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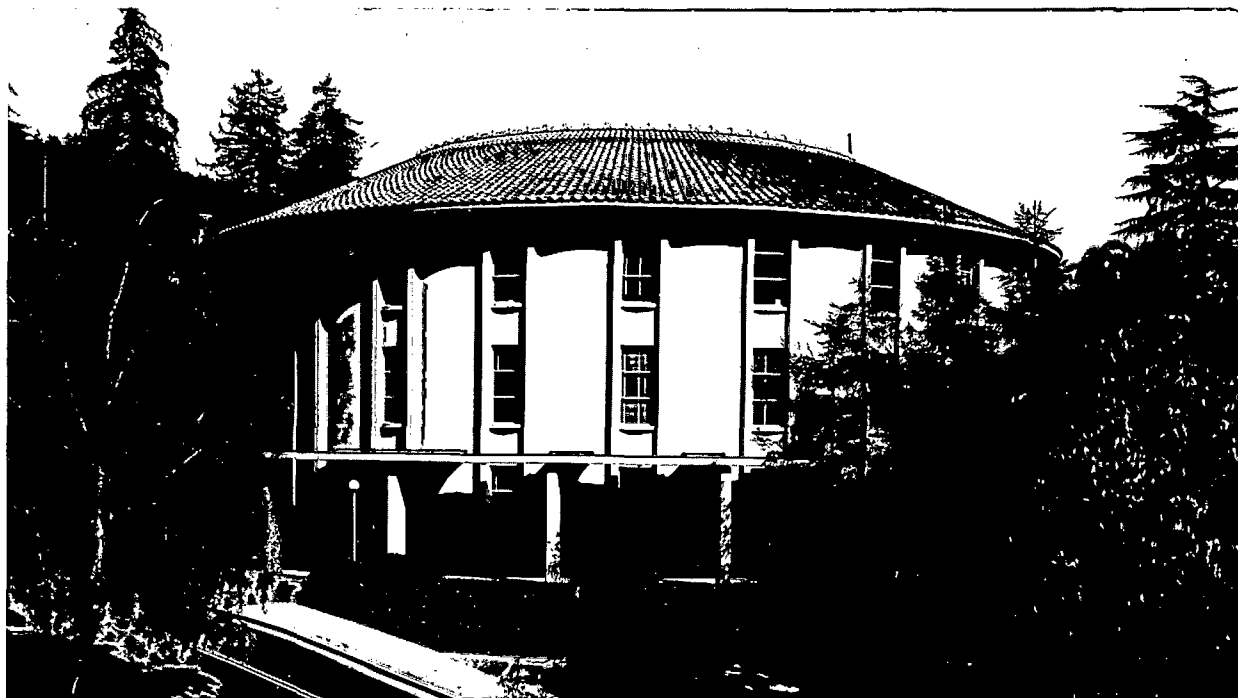## CHEMICAL BIODYNAMICS DIVISION

DYNAMIC POLARIZATION OF THE EPR SPECTRUM OF SPATIALLY-FIXED
RADICAL PAIRS: Relevance to the Photosynthetic Light Reactions

Mary B. McLean and Kenneth Sauer

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DYNAMIC POLARIZATION OF THE EPR SPECTRUM OF

SPATIALLY-FIXED RADICAL PAIRS: Relevance

to the Photosynthetic Light Reactions

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ABSTRACT

We develop a model which describes the polarization of the EPR spectrum of pairs of spatially-fixed radicals which are created by chemical or photochemical reactions. In such pairs, the exchange interaction is likely to be constant and nonzero during the radical pair lifetime. The double degeneracy of the free doublet EPR signal from each radical is removed when the exchange interaction is nonzero, yielding an exchange-split EPR spectrum with four transitions for the radical pair. These transitions are highly polarized by radical pair formation, even when the pair precursor is pure singlet. The analysis predicts that there will be an observable polarization of the EPR spectrum of spatially-fixed pairs whenever the exchange interaction is nonzero and both the magnetic relaxation time and the chemical lifetime of the pair state are long enough to permit the detection of polarized EPR signals.

INTRODUCTION

Polarized electron paramagnetic resonance (EPR) spectra have been widely used to study the mechanisms and kinetics of reactions in solution which involve radical pair intermediates[1,2]. However, only a few reactions[3-7] other than the photosynthetic light reactions have been studied in which the radical pair intermediates are spatially fixed. During the light reactions of algae[8-10], green plants[8-12] and bacteria[13-16], polarized EPR signals have been observed which demonstrate that the radical pair state is an important intermediate in reactions between spatially fixed species. Theoretical analysis of polarized EPR spectra can yield important information such as the distance between the radicals[11,14], the magnitude of exchange coupling[11,16,17], the orientation of the magnetic axes in ordered or partially ordered samples[14,17], and reaction kinetics[11,16].

Theoretical models describing Chemically or Light Induced Magnetic Polarization (CIMP or LIMP) have considered the following kinetic process involving two electrons[1,2]. The electrons start out in the ground state of a reactant molecule, M, where they are correlated by an exchange interaction of molecular magnitude. A radical reaction can be initiated when a ground state singlet ^1M is photoexcited to a state $^1M^*$ which then undergoes dissociation or charge separation, or when ^1M reacts chemically or photochemically with another species, M'. The result in any case is radical pair formation. Most of the theoretical treatments[1,2,19-26] consider the case that the radicals

are free to move about in solution, and rapid spatial separation of the pair causes the exchange interaction to vanish. The exchange interaction is then nonzero only during subsequent collisional encounters. Hence the EPR observable is a superposition of spin 1/2 free radical doublet spectra[*]. Friesner et al[17] used the theory of Adrian[19,20] to describe the polarization of the light-induced EPR signal of the membrane-bound primary donor P700 in spinach chloroplasts at room temperature. The donor and acceptor radicals are spatially fixed in the membranes; nevertheless, the electron donated by P700 moves rapidly down a chain of acceptors, and the EPR observable is the radical doublet of P700^{+}. Pedersen's theory of spin polarization in photosynthetic systems[18] also assumes the EPR observables to be uncoupled radical doublet spectra.

