Some theoretical aspects of chemically induced dynamic nuclear polarization[*]

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An analysis of aspects of the theory of chemically induced dynamic nuclear polarization (CIDNP) is given in terms of rigorous numerical solutions to the stochastic Liouville equation, in accordance with the methods previously developed for CIDEP. This analysis includes not only a model in which the exchange interaction is of finite extent in the spin Hamiltonian (EFA model) but models in which the exchange interaction explicitly affects the reactive trajectories (EFP model) by their inclusion in a spin-dependent diffusion equation and in which charge interactions between reacting ionic radicals and their surroundings are accounted for in the Debye–Hückel fashion. Several useful and simple relationships are found for the CIDNP phenomenon, and their dependence upon the model is discussed. It is found that the CIDNP polarizations are readily described in terms of two fundamental parameters—Λ, the spin-independent probability of reaction of singlets per collision, which includes *all* re-encounters, and F*, which measures the conversion from triplets to singlets for the whole collision. Exact relations for the CIDNP polarizations are given in terms of these two parameters and are found to be nearly independent of model. The parameter Λ is shown to be simply related to $k(r)$, the singlet reaction rate when the radicals are in contact, and to τ_1, the effective lifetime of the reacting pair. Simple expressions for τ_1 are given for all the models, and these results are compared with those for the usual discussions of diffusion rates on chemical kinetics. It is found that for normal diffusion rates, F* obeys the relation $(1/2)\sqrt{Q\tau_d}$, very similar to that first proposed by Adrian, where Q is half the difference in resonant frequencies of the radicals, and $\tau_d = d^2/D$ with D the relative diffusion coefficient and d the distance of closest approach. This relation is not appropriate for viscous systems, and the correct results are given for such cases. The effects of the finite range of the exchange interaction and the longer range Coulombic interactions between radicals upon F* for the different models are also obtained. In particular, for EFA the finite range of exchange yields an "excluded volume" effect wherein singlet–triplet mixing (or Q mixing) is ineffective. The model dependent effects upon F* are closely related to the recurrence probabilities, and further results are obtained implying a simple expression for the first encounter probabilities of separated radicals under the effects of the different interactions. The polarizations are related to the time-dependent CIDNP intensities that one may observe for a typical scheme of radical production, reaction, and relaxation.

I. INTRODUCTION

In several recent papers, we have developed a detailed theoretical analysis for the phenomenon of chemically induced dynamic electron polarization (CIDEP).[1–3] This theory, based upon the stochastic Liouville equation, was able to simultaneously include realistic descriptions of both the spin-dependent interactions important in the radical-pair mechanism as well as the relative molecular diffusion for spin-dependent reactive trajectories. The advantage of such a general analysis is that it is not limited, as were the simplified earlier submodels, by simplifying, but not justified, assumptions about the spin-dependent interactions and/or the diffusive trajectories. It was shown that for CIDEP, qualitatively new and important features are obtained, but it also confirmed, for nonviscous media, the crucial role played by radical reencounters, as first proposed by Adrian. It also allowed for quantitative predictions of CIDEP enhancements, which are of the order of those observed experimentally. We shall show in future work how improved descriptions of the molecular dynamics and spin-interactions may also be introduced into an analysis of CIDEP.

Chemically induced dynamic nuclear polarization (CIDNP) is, from the theoretical point of view, a closely related phenomenon. There has been considerable earlier activity in developing simple theories for it based upon the radical-pair mechanism. The analyses of Adrian[4] and Kaptein[5] based upon radical reencounters have been most successful in predicting experimental results. We note, first of all, that our methods for analyzing CIDEP are equally appropriate for CIDNP.[1] In fact, much of the results given in I and II[2,3] are appropriate for a discussion of CIDNP, although they were not discussed from that point of view, largely because the greater theoretical difficulty was in an analysis of CIDEP, which is much more sensitive to the details of the exchange interaction. Nevertheless, it was felt worthwhile to analyze the results from our general approach in a manner appropriate for CIDNP to further clarify the theory for this phenomenon, about which a variety of conflicting simple models had earlier been proposed. We note in this context that Evans *et al.*[6] have recently presented some results of a stochastic Liouville solution for a simplified model, but we have already pointed out in II that their simplified model, based on delta function representations of the exchange and chemical reactions and neglect of boundary conditions for the relative diffusion of radicals, does not even reproduce many of the important qualitative features for CIDEP that our more realistic models show. While these considerations are not so crucial for CIDNP, it was still believed to be worthwhile to see what the implications of more realistic models are. We have, however, found in our analysis of CIDNP, that although

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its features are easier to predict than CIDEP, there are certain characteristic aspects of the molecular dynamics to which CIDNP is particularly sensitive, and for which several relations exist that are useful both for prediction of CIDNP intensities and for understanding the nature of the molecular (reactive) dynamics. Furthermore, our results are obtained not only for simple diffusive trajectories, but also with Coulombic (shielded ionic interactions) and exchange forces in these trajectories, and the generality of the CIDNP theory is examined in the light of these results as well.

