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Dynamic level-crossing model of antiphase electron spin polarization in spin-correlated radical pairs

Frank J. Adrian[a)]

Institute for Physical Chemistry, Technical University Darmstadt, 64287 Darmstadt, Germany and Faculty for Chemistry, University of Konstanz, 78431 Konstanz, Germany

The unusual antiphase electron spin polarizations, attributed to residual spin correlations in incompletely separated radical pairs, are treated by a dynamic model in which the polarized electron spin transitions occur as the radicals diffuse through the separations where the transitions are in resonance with the microwave field. This model shows that the inter-radical exchange interaction, and in some cases magnetic dipolar interactions as well, can produce the observed polarizations despite varying rapidly with diffusive motions of the radicals. However, the apparent fixed splitting of the emissive and absorptive components of the antiphase line is usually determined by the intrinsic width of the unpolarized electron spin resonance (ESR) line rather than by the inter-radical interactions. Surprisingly, a static model, in which the radicals are immobile during the short ESR observation period, yields the same polarization as the dynamic model under quite general conditions. © *1995 American Institute of Physics.*

I. INTRODUCTION

When transient free radicals are photochemically generated in media where diffusion is slow and/or restricted, such as micelles or solutions at low temperatures, their electron spin resonance (ESR) spectra often exhibit a novel polarization, different from those generated by the more familiar triplet (TM) and radical pair (RPM) mechanisms of chemically induced electron spin polarization (CIDEP). This polarization, often called antiphase CIDEP because it appears to split each spectral line into two components with the low and high field portions in emission and absorption, respectively, was first observed by Sakaguchi *et al.*[1] in the free radical products of the photolysis of benzophenone in an aqueous solution of sodium *n*-dodecyl sulfate. Closs *et al.*[2] and, independently, Buckley *et al.*[3] ascribed this phenomenon to incompletely separated radical pairs, whose components are still partially spin correlated (spin-correlated radical pairs or SCRPs) by nonzero spin-dependent exchange (i.e., valence) and/or magnetic dipolar interactions between them. A key element of their model, illustrated in Fig. 1, is partial or complete removal of the exchange and dipolar energies from the center triplet (T_0) and singlet (S) pair states by electron-nuclear hyperfine and other magnetic mixing of these states at separations where they are nearly degenerate, while the other triplet pair states (T_1 and T_{-1}) remain pure, with their exchange and dipolar energies unchanged. Consequently, the transitions from the T_1 and T_{-1} states to the mixed $S-T_0$ states occur at different energies, and, for an initial triplet pair, are emissively and absorptively polarized, respectively, because the pure T_1 and T_{-1} states each retain one-third the population of the initial triplet state, while each of the two mixed $S-T_0$ states receives half the original population of the T_0 state. This is illustrated in Fig. 1 for the extreme, but common, case where the radicals have separated to the point where the original T_0 state has been magnetically mixed with

the S state to the point of randomization, that is, it can be regarded as equal amounts of the states $\alpha_1\beta_2$ and $\beta_1\alpha_2$, where α and β denote, respectively, electron spins aligned parallel and antiparallel to the applied field. Since the exchange energy of these states, which are equal admixtures of singlet and triplet, is zero, the two transitions of either radical, $\alpha_1\alpha_2 \rightarrow \beta_1\alpha_2$ and $\beta_1\beta_2 \rightarrow \alpha_1\beta_2$ for radical 1 and $\alpha_1\alpha_2 \rightarrow \alpha_1\beta_2$ and $\beta_1\beta_2 \rightarrow \beta_1\alpha_2$ for radical two, are separated by twice the exchange energy of the T_1 and T_{-1} states, with the high-energy (low-field) line in emission and the low-energy (high-field) line in absorption.

This model has received considerable experimental support, including the more detailed experiments of Closs *et al.*[2] on the original micellar system, observations of CIDEP in polymethylene biradicals produced by photolytic cleavage of cycloalkanones,[4] and investigations of the ketyl radical product of the photolysis of acetone in isopropanol at low temperatures by Buckley *et al.*[3] and also by Tominaga *et al.*[5,6] More recently, antiphase CIDEP has been observed in the photoinduced electron transfer from zinc-tetraphenylporphyrin to duroquinone in both micellar systems,[7] and in low-temperature ethanol solution using pulsed Fourier-transform ESR, which provides superior time resolution of the transient SCRPs.[8] The model is undoubtedly correct in its essential features of an interaction between incompletely-separated members of a radical pair, combined with loss of this interaction in the T_0 (or S) state due to $S-T_0$ mixing. There are important details to be resolved, however, notably, how the exchange interaction can cause an apparent definite splitting of the normal ESR lines when it changes rapidly with even small diffusive displacements of the radicals, and whether magnetic dipolar interactions can play a role in the process. The first of these points has been noted by Shushin, who suggested the antiphase polarizations are observed in weakly bound radical pairs prior to their thermally activated escape from the binding potential well.[9] Although such temporary pair binding can play an important role in delaying the separation of the pairs long enough that
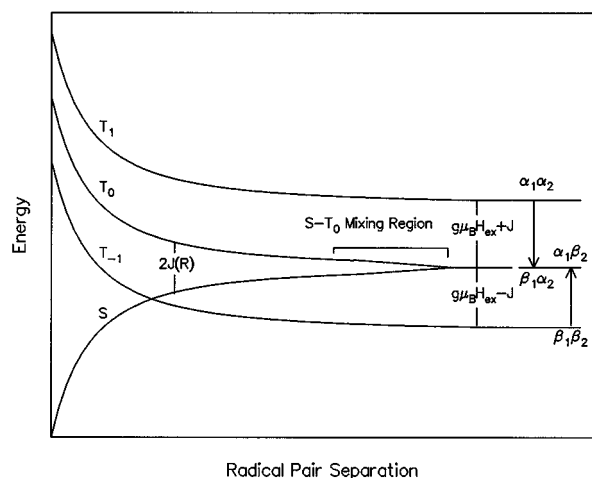
FIG. 1. Energy level diagram of an incompletely separated radical pair as a function of separation, showing the $S-T_0$ mixing region, and the polarized transitions of the incompletely separated radicals following removal of the inter-radical splittings from the T_0 and S states by the mixing.
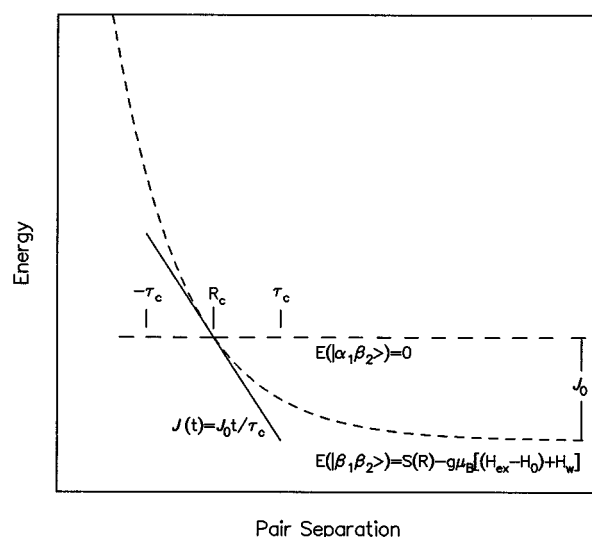