Two distinct models have been developed which describe mechanisms by which a non-Boltzmann population of the energy levels of radical doublets can be achieved: the Triplet Mechanism[1,2,23-26], and the Radical Pair Mechanism[1,2,18-23]. In the Triplet Mechanism, the molecular precursor to the radical pair has some population in its triplet spin sublevels, either because it is a ground state triplet, or because the triplet sublevels have been populated by intersystem crossing from the singlet manifold after excitation and before radical separation. In either case, the triplet population produces an initially non-Boltzmann population difference between the α and β doublet states of the radicals after separation. In the Radical Pair Mechanism, there are two ways in which a non-Boltzmann

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[*]"Doublet" refers to spin multiplicity, $(2S + 1) = 2$ for spin 1/2.

population of the radical spin sublevels can occur, and both result
from mixing of the singlet and triplet T_0 states when the exchange
interaction is small or zero. "Net polarization"[19] occurs when
radicals of a pair which have separated reencounter one another
later. These encounters produce singlet-T_0 mixing when the
exchange interaction is briefly nonzero, and this results in a net
excess of α spins on one radical and an equal excess of β spins
on the other. "Multiplet effects"[19] occur when radicals in solution
undergo spin selective reactions with other radicals, resulting in
a depletion of the singlet population. Non-Boltzmann population of
the hyperfine sublevels results from the dependence of the singlet-T_0
mixing rate on the hyperfine states, and this influences the probability
that a given pair has singlet character.

We shall concentrate for simplicity on systems in which the
molecular precursor to radical pair formation is a singlet state and
the Triplet Mechanism does not operate. We consider a model in which
the polarization of the EPR spectra arises in systems of radical
pairs which are not free to move about in solution, but are fixed
together in a definite spatial relationship. The difference between
the new model and the other models[17-26] is that the EPR spectrum
which is observed to be polarized is not simply a superposition
of radical doublets. When there is a nonzero, time-independent
exchange interaction, as is likely to be the case when the radicals
are spatially fixed, the double degeneracy of the uncoupled radical
doublet EPR transitions is removed. If the radical pair state
exists long enough to be observed by EPR, and if the polarization

does not relax to the Boltzmann population before it can be detected,
then we can observe initial polarization which is induced simply by the
population of the radical pair states by pair formation from a
singlet precursor. A similar argument can be made for the case of
a precursor with triplet character, but we omit it for simplicity.

THEORY

We consider the case where the two radicals have different,
isotropic g-values and are coupled by an isotropic exchange
interaction. We do not include the effects of anisotropic dipolar,
exchange or hyperfine interactions; however, the theory can be
generalized to include these effects. In Appendix A, the effect
of isotropic hyperfine interactions is discussed.

The Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}(t) \tag{1}$$

where

$$\hat{H}_0 = \beta B_0(g_1\hat{S}_{1Z} + g_2\hat{S}_{2Z}) - J(2\hat{S}_1 \cdot \hat{S}_2 + 1/2) \tag{2}$$

and the oscillatory Hamiltonian $\hat{H}(t)$, resulting from a microwave
field $B_1(t)$ which is linearly polarized in the X direction, is
given by

$$\hat{H}(t) = 2\beta B_1\cos\omega_0 t(g_1\hat{S}_{1X} + g_2\hat{S}_{2X}) \tag{3}$$

where $2B_1$ is the amplitude and ω_0 is the frequency of $B_1(t)$.

THE RADICAL PAIR EPR SPECTRUM

In the singlet-triplet basis, the eigenvalues and eigenvectors of $\hat{H}_0$ are well known [27] and are given in Table 1. The transitions which will be observed in the radical pair spectrum are found by evaluating the matrix elements of $\hat{H}(t)$ in the basis that diagonalizes $\hat{H}_0$. Eq. 3 may be written in the form

$$\hat{H}(t) = [1/2(g_1^2 + g_2^2)]^{1/2} \, B_1 \hat{H}'(t) \tag{4}$$

where

$$\hat{H}'(t) = [\exp(i\omega_0 t) + \exp(-i\omega_0 t)] \, \hat{H}_\chi \tag{5}$$

and $\hat{H}_\chi$ is the spin operator

$$\hat{H}_\chi = (1 + \lambda^2)^{-1/2} [\hat{S}_\chi + \lambda(\hat{S}_{1\chi} - \hat{S}_{2\chi})] \tag{6}$$

In Eq. 6, $S_\chi = S_{1\chi} + S_{2\chi}$ and $\lambda = \delta/\epsilon$, where $\delta = \beta B_0 (g_1 - g_2)/2$ and $\epsilon = \beta B_0 (g_1 + g_2)/2$. Then the transition probabilities for the four transitions denoted μ, where $\mu = 1-4$, are given by

$$W_\mu = 1/2(g_1^2 + g_2^2) \quad \beta^2 B_1^2 A_\mu f_\mu(B) \tag{7}$$

The $f_\mu(B)$ are shape functions obtained from time-dependent perturbation theory, as described in Appendix B. A_μ is given by

$$A_\mu = |<f \mid \hat{H}_\chi \mid i>|^2 \tag{8}$$

where i denotes the initial and f denotes the final state of transition μ. The A_μ are usually called "relative intensities" because they satisfy

$$\sum_\mu A_\mu = 1 \tag{9}$$

It is straightforward to calculate the transition energies ΔE_μ and the A_μ from Table 1 and Eq. 8, and the results are given in Table 2.

We note from Tables 1 and 2 that in the limit that $J \gg \delta$, the + state is the singlet state and transitions 1 and 4 vanish, because transitions between the singlet and triplet states are spin forbidden. The - state is the T_0 state in this limit, and transitions 2 and 3 are the $\Delta M_S = \pm 1$ triplet transitions. The transitions involving the + state are called "S" resonances and those involving the - state are called "T" resonances.

At the other limit, when $J \to 0$, transitions 1 and 2 collapse to a doubly degenerate transition at the energy $g_2 \beta B_0$, and transitions 3 and 4 collapse to $g_1 \beta B_0$. Thus we obtain two doubly degenerate radical doublet spectra at the limit of zero exchange interaction, as expected.

In the intermediate region, where $J \sim \delta$, the degeneracy of the doublets at $g_1 \beta B_0$ and $g_2 \beta B_0$ is removed, and each transition is split into an S and a T component. This is the region in which spatially-fixed radicals may exhibit EPR polarization. We will see later that when $J = 0$ or when $J \gg \delta$, it is not possible to observe polarization.

