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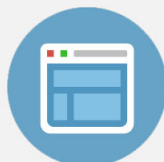
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# Analytic solution of the stochastic-Liouville model of spin exchange<sup>a)</sup>

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An analytic solution is obtained for the stochastic-Liouville model of spin exchange between a pair of radicals undergoing isotropic diffusion in solution and interacting via an exchange interaction that decays exponentially with radical separation. The resulting spin exchange cross section is the sum of a "strong encounter" term that is approximately equal to the biomolecular reaction cross section and a "grazing encounter" term that is due to encounters in the tail of the exchange interaction. The latter term may range from negligible to twice the former term for plausible values of the diffusion rate and the range of the exchange interaction. It is shown that the theory combined with experimental data on the spin-exchange contribution to spin-lattice relaxation can provide an estimate of the range of the exchange interaction between two radicals.

## INTRODUCTION

Heisenberg spin exchange, in which two paramagnetic species exchange their spins during an encounter, has been known and investigated for some time, primarily by observing its concentration- and viscosity-dependent effects on the electron spin resonance (ESR) linewidths and saturation properties of free radicals in solution. Until recently such investigations were largely confined to solutions of stable free radicals,<sup>1,2</sup> it being difficult to generate reactive radicals in sufficient concentrations to produce sizable, readily observed, spin-exchange effects. One notable exception is a measurement of the spin-exchange contribution to relaxation in a reactive acetate ion radical ( $\text{CH}_2\text{CO}_2^-$ ) produced in high concentration by a Van de Graaff electron beam.<sup>3</sup>

This situation has changed, however, with extensive recent applications of high-power, pulsed, ultraviolet excimer lasers combined with rapid-response ESR spectroscopic techniques to observe transient radical products of photochemical reactions.<sup>4-6</sup> The initial radical concentrations produced by these lasers are not only high enough to produce readily observable effects on the linewidths and other conventional ESR parameters, but, more importantly, they can have a number of interesting and hitherto unobserved effects on the chemically induced electron spin polarizations (CIDEP) which are commonplace in radicals produced by laser flash photolysis. One such effect of chemical exchange on these polarizations has already been reported,<sup>7</sup> and spin exchange generally has the same effects as chemical exchange.<sup>8</sup>

These recent developments increase the need for a more quantitative treatment of spin exchange than the phenomenological models which are generally used to investigate spin-exchange effects on ESR linewidths and relaxation.<sup>1</sup> The best approach to such a quantitative treatment appears to be the stochastic-Liouville model as applied by Freed and Pedersen to the CIDEP problem<sup>9</sup> and also used by them for

numerical calculations of spin-exchange cross sections.<sup>10</sup> It is also possible to solve the stochastic-Liouville equation of CIDEP analytically for a restricted but very useful range of parameters<sup>11</sup> and, as will be described here, this treatment can be extended to give an analytic expression for spin exchange. This expression, which relates the spin-exchange cross section to such parameters as the diffusion rate and the range of the exchange interaction, should be useful in analyzing the effects of spin exchange in CIDEP. The analysis also emphasizes the close relationship between spin exchange and the radical pair mechanism of CIDEP.

## THEORY

As shown previously<sup>11</sup> the stochastic-Liouville equation for the evolution of the electron spin state of a pair of radicals undergoing isotropic diffusion in a liquid can be written as

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{\partial^2 \hat{\rho}}{\partial r^2} + \Omega(r) \times \hat{\rho}(r, t). \quad (1)$$

