One of the groups is ionized and in a doublet electron spin state. However, the charge and, concomitantly, the unpaired electron spin can exchange between D_a and D_b. For this exchange one should distinguish two limiting situations:
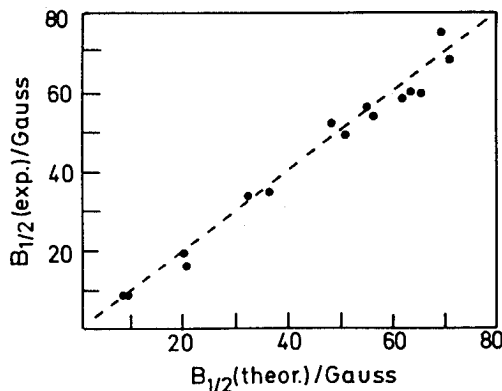

FIG. 1. Experimental $B_{1/2}$ values $B_{1/2}$ (exp) plotted against the theoretical values $B_{1/2}$ (theor) as determined through Eq. (15); the values $B_{1/2}$ are taken from Ref. 9.

(1) The exchange interaction between the groups D_a and D_b is strong such that the "jump rate" is much faster than the vibrational relaxation within the groups; in this limit the charge must be considered delocalized in a coherent quantum state over both D_a and D_b.

(2) The exchange interaction is weak, e.g., for a longer bridge, such that the jump rate is slower than vibrational relaxation in each group; in this limit the unpaired electron can be considered localized on one group at each instant of time.

In case (1) the hyperfine coupling constants a_{ik} assume half the values of those in separate doublets. In this case holds

$$B_1^2(d) = \tfrac{1}{2}B_1^2(s),   (16)$$

where $B_1(s)$ and $B_1(d)$ describe the B_1 values of Eq. (13) for a separated and for two strongly coupled groups, respectively. In this limit one expects that the $B_{1/2}$ value of the magnetic field dependent triplet yield will be diminished upon replacement of $^2D_a^+$ by $^2D_a^+ - X - {}^1D_b \leftrightarrow {}^1D_a - X - {}^2D_b^+$. The change of the $B_{1/2}$ value can be estimated by means of Eq. (15). For example, considering the system pyrene–dimethylaniline, one determines on the basis of the hyperfine coupling constants given in Ref. 4, a $B_{1/2}$ value of about 61 G which is close to the experimental value of 57 G. In the case of two strongly coupled dimethylanilines one predicts a lowering of the $B_{1/2}$ value to 45 G.

If situation (2) applies one has to distinguish two further limiting possibilities, fast (slow) exchange with an exchange rate τ_e^{-1} where τ_e is much smaller (larger) than the time constant τ for the electron spin motion given in Eq. (13). In the case of fast exchange one expects that the electron spin precession (8) is governed by the angular velocity $1/2(\omega_a + \omega_b)$ where ω_a and ω_b describe the precession in the separated groups ^2D_a and ^2D_b. This situation cannot be distinguished then, as far as the electron spin motion is concerned, from the situation (1) above. For a proof we consider the equation of motion (8) and assume for the sake of simplicity that the jump events take place at discrete times $n\tau_e$, $n = 1, 2, \ldots$. The variation of the spin operator $S(t)$ after $2n$ time steps τ_e is

$$\Delta S = \tau_e(n\omega_a + n\omega_b) \times S(t),   (17)$$

where terms of order $\omega_a\tau_e$ and $\omega_b\tau_e$ have been neglected. This variation of $S(t)$ corresponds to the equation of motion

$$\frac{dS}{dt} = 1/2(\omega_a + \omega_b) \times S(t).   (18)$$

Hence, one expects that for fast exchange between groups of the type (2) the spin motion approaches the behavior expected for strong coupling (1).

Next we consider the case of very slow exchange, i.e., $\tau_e \gg \tau$. In the limit that at most one exchange event takes place during the geminate recombination process (1) one can describe the evolution of $S(t)$ in analogy to a description given in Ref. 11,

$$S(t) = \left[\exp(-t/\tau_e)\langle B(t)\rangle_a + \tau_e^{-1}\int_0^t dt'\right.$$
$$\left. \times \exp(-t')\langle B(t')\rangle_a\langle B(t-t')\rangle_b\right]S(0),   (19)$$

where $\langle \ \rangle_a$ and $\langle \ \rangle_b$ denote the nuclear spin averages for the groups D_a and D_b of the bridged compound. The time evolution (19) reproduces exactly the behavior of paramagnetic–diamagnetic exchange by random encounters as described in Refs. 6, 7, and 11.