POLARIZATION OF THE RADICAL PAIR EPR SPECTRUM

When the radical pair is formed from a singlet precursor, the system is prepared in a non-stationary state of $\hat{H}_0$. The population N_i of eigenstate i is determined by the probability $|\langle S|i \rangle|^2$, which does not depend on the time. If the Triplet Mechanism[23-26] does not operate, then pair formation results in zero population of the

triplet T_1 and T_{-1} sublevels. If there are N radical pairs and if we denote the level i population as $N_i = P_i N$, where $P_i = |\langle S|i\rangle|^2$, then the population differences ΔN_μ are determined by

$$\Delta P_1 = P_{T_1} - P_+ = - |\langle S|+\rangle|^2$$

$$\Delta P_2 = P_- - P_{T_{-1}} = |\langle S|-\rangle|^2$$

$$\Delta P_3 = P_{T_1} - P_- = - |\langle S|-\rangle|^2$$

$$\Delta P_4 = P_+ - P_{T_{-1}} = |\langle S|+\rangle|^2$$

(10)

Figure 1 shows the radical pair spin energy levels and the four transitions for the case that $J = \delta/\sqrt{3}$, when both $J > 0$ and $\delta > 0$. The populations of the radical pair energy levels given in Eq. 10 result in positive intensities for the transitions to the T_1 state and negative intensities for transitions to the T_{-1} state. These polarities are indicated in Figure 1 by the labels E and A, where E denotes a signal in emission and A denotes a signal in absorption.

According to Eq. 10 and the time-dependent perturbation theory of Appendix B, the intensity of the polarized radical pair EPR spectrum is proportional to

$$I(t) = |\langle T_1| \hat{H}'(t)|t\rangle|^2 - |\langle T_{-1}| \hat{H}'(t)|t\rangle|^2$$

(11)

where $|t\rangle$ is the state of the system at time t, which is given by

$$|t\rangle = \exp(-i\omega t)C_+(t)|+\rangle + \exp(i\omega t)C_-(t)|-\rangle$$

(12)

and

$$C_i(t) = \langle i| \exp(-i\hat{H}(t)t) |S\rangle$$

(13)

We note that Eq. 11 will give cross terms of the form $\langle f | \hat{H}'(t) | i \rangle \langle i' | \hat{H}'(t) | f \rangle$ where $i \neq i'$. These cross terms represent coherence between the transition amplitudes which arises when the system is prepared in a non-stationary state of $\hat{H}_0$. However, in Appendix B we will show that the cross terms in Eq. 11 are zero and that we may define the intensity

$$I(B) \equiv \sum_\mu \rho_\mu A_\mu f_\mu(B) \tag{14}$$

where ρ_μ is the polarization, A_μ is the "relative intensity" from Eq. 8 and $f_\mu(B)$ are shape functions centered at ΔE_μ. The polarization ρ_μ is defined by

$$\rho_\mu \equiv \text{sgn}(\mu) \Delta P_\mu \tag{15}$$

where $\text{sgn}(\mu)$ is the sign and ΔP_μ is given by Eq. 10. The signs $\text{sgn}(\mu)$ depend on the signs of J and δ and are given by

$$\text{sgn}(\mu) = (-1)^{\mu-1} \text{sgn}(J)\text{sgn}(\delta) \tag{16}$$

where $\text{sgn}(J)$ and $\text{sgn}(\delta)$ are the signs of J and δ. We will assume that both J and δ are positive, so that $\text{sgn}(1) = \text{sgn}(3) = +1$ and $\text{sgn}(2) = \text{sgn}(4) = -1$. According to Eq. 10 and Table 1, the ΔP_μ are given by

$$\begin{aligned} \Delta P_1 &= \Delta P_4 = |a_1|^2 \\ \Delta P_2 &= \Delta P_3 = |a_2|^2 \end{aligned} \tag{17}$$

Substituting Eq. 16 into Eq. 14 gives the polarized intensity

$$I(B) = |a_1|^2 [A_1 f_1(B) - A_4 f_4(B)] - |a_2|^2 [A_2 f_2(B) - A_3 f_3(B)] \tag{18}$$

Usually λ is small enough that $A_1 \simeq A_4 \simeq |a_2|^2$ and $A_2 \simeq A_3 \simeq |a_1|^2$, so that

$$I(B) \simeq (\delta/2\omega)^2[f_1(B) - f_2(B) + f_3(B) - f_4(B)] \qquad (19)$$

We note that the zero magnetization of the singlet state precursor is conserved, since $\sum_\mu \rho_\mu = 0$, and that there is no observable polarization when either $J = 0$ or $J \gg \delta$. The polarization in Eq. 19 is comparable to or smaller than the room temperature Boltzmann factor, which is $O(10^{-3})$, when $J \gtrsim 15\delta$.

We have assumed that no population of the T_1 and T_{-1} levels occurs from a singlet precursor when there is no intersystem crossing, but it has been pointed out[19,28] that when the change in J is adiabatic rather than sudden, the T_1 or T_{-1} level (depending on the sign of J) may be populated. This occurs because the singlet and triplet T_1 or T_{-1} levels cross during the change in J. However, we expect that in most cases the change in J attending pair formation will not be adiabatic when the radical sites are spatially fixed. The polarization is easily calculated using arguments similar to the present ones in the case[19] that B_0 is small or zero, when the singlet and triplet levels are nearly degenerate and all three triplet sublevels are populated.

Eq. 17 represents the maximum theoretical value of the polarization and does not depend on the time. Time dependence of the polarization results from the interaction of the spin system with the microwave field $B_1(t)$[29], from other relaxation processes which cause the polarization to decay to the Boltzmann population, and from chemical reactions. A complete

solution of the equations of motion of the radical pair spins including relaxation is beyond the scope of this paper. In the Results and Discussion section, we will consider several cases where EPR polarization is influenced by chemical reactions.