Here,  $r$  is the dimensionless interrational distance, scaled in units of the radical-radical collision distance ( $\sigma$ ), and  $t$  is the dimensionless time, scaled in units of  $\sigma^2/D$  where  $D$  is the diffusion constant for the relative diffusion of the two radicals. The components of the spin-state vector  $\hat{\rho}$  are real, physically significant, linear combinations of the elements of the spin density matrix, i.e.,

$$\hat{\rho} = r \begin{pmatrix} \rho_{ST_0} + \rho_{T_0S} \\ -i(\rho_{ST_0} - \rho_{T_0S}) \\ \rho_{SS} - \rho_{T_0T_0} \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (2a)$$

where  $S$  and  $T_0$  are, respectively, the singlet and  $M_S = 0$  triplet spin states of the radical pair. Thus,  $x$  is the electron spin polarization of the pair and  $z$  is its relative singlet vs triplet character. The vector  $\Omega$  which determines the evolution of  $\hat{\rho}$  is

$$\Omega(r) = - \begin{pmatrix} a \\ 0 \\ J_0 e^{-\lambda r} \end{pmatrix}, \quad (2b)$$

where  $a$  is the hyperfine-state-dependent difference in the

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magnetic energies of the two radicals that mixes the  $S$  and  $T_0$  states ( $a$  will not be further specified here because it is unimportant in the spin-exchange problem) and  $J_0 e^{-\lambda r}$  is the splitting of the  $S$  and  $T_0$  states by the valence or exchange interaction between the radicals. Here,  $J_0$  and  $\lambda$  are also scaled quantities related to the corresponding dimensioned quantities  $\tilde{J}_0$  and  $\tilde{\lambda}$  by the equations<sup>11</sup>

$$\tilde{J}_0 = \frac{1}{2}(D/\sigma^2)J_0; \quad \tilde{\lambda} = \lambda/\sigma. \quad (3)$$

In the CIDEP problem the radical pair is initially in an unpolarized pure  $S$  or  $T_0$  state with its components sufficiently close together that  $J_0 e^{-\lambda r} \gg a$  and the desired quantity is the polarization after a sufficiently long time interval that the components of the radical pair are certain to be far apart and unlikely to reencounter. This polarization is the integral of  $x(r \gg 1, t \rightarrow \infty)$  over the volume of the system, i.e.,

$$P_\infty = \lim_{t \rightarrow \infty} 4\pi \int_1^\infty r x(r, t) dr = 4\pi \bar{x}(r \gg 1, s \equiv 0), \quad (4)$$

where  $\bar{x}$  is the Laplace transform of  $x$ . This result was obtained using the well-known relation<sup>12</sup>  $\lim_{t \rightarrow \infty} x(r, t) = \lim_{s \rightarrow 0} s \bar{x}(r, s)$  and the asymptotic ( $r \gg 1$ ) behavior of  $\bar{x}(r, s)$  as determined from the Laplace transformed version of Eq. (1).<sup>11</sup>

In the spin-exchange problem, on the other hand, we initially have two radicals with opposite electron spins, which is a polarized state from the standpoint of the radical pair mechanism of CIDEP, separated by some intermediate distance such that  $J_0 e^{-\lambda r} \approx 0$  and we are concerned with the possible encounter and resulting interchange of the spins of the two radicals. This will be given by the difference between the final polarization as determined from Eq. (4) and the initial polarization of unity which corresponds to the initial conditions

$$x(r, 0) = \delta(r - r')/4\pi r'; \quad y(r, 0) = z(r, 0) = 0; \quad J_0 e^{-\lambda r} \approx 0. \quad (5a)$$

The boundary conditions for the two problems are the same,<sup>11</sup> namely a reflective inner boundary condition

$$\left[ \frac{\partial(u/r)}{\partial r} \right]_{r=1} = 0 \quad (5b)$$

which insures that the radical separation does not become less than  $\sigma$ , and the outer boundary condition

$$\lim_{r \rightarrow \infty} ru = 0; \quad u = x, y, z \quad (5c)$$

which insures that the integrals of the spin densities over all space are finite.