FIG. 2. Illustration of the crossing, in the rotating frame, of the levels involved in the absorptively polarized $\beta_1\beta_2 \rightarrow \alpha_1\beta_2$ transition (dashed lines) and the linearly-varying level approximation (solid line).

the transient SCRPs are present at times accessible to the ESR technique,[6,8] the exchange interaction between a bound pair is likely so strong as to preclude the required $S-T_0$ mixing.

Here, these questions are addressed by a dynamic level-crossing model in which the transitions responsible for the antiphase polarizations occur as the radicals diffuse through those separations at which the combined Zeeman, hyperfine, and exchange or dipolar splittings bring these transitions into resonance with the ESR microwave field. This model will show that the rapidly varying inter-radical interactions between diffusing radicals can produce antiphase polarizations, with an apparent fixed splitting of the antiphase components, although the splitting usually is determined by the intrinsic width of the unpolarized ESR line rather than by the inter-radical interactions. A surprising and useful result is that, under quite general conditions, this dynamic model predicts the same polarizations as a static model in which the radicals comprising the pair are immobile on the time scale of the ESR experiment. Finally, it is also found that under some conditions the magnetic dipolar interactions, as well as the exchange interactions, can contribute to the antiphase polarizations.

II. MODELS OF ANTIPHASE POLARIZATION

The treatment of antiphase polarizations in this section is for the direct detection mode of ESR observation used in most investigations to date. Here, the detected ESR signal is due to the change induced in the z component of the magnetization by a relatively weak microwave field during an observation time window $t \geqslant t' \geqslant t + \tau$. However, as is discussed in somewhat more detail at the end of this section, the results generally will be applicable to pulsed Fourier transform ESR, whose superior time resolution is making it increasingly the method of choice for investigation of transient radicals, especially polarized ones.

A. The dynamic level-crossing model

For conciseness, we consider only the absorptive transition ($\beta_1\beta_2 \rightarrow \alpha_1\beta_2$) of the first radical [$R^{(1)}$] of the incompletely separated triplet pair illustrated in Fig. 1, and neglect possible hyperfine splittings of this transition. (Of course, this transition or that of its partner must have a hyperfine splitting large enough to mix the S and T_0 states or this mixing must be provided by a difference in the g factors of the two radicals.) Treatment of this one transition and its results are completely general and applicable to other transitions with only minor changes, such as changing the position of the line in the case of different hyperfine sublevels or changing some signs in the case of the emissive $\alpha_1\alpha_2 \rightarrow \beta_1\alpha_2$ transition.

In the usual Bloch-equation frame rotating about the z axis at the microwave frequency ω_0, the energies of the $\alpha_1\beta_2$ and $\beta_1\beta_2$ states are as shown in Fig. 2. Mixing of these states by the microwave magnetic field $2H_1$ (constant component H_1 in the rotating frame) induces transitions between these levels, with a corresponding change in magnetization and ESR absorption or emission, as the radicals diffuse through the level crossing separation R_c, determined by the resonance condition

$$S(R_c) - g\mu_B[(H_{ex} - H_0) + H_w] = 0. \tag{1}$$

Here, the separation-dependent splitting $S(R)$ due to the spin-dependent inter-radical interactions can be simply the exchange splitting, as shown in Fig. 1, or something more complicated, g is the electronic g factor, μ_B is the Bohr magneton, H_{ex} is the external field, H_0 ($=\omega_0/g\mu_B$) is the center of the ESR transition, and H_w represents unresolved hyperfine interactions and other contributions to the intrinsic width of this transition in the separated radicals.

This level-crossing transition is formally identical to the previously treated $S-T_{-1}$ radical pair mechanism of CIDEP due to hyperfine mixing of the S and T_{-1} states in the region

where these levels cross.[10,11] Especially useful here is a simple, physically-insightful, solution of this problem based on the approximation that, apart from rapid, short-term, diffusive displacements whose effects are averaged out on the time scale of the state-mixing interaction, the separation of the states varies linearly with time during diffusive passage through the level crossing,[12] as illustrated for the present situation in Fig. 2. Under typically encountered conditions, this approximation gives the same results for the $S-T_{-1}$ case[12] as solution of an integral equation form of the Stochastic–Liouville model.[11] Here, it gives the following expression for the change in magnetization during diffusion through the $\beta_1\beta_2 \rightarrow \alpha_1\beta_2$ transition:

$$\Delta M_{AP}(H+H_w) = -\frac{\mu_B}{6} \frac{\pi(g\mu_B H_1)^2 \tau_c}{|J_0|}, \qquad (2)$$

where, $\mu_B/6$ is the initial magnetization difference due to overpopulation of the $\beta_1\beta_2$ state, $g\mu_B H_1$ is the state mixing by the microwave field, and J_0/τ_c is the rate of change of the separation of the states during the level crossing in the linear approximation

$$J(t) = S[R(t)] - g\mu_B[(H_{ex}-H_0)+H_w]$$
$$= J_0 t/\tau_c; \quad -\tau_c \geqslant t \geqslant \tau_c. \qquad (3)$$