For faster exchange when more than one exchange event is likely to take place during the recombination process (1) one has to consider that the $^2D_a^+ - X - {}^1D_b \leftrightarrow {}^1D_a - X - {}^2D_b^+$ transitions involve *two random but fixed nuclear spin alignments and not a new alignment after each exchange.* In case of exchange between two random, but fixed nuclear spin alignments one has to replace the spin evolution operator $B(t)$ by the following series expansion of its Laplace transform:

$$\tilde{B}(s) = \sum_{n=1}^{\infty} \tilde{B}^{(n)}(s),   (20)$$

where

$$\tilde{B}^{(1)}(s) = \tilde{B}_a(s + \tau_e^{-1}),$$
$$\tilde{B}^{(2)}(s) = \tau_e^{-1}\tilde{B}_b(s + \tau_e^{-1})\tilde{B}_a(s + \tau_e^{-1}),   (21)$$
$$\tilde{B}^{(2n+1)}(s) = \tau_e^{-1}\tilde{B}_a(s + \tau_e^{-1})\tilde{B}^{(2n)}(s),$$
$$\tilde{B}^{(2n+2)}(s) = \tau_e^{-1}\tilde{B}_b(s + \tau_e^{-1})\tilde{B}^{(2n+1)}(s).   (22)$$

This yields

$$\tilde{B}(s) = [1 + \tau_e^{-1}\tilde{B}_b(s + \tau_e^{-1})][1 - \tau_e^{-2}\tilde{B}_a(s + \tau_e^{-1})$$
$$\times \tilde{B}_b(s + \tau_e^{-1})]^{-1}\tilde{B}_a(s + \tau_e^{-1}).   (23)$$

Equations (20) to (23) furnish the main result of this paper. These equations can be generalized in a straightforward way to describe exchange between three, four, . . . groups. Unfortunately, the averages $\langle \ \rangle_a$ and $\langle \ \rangle_b$ over this operator are difficult to perform. We will carry out the average below for the case of spin motion in high magnetic fields, a situation which renders the operator $B(t)$ diagonal. For the case of exchange by random encounters the average overall molecular sites a, b, c, . . . visited by the hopping electron has to be performed. As a result the operator corresponding to Eq. (23) becomes

$$\tilde{B}(s) = C[1 - \tau_e^{-2}C^2]^{-1}[1 + \tau_e^{-1}C] = C[1 - \tau_e^{-1}C]^{-1},   (24)$$

where $C = \langle B(s + \tau_e^{-1})\rangle$ is a diagonal operator. As to be expected this expression reproduces the evolution operator for exchange by random encounters derived in Refs. 6 and 7.

However, in the case of exchange between only two sites the effect that exchange processes repeatedly return the electron spin to the same molecular site with the same nuclear spin configuration introduces memory effects which are difficult to deal with. If this memory effect is neglected one would predict for very fast exchange that the effective B_1 value of Eq. (13) vanishes and, that

according to Eq. (15) the $B_{1/2}$ value for the respective pyrene–(dimethylaniline)$_2$ system should be only 18 G. However, this prediction is at variance with the expected spin dynamics derived from the evolution equation (18). This equation implies that for fast hopping of the electron between groups D_a and D_b the B_1 value should be given by Eq. (16) and, accordingly, the $B_{1/2}$ value should rather be about 45 G. If one is able, by appropriate synthesis of compounds $D_a - X - D_b$ for a pyrene–(dimethylaniline)$_2$ system, to vary the exchange time τ_e over a wide range one should observe for $\tau_e \gg 10$ ns a $B_{1/2}$ value of about 57 G and for $\tau_e \ll 1$ ns a $B_{1/2}$ value of about 45 G. For these extremes the magnetic field dependence should be similar to the situation without exchange, i.e., as observed in Refs. 1 and 2.