II. THEORETICAL APPROACH

As in I and II, we solve the stochastic Liouville equation for the spin-density matrix $\rho(\mathbf{r}_i, t)$:

$$\partial\rho(\mathbf{r}_i, t)/\partial t = -i\mathcal{H}^x(\mathbf{r}_i)\,\rho(\mathbf{r}_i, t) + D\Gamma_{\mathbf{r}}\,\rho(\mathbf{r}_i, t) \qquad (2.1)$$

to describe the combined spin and (reactive) diffusive dynamics of a pair of radicals a and b. A glossary of the main symbols appears at the end of II, and we will define any new symbols needed here. Note that $\Gamma_{\mathbf{r}}$ is the operator for relative diffusion, which can be spin dependent. Furthermore, as in I and II, we only consider spherically symmetric interactions, so Eq. (2.1) may just be rewritten in terms of r, the interradical separation. We consider for $\Gamma_{\mathbf{r}}$ the following kinds of models (but not in this order):

(1) a model with exchange forces present in $\Gamma_{\mathbf{r}}$ (EFP),

(2) a model with exchange forces absent (EFA), but a spin-selective chemical reaction at the contact distance d which depletes only singlets (i.e., only ρ_{ss} is affected, cf. II), and

(3) Coulombic interactions between charged radical ions partly screened by the ionic atmosphere added to case 2. In all cases, we employ an exchange interaction decaying exponentially with interradical separation:

$$J(r) = J_0 \exp[-\lambda(r-d)], \quad r \geq d$$

and we define $r_{EX} \equiv \lambda^{-1} 5 \ln 10$. We discuss here only the high-field case and consider just $S-T_0$ mixing as in I and II. The proper dimensionless units for the problem are $J_0 d^2/D$, Qd^2/D, r_{EX}/d, $\hbar J_0/k_B T$, kd^2/D, and $\Delta r/d$, with Δr being the finite difference increment.

In I and II, we have given results for the quantity $\mathfrak{F}$, the probability the radical pair reacts per collision. (We mean by a "collision" the first encounter, as well as all possible reencounters before the radicals finally diffuse away).[2,3] The CIDNP phenomenon is best discussed in terms of the quantity $\mathfrak{F}-\mathfrak{F}_0$, where $\mathfrak{F}_0$ is the value of $\mathfrak{F}$ calculated for $Q=0$, i.e., it excludes any effects from singlet–triplet $(S-T_0)$ mixing. Thus, $\mathfrak{F}-\mathfrak{F}_0$ specifically gives the extra probability of reaction due to the $S-T_0$ mixing. We show in Sec. IV how $\mathfrak{F}-\mathfrak{F}_0$ enters into the final over-all expressions to predict experimentally observed CIDNP intensities. One may calculate $\mathfrak{F}-\mathfrak{F}_0$ by calculating separately $\mathfrak{F}$ and $\mathfrak{F}_0$, wherein all parameters, except the value of Q, are held constant.

As in I and II, we calculate separate results for singlet (S) initial, triplet (T_0) initial, and random initial (R.I.) precursors (equal amounts of S and T_0). All other cases are obtained as simple superpositions of these.[2,3] (Of course, R.I. is a superposition of S and T_0 also). We indicate results for $\mathfrak{F}$, etc., as $\mathfrak{F}(S)$, $\mathfrak{F}(T_0)$, etc., to show the particular initial condition utilized.

III. RESULTS AND DISCUSSION

The proper finite difference expressions were solved by Gaussian elimination for real banded matrices. The computing time is typically ~3 sec on a CDC 6400 computer.