RESULTS AND DISCUSSION

Figures 2 and 3 illustrate that the fitting parameters are the exchange interaction, J, and the ratios Δ_μ/δ, where Δ_μ are the halfwidths of the $f_\mu(B)$ and δ is the difference in resonance frequency of radicals 1 and 2. The top three traces of Figures 2 and 3 show the polarized spectra as a function of J when δ is constant, assuming for simplicity that the four $f_\mu(B)$ are gaussian derivatives of equal homogeneous linewidths, so that $\Delta_\mu = \Delta$. The lowest traces of Figures 2 and 3 represent the unpolarized and uncoupled doublet spectra. We see that the $f_\mu(B)$ are well separated at $J = 0$ in Figure 2, where $\Delta/\delta = 0.25$, and they overlap at $J = 0$ in Figure 3, where $\Delta/\delta = 0.75$. The case of inhomogeneously broadened $f_\mu(B)$ is discussed in the Appendix. Inhomogeneous lines will give spectra with the same qualitative appearances as in Figures 2 and 3.

In summary, there are two distinguishable cases in which spatially-fixed radicals, which are created in chemical or photochemical reactions, can give rise to EPR polarization.

Case (1) When J remains nonzero during the time of the EPR measurements for spatially-fixed pairs, the model that we presented above will apply and an EPR experiment will measure the four

nondegenerate transitions of the coupled pair spectrum with polarized

intensities proportional to the population differences given by

Eq. 10. The conditions for observing the polarized EPR spectrum of

a radical pair are that both the chemical lifetime and the

magnetic relaxation time of the pair are sufficiently long to

permit detection of the polarization.

In many cases, the radicals will undergo subsequent chemical

reactions which give rise to additional EPR polarization. If, for

example, the pair decays chemically by a back reaction faster than

magnetic relaxation can occur, then population of the molecular triplet

energy levels will yield the diagnostic "radical pair" polarized

EPR triplet signal[13]. If the pair (which we shall call "the primary

pair") decays chemically by a forward reaction, creating a secondary

radical pair faster than magnetic relaxation can occur, then

we may observe polarization of the EPR spectrum of the secondary

pair. The exchange interaction, J_2, between the radicals in the

secondary pair is not equal, in general, to the exchange interaction, J_1,

between the radicals in the primary pair. When J_2 is nonzero during

the time of the EPR measurement, the EPR experiment will measure

the four transitions of the secondary pair spectrum with polarized

intensities proportional to the population differences of Eq. 10.

However, the initial conditions for the secondary pair are not

the same as the initial conditions for the primary pair given by

Eq. 10, because the state of the system, which is pure singlet

at the time of formation of the primary pair, will evolve

during the lifetime of the primary pair. As a result, the system

will be in a pure state which is a superposition of the singlet and T_0 states at the time of formation of the secondary pair, if there is no magnetic relaxation. The coefficients of the superposition will determine the initial conditions of the secondary pair, and will thus determine the probability that the system is in the $|+>$ or $|->$ state of the secondary pair. The expressions for ΔP_μ given in Eq. 10 must be modified to include the change of initial conditions for the secondary pair. The conditions for observing the polarized EPR spectrum of the secondary pair are the same as the conditions for the primary pair, i.e., the chemical lifetime and the magnetic relaxation time of the pair must be long enough to permit detection of polarization. Clearly, it is possible to observe the polarization of the secondary pair spectrum when the polarization of the primary pair spectrum cannot be observed, or to observe both at different times in time-resolved experiments, et cetera.

Case (2)   If the exchange interaction J_2 is zero between the radicals in a secondary pair, then the "net polarization"[19] mechanism of the Radical Pair Mechanism applies. In this case, we will observe the EPR spectra of uncoupled doublet radicals with polarized intensities proportional to the population differences between the α and β radical spin energy levels given by

$$2 < t|S_{1Z}|t > = P_{\alpha 1}(t) - P_{\beta 1}(t) \tag{20}$$

where $P_{\alpha 1}(t)$ and $P_{\beta 1}(t)$ are the respective probabilities that spin 1 is α or β when the system is in a state $|t>$ at time t, and $< t|S_{2Z}| t> = - < t|S_{1Z}|t >$. We stress two points: (1) Eq. 14 is

applicable only when $J_2 = 0$ and the EPR spectrum corresponds to uncoupled doublet radicals; and (2) If the exchange interaction between the two electrons is always zero, then Eq. 20 is always zero, in the absence of spin-selective reactions ("multiplet effects"[19]). Friesner et al[17] showed that "net polarization" of the EPR spectrum of the uncoupled secondary pair arises from the nonzero exchange interaction, J_1, between the radicals in the primary pair. Time evolution of the state of the system under J_1 prepares the secondary pair in a condition such that Eq. 20 is nonzero.

In a given experimental situation, spatially-fixed species may be involved in reactions which are more complex than the simple cases we have discussed. It may be possible in such cases to construct a model describing observed EPR dynamics using simple arguments including the theoretical model we presented above and/or the "net polarization" model. However, in other cases, the Hamiltonian of Eq. 1 may be inadequate because anisotropic interactions are important, such as dipolar interactions or g tensor anisotropy with attendant anisotropic exchange interactions. Friesner et al[17] included the effect of g tensor anisotropy of the acceptor radical X^- in the "net polarization" of the primary donor radical $P700^+$ at room temperature in spinach chloroplasts. Frank et al[11] used the polarization model presented here in their simulations of LIMP signals observed in spinach chloroplasts during primary photochemistry at 10 Kelvin. They found that the theoretical fit to experimental data improved when dipolar interactions were included.

In conclusion, we suggest that LIMP or CIMP should be looked
for in other systems where spatially-fixed radical pair intermediates
are known or suspected to be involved. Time-resolved EPR studies
should yield observable polarized spectra which are analyzable
by the present model whenever the chemical lifetime and the magnetic
relaxation time are long enough to permit the detection of polarized
EPR signals.

