A unified approach to spin polarization (CIDEP) and relaxation by Heisenberg spin exchange. II. Evaluation of the interradical distance dependence

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In paper I, a theory of Heisenberg spin exchange (HSE) was formulated to treat both electron spin polarization (CIDEP) and relaxation. In this paper (II), the expressions have been extended to consider the dependence of the exchange strength $J(r)$ on the interradical distance r. Analytic expressions for the CIDEP enhancement E and the spin exchange frequency ν_{ex} have been obtained by adopting an exponential model for $J(r)$ and integrating over a distribution of encounter distances r based on a Brownian diffusion model. A semiempirical expression for E has also been developed by replacing the usual diffusion parameters with experimentally measurable properties that are functions of diffusion. The behavior of ν_{ex} and E on the exchange strength $J(r)$ and the steepness of the distance dependence κr_0 is illustrated. The analytic results are consistent with existing numerical calculations and agree remarkably well with recent experimental measurements. The role of viscosity is treated to explain recent results for relaxation (ν_{ex}) and polarization (E) measurements of (i) acetate radical anion, (ii) H and D atoms, and (iii) acetone photoreduction.

I. INTRODUCTION

In the preceding paper (I),[1] it was shown how the seemingly disparate processes of chemically induced dynamic electron spin polarization (CIDEP) and relaxation, induced by Heisenberg spin exchange (HSE), could be unified under a single formalism. The details for obtaining a transient solution for the complete radical pair (RP) density matrix were presented by invoking reasonable assumptions and by factoring the RP Hamiltonian. Examples were given for the $\dot{R}H$ and $\dot{R}H_2$ radical spin systems as well as for general spin systems represented by n-line ESR spectra. Implications to reactive radicals were discussed and nonphenomenological Bloch-type equations were formulated and solved in a form suitable for describing time-resolved ESR experiments.

The exchange interaction in paper I[1] is model independent in regard to the dependence on interradical distance. In this paper, we extend the theory to include a specific model for this dependence. We also attach a stronger physical definition to encounter time and encounter distance and consider long range exchange interactions where $J(r)$ is still sufficiently large to induce exchange effects.

The objective of the present paper is (i) to develop simple analytic expressions for E and ν_{ex} which incorporate a realistic model for the $J(r)$ interradical distance dependence and (ii) to relate E, not only to microscopic diffusion parameters, but also to experimentally measurable quantities that are a function of diffusion. The present approach complements a collection of related work,[2–4] though possibly more exacting, require tedious computation[2,3] or numerical solution[4] and which convey little physical insight. Here we derive working relations for E and ν_{ex} that are straightforward to use. A comparison of calculated results with recent experimental measurements[5–9] of E and ν_{ex} demonstrates the utility and quality of the expressions.

The present paper is organized as follows: In Sec. II, the pertinent equations from paper I[1] are reestablished thus forming the basis for the subsequent sections. In Sec. III, a method for considering the dependence of the exchange interaction on interradical distance $J(r)$ is considered. Analytic expressions are developed for relaxation and the exchange frequency (Sec. III A) and for the CIDEP enhancement (Sec. III B). Included in the latter topic is a semiempirical approach to the enhancement factor. In Sec. IV, calculated values of E and ν_{ex} for various models of $J(r)$ and diffusion are compared with experiment. Finally, the results of this work are summarized in Sec. V.

II. GENERAL EQUATIONS

In paper I,[1] we derived modified Bloch equations for longitudinal and transverse magnetization which explicitly accounted for relaxation and polarization (CIDEP) by Heisenberg spin exchange (HSE). In this paper, we develop further the terms for the exchange frequency ν_{ex} and the CIDEP enhancement E, which are manifested in the properties of longitudinal magnetization M_z. We therefore reiterate below, equations from paper I that are pertinent to the present discussion:

$$\dot{M}_{z,\lambda} = -\alpha_1(t)[M_{z,\lambda} - M^0_{z,\lambda}] + w_\lambda \nu_{ex}(t) \sum_{\lambda' \neq \lambda} [M_{z,\lambda'} - M^0_{z,\lambda'}] + \dot{M}^{CID}_{z,\lambda} + \frac{\omega_1}{\sqrt{2}}[M_{+,\lambda} - M_{-,\lambda}], \tag{2.1}$$

$$\alpha_1(t) = T_{10}^{-1} + T_{1ex}^{-1}(t) + T_R^{-1}(t), \tag{2.2}$$

$$T_{1ex}^{-1}(t) = (1 - w_\lambda)\nu_{ex}(t), \tag{2.3}$$

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$$\dot{M}_{z,\lambda}^{\mathrm{CID}} = -d_\lambda G \sum_{\lambda' \neq \lambda} d_{\lambda'} \left\{ \nu_e(t) C_{\lambda'} + \frac{2Q_{\lambda'}}{J} \nu_{\mathrm{ex}}(t) D_{\lambda'} \right\}, \tag{2.4}$$

where

$$\nu_{\mathrm{ex}}(r,t) = P(r)\nu_e(t), \tag{2.5a}$$

$$w_\lambda = \frac{d_\lambda}{\Sigma_\lambda d_\lambda}, \tag{2.5b}$$

$$G(r) = \frac{J(r)\tau_e}{1 + J(r)^2\tau_e^2}, \tag{2.6a}$$

$$P(r) = \frac{1}{2}\left[\frac{J(r)^2\tau_e^2}{1 + J(r)^2\tau_e^2}\right], \tag{2.6b}$$

$$Q_{\lambda'} = \omega_\lambda - \omega_{\lambda'}. \tag{2.7}$$

The terms contained in the above expressions for line λ are defined as follows: $\alpha_1(t)$ is a decay rate encompassing uncoupled relaxation T_{10}^{-1}, HSE induced relaxation $T_{1\mathrm{ex}}^{-1}$, and chemical decay T_R^{-1}. The exchange frequency ν_{ex} is given by a product of the encounter frequency ν_e (τ_f^{-1} in paper I[1]), and a probability $P(r)$ that depends on the exchange interaction $J(r)$ and encounter time τ_e. $J(r)$ is assumed to be inherently negative and is therefore defined, as in paper I, such that $\frac{1}{2}J(r)$ is the negative of the exchange integral. The terms $G(r)$, $P(r)$, and $J(r)$ are functions of the interradical distance r. $M_{z,\lambda}^{\mathrm{CID}}$ denotes nonequilibrium magnetization due to CIDEP and w_λ is the relative weight of line λ, where d_λ is the degeneracy. $C_{\lambda'}$ and $D_{\lambda'}$ are CIDEP terms that were introduced in paper I and are evaluated in Appendix A. Finally, ω_1 is the nutation frequency for an on-resonance excitation field and ω_λ is the ESR frequency (in s^{-1}) of line λ. The expressions, thus far, assume $J(r) \gg Q_{\lambda'}$. Very weak exchange interactions are treated in paper I.

It is useful to express the frequencies of RP encounters ν_e, exchange ν_{ex}, and reactive recombination T_R^{-1}, as a function of bimolecular rate constants and radical concentration $c(t)$ as follows:

$$\nu_e(t) = 2k_e c(t), \tag{2.8}$$

$$\nu_{\mathrm{ex}}(t) = \langle P \rangle \nu_e(t) = 2k_{\mathrm{ex}} c(t), \tag{2.9}$$

$$T_R^{-1}(t) = 2k_2 c(t). \tag{2.10}$$

The rate of CIDEP magnetization ($\dot{M}_{z,\lambda}^{\mathrm{CID}}$) may also be related to radical concentration by the following expression[5–8]:

$$\dot{M}_{z,\lambda}^{\mathrm{CID}} = 2E_\lambda M_{z,\lambda}^0 k_2 c(t), \tag{2.11}$$

where E_λ is the intrinsic enhancement factor per reactive radical pair (RP) encounter and $M_{z,\lambda}^0$ is the Boltzmann magnetization for line λ. Rearranging Eqs. (2.4) and (2.11) and using Eqs. (2.5)–(2.9) gives the important expression

$$E_\lambda(r) = -\frac{k_e G(r)}{k_2 M_z^0} \sum_{\lambda' \neq \lambda} d_{\lambda'} \{ C_{\lambda'} + G(r) Q_{\lambda'} \tau_e D_{\lambda'} \}. \tag{2.12}$$

We have also made use of the relation $M_{z,\lambda}^0 = d_\lambda M_z^0$. It is emphasized here that E_λ is *independent* of concentration.

Finally, we will have occasion to use a simple model of diffusion to relate frequency ν and duration τ of various diffusive events to some characteristic distance r. For Brownian diffusion,[10] these terms are given by

$$\nu = 2kc(t) = 4\pi D r N_A c(t), \tag{2.13}$$

$$\tau = \frac{r^2}{6D}, \tag{2.14}$$

where

$$D = \frac{k_B T}{3\pi r_0 \eta}. \tag{2.15}$$

D is the Stokes–Einstein diffusion coefficient, N_A is Avogadro's number, η is viscosity, and k_B is Boltzmann's constant.