Since the radical reencounters are treated in a finite region of space, one has to choose r_N (the position of the outer absorbing or collecting wall) large enough that no further increase of r_N would affect the results significantly. This matter, as well as other aspects of obtaining convergent solutions, are discussed in I and II. However, it is significant to note that much larger regions of space, implying reencounters after much greater separations, were required in calculating $\mathfrak{F}-\mathfrak{F}_0$ than the CIDEP quantity of corresponding importance: P_a^{∞}, the polarization of radical a for $t\to\infty$. In particular (for $D=10^{-5}$ cm^2/sec, $Q=10^8$ sec^{-1}, $d=4$ Å), $\mathfrak{F}(T_0) - \mathfrak{F}_0(T_0) = \mathfrak{F}(T_0)$ only converges for $r_N \geq 500$ Å, while $P^{\infty}(T_0)$ converges for $r_N \sim 175$ Å. When $D=10^{-4}$ cm^2/sec, one gets $r_N \sim 1500$ Å and ~200 Å, respectively. Slower diffusion rates require correspondingly smaller values of r_N. This reflects the fact that for T_0 initial, one forms singlet via Q mixing in two (quantum mechanically coherent) steps [cf. Eq. (2.34) of I];

$$\rho_{T_0} \overset{Q}{\rightleftarrows} \rho_{S,T_0} - \rho_{T_0,S} \overset{Q}{\rightleftarrows} \rho_S - \rho_{T_0} ,$$

and it is the ρ_S which then reacts when the radicals reencounter; while for CIDEP polarizations P^{∞}, the Q mixing of only the first step, $\rho_T \to \rho_{S,T_0} - \rho_{T_0,S}$, is needed, the process being completed by the effects of $J(r)$ when the radicals reencounter: $\rho_{S,T_0} - \rho_{T_0,S} \overset{J}{\rightleftarrows} \rho_{S,T_0} + \rho_{T_0,S}$.

Our numerical results for the case of EFA [case (2)] (where at $t=0$ the particles are in contact) may be summarized by a series of relatively simple expressions. First define

$$\Lambda \equiv \mathfrak{F}_0(S) \qquad (3.1)$$

and

$$\mathfrak{F}^* \equiv \lim_{\Lambda\to 1} \mathfrak{F}(T_0) = \lim_{\Lambda\to 1} [\mathfrak{F}(T_0) - \mathfrak{F}_0(T_0)] . \qquad (3.2)$$

Thus, Λ is *precisely* the fractional probability of reaction (for $Q=0$) of singlets for the whole collision including all reencounters, while $\mathfrak{F}^*$ measures the conversion from triples to singlets for the whole collision. Then one obtains from the numerical solutions the *exact* relation

$$-[\mathfrak{F}(S) - \mathfrak{F}_0(S)] = -[\mathfrak{F}(S) - \Lambda] = +(1-\Lambda)\,\mathfrak{F}(T) . \qquad (3.3)$$

Eq. (3.3) shows that the net decrease in reaction for pure singlets per collision due to $Q \neq 0$ is just the probability a singlet does not react for $Q=0$ (i.e., $1-\Lambda$) times the probability pure triplets do ultimately react because of Q mixing. The factor $(1-\Lambda)$ corrects for the fact that if singlets react fast, then they are not available to be converted to triplets by Q mixing. If one now uses the superposition principle to write

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TABLE I. Relationships between different initial spin conditions for fractional reactivities.[a,b]

	Singlet		Triplet	R.I.
k	$\mathcal{F}_0=\Lambda$	$-(\mathcal{F}-\mathcal{F}_0)$	$\mathcal{F}$	$(\mathcal{F}-\mathcal{F}_0)/\mathcal{F}_0$
10^9	4.9712×10^{-3}	3.043×10^{-4}	3.058×10^{-4}	3.057×10^{-4}
10^{10}	4.7583×10^{-2}	2.795×10^{-3}	2.935×10^{-3}	2.935×10^{-3}
10^{11}	0.33316	1.395×10^{-2}	2.092×10^{-2}	2.092×10^{-3}
10^{12}	0.83323	9.008×10^{-3}	5.401×10^{-2}	5.401×10^{-2}
10^{14}	0.99800	1.306×10^{-4}	6.539×10^{-2}	6.539×10^{-2}
10^{18}	1.0	0.0	6.553×10^{-2}	6.553×10^{-2}

[a] EFA model, cf. Eq. (3.5).