The solution of the stochastic-Liouville equations for the spin-exchange case is very similar to that of the CIDEP case except for the simplification that here we can neglect the magnetic singlet-triplet mixing ( $a = 0$ ) with the result that we have only two coupled equations in  $x$  and  $z$ . ( $y$  is always zero and we do not have to uncouple  $y$  and  $z$  by defining the new variables  $u_\pm = y \pm iz$  as was done in the CIDEP case.<sup>11</sup>) The first step is aforementioned Laplace transformation of Eq. (1) to eliminate the time derivative, which transformation is especially advantageous because of the fact that the desired quantity is expressible directly in terms of the Laplace transformed variables via Eq. (4). Second,

the coupled transformed differential equations are converted to a single integral equation by using the Green function of the operator  $(d^2/dr^2 - \sqrt{s^2})$  for the boundary conditions given by Eq. (5).<sup>13</sup> For  $s \ll 1$ , which corresponds to the desired  $t \rightarrow \infty$  limit, this Green function is

$$h_{\sqrt{s}}(\xi, \eta) \approx -r_<(\xi, \eta),$$

where  $r_<$  denotes the lesser of the two arguments. The resulting integral equation for  $x$  in the small  $s$  limit is

$$\bar{x}(r, s \equiv 0) = \frac{r_<(r, r')}{4\pi r'} - J_0^2 \int_1^\infty d\eta r_<(r, \eta) e^{-\lambda \eta} \times \int_1^\infty d\xi r_<(\eta, \xi) e^{-\lambda \xi} \bar{x}(\xi, s \equiv 0). \quad (6)$$

To proceed we symmetrize the kernels of the integral equation by multiplying both sides of Eq. (6) by  $e^{-\lambda(r+r')/2}$  and introduce the change of variable

$$e^{-\lambda(r+r')/2} \bar{x}(r, s \equiv 0) = \phi(r) + \frac{e^{-\lambda(r+r')/2} r_<(r, r')}{4\pi r'}. \quad (7)$$

The motivation for this change is that  $\bar{x}(r, s \equiv 0)$  and  $r_<(r, r')/4\pi r'$  correspond to the final and initial polarizations of the radical pair, so that  $e^{\lambda(r+r')/2} \phi$  represents the difference in these polarizations, which is the desired loss of polarization due to spin exchange. The integral equation for  $\phi$  is

$$\begin{aligned} \phi(r) = & -\frac{J_0^2}{4\pi r'} \int_1^\infty d\eta \mathcal{K}^{(1/2)}(r, \eta) \\ & \times \int_1^\infty d\xi \mathcal{K}^{(1/2)}(\eta, \xi) \mathcal{K}^{(1/2)}(\xi, r') \\ & - J_0^2 \int_1^\infty d\eta \mathcal{K}^{(1/2)}(r, \eta) \\ & \times \int_1^\infty d\xi \mathcal{K}^{(1/2)}(\eta, \xi) \phi(\xi), \end{aligned} \quad (8)$$

where

$$\mathcal{K}^{(1/2)}(r, \xi) = e^{-\lambda(r+\xi)/2} r_<(r, \xi). \quad (9)$$

As in the CIDEP case<sup>11</sup> we solve Eq. (8) by expanding  $\phi$  in terms of the complete orthonormal set of eigenfunctions of the symmetric, positive-definite integral operator  $\mathcal{K}^{(1/2)}$ , as defined by the equation

$$\frac{1}{\mu_i} \varphi_i(r) = \int_1^\infty \mathcal{K}^{(1/2)}(r, \xi) \varphi_i(\xi) d\xi. \quad (10)$$