In the original treatment,[12] the time variation of $J(t)$ was estimated from the rate of diffusive change of the maximum in a distribution of radical pair separations starting with a delta-function distribution peaked at the level-crossing separation R_c. A useful feature of this approach is that it shows the duration of the level crossing for an exponentially decreasing splitting $[S(R) \propto e^{-\lambda R}]$ is approximately

$$2\tau_c = \lambda/R_c D, \qquad (4)$$

where D is the diffusion constant. More useful here is a variant of this approach which focuses on the average speed of diffusion in the radial direction ($\bar{u}_{D,R}$), since this quantity will be found to cancel in the final expression for the polarization. In this approach, $J(R)$ is expanded about R_c, giving $(dS/dR)_{R_c}(R-R_c)$, and the time variation of $R-R_c$ approximated as $\bar{u}_{D,R}t$, to obtain $J(t) = (dS/dR)_{R_c}\bar{u}_{D,R}t$. Comparison of this result with Eq. (3) gives $J_0/\tau_c = (dS/dR)_{R_c}\bar{u}_{D,R}$, whose substitution in Eq. (2) gives

$$\Delta M_{AP}(H+H_w) = -\frac{\mu_B}{6} \frac{\pi(g\mu_B H_1)^2}{|dS/dR|_{R_c}\bar{u}_{D,R}}, \qquad (5)$$

where Eq. (1) determines R_c as a function of $H+H_w$.

This change in magnetization during diffusion of a single pair through the resonant level crossing at R_c must be multiplied by the number of pairs making such a diffusive passage during the ESR observation window $t \leqslant t' \leqslant t+\tau$ to get the observed magnetization change and corresponding ESR signal. The number of such pairs is

$$N_c(R_c,t;\tau) = 4\pi R_c^2 P(R_c,t)\bar{u}_{D,R}\tau, \qquad (6)$$

where $P(R_c,t)$ is the density of pairs whose components are separated by R_c at time t, and it should be noted that Eq. (6) includes a factor of 2 to account for pairs diffusing in both directions and an offsetting factor of one-half because only half the pairs in a position to diffuse through R_c are moving in the proper direction to do so.

Thus, the total change in magnetization in the interval t to $t+\tau$ is

$$\Delta M_{AP}(H+H_w,t;\tau) = -\frac{\mu_B}{6} \frac{\pi(g\mu_B H_1)^2\tau}{|dS/dR|_{R_c}} 4\pi R_c^2 P(R_c,t). \qquad (7)$$

An important feature of this result is that it depends on diffusion only insofar as it determines the distribution of radical pair separations at a given time, with the more complicated aspects of diffusion such as diffusive speed dropping out as the decreased magnetization change with increased speed of passage through the level crossing is exactly offset by the increased number of such crossings. Because the polarization depends only on the distribution of pair separations at a given time, and not on the rate of change of these distributions, the present treatment of radicals diffusing in an isotropic open space, where they can be described simply by their separation R, is readily extended to radicals in micelles and other restricted media where it may be necessary to consider the positions of the individual radicals. These cases can be treated by using appropriate distributions of the radicals comprising the pair, such as $P_1(\mathbf{R}_1,t)P_2(\mathbf{R}_2,t)$ or $P(\mathbf{R}_1,\mathbf{R}_2,t)$ with correspondingly position-dependent surface elements through which the diffusive level crossings occur, and ultimately integrating over the positional coordinates $\mathbf{R}_1$ and $\mathbf{R}_2$ subject to the condition that the pair separation always be R_c.

To complete this model of the antiphase polarizations, it is necessary to average over the internal fields of the radical that produce its intrinsic unpolarized linewidth. In carrying out this averaging to obtain the intensity of the antiphase ESR line, it is convenient to introduce the new variables

$$H = H_{ex}-H_0; \quad H' = H_{ex}+H_w-H_0, \qquad (8)$$

where H is the field position of the line measured from its center at H_0, and H' is the integration variable. If the unresolved hyperfine splittings and other sources of line broadening produce a Gaussian line shape of root-mean-square width σ, that is, $I_w(H_w) = (1/\sqrt{2\pi}\sigma)\exp(-H_w^2/2\sigma^2)$. The resulting ESR transition intensity, which is positive (absorptive) for a negative magnetization change, is

$$I_{AP}(H) \propto \frac{\mu_B}{6} \pi(g\mu_B H_1)^2\tau \frac{4\pi}{\sqrt{2\pi}\sigma}$$
$$\times \int_{-\infty}^{\infty} \frac{R_c^2(H')P[R_c(H'),t]}{|dS/dR|_{R_c(H')}} e^{-(H'-H)^2/2\sigma^2}dH', \qquad (9)$$

where R_c and its functions are related to H' by Eqs. (1) and (8).

B. The static model

To determine the antiphase polarization in a truly static model where the distribution of radical pair separations is

constant, and also to determine the antiphase polarization as the ratio of the intensity of the antiphase line to that of the corresponding unpolarized line, it is necessary to determine the change in magnetization due to ordinary ESR transitions in the observation window $t \leqslant t' \leqslant t + \tau$. This magnetization change is calculated from the following Bloch equations,[13] in which relaxation is neglected as it is slow compared to the rates of appearance and disappearance of the antiphase polarizations,

$$du/dt = -(\omega - \omega_0)v, \quad dv/dt = (\omega - \omega_0)u + \omega_1 M_z,$$

$$dM_z/dt = -\omega_1 v,$$
(10)

where $\omega_1 = g\mu_B H_1$, and $(\omega - \omega_0) = g\mu_B(H - H_0)$. Differentiation of the equation for dv/dt by t, and substituting from the other equations, gives a second order equation for v, which is readily solved. For the conditions $v = 0$, $u = 0$ and $M_z = M_0$ at $t = 0$, this solution is $v = (\omega_1 M_0/\Omega)\sin(\Omega t)$, where $\Omega = [(\omega - \omega_0)^2 + \omega_1^2]^{1/2}$. Using this result in the equation for dM_z/dt, gives the change in M_z in the time interval $t \geqslant t' \geqslant t + \tau$, where $\omega_1 \tau \ll 1$, as

$$\Delta M_z = -M_0 \frac{\sin(\Omega t)}{\Omega} \omega_1^2 \tau = -M_0 \frac{\sin(t\Omega)}{\Omega} (g\mu_B H_1)^2 \tau.$$
(11)