[b] Parameters used: $d=4$ Å, $\Delta r=0.25$ Å, $f=100$, $M=200$, $N=400$, $r_N=5054$ Å, $J=10^8\ \mathrm{sec}^{-1}$, $r_{EX}=4$ Å, $Q=10^8\ \mathrm{sec}^{-1}$, $D=10^{-5}\ \mathrm{cm}^2/\mathrm{sec}$.

$$\mathcal{F}(\mathrm{R.I})=\tfrac{1}{2}[\mathcal{F}(S)+\mathcal{F}(T)], \tag{3.4}$$

then Eq. (3.3) may be rewritten as

$$[\mathcal{F}(\mathrm{R.I.})-\mathcal{F}_0(\mathrm{R.I.})]/\mathcal{F}_0(\mathrm{R.I.})=\mathcal{F}(T). \tag{3.5}$$

Eq. (3.5) is seen to be the CIDNP analogue of the CIDEP relation given in I and II (for EFA and EEP provided in the latter case Λ is $\geq 10^{-3}$, see below):

$$P^{\infty}(\mathrm{R.I.})/\mathcal{F}(\mathrm{R.I.})-P^{\infty}_{k=0}(S)=+P^{\infty}_{k=0}(T), \tag{3.6}$$

where the subscript $k=0$ indicates no chemical reaction. By application of Eq. 3.3 and the superposition principle, Eq. 3.6 can be rearranged to give:

$$P^{\infty}(S)+P^{\infty}(T)=\Lambda[1+\mathcal{F}(T)]\,P^{\infty}_{k=0}(T) \tag{3.7}$$

A symmary of typical results which justify Eq. (3.3) or (3.5) appears in Table I.

The physically important parameter Λ is found to obey the simple relation

$$\Lambda=(\mathcal{F}\tau_1/(1+k\tau_1). \tag{3.8}$$

For case 2, where the "sphere of influence" of $k(r)$ extends from d to $d+\Delta r_k$, one obtains for $\Delta r_k=\Delta r/2$

$$\tau_1=d\,\Delta r/2D, \tag{3.9}$$

where τ_1 is a characteristic lifetime of the interacting pair, which is identical to that found for a contact exchange model in CIDEP (cf. I). It was pointed out in I that one could rewrite $\tau_1^{-1}\simeq 4\pi Dd/\Delta V$ with ΔV the "reaction volume" in accordance with earlier theories for lifetimes of reacting pairs.[7a] These theories arbitrarily define ΔV as the total volume swept by the interacting pair: $\frac{4}{3}\pi d^3$, but our results show that $\Delta V\simeq 4\pi d^2(\Delta r/2)$, the annular volume of the "contact region". This is precisely the annular volume in the finite difference approximation. We have, by letting k range over several increments in Δr(cf. Table II), found that Eq. (3.8) still holds, and a more appropriate definition, for particles initially in contact, is

$$k\tau_1\equiv D^{-1}\int_d^{d+\Delta r_k} rk(r)dr\rightarrow D^{-1}\sum_{i=0}^{n=(\Delta r_k/\Delta r-1/2)} V(i)k(r_i), \tag{3.10}$$

with $V(i)=r_i\Delta r$ for $i>0$ (and $\frac{1}{2}d\Delta r$ for $i=0$) the radial weighting factor discussed in I. The arrow in Eq. (3.10) implies conversion to the finite difference form. This lifetime τ_1, it is clear, is to be interpreted as the effective time for reaction for the whole collision and not just for the single encounter of a pair of particles initially in contact.[7b] These points are not at all clear in the usual treatments of τ_1.[7a,8]

The role of the parameter $\mathcal{F}^*$ is seen in the following relation:

$$\mathcal{F}(T_0)=\Lambda\mathcal{F}^*[1+\mathcal{F}^*(1-\Lambda)]^{-1} \tag{3.11a}$$

(and typical results appear in Table III), which by Eq. (3.3) becomes

$$-[\mathcal{F}(S)-\Lambda]=\Lambda(1-\Lambda)\mathcal{F}^*[1+\mathcal{F}^*(1-\Lambda)]^{-1} \tag{3.11b}$$

and, by superposition,

$$[\mathcal{F}(\mathrm{R.I.})-\mathcal{F}_0(\mathrm{R.I.})]=\tfrac{1}{2}\Lambda^2\mathcal{F}^*[1+\mathcal{F}^*(1-\Lambda)]^{-1}\ . \tag{3.11c}$$

An approximate form of Eq. (3.11a), viz. $\mathcal{F}(T_0)\simeq\mathcal{F}^*\Lambda$, which becomes Eq. (3.11a) as $\Lambda\rightarrow1$, may be interpreted to mean that the probability of reaction for initially triplet radical pairs equals the probability that triplets are converted to singlets ($\mathcal{F}^*$) multiplied by the probability that the singlets react (Λ).