As shown previously<sup>11</sup> these normalized functions are

$$\varphi_i(r) = \pi^{1/2} \mu_i^{1/4} e^{\lambda/4} \xi_i^{-1/2} e^{-\lambda r/2} \mathcal{Z}_0[\omega_i e^{-\lambda(r-1)/2}], \quad (11a)$$

where

$$\mu_i^{1/2} = \lambda e^{\lambda/2} \omega_i/2, \quad (11b)$$

$$\xi_i = \frac{1}{2} \pi \omega_i [\mathcal{Z}_0^2(\omega_i) + \mathcal{Z}_1^2(\omega_i)], \quad (11c)$$

and  $\mathcal{Z}_0$  and  $\mathcal{Z}_1$  are the usual zeroth and first order Bessel functions. The quantity  $\omega_i$  is determined by the requirement that expansion of  $\phi$  in terms of the  $\varphi_i$  is equivalent to expanding  $\bar{x}(r, s \equiv 0)$  in terms of  $e^{\lambda r/2} \varphi_i$ , cf. Eq. (7), and consequently, the functions  $e^{\lambda r/2} \varphi_i$  must satisfy the boundary con-

dition given by Eq. (6a). The resulting equation for  $\omega_i$  is

$$\omega_i = \frac{2}{\lambda} \frac{\mathcal{Z}_0(\omega_i)}{\mathcal{Z}_1(\omega_i)} = \frac{2}{\lambda} \cot(\omega_i - \frac{\pi}{4}) \cong \left(i + \frac{1}{4}\right)\pi, \quad (12)$$

where the last two expressions on the right-hand side of Eq. (12) were obtained using the asymptotic behavior of the Bessel functions<sup>14</sup> for large arguments and the properties of the cotangent function, respectively. Although this last and simplest expression for  $\omega_i$  is strictly valid only for large  $i$ , it will turn out to be applicable to all but the first eigenvalue for the values of  $\lambda$  typically encountered in this problem.

Solution of Eq. (8) by expansion in the eigenfunctions of  $\mathcal{H}^{(1/2)}$  is straightforward if we note that the inhomogeneous term in this equation is also a product of the operators  $\mathcal{H}^{(1/2)}$  and interchange the order of integration when determining the integral of the product of this term and the  $\varphi_i$  that appear in its expansion. The result is

$$\phi(r) = -\frac{J_\sigma^2}{4\pi r'} \sum_{i=0}^{\infty} \frac{\varphi_i(r')\varphi_i(r)}{\mu_i(\mu_i^2 + J_\sigma^2)}. \quad (13)$$

Although compact, this expression is not particularly useful as it stands and to explore its properties it must be rewritten in terms of the expanded forms of  $\varphi_i$  and  $\mu_i$  using Eq. (11). While doing this we also use Eqs. (4) and (7) to obtain from  $\phi$  the desired loss of polarization due to spin exchange. Remembering that the initial polarization is unity one obtains  $\Delta P_{\text{ex}} = 1 - P_\infty$

$$= \frac{\pi J_\sigma^2}{r'} \sum_{i=0}^{\infty} \frac{\mathcal{Z}_0(\omega_i e^{-\lambda(r'-1)/2})}{\xi_i(\frac{1}{2}\lambda\omega_i) \left[ (\frac{1}{2}\lambda\omega_i)^4 + J_\sigma^2 \right]}, \quad (14)$$

where  $J_\sigma = J_0 e^{-\lambda}$  is the value of the exchange interaction at the collision separation of the radicals, and we have used the fact that at large  $r$   $\mathcal{Z}_0(\omega_i e^{-\lambda(r-1)/2}) = \mathcal{Z}_0(0) = 1$ .