In the more common situation that M_0 is a distribution of magnetization such that the magnetization in a given field region is $(dM_0/dH)\Delta H$ or, alternatively, $(dM_0/dH)\Delta\omega/g\mu_B$, then the above expression must be replaced by the integral

$$\Delta M_z = -[(g\mu_B H_1)^2 \tau/g\mu_B] \int_{-\infty}^{\infty} \frac{dM_0}{dH} \frac{\sin(t\Omega)}{\Omega} d\omega$$

$$\simeq -[\pi(g\mu_B H_1)^2 \tau/g\mu_B] \frac{dM_0}{dH}.$$
(12)

The approximate result on the far right-hand side of Eq. (12) is valid if, as is typically the case, ω_1 is small compared to the ESR linewidth and t is neither so small that $\omega_1 t \ll 1$, in which case virtually no ESR absorption occurs, nor so large that $\omega_1 t > 1$, in which case the ESR transition is substantially saturated prior to the observation window at t to $t + \tau$. Under these conditions dM_0/dH is nearly constant over the narrow frequency range spanned by the function $\sin(t\Omega)/\Omega \simeq \sin[t(\omega - \omega_0)]/(\omega - \omega_0)$, for which the integration gives π.

For a distribution of radical pair separations, as given by $P(R,t)$, the antiphase magnetization in the field range ΔH at the field corresponding to separation R_c is the magnetization of those pairs whose separations lie in a spherical shell of width ΔR and radius R_c, where ΔR is the change in R required to maintain the resonance condition of Eq. (1) when H_{ex} changes by ΔH. Thus,

$$(dM_{AP}/dH)_{R_c} = \frac{\mu_B}{6} 4\pi R_c^2 P(R_c,t)|dR/dH|_{R_c}$$

$$= \frac{\mu_B}{6} \frac{4\pi R_c^2 P(R_c,t)g\mu_B}{|dS/dR|_{R_c}}.$$
(13)

Inserting this result in Eq. (12) gives the same result for $\Delta M_{AP}(H + H_w,t;\tau)$ as the dynamic model result in Eq. (7).

C. Comparison of the static and dynamic models

Thus, the dynamic and static models predict the same antiphase polarization under the rather general conditions of a small enough microwave field that the on-resonance members of a static distribution of pair separations are not partially saturated by the time of observation, and the validity of the linearly-varying level model used to calculate the dynamic polarization. Importantly, when conditions are such that one of these models is invalid, the other usually will be sufficiently physically realistic that the polarization will still be given by Eqs. (7) and (9).

For example, if the duration of the level crossing, given by Eq. (4) for an exponentially decreasing interaction ($\propto e^{-\lambda R}$), is shorter than or comparable to the ESR observation time τ, then the dynamic model is the more realistic. Reduction of the polarization predicted by Eqs. (7) and (9) due to saturation is less likely in the dynamic case because a given pair is in resonance only during level crossings, which reduces the average change in magnetization per radical pair considerably below that in the static case where the same pairs are in resonance during the entire time of exposure to the microwave field.

In addition to the adequacy of the linearly-varying level approximation itself, this model of mixing during level crossings,[12] as well as the corresponding solution of the integral Stochastic–Liouville equation,[10,11] requires that the mixing interaction (here the microwave field) not produce large changes during the level crossing. This second condition is not a problem in continuous-wave, direct-detected, ESR, but definitely is for pulsed, Fourier-transform, ESR. Although the model itself[12] gives a somewhat stringent condition for the validity of the linear approximation (here, $g\mu_B|H - H_0|\tau_c \geqslant 1$), comparison of the results of this model[12] with solution of the integral Stochastic–Liouville equation[11] indicates it is valid under the considerably less stringent condition,

$$[4g\mu_B(H - H_0)/\lambda^2 D]^{1/2} \geqslant 0.1.$$
(14)

For the values of λ and D that give significant antiphase polarizations, this condition will be satisfied except for very small values of $H - H_0$ close to the center of the line, where the positive and negative parts of the antiphase polarization cancel in any case.

In pulsed Fourier transform ESR the large change in magnetization produced by the strong microwave field present during the pulse invalidates the present dynamic model. Usually, however, this pulse will be short enough (typically 15 ns) (Ref. 8) that the range of resonant frequencies ($\omega_0 \pm \tau_p^{-1}$, where τ_p is the duration of the pulse) is large compared to both the antiphase line splitting, and, from Eqs.
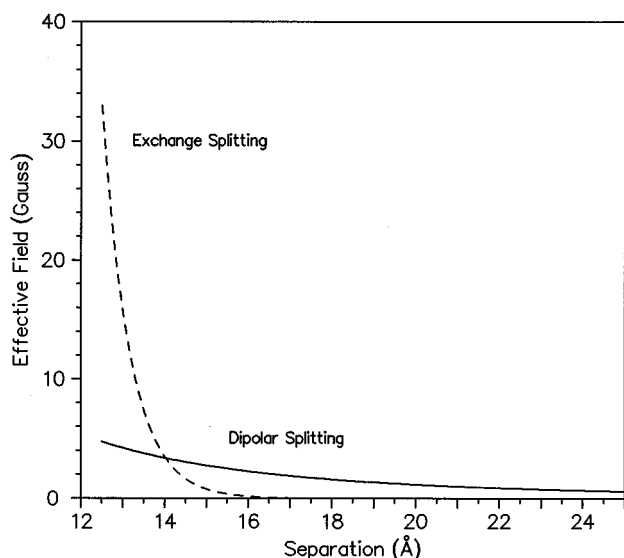
FIG. 3. Illustration of the effective magnetic splittings due to the exchange (- - -) and magnetic dipolar interactions (—) as a function of pair separation. The exchange interaction is $J_0 e^{-\lambda R}$ with $\lambda = 1.5$ Å^{-1}, and $J_0 = 4.6 \times 10^9$ G (corresponding to an exchange energy at $R = 4$ Å of $5 k_B T$ at $T = 300$ K). The dipolar splitting is $g \mu_B / 2 R^3$.

(3) and (4), the change in this splitting during passage through the level crossing, whose duration will be comparable to or longer than τ_p for the values of λ and D in Eq. (4) that yield significant antiphase polarizations. Under these conditions, the static model, which neglects the change in resonant frequency due to motion of the radicals during the microwave pulse, is applicable. Again, the polarization and line shape will be given by Eq. (9), since the change in magnetization will be the same for the polarized and unpolarized lines, even though it is different from that given by Eq. (12).