APPENDIX A

$\hat{H}_0$ of Eq. 2 is modified to include the hyperfine interaction
by adding the hyperfine terms

$$\hat{H}_0' = \hat{H}_0 + \sum_i^{N_1} A_i I_i \cdot S_1 + \sum_j^{N_2} A_j I_j \cdot S_2 \tag{A1}$$

where N_1 and N_2 are the number of nuclei coupled to S_1 and S_2,
respectively. We assume that the hyperfine states are quantized
along B_0, and neglect second order terms of the form $I_X S_X$ and $I_Y S_Y$.
We adopt the basis set $|M_S \Pi_p \Pi_q \rangle$, where M_S is the eigenvalue of
$S_Z = S_{1Z} + S_{2Z}$ (that is, the singlet-triplet electron spin basis),
$\Pi_p = \Pi_i m_{1i}$ and $\Pi_q = \Pi_j m_{2j}$, and m_{1i} and m_{2j} are the eigenvalues of
I_{iZ} and I_{jZ} in the pth hyperfine state of spin 1 and the qth
hyperfine state of spin 2. Then we define the hyperfine energies

for S_1 and S_2 in their p^{th} and q^{th} respective hyperfine states as

$$\alpha_1^{\,P} \equiv \sum_i^{N_1} A_i m_{1i}$$

$$\alpha_2^{\,q} \equiv \sum_j^{N_2} A_j m_{2j}$$

(A2)

For example, if all the hyperfine nuclei are spin 1/2 and the A_i and A_j are all different, then there are $2^{(N_1)}$ values of $\alpha_1^{\,P}$ and $2^{(N_2)}$ values of $\alpha_2^{\,q}$.

$\hat{H}_0'$ in the chosen basis is then

$$< M_S \Pi_p \Pi_q | \hat{H}_0' | M_S' \Pi_p' \Pi_q' > = [< M_S | \hat{H}_0' | M_S'> + (\alpha_1^{\,P} + \alpha_2^{\,q}) M_S \delta_{M_S M_S'}$$

$$+ (\alpha_1^{\,P} - \alpha_2^{\,q}) < M_S | S_{1Z} - S_{2Z} | M_S' >] \delta_{pp'} \delta_{qq'} \qquad (A3)$$

where $\delta_{pp'}$, $\delta_{qq'}$ have the form $\Pi \delta_{m_i m_i'}$. Diagonalization of the Hamiltonian matrix for the p,qth radical pair hyperfine state can easily be shown to yield the expressions in Tables 1 and 2 if we make the substitutions

$$\varepsilon = \varepsilon^{p,q} = 1/2(\varepsilon_1^{\,P} + \varepsilon_2^{\,q})$$

$$\delta = \delta^{p,q} = 1/2(\varepsilon_1^{\,P} - \varepsilon_2^{\,q})$$

(A4)

where $\varepsilon_1^{\,P} = g_1 \beta B_0 + \alpha_1^{\,P}$ and $\varepsilon_2^{\,q} = g_2 \beta B_0 + \alpha_2^{\,q}$.

To obtain the polarized radical pair spectrum including the hyperfine interaction, one would write the intensity of the spectrum from the p,qth pair hyperfine state as

$$I^{p,q}(B) = \sum_\mu \rho_\mu^{pq} A_\mu^{pq} f_\mu^{pq}(B)$$

(A5)

where in each case $\rho_\mu^{pq} \equiv S_\mu P_\mu^{pq}$, as defined in Eq. 15.

In general, the hyperfine energies on radicals 1 and 2 may cross, i.e., some $\varepsilon_1^p > \varepsilon_2^q$ and some $\varepsilon_1^{p'} < \varepsilon_2^{q'}$. The effect of this crossing must be included in the expressions ρ_μ^{pq}. For example, when $\varepsilon_1^p > \varepsilon_2^q$, the S resonance on radical 1 is emissive and shifts to lower energies as J increases. On the other hand, when $\varepsilon_1^{p'} < \varepsilon_2^{q'}$, the S resonance on radical 1 is absorptive and shifts to higher energies as J increases. We assume that the expressions ρ^{pq} are corrected for these effects.

In the case of resolved hyperfine structure when N_1 and N_2 are small, the polarized radical pair spectrum may be convoluted to the total EPR intensity $I(B)$ by multiplying each $I^{pq}(B)$ by its coefficient in the binomial expansion, and summing over all combinations of p and q, i.e.

$$I(B) = \sum_p \sum_q a_p a_q I^{pq}(B) \tag{A6}$$

where a_p and a_q are the binomial coefficients.

In the case that the hyperfine structure enters primarily as an inhomogeneous broadening, the binomial distribution is well approximated by a gaussian distribution. If the two J = 0 spectra do not overlap, then there is no crossing of hyperfine energies, i.e., if $g_1 > g_2$ and there is zero overlap, then no $\varepsilon_1^p < \varepsilon_2^q$. The radical pair spectrum for J $\neq 0$ can then be calculated without taking explicit account of the hyperfine interaction, by adopting for the $f_\mu(B)$ gaussians of the appropriate widths and using the expressions in Tables 1 and 2 and eq. 14. However, when the lines overlap at J = 0, the hyperfine interaction must enter the theory

explicitly. For computer simulations, the calculations are essentially the same in the inhomogeneous case as in the case of resolved hyperfine structure, and Eq. [A6] is used.

APPENDIX B

We will use time-dependent perturbation theory to justify Eq. 14 above, in the case that the system is prepared in a non-stationary state of the unperturbed Hamiltonian H_0. However, we will adopt a more general notation than that used above.

If the Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \tag{B1}$$

then the state of the system at time t in the interaction representation is given by

$$|t\rangle = \Sigma_i |i\rangle \exp(-iE_i t) C_i(t)$$

$$\tag{B2}$$

$$C_i(t) = \langle i| \exp(-i\hat{V}(t)t) |S\rangle$$

where $|S\rangle$ is the state of the system before the perturbation $\hat{V}(t)$ is turned on, and $|i\rangle$ is the eigenstate of $\hat{H}_0$ with the eigenvalue E_i. We are assuming that $\hbar = 1$. The time-dependent Schroedinger equation is then

$$i \frac{d|t\rangle}{dt} = [\hat{H}_0 + \hat{V}(t)] |t\rangle \tag{B3}$$

We now suppose that $\hat{V}(t)$ is periodic and given by

$$\hat{V}(t) = \hat{V} [\exp(i\omega_0 t) + \exp(-i\omega_0 t)] \tag{B4}$$

Substituting Eqs. B2 and B4 into Eq. B3, multiplying from the left by $\langle j| \exp(iE_j t)$, and integrating from 0 to τ, we obtain

$$C_j(\tau) = \Sigma_i' V_{ji} C_i(\tau) [\exp(-i(\omega_{ij}-\omega_0)\tau) - 1](\omega_{ij}-\omega_0)^{-1} \tag{B5}$$

where $\omega_{ij} = (E_i - E_j)$ and V_{ji} is the transition moment $<j|\hat{V}|i>$. The prime on the sum denotes that we are assuming that all of the $\omega_{ij} > 0$ and that only the $\exp(i\omega_0 t)$ component of $\hat{V}(t)$ is effective. It is straightforward to generalize to all ω_{ij}.