Further simplification of Eq. (14) is based on the values of its parameters. A typical range for the collision separation of the radicals is  $3 \leq \sigma \leq 8 \text{ \AA}$  while the diffusion constant will typically be  $10^{-6} \leq D \leq 10^{-4} \text{ cm}^2/\text{s}$ . Thus, the time scale for the system is approximately  $10^{-11} \leq \sigma^2/D \leq 5 \times 10^{-9} \text{ s}$ . It is reasonable to expect that the actual value of the exchange interaction at the collision separation  $\sigma$ , i.e.,  $\tilde{J}_\sigma$ , will be of the order of the thermal energy  $kT$  since the repulsive exchange energy at this separation must be large enough to prevent closer approach by a pair of radicals with typical thermal kinetic energies. Thus, at  $T = 300 \text{ K}$  we have, using Eq. (3),  $800 \leq J_\sigma = 2\tilde{J}_\sigma \sigma^2/D \leq 4 \times 10^5$  for the aforementioned values of  $\sigma^2/D$ . Theoretical<sup>15</sup> and experimental<sup>16,17</sup> estimates of the range of the exchange interaction are of the order  $4 \leq \tilde{\lambda} = \tilde{\lambda}\sigma \leq 10$  where  $\tilde{\lambda}$  is the actual unscaled value of this quantity. For example, a detailed analysis of CIDEP of the diethoxyphosphonyl radical<sup>17</sup> produced by photolysis of di-tertbutyl peroxide in diethylphosphite yielded  $\tilde{\lambda} = 1.7 \text{ \AA}^{-1}$  and  $\tilde{\lambda}\sigma = 9.5$ , consistent with the foregoing estimate.

For the indicated range of  $\lambda$  it turns out that all the  $\omega_i$  except  $\omega_0$  are satisfactorily determined by the last term on the right-hand side of Eq. (12) and a similar evaluation of Eq. (11c) using the asymptotic formulas for  $\mathcal{Z}_0$  and  $\mathcal{Z}_1$  shows that  $\xi_i \cong 1$  for  $i > 0$ . On the other hand,  $\omega_0$  and  $\xi_0$  are readily determined from the power series expansions of  $\mathcal{Z}_0$  and  $\mathcal{Z}_1$ . If we take only terms up to order  $\omega_0^4$  in the expan-

sion of these functions, then Eqs. (12) and (11c) give, respectively,

$$\omega_0 = \left(\frac{8}{2\lambda + 1}\right)^{1/2}; \quad \xi_0 = \frac{\pi}{2} \left(\frac{2\lambda}{2\lambda + 1}\right)^2 \omega_0, \quad (15)$$

where we have taken  $1 + 1/(4\lambda^2 + 4\lambda + 1) = 1$  to simplify the expressions for  $\xi_0$ .

Also, for the estimated range of  $\lambda$ , it can be seen from the term  $[(\frac{1}{2}\lambda\omega_i)^4 + J_\sigma^2]$  in the denominator of Eq. (14) and the facts that  $\mathcal{Z}_0(\omega_i e^{-\lambda(r'-1)/2}) \leq 1$  and  $\xi_i \cong 1$  that terms for which  $\omega_i^2$  is significantly greater than  $J_\sigma$  will make only negligible contributions to the series. Then, since  $J_\sigma e^\lambda = J_0$ , the arguments of the important terms in Eq. (14) will not be significantly greater than  $J_0^{1/2} e^{-\lambda r'/2}$ , which is the square root of the exchange interaction at the initial separation  $r_1$ . However,  $r_1$  must be large enough that the exchange interaction is small, otherwise spin exchange may have already occurred and invalidated the assumption of total polarization. Thus, we have  $\mathcal{Z}_0(\omega_i e^{-\lambda(r'-1)/2}) \cong 1$  for all the significant terms in Eq. (14). Although satisfying this condition might seem to present no problems, since Eq. (14) imposes no limits on  $r'$ , there is a practical limit imposed by the fact that the duration of a possible spin-exchange encounter, which increases with the starting separation  $r'$ , must not be so long that one of the two radicals is likely to encounter a third radical during this time. This is not a problem, however, even in excimer laser experiments where relatively high initial radical concentrations are produced.