In summary, Eqs. (7) and (9) should give a good estimate of the shape and polarization of the antiphase lines in most cases.

III. INTER-RADICAL INTERACTIONS AND ANTIPHASE POLARIZATION

The spin-dependent inter-radical interactions, illustrated in Fig. 3, are the short-range exchange interaction and the longer-range, orientation-dependent, magnetic dipolar interaction. Although, as discussed later, the latter as well as the former can produce antiphase polarization, it can do so only at separations where the exchange interaction is very small. The exchange interaction will dominate the antiphase polarization process at separations where it is nonzero despite the presence of magnetic dipolar interactions because these interactions, which change much more slowly with separation than the exchange interaction, can be compensated for by small changes in pair separation.

A. The exchange interaction

We take the usual form for the exchange interaction,

$$\mathcal{H}_{ex} = 2 J_0 e^{-\lambda R} (\mathbf{S}_1 \cdot \mathbf{S}_2 + \tfrac{1}{4}), \tag{15}$$

where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spins of the radicals, and assume that the radicals have separated to the point where the T_0 and S states have been mixed by a hyperfine or other magnetic interaction $\mathcal{H}_{mag} \gg \mathcal{H}_{ex}$ for a time of the order $\hbar / \mathcal{H}_{mag}$. This mixing converts the initial T_0 (or S) state into the uncorrelated spin states $\alpha_1 \beta_2$ and $\beta_2 \alpha_1$, so the splitting $S(R)$ in Eq. (1) is $J_0 e^{-\lambda R}$, and the resonance condition becomes

$$J_0 e^{-\lambda R_c} \pm g \mu_B H' = 0, \tag{16}$$

where H' is given by Eq. (8), and the minus and plus signs apply to the absorptive $(\beta_1 \beta_2 \rightarrow \alpha_1 \beta_2)$ and emissive $(\alpha_1 \alpha_2 \rightarrow \beta_1 \alpha_2)$ transitions, respectively. The case where the condition $\mathcal{H}_{mag} \gg \mathcal{H}_{ex}$ does not hold is readily treated, leading to a more complicated form for $S(R)$ and the possibility of pairs of absorptive and emissive transitions, since the (S, T_0) states in this case are neither pure S and T_0 states or pure $\alpha_1 \beta_2$ and $\beta_2 \alpha_1$ states.[2,3]

For the resonance condition of Eq. (16), $|dS/dR|_{R_c} = |\lambda g \mu_B H'|$, for both transitions. Substituting this result in Eq. (9) along with an expression for $P(R,t)$ such as the simple form corresponding to pairs initially at zero separation,[14]

$$P(R_c, t) = \frac{1}{(4 \pi D t)^{3/2}} e^{-R_c^2 / 4 D t}, \tag{17}$$

gives the antiphase polarization for the exchange case. It is convenient to express this polarization relative to the maximum intensity of the unpolarized ESR line, which is readily shown to be

$$I_0 \propto \mu_B \left(\frac{g \mu_B H_0}{2 k_B T} \right) \frac{\pi (g \mu_B H_1)^2 \tau}{g \mu_B \sigma} \frac{1}{\sqrt{2 \pi}}, \tag{18}$$

upon taking for dM_0/dH in Eq. (12) a line with the thermal equilibrium magnetization per spin of $\mu_B (g \mu_B H_0 / 2 k_B T)$, and the Gaussian shape used to calculate the antiphase polarization in Eq. (9). The resulting antiphase polarization is

$$\frac{I_{AP,ex}(H,t)}{I_0} = \frac{4}{3 \sqrt{\pi}} \left(\frac{k_B T}{g \mu_B H_0} \right) \int_{-\infty}^{\infty} I_{AP,ex}^{(0)}(H',t)$$
$$\times e^{-(H'-H)^2 / 2 \sigma^2} dH', \tag{19a}$$

where

$$I_{AP,ex}^{(0)}(H',t) = \frac{1}{\lambda R_c} \left(\frac{R_c^2}{4 D t} \right)^{3/2} e^{-R_c^2 / 4 D t} \frac{1}{H'}. \tag{19b}$$

The function $I_{AP,ex}^{(0)}(H',t)$ gives the intensity and shape of the antiphase polarized line if the width of the normal unpolarized line is negligible, an unlikely occurrence in the exchange case because of the $1/H'$ singularity in $I_{AP,ex}^{(0)}(H',t)$. Since the resonance condition of Eq. (16) restricts H' to $H' \geq 0$ and $H' \leq 0$, respectively, for the absorptive and emissive parts of the antiphase line, Eq. (19) gives the entire antiphase line shape, with H' in the denominator of Eq. (19b) providing the sign change at $H' = 0$.

Because the exchange interaction varies very rapidly with separation, as shown in Fig. 3, R_c and the functions of $R_c(H')$ in $I_{AP,ex}^{(0)}(H',t)$ usually do not change significantly

The polarizations decay as $t^{-3/2}$, which gives decay rates of the order of one-third of the reciprocals of these times of maximum polarization. Of course, the antiphase polarizations will be less transitory for radicals confined in micelles. To date, antiphase lines have been observed in solution only at low temperatures where diffusion is slow, and even so, it appears in some cases that a delay in the separation of the radicals, due to a structured solvent[6] or a Coulomb attraction between charged radicals,[8] plays a significant role in determining the time after radical pair generation at which the antiphase lines are observed.