III. EVALUATION OF THE INTERRADICAL DISTANCE DEPENDENCE

A. Relaxation and the exchange frequency

The theory presented here considers two contributions to electron spin relaxation: (i) an explicit account of concentration dependent HSE which describes the coupling of different lines in an ESR spectrum [cf. Eqs. (2.1)–(2.4)], and (ii) a phenomenological term which accounts for concentration independent and uncoupled relaxation. The latter term would include spin–lattice-type mechanisms as well as spin–orbit, spin–rotation, and g-factor anisotropy interactions.[11–12] A competitive bimolecular relaxation mechanism may occur as a result of the electron–electron dipolar interaction between two radicals. However, experimental results[12] apparently indicate that this mechanism only becomes dominant at radical concentrations $\geqslant 10^{-2}$ M, whereas concentrations in excess of 10^{-3} M are rarely produced experimentally for *reactive* radicals.

1. The averaged exchange frequency

The exchange frequency is often expressed as a product of the exchange probability per encounter P times the encounter frequency ν_e. The form of P is quite explicit and naturally is a function of J and τ_e [Eq. (2.6b)], however, the definition of an encounter is often dealt with vaguely. ν_e is usually associated with the hard-sphere collision frequency ν_0, which implies a contact exchange model in which ν_{ex} cannot exceed $\nu_0/2$ [Eqs. (2.5) and (2.6)]. The contact model, however, ignores interaction distances greater than a molecular diameter which can lead to $\nu_{\mathrm{ex}} \geqslant \nu_0/2$. To consider this possibility, we express J as a function of the interradical distance r and average the exchange probability $P(r)$ over a distribution of impact parameters $y(r)$ according to the expression

$$\langle P \rangle = \frac{\int P(r) y(r) dr}{\int y(r) dr}. \tag{3.1}$$

We express the distance dependence of $J(r)$ as

$$J(r) = J_0 e^{-\kappa(r - r_0)}, \tag{3.2}$$

where J_0 is the hard-sphere exchange interaction [i.e., $J_0 \equiv J(r_0)$] and κ (in units of $1/r_0$) is the steepness parameter which governs how fast $J(r)$ decreases with r. The contact exchange model is represented in the limit $\kappa \to \infty$.

The distribution of impact parameters, $y(r)$, may be associated with a frequency at which two radicals approach to a distance r [i.e., $y(r) = \nu/\nu_0$]. Using a Brownian diffusion

model [Eqs. (2.13)–(2.15)] one obtains the relation

$$y(r) = \frac{r}{r_0}. \tag{3.3}$$

One might alternatively derive a similar expression for $y(r)$ based on pair distribution functions.[13]

We define an encounter distance r_e beyond which the exchange probability $P(r)$ becomes negligible (e.g., $J_e\tau_e \sim 0.1$). This value is used as the upper limit to integration in Eq. (3.1). Although, it should be possible to integrate beyond this value (i.e., to ∞), because of the simple form of $y(r)$ it is best to restrict the range of integration to a region that truly represents effective exchange encounters. By rearranging Eq. (3.2) and defining $J_e \equiv J(r_e)$, one obtains

$$r_e = \left[1 + \frac{1}{\kappa r_0} \ln \frac{J_0}{J_e}\right] r_0. \tag{3.4}$$

The exchange frequency may then be expressed as

$$\nu_{ex} = \langle P \rangle \nu_e = \langle P \rangle \left[1 + \frac{1}{\kappa r_0} \ln \frac{J_0}{J_e}\right] \nu_0, \tag{3.5}$$

where we have related ν_e and ν_0 using Eqs. (2.13)–(2.15) and (3.4).

The evaluation of $\langle P \rangle$ [Eq. (3.1)] is difficult even for the simple form of $y(r)$ in Eq. (3.3). However, reasonable analytic expressions may be obtained if we recognize that $y(r)$ varies much less than $P(r)$ over the effective range of exchange $r_e - r_0$ [since $J(r)$ is very steep] and may therefore be taken to be constant [i.e., $y(r) \simeq 1$] over the range of integration in the numerator of Eq. (3.1). Solving for $\langle P \rangle$ from r_0 to r_e then gives the manageable expression

$$\langle P \rangle = \frac{1}{2}\left\{\frac{\ln[1 + (J_0\tau_e)^2] - \ln[1 + (J_e\tau_e)^2]}{\ln(J_0/J_e)}\right\}. \tag{3.6}$$

An important distinction must be made regarding the encounter duration for hard-sphere collision vs longer range exchange (i.e., τ_0 vs τ_e). Clearly, as the interaction region $r_e - r_0$ increases, so does the encounter duration τ_e. The relation between τ_e and τ_0 may be derived from Eqs. (2.14) and (3.4) to give

$$\tau_e = \left[1 + \frac{1}{\kappa r_0} \ln \frac{J_0}{J_e}\right]^2 \tau_0. \tag{3.7}$$

In the contact exchange limit ($\kappa r_0 \to \infty$), τ_e naturally reduces to τ_0.

2. Model calculations

In Fig. 1, the dependence of ν_{ex} (expressed as a probability ν_{ex}/ν_0) for various values of τ_0 and κr_0 are compared to that for the contact exchange interaction ($\kappa r_0 \to \infty$). As expected, the calculated dependence of ν_{ex} on $J(r)$ differs markedly from the contact model. In the latter case, ν_{ex} reaches a limiting value of $\nu_0/2$. Equation (3.5), on the other hand, shows that ν_{ex} continues to increase with J_0, even in the strong exchange limit ($J_0\tau_0 \gg 1$), since the cross section for exchange continues to increase. As shown in Fig. 1(b), the rate of increase of ν_{ex} with J_0 depends on the steepness of $J(r)$ as measured by a parameter κr_0. Equation (3.6) tends to overestimate the exchange probability $P(r)$ for very large J_0 or for long range interactions (i.e., small κr_0) since the

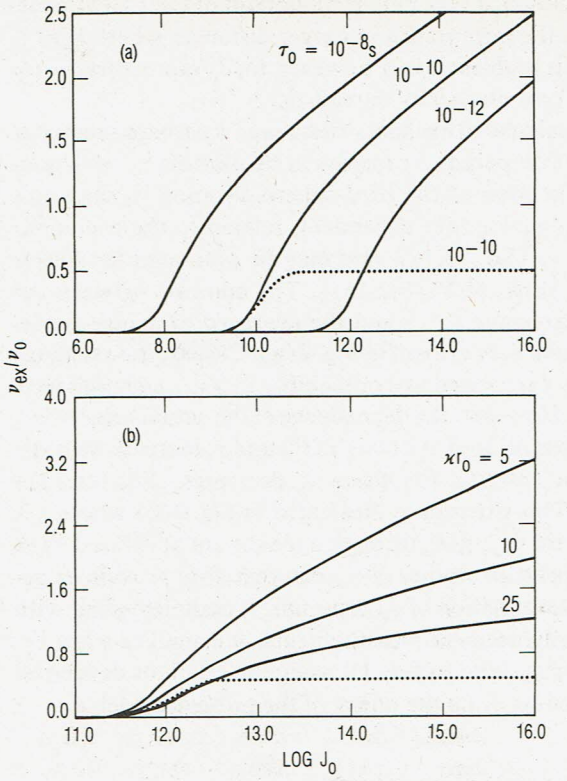

FIG. 1. Calculated dependence of the spin-exchange frequency ν_{ex} on $J(r)$: (a) as a function of τ_0 with $\kappa r_0 = 10$ and (b) as a function of the steepness parameter κr_0 with $\tau_0 = 10^{-12}$ s. A contact exchange model ($\cdots$) is given for comparison. Rates are expressed in units of ν_0 and the exchange threshold is taken to be $J_e\tau_e = 0.1$.

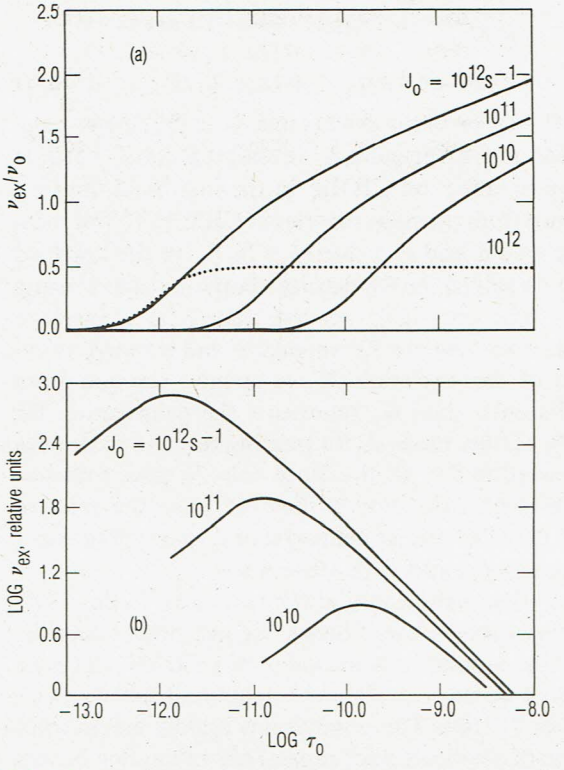

FIG. 2. Calculated dependence of ν_{ex} on the viscosity dependent parameter τ_0: (a) Rate expressed in units of ν_0. Contact exchange model ($\cdots$) is given for comparison. (b) Relative rate of ν_{ex}. Actual values ν_{ex} depend on a specific value of ν_0 or ν_e which in turn depends on radical concentration.

approximation $y(r) \simeq 1$ in the numerator of Eq. (3.1) underestimates the importance of longer distances where $P(r)$ is small. This problem arises, however, for J_0 values that are for the most part physically unrealistic.