Following the foregoing discussion, we evaluate the first term in Eq. (14) separately from the others using Eq. (15) for  $\omega_0$  and  $\xi_0$ , and the asymptotic forms  $\omega_i = (i + \frac{1}{4})\pi$  and  $\xi_i = 1$  for the remaining terms. With the aid of the fact that  $J_0^2 \gg (\frac{1}{2}\lambda\omega_0)^4$  this gives

$$\Delta P_{\text{ex}} = \frac{1}{r'} \left( \frac{2\lambda + 1}{2\lambda} \right)^3 + \frac{2}{\lambda r'} \times \sum_{i=1}^{\infty} \frac{1}{(i + \frac{1}{4}) \{1 + [\pi^4 \lambda^4 (i + \frac{1}{4})^4 / 16 J_\sigma^2]\}}. \quad (16)$$

Since  $J_\sigma$  is very large, we can approximate the foregoing sum by an integral. Set  $p = \alpha(1 + \frac{1}{4})$  and  $\Delta p = \alpha$  where  $\alpha = \pi\lambda / 2J_\sigma^{1/2} \ll 1$ , then by reversing the trapezoidal rule for integration, we have

$$\begin{aligned} & \sum_{i=1}^{\infty} \frac{1}{(i + \frac{1}{4}) [1 + \alpha^4 (i + \frac{1}{4})^4]} \\ &= \frac{2}{5[1 + (5\alpha/4)^2]} + \int_{5\alpha/4}^{\infty} \frac{dp}{p(1 + p^4)} \\ &\cong \frac{2}{5} + \ln \frac{8J_0^{1/2}}{5\pi\lambda}, \end{aligned} \quad (17)$$

where we have used the fact that  $1 \gg (5\alpha/4)^4$  in deriving the last term on the right-hand side of this equation and the integral is a standard form.<sup>18</sup> Thus we have finally for the loss of polarization due to spin exchange in a pair of radicals starting with total polarization at a separation  $r'$ :

$$\Delta P_{\text{ex}} = \frac{1}{r'} \left( \frac{2\lambda + 1}{2\lambda} \right)^3 = \frac{1}{\lambda r'} \left( \frac{4}{5} + \ln \frac{64J_\sigma}{25\pi^2\lambda^2} \right). \quad (18)$$

Using Eq. (18) and noting that the rate constant for

biomolecular encounters between radicals at a separation  $r'$  is  $4\pi r'\sigma D$ ,<sup>19</sup> we obtain the following expression for the spin-exchange rate constant:

$$k_{\text{ex}} = \frac{1}{4}k_e \left[ \left( \frac{2\tilde{\lambda}\sigma + 1}{2\tilde{\lambda}\sigma} \right)^3 + \frac{1}{\tilde{\lambda}\sigma} \left( \frac{4}{5} + \ln \frac{128\tilde{J}_\sigma}{25\pi^2\tilde{\lambda}^2 D} \right) \right]. \quad (19)$$

Here,

$$k_e = 4\pi\sigma D \quad (20)$$

is the rate constant for radical–radical encounters at the collision separation  $\sigma$ ,<sup>19</sup> we have introduced the dimensioned equivalents of  $\lambda$  and  $J_\sigma$  given by Eq. (3), and the factor  $1/4$  appears in Eq. (19) because spin exchange can occur only during collisions between radicals with opposite spins and complete depolarization ( $\Delta P_{\text{ex}} = 1$ ) corresponds to only a 50% chance that spin exchange actually occurs. Finally, it should be noted that spin exchange between chemically identical radicals will be effective only if their nuclear spin state differ, which restriction is readily treated by regarding such nuclear spin states of the same radical as different species with different concentrations.

## DISCUSSION

We note that apart from the factor  $[(2\tilde{\lambda}\sigma + 1)/2\tilde{\lambda}\sigma]^3$ , which is usually close to unity, the first term in Eq. (19) is just the reaction cross section ( $k_d = \frac{1}{4}k_e$ ) for two radicals which recombine or react in some fashion anytime they reach a separation  $\sigma$  in the spin singlet state, which last condition prevails in one-fourth of the encounters. Clearly such “strong” encounters will invariably result in spin exchange. The second term in Eq. (19) then can be related to partial spin exchange produced in weaker grazing encounters of the radicals at separations greater than the collision diameter. The magnitude of this partial spin exchange depends, as expected, on the range of the exchange interaction and, to a lesser extent, on the diffusion constant (this dependence is in addition to that contained in  $k_e$ ) and the magnitude of the exchange interaction at the collision separation. For the aforementioned ranges of the parameter values ( $800 \leq \tilde{J}_\sigma \sigma^2/D \leq 4 \times 10^5$  and  $4 \leq \tilde{\lambda}\sigma \leq 10$ ) the magnitude of this second term can range from negligible to twice the first term.