The factor $[1+\mathcal{F}^*(1-\Lambda)]^{-1}$ may be understood in terms of its infinite series expansion $\sum_{r=0}^{\infty}(-)^r\mathcal{F}^{*r}(1-\Lambda)^r$, where for example the $r=1$ term $\mathcal{F}^*(1-\Lambda)$ corrects for the fact that some initially triplet radical pairs, which would first be converted to singlet by Q mixing and then reencounter and react with certainty if $\Lambda=1$, would, for $\Lambda<1$, not react and be converted back to triplet for subsequent encounters. (Note that $\mathcal{F}^*$ by dynamic reversibility in quantum mechanics measures conversion from singlets to triplets and *vice versa* for a collision.) The higher order corrections along these lines appear as the other terms in the series. {Evans *et al.*[6] give results that do not have the correct $[1+\mathcal{F}^*(1-\Lambda)]^{-1}$ correction factor, nor do they properly interpret their dimensionless parameter analogous to our Λ.}

A comparison of Eq. (3.11a) and its simplified form with the actual results appears in Table III.

When the initial separation $r_I>d$, then we have found that Eqs. (3.11) may be modified as follows:

$$\Delta\mathcal{F}(\mathrm{R.I.}\ r_I)/\Delta\mathcal{F}(\mathrm{R.I.},\ d)=t_f, \tag{3.12}$$

where $\Delta\mathcal{F}(\mathrm{R.I.}\,r_I)=\mathcal{F}(\mathrm{R.I.})-\mathcal{F}_0(\mathrm{R.I.})$ with initial separation of r_I, and t_f is the transfer factor,[3] which for a

TABLE II. Typical examples justifying expression for τ_1.[a,b]

Range of reaction (Å)	$\tau_1\times10^{11}$ sec[c]	$\tau_1\times10^{11}$ sec[d]
0.25	0.9977	1.0
0.75	3.24	3.25
1.25	5.73	5.75
1.75	8.48	8.50

[a] Cf. Eqs. (3.9), (3.10).

[b] Parameters used: $d=4$ Å, $\Delta r=0.25$ Å, $M=200$, $N=400$, $r_N=5054$ Å, $D=10^{-5}\ \mathrm{cm}^2/\mathrm{sec}$.

[c] Calculated from computed results for Λ as a function of k by Eq. (3.8).

[d] Calculated from Eq. (3.10).

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TABLE III. Fractional reactivity $\mathfrak{F}$ as a function[a,b] of $\mathfrak{F}^*$ and Λ.

	$Q=1\times10^8\ \mathrm{sec}^{-1}$			$Q=1\times10^9\ \mathrm{sec}^{-1}$		
Λ	$\mathfrak{F}^c$	$\mathfrak{F}^d$	$\mathfrak{F}^*\Lambda^e$	$\mathfrak{F}^c$	$\mathfrak{F}^d$	$\mathfrak{F}^*\Lambda^e$
4.99×10^{-4}	3.071×10^{-5}	3.071×10^{-5}	3.270×10^{-5}	8.467×10^{-5}	8.467×10^{-5}	1.019×10^{-4}
4.97×10^{-3}	3.058×10^{-4}	3.058×10^{-4}	3.257×10^{-4}	8.435×10^{-4}	8.435×10^{-4}	1.015×10^{-3}
4.75×10^{-2}	2.935×10^{-3}	2.935×10^{-3}	3.119×10^{-3}	8.133×10^{-3}	8.133×10^{-3}	9.714×10^{-3}
0.33316	2.092×10^{-2}	2.092×10^{-2}	2.183×10^{-2}	5.987×10^{-2}	5.987×10^{-2}	6.801×10^{-2}
0.83323	5.401×10^{-2}	5.401×10^{-2}	5.460×10^{-2}	0.1645	0.1645	0.1701
0.998	6.539×10^{-2}	6.539×10^{-2}	6.540×10^{-2}	0.2037	0.2037	0.2037
1.0	6.553×10^{-2}	6.553×10^{-2}	6.553×10^{-2}	0.20415	0.20415	0.20415

[a] EFA model for triplet initial case, cf. Eq. (3.11a).

[b] Parameters used: $d=4$ Å, $\Delta r=0.25$ Å, $f=100$, $M=200$, $N=400$, $r_N=5054$ Å, $J_0=10^8\ \mathrm{sec}^{-1}$, $r_{\mathrm{EX}}=4$ Å, $D=10^{-5}\ \mathrm{cm}^2/\mathrm{sec}$. k values range from 10^8–10^{18}.