The calculated exchange frequency is perhaps most conveniently compared to experiment by plotting ν_{ex} as a continuous function of the hard-sphere duration τ_0 since this parameter is viscosity dependent, related to the encounter duration τ_e [Eq. (3.7)], and may be estimated for simple diffusion [Eqs. (2.13)–(2.15)]. The contrast between the contact exchange (···) and the averaged exchange model (—) is again very evident in Fig. 2(a). Clearly, the exchange frequency (expressed as a probability ν_{ex}/ν_0) increases with J_0 and τ_0. However, the dependence of the actual value of ν_{ex} is more complicated. Although $\langle P \rangle$ and τ_0 increase with viscosity, the collision frequency ν_0 decreases [Eqs. (2.13)–(2.15)]. This situation is illustrated in Fig. 2(b) where it is apparent that ν_{ex} goes through a maximum at $J_0\tau_0 \sim 1$. Viscosity dependent studies of ν_{ex} can therefore provide an accurate determination of J_0, especially if complemented with CIDEP enhancement measurements. We analyze a few experimental systems in Sec. IV using the relations developed here to demonstrate the utility of the present model.

B. CIDEP enhancement factor

We begin with Eq. (2.12) for the CIDEP enhancement E_λ for line λ. The terms $C_{\lambda'}$ and $D_{\lambda'}$ are transformed from a free radical representation to a singlet–triplet RP representation in Appendix A and are evaluated in Appendix B. The use of Eqs. (2.12) and (A9) and (A10) then leads to

$$E_\lambda(r) = -\frac{k_e G(r)}{k_2 M_z^0} \sum_{\lambda' \neq \lambda} d_{\lambda'} \{ [\rho_{ST_0,\chi_I} + \rho_{T_0S,\chi_I}]_{\lambda'} + G(r) Q_{\lambda'} \tau_e [\rho_{SS,\chi_I} - \rho_{T_0T_0,\chi_I}]_{\lambda'} \}. \quad (3.8)$$

The transformation of the density matrix to the singlet–triplet representation (Appendix A) reveals that the $T_\pm$ triplet states have no affect on CIDEP in the high field limit[1]; a result known from previous theories of CIDEP.[2–4] The present theory would lead to a theory of S–T_- in the low field limit since we solved the RP density matrix in paper I[1] using a complete basis set. Again we note that E_λ is an intrinsic enhancement *per reactive* RP encounter and is therefore independent of concentration. If we assume reaction from singlet RPs only, then E_λ represents the polarization for triplet RPs. (Other methods for treating reactive recombination are noted in Sec. IV B.) Since only T_0 gives polarization in our high field model, then we have the relation $E_\lambda = \frac{1}{3} E(T_0)$. The precise definition of E is very important when comparing results with other work.

The physical significance of the two terms in Eq. (3.8) has been discussed before,[14] hence, we just briefly describe their role. The second term indicates that CIDEP can arise from random encounters if there is a net multiplicity of either the S or T_0 state. This condition is usually met in solutions of reactive radicals since radical recombination occurs preferentially from the S state. However, close inspection of the leading quantity indicates that this contribution to CIDEP can only be appreciable in the narrow regime where $Q_{\lambda'} \simeq J \simeq \tau_e^{-1}$. Since $Q_{\lambda'}$ is on the order of a hyperfine splitting ($\sim 10^8\ s^{-1}$) and τ_e on the order of the correlation time of a diffusive step in liquids ($\sim 10^{-10}$–$10^{-11}\ s^{-1}$), CIDEP occurring from random encounters is usually negligible. The second term, however, does have the historical significance of being the first proposed explanation of RP CIDEP.[15]

The first term in Eq. (3.8) would also appear to be negligible since the phase correlation term $[\rho_{ST_0} - \rho_{T_0S}]$ is zero for a *random* ensemble of RP encounters. However, RPs can acquire phase correlation if they should separate and reencounter following a previous encounter. Hence, radical pairs that give rise to CIDEP retain memory of their previous history. The evaluation of the memory function for the encounter/separation/reencounter scheme is common to all theories of RP CIDEP[2–4,14] and is given in Appendix B. By inserting Eq. (B4) into Eq. (3.8) and dropping the unimportant second term, we obtain

$$E_\lambda(r) = -\frac{k_e G(r)}{k_2 M_z^0} [\rho_{SS} - \rho_{T_0T_0}] \times \sum_{\lambda'} d_{\lambda'} \int_0^\infty f(t') \sin Q_{\lambda'} t'\, dt'. \quad (3.9)$$

The summation is now written for all lines λ' rather than for $\lambda' \neq \lambda$ since the term for $\lambda = \lambda'$ equals zero. In Eq. (3.9) we have assumed that the net multiplicity $[\rho_{SS} - \rho_{T_0T_0}]$ resulting from singlet reactive recombination in the initial encounter is independent of the RP nuclear spin state χ_I.

It is important to realize that the terms in Eq. (3.9) describe the following sequence of events which must occur for the production of RP CIDEP: (i) Geminate RP formation usually by photolysis (G pairs) or random RP encounters with preferential S state reactive recombination (F pairs). Both processes give net triplet multiplicity (cf. $[\rho_{SS} - \rho_{T_0T_0}]$ term). (ii) Separation of unreacted pairs to a distance where $J(r) \leqslant Q_{\lambda'}$ so that S–T_0 mixing can occur (cf. $\sin Q_{\lambda'} t$ term), and (iii) reencounter of the same RPs, with probability $f(t)$, to give CIDEP with an enhancement that is dependent on $J(r)$ and τ_e [via the function $G(r)$, Eq. (2.6a)].

We begin by developing an expression for the CIDEP enhancement E_λ that accounts for the interradical distance dependent nature of the exchange interaction $J(r)$. Beginning with Eq. (3.9), we shall be concerned with (i) the integration of $G(r)$ over a distribution of r, analogous to Eq. (3.1), (ii) evaluation of the net multiplicity term by geminate RP formation (G pairs) or singlet reactive recombination of diffusive encounters (F pairs), and (iii) evaluation of the reencounter probability expression. The latter term will be formulated in terms of characteristic distances for RP diffusive reencounters, as well as by a semiempirical expression which relates the properties of RP diffusive dynamics to measurable experimental parameters (i.e., k_{ex}, k_2).

1. The averaged enhancement factor

Integration over r: The expression for $G(r)$ [Eqs. (2.6a) and (3.2)] in Eq. (3.9) is integrated according to Eq. (3.1) in the same manner used to obtain the averaged exchange probability [Eq. (3.6)]. We assume that the distribution of

impact parameters $y(r)$ varies slightly compared to $G(r)$ over the limits of integration and is therefore treated as a constant in the integral of the numerator. The true function $y(r)$ is used everywhere else. This operation leads to

$$\langle G \rangle = \frac{\tan^{-1} J_0\tau_e - \tan^{-1} J_e\tau_e}{\ln(J_0/J_e)}. \tag{3.10}$$

Net multiplicity: For triplet geminate RPs (G pairs), the net multiplicity $[\rho_{SS} - \rho_{T_0T_0}]$ will simply be $-\frac{1}{3}$. To describe the net multiplicity resulting from diffusive encounters (F pairs), we define λ_s as the probability of singlet reactions. If we assume that triplet pairs are unreactive (or that at least $\lambda_T \ll \lambda_S$), then the net multiplicity acquired by F pairs may be expressed as

$$[\rho_{SS} - \rho_{T_0T_0}] = \tfrac{1}{4}[(1-\lambda_S) - (1-\lambda_T)] \simeq -\frac{\lambda_S}{4}. \tag{3.11}$$

We have the additional relation that λ_S is related to the ratio of bimolecular rate constants for reactive recombination k_2 to give $\lambda_S \sim 4k_2/k_e$ (where we still assume negligible triplet state reaction). Hence, Eq. (3.11) may be rewritten as

$$[\rho_{SS} - \rho_{T_0T_0}] = -\frac{k_2}{k_e}. \tag{3.12}$$

Reencounter probability: The function $f(t)$ derives from Noyes' concept[16] of secondary recombination. One is free to use his own model for the diffusion properties of $f(t)$, however, we use a solution of the Smoluchowski equation first used in CIDNP by Deutsch.[17] We adopt Adrian's treatment[14] which states that the reencounter probability from a distance where S–T_0 mixing can occur, to a distance where exchange effects can occur, in the time interval $t + dt$, is given by

$$f(t)dt = \left(\frac{3}{4\pi}\right)^{1/2}\left(\frac{r_Q - r_e}{r_Q}\right)\left(\frac{t}{\tau_e}\right)^{-3/2} \times \exp\left\{-\frac{3}{4}\left(\frac{r_Q - r_e}{r_e}\right)^2\frac{\tau_e}{t}\right\} d\left(\frac{t}{\tau_e}\right). \tag{3.13}$$

We have defined r_Q as the distance where $J(r)$ becomes comparable to $Q_{\lambda'}$ (thus allowing S–T_0 mixing to occur), r_e as the distance where exchange effects become active, and τ_e as the time between diffusive displacements of the radicals which we equate with the encounter time. We simplify Eq. (3.13) by noting that the onset of S–T_0 mixing occurs for times t afterwhich the exponential term has become unity (i.e., $Q_{\lambda'}^{-1} \sim t \gg \tau_e$). This simplification becomes arguable in cases of high viscosity. The evaluation of the integral in Eq. (3.9), using the function $f(t)$, is given in Appendix C.