B. Magnetic dipolar interactions

For the widely separated radicals of interest here their magnetic dipolar interaction can be approximated as that between point dipoles,

$$\mathscr{H}_D = -(g^2\mu_B^2/4R^3)(3\cos^2\theta-1)[3S_z^2-S(S+1)],$$
(22)

where $\mathbf{S}$ is the total spin of the pair, S_z is the component of $\mathbf{S}$ along the magnetic field, and θ is the angle between the inter-radical axis and the magnetic field. Since the $\alpha_1\beta_2$ and $\beta_1\alpha_2$ states have equal amounts of S and T_0 character, they have one half the dipolar splitting of the T_0 state, so the resonance condition of Eq. (16) for the dipolar case is

$$(g^2\mu_B^2/4R_c^2)(1-3\cos^2\theta)\pm H'=0.$$
(23)

These dipolar interactions can contribute to the antiphase polarization if the cancellation between the positive and negative contributions from differently oriented pairs is not too extensive and the polarizations are not averaged to zero by reorientation of the pairs on the time scale of the polarization process. Possible advantages of the dipolar splitting over the exchange interaction is that it is longer ranged, which provides a longer time in the level-crossing region, and produces polarizations at longer times after formation of the pair when the radicals are further apart. Comparison of Eqs. (16) and (23) shows that the antiphase polarization pattern should be the same for the dipolar and exchange interactions, that is emissive/absorptive for an initial triplet pair, because the contribution of the many pairs oriented at an angle of $\theta=\pi/2$ with respect to the external field, for which the signs of the dipolar and exchange splittings are the same, outweighs that from the smaller number of pairs oriented near $\theta=0$. Because of rotational averaging, dipolar interactions are less likely to be important in micelles, whose rotation in a low viscosity solvent is relatively rapid,[2] than in viscous solutions, where reorientation requires that the radicals diffuse angularly with respect to each other through the solution itself. The rotational correlation time in this case, where the reorientation can be described in terms of the two radicals diffusing on the surface of a sphere of radius R_c, is obtained by a modification of the well known equation for the dipolar correlation time due to diffusive reorientation of a molecule in solution.[17] The modification, which consists of replacing a factor of a^2, where a is the average radius of the radicals, by R_c^2, and using the diffusion constant for linear diffusion rather than that for rotational diffusion, gives the result

$$\tau_R = 4\pi\eta R_c^2 a/3k_BT = 2R_c^2/9D,$$
(24)

where, η is the solution viscosity, and the diffusion constant D is taken to have the Stokes–Einstein value, $D=k_BT/6\pi a\eta$.

For the rather short distances involved in the passage through resonance, the R^{-3} dependence of the dipolar splitting can be fitted to an exponential $e^{-\lambda_{\text{eff}}R}$, with $\lambda_{\text{eff}}=3/R_c$ at the level crossing separation. Equation (4) then gives the duration of the level crossing as $R_c^2/3D$. This is only slightly longer than the rotational correlation time for dipolar averaging in Eq. (24), so the dipolar interaction should at least partially survive the rotational averaging. Furthermore, this level-crossing time is rather long, of the order of the time required for the radicals to reach the separation R_c, and usually will be longer than the ESR observation window (τ). In this case the static model, which neglects all diffusive changes including rotational averaging, is applicable, All things considered, dipolar interactions are likely to contribute to the antiphase polarizations, in at least some cases.

The calculation of the antiphase polarization due to dipolar splitting is similar to that of the exchange case, that is, use of Eq. (9) with the resonance condition given by Eq. (23), except that the dependence of this equation on θ requires an additional integration over radical pair orientation. Actually, it is more convenient to make R_c the independent variable and integrate over it rather than orientation. Also, it is simpler to calculate $I_{\text{AP},D}(H)$ for $H\geq0$ only and use the fact that $I_{\text{AP}}(-H)=-I_{\text{AP}}(H)$. The dipolar splittings yielding absorptive polarization for $H\geq0$ [minus sign in Eq. (23)] come from angular orientations related to R_c by the equation,

$$\cos\theta_+ = \frac{1}{\sqrt3}\left(1-\frac{2HR_c^3}{g\mu_B}\right)^{1/2}$$
$$0\leq R_c\leq(g\mu_B/2H)^{1/3},$$
(25a)

while the corresponding emissive polarizations [plus sign in Eq. (23)] come from the orientations,

$$\cos\theta_- = \frac{1}{\sqrt3}\left(1+\frac{2HR_c^3}{g\mu_B}\right)^{1/2}$$
$$0\leq R_c\leq(g\mu_B/H)^{1/3}.$$
(25b)

It is also convenient to scale the fields to the magnetic dipolar splitting for $\pi/2$-oriented radicals at the distance $(4Dt)^{1/2}$. This dipolar field is

$$H_D = g\mu_B/2(4Dt)^{3/2},$$
(26)

and the corresponding dimensionless scaled field and line widths are

$$\bar H = H/H_D; \quad \bar\sigma = \sigma/H_D.$$
(27)

Written in terms of these scaled field variables, the equation for the antiphase-polarization due to dipolar splitting is found to be

$$\frac{I_{\text{AP},D}(\bar H,t)}{I_0} = \frac{4}{3\sqrt\pi}\left(\frac{k_BT}{g\mu_BH_0}\right)\int_{-\infty}^{\infty}\text{sgn}(\bar H')I_{\text{AP},D}^{(0)}(|\bar H'|)$$
$$\times e^{-(\bar H'-\bar H)^2/2\bar\sigma^2}d\bar H',$$
(28a)

where $\mathrm{sgn}(x) = -1, 0, 1$ for $x < 0, = 0, > 0$,

$$I_{\mathrm{AP},D}^{(0)}(\bar{H}') = \frac{1}{2\sqrt{3}} \left[\int_0^{(1/\bar{H}')^{1/3}} \frac{1}{(1 - \bar{H}'x^3)^{1/2}} x^5 e^{-x^2} dx \right.$$

$$\left. - \int_0^{(2/\bar{H}')^{1/3}} \frac{1}{(1 + \bar{H}'x^3)^{1/2}} x^5 e^{-x^2} dx \right],$$

$$(28\mathrm{b})$$

and x is the dimensionless integration variable $R_c/(4Dt)^{1/2}$. $I_{\mathrm{AP},D}^{(0)}(\bar{H}')$, which is the dipolar analog of the exchange line shape function in Eq. (19b), determines the shape and intensity of the dipolar antiphase line if the width of the unpolarized line is negligible. It is, of course, an implicit function of time through its dependence on the time-dependent scaling field H_D.