In order to predict the field dependence for the intermediate situation 10 ns $> \tau_e > 1$ ns one needs to determine the spin operator (23). For this purpose we suggest that one may actually evaluate the series expansion implied by Eqs. (20)–(22), employing the single site operator (10) and to carry out the average explicitly by means of a computer code capable of algebraic manipulations, like SMP.[12]

Expression (23) can be evaluated for the case of large magnetic fields. We will carry out this calculation as a demonstration of our theory. In the limit of large fields the operator (10) simplifies since for $\theta = 0$ one obtains

$$\mathbf{B}(t) = \begin{pmatrix} \exp(i\omega t) & 0 & 0 \\ 0 & \exp(-i\omega t) & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (25)$$

i.e., a diagonal single site evolution operator. As a result, Eq. (23) assumes a diagonal form as well with elements ($\omega_0 = g\mu_B/\hbar$),

$$\mathbf{B}(t) = \begin{pmatrix} e(t)\exp(i\omega_0 t) & 0 & 0 \\ 0 & e(t)\exp(-i\omega_0 t) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (26)$$

$e(t)$ replaces $e_0(t/\tau)$ in Eq. (13). From this follows according to Eq. (4),

$$p_T(t) = 1/2 - 1/2 e(t) e_0(t/\tau_2), \qquad (27)$$

where the electron on $^2D_1$ is being exchanged. In analogy to Eq. (23) the correlation function $e(t)$ is given by[13]

$$e(t) = L^{-1} \langle [s' - iI_a]^{-1}[1 - \tau_e^{-2}(s' - iI_a)^{-1}(s' - iI_b)^{-1}]$$
$$\times [1 + \tau_e^{-1}(s' - iI_b)^{-1}] \rangle_{a,b} \qquad (28)$$

where L^{-1} denotes the inverse Laplace transform $s' = s + \tau_e^{-1}$ and

$$\langle \cdots \rangle_{a,b} = (\tau^2/4\pi) \int_{-\infty}^{\infty} dI_a \int_{-\infty}^{\infty} dI_b$$
$$\times \exp[-(1/4)\tau^2(I_a^2 + I_b^2)] \cdots . \qquad (29)$$

For a further evaluation one may expand Eq. (27) in terms of partial fractions

$$e(t) = L^{-1} \langle [i(y + R) + 1]/[2iR(s' - i(x + R)]$$
$$- [i(y - R) + 1]/[2iR(s' - i(x - R)] \rangle_{x,y}, \qquad (30)$$

where $x = (I_a + I_b)/2$, $y = (I_a - I_b)/2$, $R = (y^2 - 1)^{1/2}$, and

$$\langle \cdots \rangle_{x,y} = \frac{1}{2\pi} (\tau/\tau_e)^2 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy$$
$$\times \exp[-1/2(\tau/\tau_e)^2(x^2 + y^2)] \cdots . \qquad (31)$$

Carrying out the x average and the inverse Laplace transform yields

$$e(t) = \exp[-t/\tau_e - 1/2(t/\tau)^2] \langle \{[i(y + R) + 1]/2iR\}$$
$$\times \exp(iRt/\tau_e) - \{[i(y - R) + 1]/2iR\}$$
$$\times \exp(-iRt/\tau_e) \rangle_y, \qquad (32)$$

and, since the y distribution is even,

$$e(t) = \exp[-t/\tau_e - 1/2(t/\tau)^2]$$
$$\times \langle \cos Rt/\tau_e + R^{-1} \sin Rt/\tau_e \rangle_y. \qquad (33)$$

This function can be expanded in terms of products of Bessel functions. However, the result appears to be neither illuminating nor useful. Alternatively, the factor $\langle \ \rangle_y$ in Eq. (33) can be expanded in powers of t/τ_e,

$$\langle \ \rangle_y = \sum_{\nu=0}^{\infty} (-1)^\nu (t/\tau_e)^{2\nu} \left[1 + \frac{t/\tau_e}{2\nu + 1} \right]$$
$$\times \frac{1}{(2\nu)!} \sum_{\mu=0}^{\nu} (-1)^{\nu-\mu} \binom{\nu}{\mu} (\tau_e/\tau)^{2\mu}$$
$$\times \begin{cases} 1 \cdot 3 \cdots (2\mu - 1) & (\mu = 1, 2, \ldots). \\ 1 & (\mu = 0) \end{cases} \qquad (34)$$

This expansion agrees with a result obtained recently in Ref. 14. Below [Eqs. (37) and (38)] we furnish a more convenient expression for the evaluation of Eq. (33).

We consider now $e(t)$ in the limits of fast and slow exchange. In case of slow exchange, i.e., $\tau_e \gg \tau$, the y distribution as defined in Eq. (31) is very broad, such that the contribution of large y values is dominant. In this limit $R = |y|$ and, hence,

$$e(t) = \exp[-1/2(t/\tau)^2] \langle \exp(iyt/\tau_e) \rangle_y$$
$$= \exp[-(t/\tau)^2], \qquad (35)$$

i.e., the spin correlation function of the situation without exchange is reproduced [see Eq. (12)].