The characteristic distances for the onset of S–T_0 mixing r_Q and for exchange encounters r_e are dependent on the steepness of $J(r)$. Equation (3.2) allows us to write

$$\frac{r_Q - r_e}{r_Q} = \frac{1}{\kappa r_Q}\ln\frac{J_e}{Q_{\lambda'}}, \tag{3.14a}$$

$$\kappa r_Q = \kappa r_0 + \ln\frac{J_0}{Q_{\lambda'}}. \tag{3.14b}$$

Substituting Eqs. (3.10), (3.12), (3.14), and (C4) into Eq. (3.9) then gives for the averaged enhancement factor the expression

$$E_\lambda = \frac{(3/2)^{1/2}}{M_z^0}\left[\frac{\tan^{-1} J_0\tau_e - \tan^{-1} J_e\tau_e}{\ln(J_0/J_e)}\right] \times \sum_{\lambda'}\frac{d_{\lambda'}}{\kappa r_Q}\ln\frac{J_e}{Q_{\lambda'}}(\text{sgn } Q_{\lambda'})|Q_{\lambda'}\tau_e|^{1/2}, \tag{3.15}$$

where (sgn $Q_{\lambda'}$) denotes the sign (i.e., $\pm$) of $Q_{\lambda'}$.

The Boltzmann magnetization M_z^0 which serves as the basis for defining enhancement, is straightforward to evaluate. At room temperature for conventional ESR fields (3.4 kG), it is given by

$$M_z^0 = \frac{1}{2}\Delta\rho_\lambda^0 \simeq \frac{\gamma H}{kT} \simeq 1.4\times 10^{-3}. \tag{3.16}$$

It is important to note that Eq. (3.15) is valid for a large range of $Q_{\lambda'}\tau_e$ values as long as $|Q_{\lambda'}\tau_e| < 1$. This upper limit is imposed by the particular model used for the recombination probability[14] and not by the integration of $G(r)$. Nonetheless, this range essentially covers all experimentally significant values of $Q_{\lambda'}\tau_e$. For instance, Eq. (3.15) smoothly describes the falloff of the square root dependence of $|Q_{\lambda'}\tau_e|$ as this term becomes larger. The asymptotic expressions of numerical solutions predict the same behavior,[4,7–9] but only for limiting cases.

2. Semiempirical expression for E_λ

All theories of CIDEP rely on diffusion parameters that are not well defined for many systems. Often, the selection of values appears rather arbitrary. It would, therefore, seem desirable to relate these parameters to real experimental observables. In this vein, we attempt to relate the rather nebulous concepts of characteristic distances for exchange encounters r_e and S–T_0 mixing r_Q that appear in $f(t)$ [Eq. (3.13)] to measurable quantities. The intention is to present a treatment with some physical basis, but not necessarily of the rigor necessary for quantitative calculations.

It is not unreasonable to associate the encounter distance r_e with a characteristic distance for bimolecular reaction r_2 (as is the case for CIDNP[14]), and the distance r_Q for S–T_0 mixing with that for the onset of spin exchange, r_{ex}. We may then write

$$\frac{r_Q - r_e}{r_Q} \simeq \frac{r_{ex} - r_2}{r_{ex}}. \tag{3.17}$$

These characteristic distances may be related to measurable rate constants using the simple diffusion model given by Eqs. (2.13)–(2.15). If we include the probability for reaction (1/4 if we assume singlet reaction only) and the probability of exchange [$P(r)$, Eq. (2.6b)] at the respective distances r_2 and r_{ex}, and make use of Eqs. (2.8) and (2.9), one obtains the relation

$$\frac{r_{ex} - r_2}{r_{ex}} = 1 - \frac{r_2}{r_{ex}} = 1 - \frac{4Pk_2}{k_{ex}} = 1 - \frac{4k_2}{k_e}. \tag{3.18}$$

The use of Eq. (3.18) in place of Eq. (3.14) in the

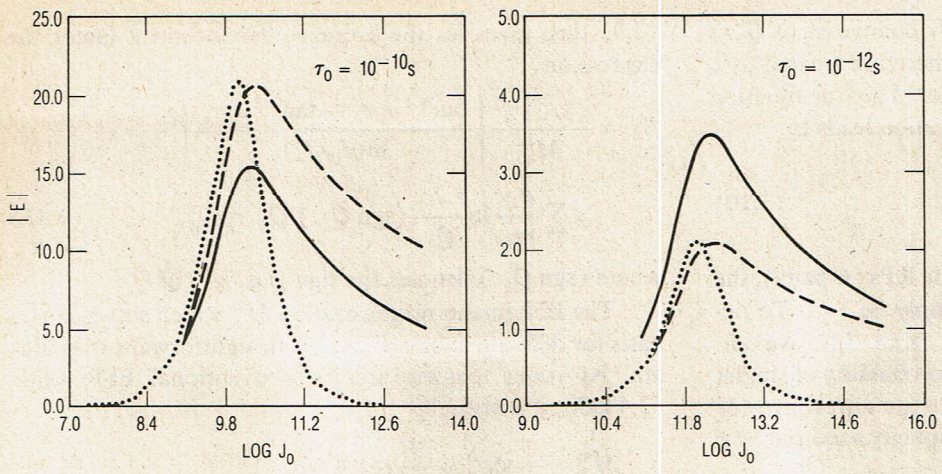

FIG. 3. The dependence of $|E|$ on J_0 for various models of the exchange interaction. The averaged expression by Eq. (3.15) (—); semiempirical averaged expression by Eq. (3.19) (---); and contact exchange model (···). Calculations are for an RH_2-type radical with line frequencies 9.33, 9.40, and 9.47 GHz (i.e., hyperfine splitting of 70 MHz). The outer lines are polarized and the middle line, which is doubly degenerate is unpolarized. For the semiempirical model, the ratio k_{ex}/k_e was expressed by P [Eq. (3.18)]. Other parameters are: $k_2 = 0.6\times10^9$ $M^{-1}s^{-1}$, $k_{ex} = 1.5\times10^9$ M^{-1}, $k_e = 3.0\times10^9$ $M^{-1}s^{-1}$, $J_e\tau_e = 0.1$, $\kappa r_0 = 10$.

expression for E_λ leads to the semiempirical expression

$$E_\lambda = \frac{(3/2)^{1/2}}{M_z^0}\left[\frac{\tan^{-1}J_0\tau_e - \tan^{-1}J_e\tau_e}{\ln(J_0/J_e)}\right] \times\left[1-\frac{4k_2}{k_e}\right]\sum_{\lambda'} d_{\lambda\lambda'}(\operatorname{sgn} Q_{\lambda\lambda'})|Q_{\lambda\lambda'}\tau_e|^{1/2}. \quad (3.19)$$

Again, we caution that the particular choice of rate constants and characteristic distances that describe the RP reencounter behavior are debatable. Furthermore, we have not completely replaced the characteristic encounter terms since values of J_e and τ_e must still be chosen. The latter term, however, may be expressed in terms of a diffusion coefficient by Eq. (2.14). In Sec. IV, we compare calculated values of E_λ to experiment as a function of the diffusion coefficient. Our intent in deriving Eq. (3.19) is to suggest a means (and not necessarily the best means) for obtaining semiempirical expressions for E_λ. The usefulness of this model, however, may be judged by comparing it with the more exact expression given by Eq. (3.15) and with experiment (Sec. IV A).

3. Model calculations

We examine the models of E_λ proposed thus far in Figs. 3 and 4. For the sake of comparison, we include results for a contact exchange expression based on the semiempirical model in Eq. (3.19). This is obtained by replacing the integrated expression for $\langle G\rangle$ in Eq. (3.10) with that given by Eq. (2.6a) and making use of the relations given in Eqs. (2.5)–(2.9). In Fig. 3, calculated values of E_λ according to Eq. (3.15) (—) and Eq. (3.19) (---) are compared along with a contact exchange model (···). The first two models clearly demonstrate the weakness of the contact model by showing that significant polarization can still occur in the so-called strong exchange region (i.e., $J_0\tau_0 \geqslant 1$). This behavior is due to longer range (noncontact) encounters, since there will always be a range of reencounter distances that will give a favorable value of $J(r)$ for CIDEP. Interestingly, the rather simple semiempirical model for E_λ gives a qualitatively similar result to that calculated using Eq. (3.15). Efforts to develop more exact semiempirical models may therefore prove promising.