In what appears to be the most quantitative investigation of spin exchange to date Syage *et al.*<sup>3</sup> have determined that for acetate ion radicals ( $\text{CH}_2\text{COO}^-$ ) in aqueous solution the spin-exchange cross section is approximately three times the reaction cross section, i.e.,  $k_{\text{ex}} = 3k_d$ . Since this result was obtained from measurement of the concentration-dependent spin–lattice relaxation rate ( $1/T_1$ ) it implies either a substantial long-range contribution to spin-exchange or strong dipolar relaxation during encounters of the radicals. The following discussions shows that the former interpretation is the more reasonable one.

We can estimate the parameters  $\sigma$ ,  $D$ , and  $J_\sigma$  in Eq. (19) and then obtain  $\tilde{\lambda}$  from the experimental result:  $k_{\text{ex}} = 3k_d$ . A space filling model of the  $\text{CH}_2\text{CO}_2^-$  radical gave  $\sigma = 4.2 \text{ \AA}$  which value is the average over the three molecular symmetry axes. The diffusion constant for an individual radical can then be determined from the formula  $D_0 = kT/4\pi a\eta$  where

$a = \frac{1}{2}\sigma$  is the molecular radius and  $\eta$  is the viscosity.<sup>20</sup> Since the viscosity of the very dilute aqueous solutions used in these experiments is effectively that of water ( $\approx 0.01 \text{ cp}$ )<sup>21</sup> we have  $D = 2D_0 = 3.1 \times 10^{-5} \text{ cm}^2/\text{s}$ . With these results together with the aforementioned estimate that  $\tilde{J}_\sigma = kT/\hbar = 3.9 \times 10^{13} \text{ s}^{-1}$  at 298 K, we find that  $\tilde{\lambda} = 0.85 \text{ \AA}^{-1}$  in Eq. (19) reproduces the observed relation between the spin-exchange and reaction cross sections. This value of  $\tilde{\lambda}$  corresponds to a relatively long-range exchange interaction between two  $\text{CH}_2\text{CO}_2^-$  radicals, which may result from partial transfer of the unpaired spins of the radicals to neighboring solvent molecules via overlap or charge exchange.<sup>15</sup>

(Incidentally, spin–lattice relaxation by dipolar interactions between encountering radicals can be neglected at the concentrations present in the experiment of Syage *et al.*<sup>3</sup> The formula<sup>22</sup>  $1/T_1 = \pi N \gamma^4 \hbar^2 / 5aD_0$  where  $\gamma$  is the magnetogyric ratio of the electron and  $N$  is the radical concentration in molecules/cm<sup>3</sup> yields a dipolar relaxation time of  $40 \mu\text{s}$  at the maximum experimental radical concentration of  $4 \times 10^{-4} \text{ M}$ .)

Furthermore, the foregoing estimate of  $\tilde{\lambda}$  is consistent with a value obtained from the following analysis of CIDEF in the acetate ion radical system under different conditions in which encounters between random pairs of radicals leads to significant electron spin polarization.<sup>23</sup> Comparison of the magnetization given by the rate equations for the population of different electron and nuclear spin states of the  $\text{CH}_2\text{CO}_2^-$  radical (these are readily obtained following previously described procedures<sup>17</sup>) with the modified Bloch equation of Verma and Fessenden<sup>24</sup> yields the following relation between their CIDEF enhancement factors, denoted  $V$ , and the molecular parameters of the system:

$$VT_c/T_1 = [\rho_{ST_0}^{(1,0)} + \frac{1}{2}\rho_{ST_0}^{(1,-1)}] / (g\beta H/kT). \quad (21)$$