[c] From general numerical solutions.

[d] Calculated from computer results of Λ and $\mathfrak{F}^*$ by Eq. (3.11a).

[e] Approximate form of Eq. (3.11a).

simple diffusive model is simply

$$t_f = d/r_I$$

and is just the reencounter probability (i.e., $1-t_f$ is the total probability that two particles initially separated by r_I will never encounter at $r=d$) discussed originally by Noyes[9] and obtained for continuous diffusion by Deutch.[10] Equation (3.12) is seen to be a simple consequence of the fact that for random initial condition, the CIDNP process only starts upon initial encounter. The result for triplet initial is

$$\mathfrak{F}(T, r_I)/\mathfrak{F}(T, d) = 1-\chi, \tag{3.13}$$

where χ is usually a small quantity ≤ 0.1 (but it becomes more significant in viscous media). It corrects for the fact that some of the triplets are converted to singlets before the first encounter. We have found that for $r_I \sim 2d$, it may be approximated by

$$\chi \simeq t_f'^2(1-t_f')\mathfrak{F}^*/[1+(1-t_f')\mathfrak{F}^*], \tag{3.13a}$$

with $t_f' = r^*/r_I$ for $r_I \geq r^*$ (but if $r_I \leq r^*$, then $t_f'=1$ and there is no correction), and r^* is defined by $J(r^*) \simeq Q/5$ [where the dependence upon $J(r)$ is a type of excluded volume effect discussed below]. It follows from Eqs. (3.12), (3.13) and (3.5) that

$$\Delta\mathfrak{F}(S, r_I)/\Delta\mathfrak{F}(S, d) = (1-\chi-\Lambda t_f)/(1-\Lambda). \tag{3.14}$$

Only when $\chi=0$ do Eqs. (3.12)–(3.14) become equivalent to the result obtained by Evans *et al.*[6,11]

Given the above relations, then, it is only necessary to determine $\mathfrak{F}^*$ in order to obtain the CIDNP polarizations for a given Λ and initial set of conditions. We have found that over much of the range of the relevant parameters, $\mathfrak{F}^*$ obeys essentially a $Q^{1/2}$ dependence as first predicted by Adrian. This is clearly a result of the reencounter phenomenon. However, as Qd^2/D becomes large, a weaker dependence upon Q than the $\frac{1}{2}$ power is observed. In the case of $J_0 d/\lambda D < 1$, the results for $\mathfrak{F}^*$ are independent of $J(r)$, and one then obtains for small Qd^2/D and $J_0 d^2/D$

$$\mathfrak{F}^* \simeq \tfrac{1}{2}(Qd^2/D)^{1/2}. \tag{3.15}$$

This is a result close to Adrian's,[4] but (1) it shows the relevant "diffusive length" is d when (a) the reaction occurs at separation d and (b) this is the distance of closest approach, and (2) it automatically includes *all* reencounters. The deviation of $\mathfrak{F}^*$ from this simple expression for larger Qd^2/D (which has not been obtained in earlier work) is shown in Fig. 1 for $J_0 d/\lambda D \ll 1$. The correction to $\mathfrak{F}^*$ for $J_0 d/\lambda D \sim 0.1(J_0 d r_{\mathrm{EX}}/D) \geq 1$ is summarized in Table IV. It is seen that the effect of $J_0 d/\lambda D \geq 1$ is to reduce the value of $\mathfrak{F}^*$. The inverse dependence upon J_0 (for large J_0) is a weak one, roughly logarithmic, while the dependence upon r_{EX}/d (for large J_0) is roughly the inverse of $\sqrt{r_{\mathrm{EX}}/d}$. This $\mathfrak{F}^*$ dependence upon J_0 and r_{EX} is enhanced as Qd^2/D is increased. These results may be understood qualitatively in terms of an "exchange volume", i.e., a region extending beyond the contact distance d wherein $J(r) > Q$, so that the possibility of Q mixing is suppressed. As we have already noted, for small Qd^2/D the effects of reencounters after longer separations play a greater role, hence this excluded volume has less effect for small Qd^2/D than for larger values of Qd^2/D. This excluded volume or exchange volume effect is seen to have similar functional dependences upon J_0 and Λ to the results for the effects of a finite range of $J(r)$ upon spin depolarization by Heisenberg spin exchange given in II. The important difference with this latter effect is the nearly negligible Q dependence in that case.