We have varied the steepness parameter κr_0 for $J(r)$ in Fig. 4. As $J(r)$ becomes steeper, the interaction region $r_e - r_0$ [Eq. (3.4)] becomes smaller, leading to a decrease in E_λ as illustrated. For a value of $\kappa r_0 = 10$, one finds that $J(2r_0) < 10^{-4}J(r_0)$. The narrowness of $r_e - r_0$ helps explain why the simple distribution function for encounter distances $y(r)$ [Eq. (3.3)] works very well. For instance, in the limit of an infinitely steep $J(r)$ dependence (i.e., contact exchange where $\kappa r_0 \to \infty$) $y(r)$ becomes unity. The narrowness of $r_e - r_0$ also explains why the choice of r_e (e.g., where $J_e\tau_e \sim 0.1$) is not a very sensitive parameter in the expression for E_λ.

It is important to recognize that the encounter time τ_e is dependent on $J(r)$. It is a "breathing value" in the sense that it increases as the range of $J(r)$ increases [i.e., as κr_0 decreases, Eq. (3.7)]. To show this, we include a calculated curve in Fig. 4 denoted by (·-·-·) which represents the curve just above it, except that we have set $\tau_e = \tau_0$. Although, qualitatively similar to the more exact curve, the assumption that τ_e is constant with J_0 underestimates the value of E, especially in cases of strong exchange.

In Fig. 5, we have plotted according to Eq. (3.15) the enhancement $|E|$ as a continuous function of the hard-

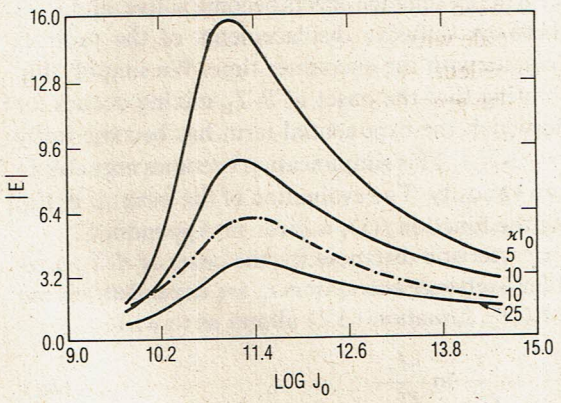

FIG. 4. The dependence of $|E|$ on the $J(r)$ steepness parameter κr_0 according to Eq. (3.15). Calculations are for τ_e given by Eq. (3.7) (—) and for $\tau_e = \tau_0$(·-·-·). ESR parameters are given in Fig. 3. Other parameters are $\tau_0 = 10^{-11}$ s^{-1} and $J_e\tau_e = 0.1$.

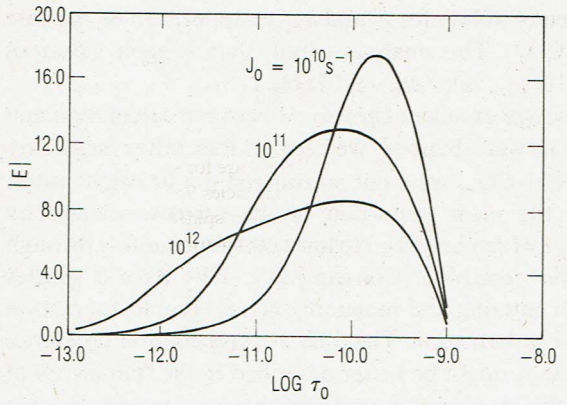

FIG. 5. The dependence of $|E|$ on the viscosity dependent parameter τ_0. Calculations are based on Eq. (3.15) using the ESR parameters in Fig. 3 and $J_e\tau_e = 0.1$.

sphere collision duration τ_0. This value may be expressed in terms of a diffusion coefficient for a particular medium according to Eqs. (2.13)–(2.15) if one has knowledge of the molecular diameter r_0 and the viscosity η. At high viscosity (large τ_0), a phase reversal in polarization is predicted by Eq. (3.15) and inferred in Fig. 5. The calculated phase reversal is only qualitative since it occurs under conditions ($Q_\lambda \cdot \tau_e \sim 1$) where the model employed for the RP reencounter probability begins to breaks down. A similar phase reversal effect appears in the asymptotic expressions of Freed and Pedersen[4,9] for large $Q_\lambda \cdot \tau_e$. This phenomenon may have implication to the puzzling phase reversal behavior observed experimentally for certain radical/solvent systems.[18–20]

Measuring E as a function of an experimentally adjustable property such as viscosity should provide the means for determining more accurately the value of J_0. This is particularly true when combined with a similar study of the exchange frequency, ν_{ex} [Sec. III A, Fig. 2(b)]. An analysis of recent experimental results in terms of viscosity is presented in the following section.

The benchmark for comparing calculated enhancement factors are the numerical solutions of the stochastic Liouville equations reported by Pedersen and Freed.[4] Although the diffusion terms in their work make it difficult to compare on an absolute scale with the present model, the qualitative agreement is excellent. The calculated magnitude of E appears though to be greater in the present model than in the numerical solutions and are in better accord with the emerging body of experimental measurements (Sec. IV). (An analysis of recent experimental results is given in Sec. IV in which asymptotic solutions of the stochastic Liouville equations are compared with the present expressions.) A small variation between the two theories occurs for *very* large (and possibly unrealistic values of J_0 where an asymptotic value of E is predicted in the numerical solutions. The use of a more accurate expression for $y(r)$ in the integration of $G(r)$ to account for the greater number of encounters at longer distances would give better agreement, however, this action would probably not allow an analytic solution for E. The analytic expressions derived here, on the other hand, are valid over a very reasonable range of exchange strengths as indicated in Figs. 3–5.

The utility of the expressions for E_λ given by Eqs. (3.15) and (3.19) is that they are analytic, convey physical sense, and can be incorporated into a set of Bloch equations[1] that are descriptive of time resolved ESR studies of reactive radicals.

IV. COMPARISON WITH EXPERIMENTS

Although, extensive measurements of CIDEP enhancement factors E and exchange frequencies ν_{ex} for transient radicals have been reported[5–9,21,22] in the literature, in only a few instances have E and ν_{ex} been measured for the same radical system.[5–8] We focus on the latter class of studies in the following discussions. Our main concern is to evaluate how well the present theory compares to (i) the experimental results and (ii) other theories used to explain the experimental results. Our analysis will, therefore, tend to follow the approach taken by the researchers in their use of previous theories. When appropriate, other approaches to analyzing the data using the present theory are suggested for obtaining additional information on RP processes.

A. Acetate radical anion

The acetate radical anion $\dot{C}H_2CO_2^-$, produced by pulse radiolysis, was recently studied by the electron spin-echo method.[5] In this work, a value of $|E| = 30 \pm 6$ was obtained and shown to be independent of concentration, as expected. HSE relaxation was also studied giving a spin exchange rate constant of $k_{ex} = 1.6\times10^9\ M^{-1}\ s^{-1}$ which assumes that no electron dipolar relaxation occurs (cf. Sec. III A).

The calculated curves in Figs. 2–5 are to some extent representative of the properties of $\dot{C}H_2CO_2^-$, however, we apply the present theory more specifically to the $\dot{C}H_2CO_2^-$ results in the following. We find it useful to calculate the hard-sphere collision frequency ν_0 and duration τ_0 using the simple diffusion model given by Eqs. (2.13)–(2.15). The pertinent data on the $\dot{C}H_2CO_2^-$, system are $T = 15\,°C$, $\eta = 1.14$, and $r_0 \simeq 4$ Å, which lead to the quantities $k_0 = 1.7\times10^9\ M^{-1}\ s^{-1}$ and $\tau_0 \simeq 2\times10^{-11}$ s.

Bearing in mind that the contact exchange model has the restriction that $k_{ex} \leqslant \frac{1}{2} k_0$, the measured value of k_{ex} is of considerable interest since it is nearly identical to k_0. This can be attributed to a long range exchange interaction and

TABLE I. Calculations of E and k_{ex} for $\dot{C}H_2CO_2^-$ for various models of $J(r)$.

J_0 (s^{-1})	κr_0	E[a] Eq. (3.15)	E[a] Eq. (3.19)	k_{ex}[a,b] ($M^{-1}\,s^{-1}$)
1×10^{12}	10	9	13	1.6×10^9
2×10^{11}	5	20	18	1.6×10^9
5×10^{10}	2.5	38	23	1.6×10^9

[a] Input parameters: $k_2 = 0.5\times10^9\ M^{-1}\ s^{-1}$, $k_e = 3.2\times10^9\ M^{-1}\ s^{-1}$, $\tau_0 = 2\times10^{-11}\ s^{-1}$ and $J_e\tau_e = 0.1$.
[b] Calculated by Eq. (3.5).