Since $\hat{V}(t)$ is a small perturbation, we assume that $C_i(\tau) \simeq C_i(0)$ in the sum of Eq. B5. In conventional time-dependent perturbation theory, it is assumed that the system starts out in one of the eigenstates, $|k>$, of $\hat{H}_0$ so that $C_i(0) = \delta_{ik}$. However, we relax this assumption and say the system is prepared in an arbitrary state given by

$$|S> = \Sigma_k' a_k |k> \tag{B6}$$

In this case we have the initial condition

$$C_i(0) = <i|S> = a_i \tag{B7}$$

Then Eq. B5 becomes

$$C_j(\tau) = \Sigma_i' V_{ji} a_i [\exp(-i(\omega_{ij}-\omega_0)\tau) - 1](\omega_{ij}-\omega_0)^{-1} \tag{B8}$$

The probability that the system makes a transition to state j is given by

$$W_j(\tau) = |C_j(\tau)|^2$$

$$= \Sigma_{i=i'}' |a_i|^2 W_{ij}(\tau) + \Sigma_{i \neq i'} X_{ii'j}(\tau) \tag{B9}$$

where

$$W_{ij}(\tau) = 4|V_{ji}|^2 \sin^2[(\omega_{ij}-\omega_0)\tau/2](\omega_{ij}-\omega_0)^{-2} \tag{B10a}$$

$$X_{ii'j}(\tau) = 2|\Gamma_{ii'j}| \frac{[\cos(\omega_{ij}-\omega_{i'j})\tau - \cos(\omega_{ij}-\omega_0)\tau - \cos(\omega_{i'j}-\omega_0)\tau + 1]}{(\omega_{ij}-\omega_0)(\omega_{i'j}-\omega_0)} \tag{B10b}$$

$$\Gamma_{ii'j} = a_i a_{i'}^* V_{ji} V_{ji'}^* \tag{B10c}$$

The goal is to calculate the total spectral intensity when the system is prepared in an arbitrary state $|S>$, given by Eq. B6. Each of the W_{ij} in Eq. B10a corresponds to the transition probability that is calculated by conventional time-dependent perturbation theory when particular initial conditions are assumed, namely that the system starts out in the ith eigenstate of $\hat{H}_0$. The presence of cross terms in Eq. B10a means that the W_{ij} and the populations of the eigenstates do not determine the total spectral intensity when the system is prepared in an arbitrary state. We shall now prove that the cross terms given by Eq. B10b are zero.

Using trigonometric identities, one can show that $X_{ii'j}(\tau)$ has the form

$$X_{ii'j}(\tau) = 8|\Gamma_{ii'j}|\cos[(\omega_{ij}-\omega_{i'j})\tau/2]\frac{\sin[(\omega_{ij}-\omega_0)\tau/2]}{(\omega_{ij}-\omega_0)}\frac{\sin[(\omega_{i'j}-\omega_0)\tau/2]}{(\omega_{i'j}-\omega_0)} \quad (B11)$$

In the limit that $\omega_{ij}^{-1} \ll \tau$ we may write

$$\frac{\sin(\omega_{ij}-\omega_0)\tau}{\pi(\omega_{ij}-\omega_0)} = \partial(\omega_{ij}-\omega_0) \quad (B12)$$

which gives

$$X_{ii'j}(\tau) = 8\pi^2|\Gamma_{ii'j}|\cos[(\omega_{ij}-\omega_{i'j})\tau/2]\partial(\omega_{ij}-\omega_0)\,\partial(\omega_{i'j}-\omega_0) \quad (B13)$$

Therefore, $X_{ii'j}(\tau)$ is zero unless $\omega_{ij} = \omega_{i'j}$, i.e. unless $E_i = E_{i'}$. When such degeneracies occur, we can choose a new representation, $|\ell>$, which transforms the cross terms $X_{ii'j}(\tau)$ to diagonal terms $W_{\ell j}(\tau)$ which have the form of Eq. B10a.

Finally, we note that the limit $\omega_{ij}^{-1} \ll \tau$ used to obtain Eq. B13 is also used in ordinary perturbation theory to obtain the result

$$W_{ij}(\tau) = 4\pi |V_{ji}|^2 \tau \, \partial(\omega_{ij} - \omega_0) \qquad (B14)$$

The total intensity of transitions to state j is then given by

$$I_j(\omega) = \Sigma_i^- |a_i|^2 W_{ij} f_{ij}(\omega) \qquad (B15)$$

where $W_{ij} = \tau^{-1} W_{ij}(\tau)$ and $f_{ij}(\omega)$ is a shape function centered at ω_{ij}.

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REFERENCES

[1]A comprehensive treatment of the theoretical approaches is contained in Chemically Induced Magnetic Polarization(1977) edited by Muus,L.T., Atkins,P.W., McLauchlan,K.A. and Pedersen,J.B.(D. Reidel,Holland).

[2]See also Chemically Induced Magnetic Polarization (1973) edited by Closs,G.L. and Lepley,A.R. (Wiley Interscience, New York).

[3]Kim,S.S. and Weissman,S.I. (1976) J.Mag.Res. 24 167-169.

[4]Kim,S.S. (1979) Chem.Phys.Lett. 61 327-330.

[5]Kim,S.S. (1978) J.Chem.Phys. 68 333-334.

[6]McBride,J.M. and Evans,G.T. (1975) Chem.Phys.Lett. 36 41-45.

[7]Vary,M.W. and McBride,J.M. (1979) Mol.Cryst.Liq.Cryst. 52 437-448.

[8]McIntosh,A.R., Manikowski,H. and Bolton,J.R. (1979) J.Phys.Chem. 83 3309-3313.

[9]Dismukes,G.C., McGuire,A., Blankenship,R. and Sauer,K. (1978) Biophys.J. 21 239-256.

[10]Dismukes,G.C.,McGuire,A., Blankenship,R. and Sauer,K.(1978) Biophys.J. 22 521.