TABLE IV. Dependence of $\mathfrak{F}^*$ upon $J(r)$.[a,b]

J_0	$D=10^{-6}$ $r_{\mathrm{EX}}=2$ Å	$D=10^{-6}$ $r_{\mathrm{EX}}=4$ Å	$D=10^{-6}$ $r_{\mathrm{EX}}=8$ Å	$D=10^{-5}$ $r_{\mathrm{EX}}=8$ Å	$D=10^{-4}$ $r_{\mathrm{EX}}=8$ Å
10^8	1.0	1.0	1.0	1.0	1.0
10^9	0.997	0.990	0.961	1.0	1.0
10^{10}	0.872	0.782	0.691	0.957	1.0
10^{11}	0.800	0.711	0.595	0.800	0.977
10^{12}	0.781	0.646	0.510	0.745	0.910
10^{13}	0.756	0.592	0.447	0.687	0.886
10^{14}	0.733	0.546	0.391	0.636	0.859
10^{15}	0.712	0.508	0.328	0.589	0.833

[a] EFA model. Results given as the ratio $\mathfrak{F}^*/\mathfrak{F}^*_{J=0}$, where $\mathfrak{F}^*_{J=0}$ is the value obtained for $J_0=0$.

[b] Parameters used: $d=4$ Å, $\Delta r=0.25$ Å, $f=20$, $M=40$, $N=208$, $r_N=854$ Å, $Q=4\times10^8\ \mathrm{sec}^{-1}$, $k=10^{18}\ \mathrm{sec}^{-1}$.

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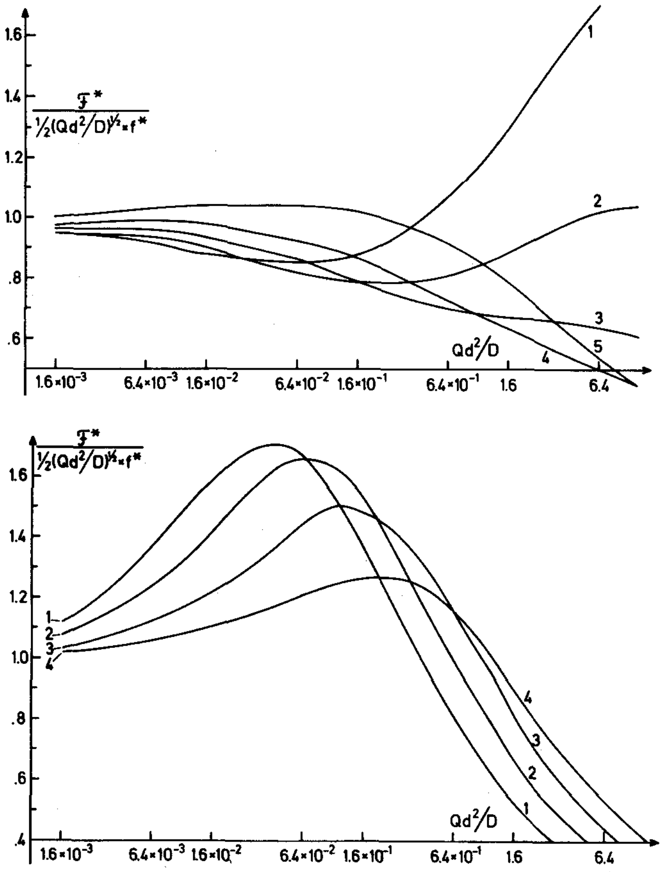

FIG. 1. (a) (Upper Graph) $\mathfrak{F}^*$ divided by $\frac{1}{2}(Qd^2/D)^{1/2}f^*$ as a function of Qd^2/D (logarithmic scale). Diffusion model includes the effect of a repulsive ionic interaction with Debye–Hückel potential. The values of κd are $\frac{1}{4}$ for Curve 1, $\frac{1}{2}$ for Curve 2, 1 for Curve 3, and 2 for Curve 4. Curve 5 is calculated for normal diffusion without any ionic interaction. Values of f^* are given in Table V. Other parameters used in the calculation of $\mathfrak{F}^*$ are $d=4$ Å, $\Delta r=0.25$ Å, $M=200$, $f=100$, $N=400$, $r_N=5054$ Å, $J_0=10^8$ sec^{-1}, and $|U(d)|=5k_BT/(1+\kappa d)$. (b) (Lower Graph) Same as Fig. 1(a), but for an attractive ionic interaction.