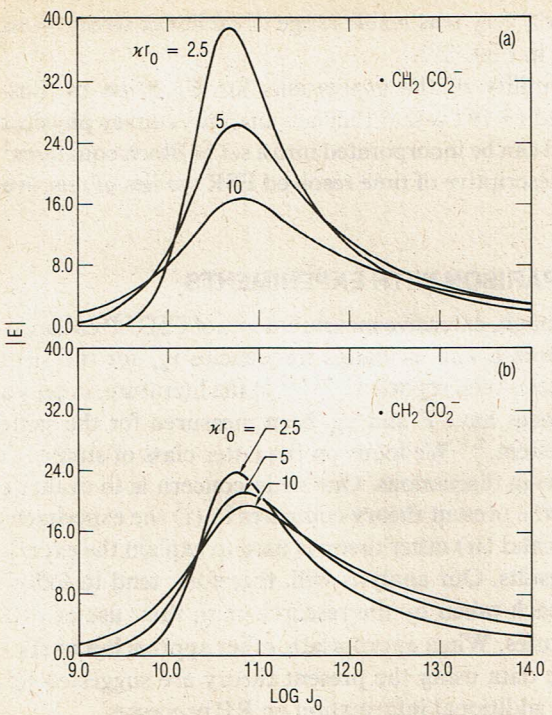

FIG. 6. The dependence of $|E|$ on $J(r)$ for the $\dot{C}H_2CO_2^-$ radical: (a) Averaged enhancement according to Eq. (3.15). (b) Semiempirical expression [Eq. (3.21)]. Parameters used in the calculations: $k_2 = 0.5\times10^9\ M^{-1}\ s^{-1}$, $k_{ex} = 1.6\times10^9\ M^{-1}\ s^{-1}$, $k_e = 3.2\times10^9\ M^{-1}\ s^{-1}$, $\tau_0 = 2\times10^{-11}\ s^{-1}$ and $J_e\tau_e = 0.1$.

demonstrates the inadequacy of the contact model. The exchange frequency ν_{ex} is a function of the magnitude J_0 and long range behavior κr_0 of $J(r)$. A series of J_0 and κr_0 values may therefore give the same value of ν_{ex}. For instance, values of $(J_0; \kappa r_0)$ ranging from $(5\times10^{10}\ s^{-1}; 2.5)$ to $(1\times10^{12}\ s^{-1}; 10)$ are consistent with the measured value of k_{ex} assuming $\tau_0 = 2\times10^{-11}$ s (Table I).

A more precise estimate of the properties of $J(r)$, however, becomes possible by combining the analysis of the ν_{ex} results with the measured CIDEP enhancement E. We have plotted the calculated dependence of E on $(J_0; \kappa r_0)$ in Fig. 6. We have likewise compiled in Table I, calculated values of E for $J(r)$ parameters consistent with the measured value of k_{ex}. Although, the dependence of $J(r)$ is not well known, previous studies[23] are consistent with values of κr_0 between 4 and 10. If we consider a long range $J(r)$ dependence, then the calculated values of E by Eq. (3.15) [Fig. 6(a)] can be brought into agreement with the measured results for both k_{ex} and E. Inspection of Table I would suggest a value of κr_0 between 2.5 and 5.

It is interesting to examine the semiempirical model given by Eq. (3.19) and plotted in Fig. 6(b). The calculation of E is less sensitive to the range of exchange parameters $(J_0; \kappa r_0)$ that were found to be consistent with the measured values of E and k_{ex} (Table I). This is because the semiempirical expression allows known properties to be fixed that might otherwise vary in a nonempirical model. One might argue that the value of $(J_0; \kappa r_0)$ that gives a similar result by both Eqs. (3.15) and (3.19), best reflects the true nature of the exchange interaction, especially if the results agree with the experimental values for E and k_{ex} as appears to be the case for $\dot{C}H_2CO_2^-$. This analysis would then suggest values of $J_0 \sim 1\times10^{11}\ s^{-1}$ and $\kappa r_0 \sim 5$ (Table I).

Although excellent agreement between calculation and experiment was obtained, we caution that other factors regarding $\dot{C}H_2CO_2^-$ were not considered in our calculations. Perhaps the most important is the negative charge on $\dot{C}H_2CO_2^-$, which may tend to limit close encounters through Coulombic repulsion. Consequently, RPs have a greater chance of entering and remaining in a favorable interaction region for polarization. The diffusive reencounter dynamics of $\dot{C}H_2CO_2^-$, might be better described in the framework of Debye's theory of reaction rates of charged particles in ionic solutions.[10,24] This analysis has been employed in the study of spin exchange in stable charged radicals[25] and more recently[26] for $\dot{C}H_2CO_2^-$. Unfortunately, such an analysis is extensive and beyond the scope of this paper.

B. H atom recombination

Beckert and Mehler[7] recently investigated the RP dynamics of hydrogen and deuterium atoms by TR ESR. Their quantitative measurements of E were analyzed using asymptotic solutions to the stochastic Liouville theory of CIDEP by Pedersen and Freed.[4] These co-workers, furthermore, investigated the concentration dependence of T_1 and T_2 so as

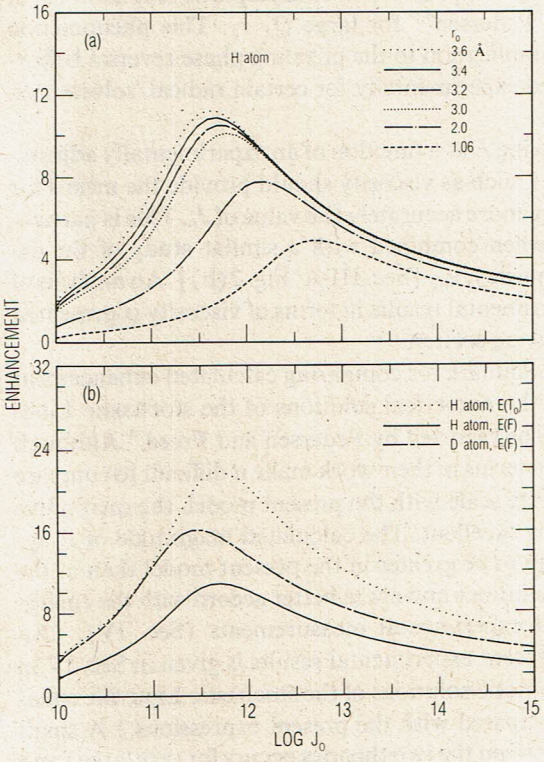

FIG. 7. Calculations of S–T_0 CIDEP from F-pair encounters of hydrogen atoms. (a) H atom polarization as a function of the distance of closest approach r_0 for a diffusion coefficient of $D_H = 7\times10^{-5}\ cm^2\ s^{-1}$. (b) Comparison of E for H and D atoms assuming $r_0 = 3.4$ Å and $D_D = 4\times10^{-5}\ cm^2\ s^{-1}$. $E(T_0)$ refers to the polarization for pure T_0 RPs. All calculations used values of $\kappa r_0 = 5$ ln 10 and $J_e\tau_e = 0.2$. Calculations were normalized to $E(F) = \frac{1}{2}E(T_0)$ in order to reproduce reaction probability model in Ref. 7.

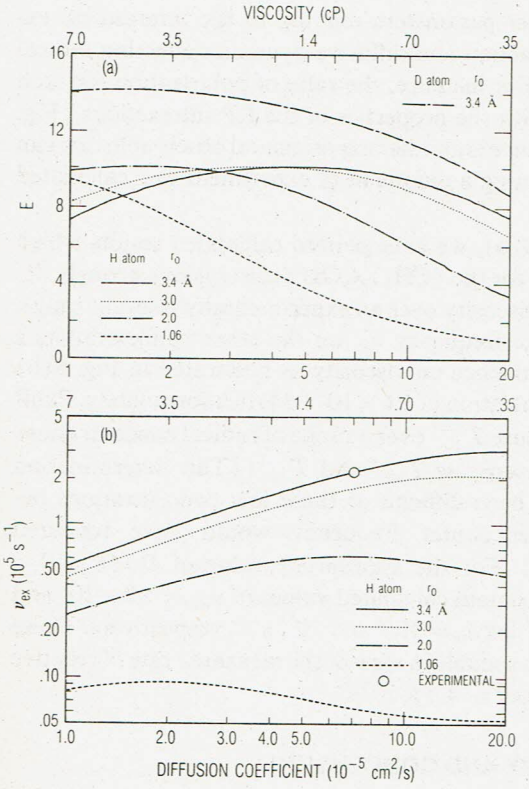

FIG. 8. Calculated dependence of E and ν_{ex} for H and D atoms as a function of the diffusion coefficient D. Calculations for various r_0 assumed $J_e\tau_e = 0.2$ and parameters from Ref. 7 of $J_0 = 10^{12}\ s^{-1}$ and $\kappa r_0 = 5$ ln 10. Viscosity scale is for H atom only and is based on the reported value of $D_H = 7\times10^{-5}\ cm^2\ s^{-1}$ and assuming $\eta \sim 1.0$ for aqueous solutions.

to determine the HSE contribution to relaxation. This work, therefore, serves as an excellent test case for comparing calculated results using the present theory to not only the experimental CIDEP and relaxation results, but also to the calculated results for E using the theory of Pedersen and Freed.