The following alternative form for $I_{\mathrm{AP},D}^{(0)}(\bar{H}')$, which is more useful for visualizing its properties, is obtained by the change of variable $y = \bar{H}'x^3$, in Eq. (28b),

$$I_{\mathrm{AP},D}^{(0)}(\bar{H}') = \frac{1}{6\sqrt{3}\bar{H}'} \left[\int_0^1 \frac{y}{(1 - y)^{1/2}} e^{-(y/\bar{H}')^{2/3}} dy \right.$$

$$\left. - \int_0^2 \frac{y}{(1 + y)^{1/2}} e^{-(y/\bar{H}')^{2/3}} dy \right]. \quad (29)$$

Clearly, $I_{\mathrm{AP},D}^{(0)}(\bar{H}')$ will be zero at $\bar{H}' = 0$ because of the exponential term $\exp[-(y/\bar{H}')^{2/3}]$. It will increase rapidly to a maximum value as $\bar{H}'$ increases from zero, reaching this maximum at a point where $\bar{H}'$ is such that the maximum value of the function $y \exp[-(y/\bar{H}')^{2/3}]$, which is $\simeq 0.4\bar{H}'$ at $y/\bar{H}' = 1.5^{3/2} \simeq 1.84$, is well within the region spanned by the first integral in Eq. (29). In this region, the first integral is considerably larger than the second because of its smaller denominator with a square root singularity at $y = 1$, which represents the contribution of the $\pi/2$-oriented radical pairs. For large values of $\bar{H}'$, where $\exp[-(y/\bar{H}')^{2/3}]$ approaches unity, expansion of this term as $1 - (y/\bar{H}')^{2/3} + \cdots$ shows that $I_{\mathrm{AP},D}^{(0)}(\bar{H}')$ decreases as $1/\bar{H}'^{8/3}$ because the two integrals in the first term of this expansion cancel exactly. That $I_{\mathrm{AP},D}^{(0)}$ decreases as $1/\bar{H}'^{8/3}$, rather than the $1/\bar{H}'$ decrease of $I_{\mathrm{AP,ex}}^{(0)}$ in Eq. (19b), suggests that the dipolar interaction will produce an antiphase line that closely resembles the derivative of a normal absorption line, without the extended tails found in the exchange case. These qualitative considerations are borne out by the calculated $I_{\mathrm{AP},D}^{(0)}(\bar{H}')$ in Fig. 6, which shows that this function has a maximum at $\bar{H}_{\max} = H_{\max}/H_D \simeq 1/8$. The dipolar antiphase line $I_{\mathrm{AP},D}/I_0$, calculated from Eq. (28) for $\bar{\sigma} = \bar{H}_{\max}$ ($\sigma \simeq H_D/8$) is given in Fig. 5, where it is compared with $I_{\mathrm{AP,ex}}/I_0$ and the derivative of the unpolarized absorption line. Clearly, the exchange and dipolar contributions to the antiphase polarizations are comparable in this case.

When the width of the unpolarized line is small compared to the width of $I_{\mathrm{AP},D}^{(0)}$, that is, $\bar{\sigma} \ll \bar{H}_{\max}$ or $\sigma \ll H_D/8$, then the antiphase-polarized line will closely resemble $I_{\mathrm{AP},D}^{(0)}$. However, the antiphase intensity relative to that of the unpolarized line i.e., the polarization ratio ($I_{\mathrm{AP},D}/I_0$), will be small because the peak intensity of the unpolarized line increases as its width decreases. Numerical calculations show
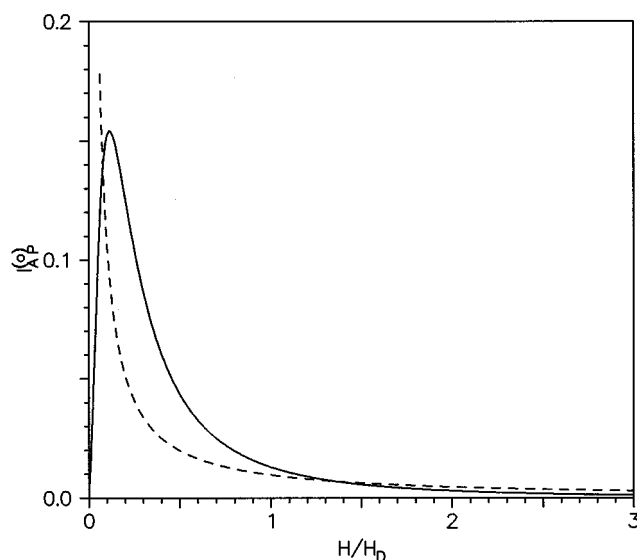

FIG. 6. The pure antiphase line shapes in the absence of broadening by the unpolarized line. —, $I_{\mathrm{AP},D}^{(0)}$; ---, $I_{\mathrm{AP,ex}}^{(0)}$ for $(4Dt)^{1/2} = 21$ Å, $R_c = 15$ Å, and $\lambda = 1.5$ Å^{-1}.

that this polarization ratio will be greatest when $I_{\mathrm{AP},D}^{(0)}$ and the unpolarized line have approximately the same width. However, both these conditions are likely to be very short lived, if they occur at all, because they require $H_D \gg \sigma$, which occurs only at early times after the formation of the pair when the radicals are quite close together. Also, the antiphase polarizations are likely to be dominated by the exchange interaction in this region unless the unpolarized lines are very narrow.

Dipolar antiphase polarizations are most likely to be observed at relatively long times and large inter-radical distances where $H_D \ll \sigma$ and, thus, $I_{\mathrm{AP},D}^{(0)}(\bar{H}')$ is nonzero only for $|\bar{H}'| \ll \sigma$. In this case, a useful analytic approximation to $I_{\mathrm{AP},D}$ can be obtained by expanding the Gaussian function in Eq. (28a) about $\bar{H}' = 0$. This gives the result

$$\frac{I_{\mathrm{AP},D}(\bar{H}, t)}{I_0} \simeq \frac{4}{3\sqrt{\pi}\bar{\sigma}} \left(\frac{k_B T}{g\mu_B H_0} \right) \frac{\bar{H}}{\bar{\sigma}} e^{-\bar{H}^2/2\bar{\sigma}^2}$$

$$\times 2 \int_0^\infty \bar{H}' I_{\mathrm{AP},D}^{(0)}(\bar{H}') d\bar{H}'$$

$$\simeq \frac{1}{8\sqrt{\pi}\bar{\sigma}} \left(\frac{k_B T}{g\mu_B H_0} \right) \frac{\bar{H}}{\bar{\sigma}} e^{-\bar{H}^2/2\bar{\sigma}^2}, \quad (30)$$