[11]Frank,H.A., McCracken,J.L.,   and Sauer,K. (1980) to be published.

[12]Frank, H.A., McLean,M.B. and Sauer,K. (1979) Proc.Nat.Acad.Sci.USA 76 5124-5128.

[13]Dutton,P.L., Leigh,J.S. and Seibert,M.(1972) Biochem.Biophys.Res. Comm. 46 406-413.

[14]Frank,H.A., Friesner,R., Nairn,J.A., Dismukes,G.C. and Sauer,K. (1979) Biochim.Biophys.Acta 547 484-501.

[15]Hoff,A.J., Gast,P. and Romijn,J.C. (1976) FEBS Lett. 73 185-189.

[16]Gast,P. and Hoff,A.J. (1979)Biochim.Biophys.Acta 548 520-535.

[17]Friesner,R.,Dismukes,G.C. and Sauer,K. (1979) Biophys.J. 25 277-294.

[18]Pedersen,J.B. (1979) FEBS Lett. $\underline{97}$ 305-310.

[19]Adrian,F.J. (1977) in ref. 1, pp. 77-105.

[20]Adrian,F.J.(1972) J.Chem.Phys. $\underline{57}$ 5107-5113.

[21]Closs,G.L. and Trifunac,A.D. (1969) J.Am.Chem.Soc. $\underline{91}$ 4552-4555.

[22]Kaptein,R. and Oosterhoff,L.J. (1969) Chem.Phys.Lett. $\underline{4}$ 195-200.

[23]Pedersen,J.B. and Freed,J.H. (1973) J.Chem.Phys. $\underline{59}$ 2656-2667.

[24]Wong,S.K., Hutchinson,D.A. and Wan,J.K.S. (1973) J.Chem.Phys. $\underline{58}$ 985-989.

[25]Atkins,P.W. and Evans,G.T. (1976) Adv.Chem.Phys. $\underline{35}$ 1-12.

[26]Elliot,A.J. and Wan,J.K.S. (1977) Accts.Chem.Res. $\underline{10}$ 161-166.

[27]Abragam,A. and Bleaney,B. (1970) Electron Paramagnetic Resonance of Transition Metal Ions (Clarenden Press, Oxford), 509-514.

[28]Trifunac,A.D., Nelson,D.T. and Mottley,C. (1978) J.Mag.Res. $\underline{30}$ 263-272.

[29]Atkins,P.W., McLauchlan,K.A. and Percival,P.W. (1973) Mol.Phys. $\underline{25}$ 281-296.

TABLE 1

The eigenstates and eigenvalues of $\hat{H}_0 = \beta B_0(g_1 \hat{S}_{1Z} + g_2 \hat{S}_{2Z}) - J(2\hat{S}_1 \cdot \hat{S}_2 + 1/2)$,

where

$|T_1> = |\alpha\alpha>$; $|T_{-1}> = |\beta\beta>$; $|S> = (|\alpha\beta> - |\beta\alpha>)2^{-1/2}$; $|T_0> = (|\alpha\beta> + |\beta\alpha>)2^{-1/2}$

$\omega = (J^2 + \delta^2)^{1/2}$; $\delta = \beta B_0(g_1 - g_2)/2$; $\varepsilon = \beta B_0(g_1 + g_2)/2$;

$a_1 = ((\omega + J)/2\omega)^{1/2}$; and $a_2 = ((\omega - J)/2\omega)^{1/2}$.

EIGENSTATE	EIGENVALUE
$|T_1>$	$\varepsilon - J$
$|+> = a_1|S> + a_2|T_0>$	ω
$|-> = a_1|T_0> - a_2|S>$	$-\omega$
$|T_{-1}>$	$-\varepsilon - J$

TABLE 2

Energies, ΔE_μ, and relative intensities, A_μ, for the transitions in the EPR spectrum of two electrons, calculated using Table 1 and Eq. 8. $\lambda = \delta/\varepsilon$.

μ	$\lvert\, i\rangle \to \lvert f\rangle$	A_μ	ΔE_μ
1	$\lvert +\rangle \to \lvert T_1\rangle$	$(2 + 2\lambda)^{-1}[\lvert a_2\rvert^2 + \lambda^2\lvert a_1\rvert^2 - 2\lambda\lvert a_1 a_2\rvert]$	$\varepsilon - J - \omega$
2	$\lvert T_{-1}\rangle \to \lvert -\rangle$	$(2 + 2\lambda)^{-1}[\lvert a_1\rvert^2 + \lambda^2\lvert a_2\rvert^2 - 2\lambda\lvert a_1 a_2\rvert]$	$\varepsilon + J - \omega$
3	$\lvert -\rangle \to \lvert T_1\rangle$	$(2 + 2\lambda)^{-1}[\lvert a_1\rvert^2 + \lambda^2\lvert a_2\rvert^2 + 2\lambda\lvert a_1 a_2\rvert]$	$\varepsilon - J + \omega$
4	$\lvert T_{-1}\rangle \to \lvert +\rangle$	$(2 + 2\lambda)^{-1}[\lvert a_2\rvert^2 + \lambda^2\lvert a_1\rvert^2 + 2\lambda\lvert a_1 a_2\rvert]$	$\varepsilon + J + \omega$

FIGURE CAPTIONS

Figure 1. Energy level diagram for the stationary states of $\hat{H}_0 = \beta B_0(g_1\hat{S}_{1Z} + g_2\hat{S}_{2Z}) - J(2\hat{S}_1 \cdot \hat{S}_2 + 1/2)$ for the case that $J = \delta/\sqrt{3}$, where $\delta = 1/2(g_1 - g_2)\beta B_0$, $T_1 = |\alpha\alpha>$, $T_{-1} = |\beta\beta>$, $|+> = a_1 |S> + a_2 |T_0>$, $|-> = a_1|T_0> - a_2|S>$, and a_1 and a_2 are defined in Table 1. There are four transitions labeled 1-4. Signals which are in absorption (emission) when the levels are populated from a singlet precursor are labeled A (E), reflecting a larger (smaller) population in the lower energy level.