Here,  $T_c$  is the second-order radical decay time, i.e.,  $R/R_0 = (1 + t/T_c)^{-1}$  where  $R$  and  $R_0$  are the radical concentrations at times  $t$  and 0, respectively,  $g\beta H$  is the electron Zeeman energy, and  $\rho_{ST_0}^{(1,0)}$  and  $\rho_{ST_0}^{(1,-1)}$  are the electron spin polarizations produced by the radical pair mechanism following encounters between radicals with opposite electron spins and proton spin states of (1,0) and (1, −1), respectively. These last quantities are given by the equation<sup>11</sup>

$$\rho_{ST_0}^{(1,-1)} = 2^{1/2} \rho_{ST_0}^{(1,0)} = (\pi/2)(A/\tilde{\lambda}^2 D)^{1/2}, \quad (22)$$

where  $A = 21.2 \text{ G} = 3.73 \times 10^8 \text{ rad/s}$  is the proton hyperfine splitting constant of the  $\text{CH}_2\text{CO}_2^-$  radical.<sup>24</sup> Using the experimental results<sup>23</sup>  $VT_c = 57 \mu\text{s}$  and  $T_1 = 1.4 \mu\text{s}$ , and the aforementioned values of the parameters in Eqs. (21) and (22), we estimate  $\tilde{\lambda} = 1.1 \text{ \AA}^{-1}$ . This value and that obtained from the spin-exchange contribution to the relaxation rate agree well considering the uncertainties in the various parameters involved in their determination, and support the concept of substantial long-range contributions to the spin-exchange cross section.

Clearly spin exchange is an important factor to consider when investigating radical systems at the concentrations readily produced by Van der Graaff beams and modern excimer lasers. For a rough estimate of the concentrations at which spin exchange becomes important we note that the

spin-exchange cross section can be several times the diffusion controlled biomolecular reaction cross section, which is of the order  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , while the relaxation times of many small radicals are several microseconds.<sup>25</sup> Thus spin exchange effects become significant at radical concentrations of roughly  $10^{-4} \text{ M}$  and higher.

A negative aspect of this is that spin exchange limits somewhat our ability to maximize CIDEP by increasing the radical concentration to the point where the chemical lifetime of the radicals determined by biomolecular recombination is substantially less than the spin-lattice relaxation time.<sup>26</sup> Although these high radical concentrations are readily achieved with excimer lasers, spin-exchange contributions to spin-lattice relaxation will offset the advantages in doing so, in which case the maximum polarization will occur around that concentration for which the spin-exchange rate equals the molecular spin-lattice relaxation rate.

Of course spin exchange cannot reduce an absolute polarization (i.e., more "up" spins than "down" or vice versa) such as that produced by the triplet mechanism, although it can distribute it among all the different radicals in the system. It can destroy only a relative polarization (i.e., equal numbers of up and down spins but more up spins associated with an up nuclear spin and vice versa) such as is commonly produced by the radical pair mechanism. Thus an initial polarization which is part triplet and part radical pair may appear to be a pure triplet polarization unless observed very soon after the formation of the pair (which can be difficult if the required observation must take place within a fraction of a microsecond) or at lower radical concentrations where the spin exchange is suppressed (which may present signal-to-noise problems). The recent observation by Depew and Wan<sup>27</sup> of an initial mixed absorption-emission CIDEP spectrum which evolves to a purely emissive spectrum may be an example of this spin-exchange effect, although it should be noted that electron exchange between the subject camphorquinone radical anion and the parent neutral camphorquinone would have the same effect.

In summary, spin exchange is a mixed blessing which can complicate observations and analysis of CIDEP, but also can provide significant information about the interactions between radicals. It is hoped the theory presented here will be helpful in these investigations.

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