CIDEP in H atoms is somewhat complicated by the large hyperfine splitting which contributes significant S–T_- polarization.[21] Beckert and Mehler[7] were able to extract out the S–T_0 contribution from F pairs, obtaining values of $E = 14$ and $E = 10$ for H atom and D atom RPs, respectively. Calculations based on Eq. (3.15) were carried out for E as a function of J_0 and the distance of closest approach r_0 and are plotted in Fig. 7(a). The present calculations use the same parameters for exchange, diffusion, and recombination employed by Beckert and Mehler in their calculations. Remarkable agreement is obtained in terms of the functional dependence of E on J_0 and r_0. The absolute values of E agree to within 30% after correcting for differences in our definitions of E and reaction probability. The model for the reaction probability in Ref. 7 results in $E(F) \simeq \frac{1}{2}E(T_0)$ as opposed to a factor of $\frac{1}{3}$ in our model (Sec. III B). We have therefore normalized our results to $\frac{1}{2}E(T_0)$ to be consistent with Beckert and Mehler.[7]

Calculations using Eq. (3.15) were also carried out for D atom RPs and are compared with results using the asymptotic solutions in Fig. 7(b). Again, excellent agreement is obtained for the functional dependence of E on J_0 and r_0. Interestingly, we predict a slightly larger enhancement for D atoms than H atoms, opposite to the results of Beckert and Mehler.[7] Nonetheless, agreement on the absolute scale is within 25% even though our treatment of the reaction probability differs.

Beckert and Mehler[7] argue that the distance of closest approach r_0 for H atom RPs is greater than the Bohr diameter of 1.06 Å and is best represented by a distance of about 3.4 Å. The value of r_0 should be manifested in the dependence of E and ν_{ex} on the rate of diffusion. We illustrate in Fig. 8 the calculated values of E and ν_{ex} for various encounter distances r_0 over an experimentally realistic range of viscosities appropriate to the H and D atom experiments.[7] These results indicate that different values of r_0 can be distinguished on the basis of the viscosity dependence of E and ν_{ex}.

The simulation of ν_{ex} in Fig. 8(b) was calculated for a concentration of H atoms of 2×10^{-5} M, representing a typical value in the experiments of Beckert and Mehler. At this concentration, these investigators obtained a value of $T_{1ex}^{-1} = 2.2\times10^5\ s^{-1}$. For a single spin-$\frac{1}{2}$ system such as H atom, one has the relation[1,27] $T_{1(2)ex}^{-1} = \nu_{ex}/2$. In cases of multiplet CIDEP, however, the actual measured or "effective" value of T_{1ex}^{-1} for the line of interest is enhanced by the contribution to decay from the other oppositely polarized lines. For H atoms, the effective rate is twice the unpolarized rate,[1] consequently, $\nu_{ex} = (T_{1ex}^{-1})_{eff} = 2.2\times10^5\ s^{-1}$. Remarkably, the calculations in Fig. 8(b) are in complete agreement with experiment if we assume the values $r_0 = 3.4$ Å and $D = 7.0\times10^{-5}\ cm^2\ s^{-1}$ that Beckert and Mehler found to best fit their other data.

The excellent agreement between the present calculations and experiment must be considered to some extent fortuitous, however, it does indicate that the present model is capable of making quantitative and certainly qualitative predictions of CIDEP polarization and HSE relaxation as a function of many properties relating to radical–radical interactions and encounter dynamics. It is also worth emphasizing that an investigation of *both* E and ν_{ex} can provide a more precise estimate of the properties of the exchange interaction $J(r)$ than either analysis alone. This conclusion was also reached in the analysis of the experimental and calculated results for $\dot{C}H_2CO_2^-$ in the previous section.

For purposes of comparison, the above treatment for the H and D atom was intended to match as closely as possible that given by Beckert and Mehler[7] using the asymptotic solutions of Pedersen and Freed.[4] A thorough analysis should include variations not only of r_0, but of other parameters affecting the interradical exchange interaction (e.g., J_0 and κr_0) as was done in the treatment for $\dot{C}H_2CO_2^-$ (Sec. IV A).

C. Photoreduction of acetone: 2-Propyl-2-ol radical

Paul[8] reported on the photoreduction of acetone with 2-propanol in aqueous solution to give 2-propyl-2-ol, $(CH_3)_2\dot{C}OH$, radical pairs. This work is notable in that he presents absolute enhancements E for all lines as well as determinations of initial concentration $c(0)$ and T_1. Furthermore, he has analyzed his CIDEP results using equations based on the numerical solutions of Pedersen and Freed.[4]

TABLE II. Experimental and calculated CIDEP enhancements for $(CH_3)_2\dot{C}OH$.

Line	Obs. (Ref. 8)	Calculated for J_0 (s^{-1})[a] 1×10^{11}	1×10^{12}	1×10^{13}	1×10^{13} (Ref. 8)
−1, 1	62	110	69	47	16
−2, 2	115	174	108	80	28
−3, 3	153	232	143	98	35

[a] Input parameters: $D = 8\times10^{-6}$ cm^2 s^{-1}, $r_0 = 4.6$ Å, $\kappa r_0 = 5$ ln 10, $J_e\tau_e = 0.2$ and $c(0) = 1.6\times10^{-6}$ M. Polarization enhancements are expressed as absolute values.

Using the same parameters as Paul, we have calculated polarized spectra for $(CH_3)_2\dot{C}OH$ using the major hyperfine interaction involving the six equivalent methyl hydrogens which gives a seven line spectrum. (The weak α-H and hydroxy-H interactions have been ignored.) The present calculations are compared to the observed and calculated results of Paul[8] in Table II. Paul restricted his calculations to an exchange interaction of $J_0 = 1\times10^{13}$ s^{-1} and obtained polarizations that were about one-quarter of the observed values. For the same parameters, we obtain much better agreement, but still fall short of the experimental values. However, an excellent agreement for all lines can be obtained by assuming a value of $J_0 \sim 1\times10^{12}$ s^{-1} (Table II). Again, we caution that our calculations are presented simply as a comparison with other methods. A full analysis should consider other parameters relating to the interradical exchange interaction and diffusive dynamics affecting radical encounters. For instance, the ratio of polarization for each line varies with the properties of the RP interactions [Fig. 9(a)] and hence is another experimental observable that can help in obtaining a unique fit of experiment to a calculated RP model.

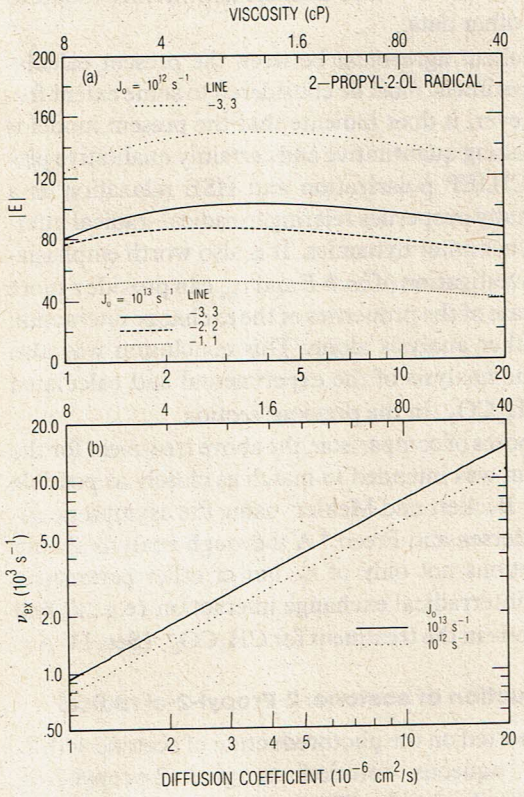

FIG. 9. Calculated dependence of $|E|$ and ν_{ex} on viscosity for $(CH_3)_2\dot{C}OH$. Calculations assumed $J_e\tau_e = 0.2$ and parameters from Ref. 8 of $\kappa r_0 = 5$ ln 10, $r_0 = 4.6$ Å, and $c(0) = 1.6\times10^{-6}$ M. Viscosity scale is based on the reported value of $D = 8\times10^{-6}$ cm^2 s^{-1} and assuming $\eta \sim 1.0$ for aqueous solutions.

In Fig. 9(a), we have plotted calculated results which show that E for the $(CH_3)_2\dot{C}OH$ radical is not strongly dependent on viscosity over an experimentally relevant range. The exchange frequency ν_{ex} on the other hand, exhibits a steeper dependence on viscosity as illustrated in Fig. 9(b) (for a concentration of 1.6×10^{-6} M). Unfortunately, Paul[8] did not measure T_1^{-1} over a range of radical concentrations in which to separate T_{10}^{-1} and T_{1ex}^{-1}. (This determination would have been difficult at these low concentrations because the encounter frequency would have rendered $T_{1ex}^{-1} \ll T_{10}^{-1}$). For the appropriate value of $D = 8\times10^{-5}$ cm^2 s^{-1}, we obtain calculated values of $\nu_{ex} = 5.2\times10^3$ and 6.5×10^3 s^{-1} for $J_0 = 10^{12}$ and 10^{13} s^{-1}, respectively. These values are reasonable in view of the measured rate of reactive recombination[8] of 4.3×10^3 s^{-1}.

V. SUMMARY AND CONCLUSION

The dependence of the exchange strength on interradical distance $J(r)$ has been applied to the problem of relaxation and CIDEP. Analytic expressions for the CIDEP enhancement E and the spin exchange frequency ν_{ex} have been obtained by integrating an exponential model for $J(r)$ over a distribution of encounter distances r based on Brownian diffusion and pair correlation. A semiempirical expression has also been presented for E in which diffusion parameters, which are ordinarily difficult to determine, are related to measurable properties such as the chemical decay rate and the encounter frequency.