In case of fast exchange, i.e., $\tau_e \ll \tau$, the y distribution is very narrow and centered around $y = 0$. This yields with $R = i$,

$$e(t) = \exp[-1/2(t/\tau)^2], \qquad (36)$$

i.e., the result expected according to the discussion above.

A numerical expression for $e(t)$ in case of intermediate τ_e can be constructed if one replaces the continuous y distribution in Eq. (33) by a discrete binomial distribution for some suitable N, i.e., $N \geq 5$,

$$e(t) = \langle f(y) \rangle_y$$
$$\simeq \sum_{j=-N}^{N} 2^{-2N} \binom{2N}{N+j} f(2j\tau_e/\tau \sqrt{N}). \qquad (37)$$
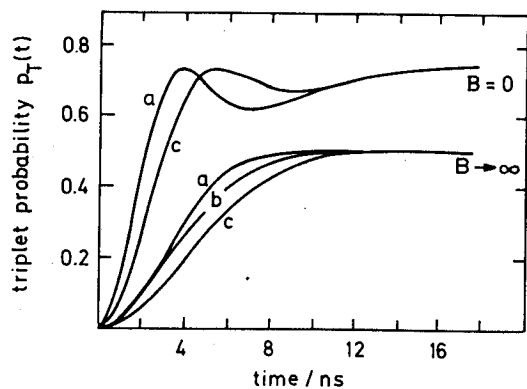
FIG. 2. Triplet probability for the pyrene–(dimethylaniline)$_2$ encounter pair starting in a singlet state (τ_1 = 4.35 ns, τ_2 = 14.13 ns at zero and very large external field; (a) $\tau_e \to \infty$, (b) τ_e = 5 ns, (c) τ_e = 0.

Equation (33) implies

$$f(u) = \exp[-t/\tau_e - 1/2(t/\tau)^2]\{\cos(\sqrt{u^2-1}\,t/\tau_e)$$
$$+ \sin(\sqrt{u^2-1}\,t/\tau_e)/\sqrt{u^2-1}). \qquad (38)$$

This result can be employed to evaluate the triplet probability $p_T(t)$ according to Eq. (27). Figure 2 represents the resulting triplet probability for the case of a pyrene–(dimethylaniline)$_2$ doublet pair. The triplet probability, e.g., curve (b) in Fig. 2, compares well with that evaluated by means of expansion (34). We found that Eq. (34) provides reliable results for the triplet probability over a broad range of τ_e values up to the limit of very fast exchange, e.g., for $\tau_e = 0.04\tau$.

We may finally note that Eq. (30) furnishes also the exact high field description, i.e., the description which does not envoke the representation of expression (6) by a continuous Gaussian distribution. The exact description involves discrete values I_a and I_b taken from the set

$$\left\{\sum_k a_{1k} m_{1k}, \ m_{1k} = -I_{1k}, -I_{1k}+1, \ldots, I_{1k}\right\}, \qquad (39)$$

where m_{1k} are the magnetic quantum numbers of the nuclear spins. For each I_a and I_b, expression (30) can be readily evaluated by means of

$$L^{-1}(s' - i\alpha)^{-1} = \exp(-t/\tau_e + i\alpha t).$$

In case of dimethylaniline the set (39) entails 1536 elements and, therefore, the exact description is not very useful. However, for molecules with a small number of dominant hyperfine coupling constants [and a small set (39)], the exact description must be used.

IV. POTENTIAL APPLICATIONS

The effect of intramolecular paramagnetic–diamagnetic exchange should allow to measure the exchange rates τ_e^{-1}. For this purpose, Eq. (23) needs to be evaluated for arbitrary fields. This evaluation appears to be rather formidable [however, see comment below Eq. (23)]. One can then match predicted yields $\phi_T(B)$ to the observations in analogy to the treatment in Ref. 8 and determine τ_e. The material constant τ_e for a given bridge X is of great interest since it characterizes the conduction properties of X. Such conduction, e.g., along the hydrocarbon tails of chlorophylls, pheophytins, and quinones in the photosynthetic reaction center, is of great importance for biological redox processes.

The theory outlined can be applied in an analogous way to describe the dynamics of triplet excitons, when the exciton migration is connected with reorientation of the molecular frame in which the triplet experiences the fine structure interaction.[11] Observation of a magnetic field dependence of triplet–triplet annihilation may yield information on the energy migration in the light harvesting systems of photosynthesis. In these systems membrane proteins which carry a small number of chromophores[15] and, thereby, furnish intramolecular exciton coupling between a small number of sites, may be investigated.

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