Figure 2. Theoretical first derivative EPR spectra when two radicals in a pair are characterized by gaussian spectra of equal linewidth which do not overlap when the exchange interaction J is zero. The lowest trace shows the EPR absorption spectrum for radicals 1 and 2 in the absence of interaction when the respective resonance frequencies are $g_1\beta B_0$ and $g_2\beta B_0$, for the case that $\delta/\varepsilon = 0.01$, where $\varepsilon = 1/2(g_1 + g_2)\beta B_0$ and $\delta = 1/2(g_1 - g_2)\beta B_0$. The gaussian halfwidths are $\delta/4$. The upper traces show the polarized spectra as a function of increasing exchange interaction when the radical pair is formed from a singlet precursor. The vertical scale is the same for the top three traces.

Figure 3. Theoretical first derivative EPR spectra when two radicals in a pair are characterized by gaussian spectra of equal linewidth which overlap when the exchange interaction J is zero, where the parameters are the same as in Figure 2, except that the halfwidths are $3\delta/4$.
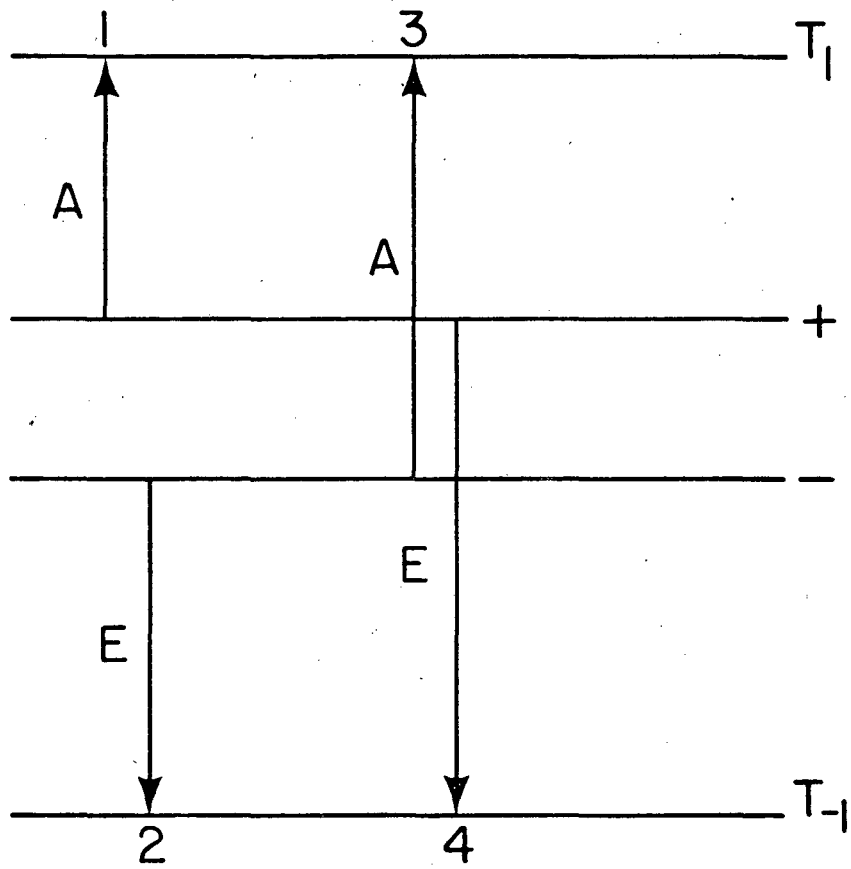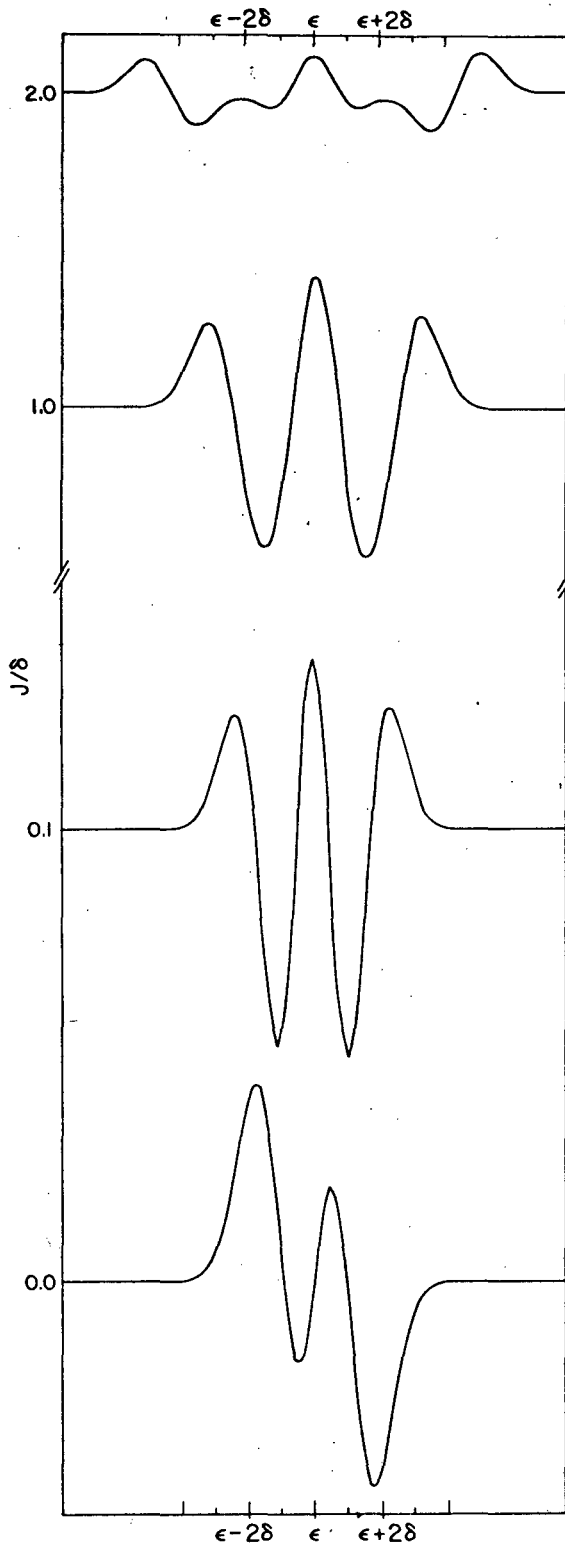
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FIGURE 1

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FIGURE 2

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FIGURE 3