where the integral was evaluated numerically. Comparison with numerical calculations shows that this expression represents $I_{\mathrm{AP},D}$ quite well for $\bar{\sigma} = \sigma/H_D \geq 5$, and is a reasonably good approximation down to $\sigma/H_D \geq 1$, which range includes most situations that are likely to be encountered. To put the above expression in terms of actual, rather than scaled fields, which facilitates comparison with Eq. (21) for the exchange case, we note from Eqs. (26) and (27) that $\bar{\sigma} = \sigma/H_D = 2\sigma(4Dt)^{3/2}/g\mu_B$, and define the Gaussian linewidth σ in terms of the separation $R_{\sigma,D}$ at which the dipolar field equals σ, that is,

$$R_{\sigma,D} = (g\mu_B/2\sigma)^{1/3}. \qquad (31)$$

Equation (30) then becomes

$$\frac{I_{\mathrm{AP},D}(H)}{I_0} = \frac{1}{8\sqrt{\pi}} \left(\frac{k_B T}{g\mu_B H_0} \right) \left(\frac{R_{\sigma,D}^2}{4Dt} \right)^{3/2} \frac{H}{\sigma} \, e^{-H^2/2\sigma^2}. \qquad (32)$$

This expression is very similar to Eq. (21) for the antiphase polarization due to the exchange interaction, since, at the longer times where it is valid, the exponential factor $[\exp(-R_{\sigma,\mathrm{ex}}^2/4Dt)]$ in Eq. (21) will be approximately unity. However, it lacks the extended tails found for the antiphase line shape in the exchange case. In fact, the derivation leading to Eq. (30) and the first-derivative line shape, was possible only because the product of the field and the dipolar line shape function $I_{\mathrm{AP},D}^{(0)}(\bar{H})$ is integrable over the range $0 \geq \bar{H} \geq \infty$, which is not the case for the corresponding exchange line shape function with its $(1/\bar{H})$ field dependence.

Comparison of Eqs. (21) and (32) indicates the exchange and dipolar contributions to the antiphase polarization will be of the same order of magnitude for typical values of 20 to 30 for λR_c. The decay of the two polarizations with time is the same, although the dipolar term may persist to somewhat longer times because the separation at which the dipolar splitting equals the linewidth ($R_{\sigma,D}$) will usually be somewhat greater than the corresponding distance for the exchange splitting ($R_{\sigma,\mathrm{ex}}$).

IV. DISCUSSION

These models of the antiphase polarization mechanism show it can lead to significant polarizations, of the order of magnitude of those observed. Although detailed comparison of theory and experiment must await further experimental data, which should be forthcoming given the greatly improved time resolution of present ESR experiments, a few points are notable.

The prediction that the antiphase-polarized lines will resemble the derivative of the normal unpolarized line both as to shape and width, rather than have a width related to the strength of the polarizing interaction, is especially well born out by the work of Tominaga et al.[5,6] on the normal protonated and deuterated forms of the acetone–isopropanol photolysis system. There, the ratios of the apparent antiphase line splittings of the resulting isopropyl–ketyl radical $[(CH_3)_2\dot{C}H]$ and its deuterated counterpart $[(CD_3)_2\dot{C}D]$ are approximately in the ratio 6:1, as expected for an unpolarized line whose width is primarily due to unresolved hyperfine interactions.

Less clear, however, is why the antiphase polarizations are observable at times of the order of microseconds in this system, even though the diffusion constant is estimated to be only 2×10^{-8} cm^2/s at the observation temperature of 186 K.[6] For this value of D, and the time development of the polarization given by Fig. 4, the maximum antiphase polarization should occur at approximately 0.2 μs for a typical level-crossing separation of 15 Å, and will be reduced by a factor of roughly 10 at 2 μs. Whether larger polarizations would have been observed at the shorter time merits further investigation, however, the time evolution of these authors' ESR

signals[5,6] suggests the development and decay of the polarization is slower than expected for radical pairs that were freely diffusing from the time of their formation. The indicated delay in the development of the polarization supports these authors' conclusion, based on their analysis of the radical pair CIDEP at various temperatures, that at low temperatures the isopropanol solvent has a cage structure which delays the separation of a considerable fraction of the radical pairs for times of the order of microseconds.[6] Similarly, a delay in pair separation due to coulomb attraction between a pair of radical ions has been proposed to account for the time scale on which the radicals and their polarizations are observed following pulsed-laser photoinduction of electron transfer from zinc-tetraphenylporphyrin to duroquinone in ethanol solution.[8]

That both the inter-radical exchange interaction and magnetic dipolar interactions can contribute to the antiphase polarizations should not complicate the analysis of these spectra excessively because they have similar time and other dependences. The best prospects for separating the two effects seems to be the considerably more extended tails of the antiphase line in the exchange case, and the possibly somewhat longer duration of the dipolar polarizations. There are some indications of extended tails in the antiphase lines observed to date, however, a more detailed examination of these line shapes as a function of time would be desirable. Observations in deuterated systems, where, as shown by Tominaga et al.,[5,6] the antiphase lines are more prominent because of the reduced radical pair polarizations, and perhaps also because of the inherently narrower lines, should be the ideal medium for such investigations. If the dipolar contributions can be distinguished from the exchange contributions, there is the interesting feature that the dipolar antiphase-polarized line is due largely to radical pairs whose axes are approximately perpendicular to the external magnetic field. Whether this can be utilized experimentally, such as orientationally selective photoexcitation of the pairs, or creation of pairs in an anisotropic medium such as a micelle or liquid crystal remains to be seen.

Finally, it is likely that antiphase polarizations will become increasingly important with increased utilization of pulsed ESR methods, which can observe the radicals at short times ($\simeq 10$ ns) where spin correlated pairs are likely to exist. As noted in the first such study,[8] the antiphase polarizations introduce an out-of-phase or dispersive component into the free-induction-decay (FID) response that can produce meaningful distortions of the spectrum obtained from Fourier transformation of the FID, even if distinct antiphase lines are not observed. Hopefully, it will be possible to obtain a more detailed picture of photochemical creation of radical pairs and their subsequent evolution, chemistry, and interactions from such observations.

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