The present model has been compared not only to recent experimental work, but to analyses based on the numerical solutions of the stochastic Liouville equations by Pedersen and Freed.[4] Several experimental systems have been examined using the present treatment in order to demonstrate the excellent quantitative capabilities. Analysis of the results for $\dot{C}H_2CO_2^-$ by the nonempirical and semiempirical methods successfully models the experimentally measured values[5] of E and k_{ex} for an exchange interaction $J(r)$ in which $J_0 \simeq 1\times10^{11}$ s^{-1} and $\kappa r_0 \simeq 5$. An analysis of the recent H and D atom work,[7] likewise, gave excellent agreement with the measured values of E and ν_{ex} as well as with the analysis of E using the asymptotic solutions of Pedersen and Freed. The present expressions were also applied to results for $(CH_3)_2\dot{C}OH$ and found to be in closer agreement with experiment than the asymptotic solutions using the same input parameters. A better value for J_0 is suggested which essentially reproduces the polarizations for each of the hyperfine lines of $(CH_3)_2\dot{C}OH$.

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APPENDIX A: EXPRESSIONS FOR CIDEP: TRANSFORMATION TO SINGLET–TRIPLET REPRESENTATION

We have previously[1] expressed the free radical and encounter pair basis states in an uncoupled representation given, respectively, by

$$|k\rangle = \left| m_s, \prod_i m_{I,i} \right\rangle \tag{A1}$$

and

$$|k\mu\rangle = |\chi_S, \chi_I\rangle, \tag{A2}$$

where

$$\chi_S = m_S^a m_S^b, \tag{A2a}$$

$$\chi_I = \chi_I^a \chi_I^b = \prod_i^a m_{I,i} \prod_j^b m_{I,j}. \tag{A2b}$$

Theories on CIDEP usually employ a coupled RP basis set in which the pair of electron spins χ_S is expressed in terms of singlet and triplet states $\chi_S^{\rm RP}$ by the relations

$$\begin{aligned} T_+ &= \alpha\alpha, \\ S_0 &= 2^{-1/2}(\alpha\beta - \beta\alpha), \\ T_0 &= 2^{-1/2}(\alpha\beta + \beta\alpha), \\ T_- &= \beta\beta. \end{aligned} \tag{A3}$$

The density matrix elements in the uncoupled representation must be transformed accordingly. If $\mathbf{S}$ is a similarity matrix that transforms the vector of basis states for the encounter pair β_e to the vector of RP states $\beta_{\rm RP}$, i.e.,

$$\beta_{\rm RP} = \mathbf{S}\beta_e. \tag{A4}$$

then the RP density matrix $\rho_{\rm RP}$ is obtained from ρ_e via the operation

$$\rho_{\rm RP} = \mathbf{S}\rho_e\mathbf{S}^{-1}. \tag{A5}$$

The density matrix elements for CIDEP are encompassed by the $C_{\mu\nu}$ and $D_{\mu\nu}$ terms [cf. paper I, Eqs. (3.3a) and (3.3b)[1]] which we rewrite as

$$C_{\mu\nu} = i\,\mathrm{Im}\,\rho_{kl}\rho_{\mu\nu} = i(\rho_{k\nu,l\mu} - \rho_{l\mu,k\nu}), \tag{A6}$$

$$D_{\mu\nu} = \mathrm{Re}\,\rho_{kl}\rho_{\mu\nu} = i(\rho_{k\nu,l\mu} + \rho_{l\mu,k\nu}), \tag{A7}$$

where we have made use of the relation $\rho_{ac}\rho_{bd} = \rho_{ab,cd} = \rho^*_{cd,ab}$. Since kl and $\mu\nu$ represent ESR transitions from $m_s = \beta$(k and μ) to $m_S = \alpha$ (l and ν), we have for the encounter pair states

$$|k\nu\rangle = |\alpha\beta, \chi_I\rangle, \tag{A8a}$$

$$|l\mu\rangle = |\beta\alpha, \chi_I\rangle. \tag{A8b}$$

It may be shown by carrying out the tedious transformation in Eq. (A5) or by judiciously grouping terms that

$$C_{\mu\nu} = (\rho_{ST_0,\chi_I} - \rho_{T_0S,\chi_I}), \tag{A9}$$

$$D_{\mu\nu} = (\rho_{SS,\chi_I} - \rho_{T_0T_0,\chi_I}). \tag{A10}$$

An explicit example of the transformation for the RH spin case has been worked out before.[26] The expressions for C_λ and D_λ are simply equated to the corresponding terms for the transition(s) comprising line λ.

APPENDIX B: EVALUATION OF THE MEMORY FUNCTION $C_{\mu\nu}$

An encounter of two radicals can only give RP CIDEP if (i) the same radicals have had a previous encounter with singlet encounters reacting to leave net triplet multiplicity, and (ii) the RPs separate to a sufficient distance between encounters to allow S–T_0 to occur via the hyperfine interactions [i.e., $J(r) \leqslant Q_{\mu\nu}$]. Hence, RPs giving rise to CIDEP have memory of their initial encounter and events leading up the the reencounter. This information is contained in the memory function $C_{\mu\nu}$, which we evaluate from the instant of initial RP separation to the onset of the RP reencounter.

The density matrix solution for the free radical in the absence of exchange and relaxation is given by

$$\rho(t) = e^{-iHt}\rho(0)e^{+iHt}. \tag{B1}$$

The exchange term does not apply here since the solution is strictly for intervals *between* encounters. Unusual situations where exchange effects and S–T_0 mixing occur simultaneously are treated in the encounter RP density matrix solution. The relaxation term is dropped since typical times for RP reencounters ($\sim 10^{-10}$–10^{-11} s) are much less than those for relaxation ($\sim 10^{-5}$–10^{-8} s). Since the Hamiltonian matrix H is diagonal in the high field limit,[1] one obtains for the elements of ρ,

$$\rho_{kl}(t) = e^{i\omega_{kl}t}\rho_{kl}(0), \tag{B2}$$

where $\omega_{kl} = H_{kk} - H_{ll}$.

Substitution of Eq. (B2) into Eq. (A6) leads to

$$\begin{aligned} C_{\mu\nu}(t) = i\{&\cos(\omega_{kl} - \omega_{\mu\nu})t\,[\rho_{ST_0,\chi_I}(0) - \rho_{T_0S,\chi_I}(0)] \\ &+ i\sin(\omega_{kl} - \omega_{\mu\nu})t\,[\rho_{SS,\chi_I}(0) - \rho_{T_0T_0,\chi_I}(0)]\}, \end{aligned} \tag{B3}$$

where we have expressed the initial conditions in the RP representation via the identities described in Appendix A [Eqs. (A6)–(A10)]. The initial condition for the cosine term in Eq. (B3) represents a phase correlation which is zero for a random ensemble of radicals. Finally, an averaged $C_{\mu\nu}$ is defined by integrating over a distribution of reencounter probabilities $f(t)$ to give

$$\begin{aligned} C_{\mu\nu} &= \int_0^\infty f(t')C_{\mu\nu}(t')dt' \\ &= [\rho_{SS,\chi_I} - \rho_{T_0T_0,\chi_I}]\int_0^\infty f(t')\sin(\omega_{kl} - \omega_{\mu\nu})t'\,dt'. \end{aligned} \tag{B4}$$

The function $f(t)$ is discussed in more detail in Sec. III B 1. The expression for C_λ is obtained by substituting Q_λ [Eq. (2.7)] for $\omega_{kl} - \omega_{\mu\nu}$.

APPENDIX C: INTEGRATION OVER THE REENCOUNTER PROBABILITY $f(t)$

For $f(t)$ given by Eq. (3.13), the integral in Eq. (3.9) is given by

$$\text{Int} \equiv \int_0^\infty f(t')\sin Q_\lambda t'\, dt'$$

$$= K\int_0^\infty \left(\frac{t'}{\tau_e}\right)^{-3/2} \sin Q_\lambda t' d\left(\frac{t'}{\tau_e}\right), \tag{C1a}$$

where

$$K = \left(\frac{3}{4\pi}\right)^{1/2}\left[\frac{r_Q - r_e}{r_Q}\right]. \tag{C1b}$$

If we introduce the change of variables $x = Q_\lambda t'$, we obtain

$$\text{Int} = K(\text{sgn}\, Q_\lambda)|Q_\lambda \tau_e|^{1/2}\int_0^\infty x^{-3/2}\sin x\, dx. \tag{C2}$$

The quantity Q_λ has been expressed as $(\text{sgn}\, Q_\lambda)|Q_\lambda|$ where sgn indicates the sign (i.e., $\pm$) of Q_λ to avoid problems with square roots. The integral in Eq. (C2) may then be integrated by parts to give the definite integral

$$\int_0^\infty x^{-3/2}\sin x\, dx = 2\int_0^\infty x^{-1/2}\cos x\, dx = (2\pi)^{1/2}. \tag{C3}$$

Equations (C1)–(C3) then give the final expression

$$\int_0^\infty f(t')\sin Q_\lambda t'\, dt'$$

$$= \left(\frac{3}{2}\right)^{1/2}\left[\frac{r_Q - r_e}{r_Q}\right](\text{sgn}\, Q_\lambda)|Q_\lambda \tau_e|^{1/2}. \tag{C4}$$

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