A. Ionic interactions

Results for ionic interactions with Debye–Hückel potentials over a range of values of κd were obtained as in II. One may summarize these results by noting first that Eqs. (3.1)–(3.5), (3.8), and (3.11) *again apply*. However, Eq. (3.9) must be modified to

$$\tau_1^{-1} = \tau_{1,u}^{-1} f^* \exp[U(d)/kT] , \tag{3.16}$$

where

$$(f^*)^{-1} = d\int_d^{\infty} \exp\left(\frac{U(r)}{kT}\right)\frac{dr}{r^2} , \tag{3.17}$$

with $U(r)$ the usual Debye–Hückel interaction [cf. II, Eq. (39)], and $\tau_{1,u}$ the value for uncharged radicals given by Eq. (3.9). This Debye-type correction is thus identical to that found in the usual analyses of chemical-reaction kinetics.[7,9] Typical results demonstrating this are given in Table V. The effects upon $\mathfrak{F}^*$ may be approximately represented (cf. Fig. 1) by

$$\mathfrak{F}^* \simeq \mathfrak{F}_u^* f^{*(1+\epsilon)} , \tag{3.18}$$

where $\mathfrak{F}_u^*$ are the results obtained for uncharged radicals [e.g., Eq. (3.15)], $\epsilon \simeq \frac{1}{4}$ for attraction, and $0 \le \epsilon \le \frac{1}{4}$ for repulsion with $Q=10^8$ sec^{-1} ($D=10^{-5}$ cm^2/sec). More generally, ϵ is somewhat sensitive to Q and κd, where κ is the usual Debye–Hückel "reciprocal thickness of the ionic layer" (cf. Fig. 1, where values of $\epsilon \simeq 0.6$ may be found). These results indicate the complex way in which the long-range (shielded) Coulomb forces can affect the reencounter dynamics so as to influence the Q mixing. Note, however, that when the interaction is of short range (i.e., κd is large), then one would expect that the only effect on $\mathfrak{F}^*$ would be to cause d to be replaced by an effective interaction distance of f^*d. For such cases, one would expect $\mathfrak{F}^* \simeq f^*\mathfrak{F}_u^*$. The small $\epsilon \neq 0$ in Eq. (3.18) then reflects the longer-range effect on the relative diffusive motion affecting the Q mixing, which is an effect different from that involved in the usual descriptions of liquid-state reaction kinetics. These features are further clarified by the results of the EFP models discussed in the next section.

We have also found that Eq. (3.12) remains applicable [as do Eqs. (3.13)] when t_f is appropriately modified. The values of t_f are conveniently calculated by our method,[3] and we have found they obey quite well (cf. Table VI) the relation

$$t_f = 1 - f^*/f^*(r_I) , \tag{3.19}$$

where

$$f^*(r_I)^{-1} = d\int_d^{r_I} \exp\left(\frac{U(r)}{kT}\right)\frac{dr}{r^2} , \tag{3.20a}$$

so that

$$f^* = \lim_{r_I \to \infty} f^*(r_I) . \tag{3.20b}$$

For r_I such that $U(r_I)/kT \ll 1$, Eq. (3.19) simply yields

$$t_f = f^*d/r_I . \tag{3.19'}$$

B. Exchange forces present

Results for EFP (i.e., the exchange interaction is included in the potential energy of the diffusion equation) with different diffusive trajectories for singlets and triplets were obtained as in II. One should bear in mind that this physical model, which includes diffusion in configuration space only, implies very fast momentum re-

TABLE V. Effect of ionic interactions upon τ_1 and $\mathfrak{F}^*$.[a]

	κd	τ_1/τ_{1u} [b,c]	$(f^*)^{-1}\exp[-U(d)/k_BT]$ [d]	$\mathfrak{F}^*/\mathfrak{F}_u^*$ [b,e]	f^* [d]
Attraction	0.25	19.34	19.44	4.31	2.81
	0.50	12.86	12.90	2.97	2.17
	1.0	7.31	7.34	1.95	1.66
	2.0	4.00	4.01	1.41	1.32
Repulsion	0.25	0.203	0.203	0.0766	0.0901
	0.50	0.213	0.213	0.144	0.167
	1.0	0.242	0.242	0.305	0.339
	2.0	0.311	0.313	0.566	0.603

[a] Parameters used: $d=4$ Å, $\Delta r=0.25$ Å, $f=100$, $M=200$, $N=400$, $r_N=5054$ Å, $Q=10^8$ sec^{-1}, $D=10^{-5}$ cm^2/sec. $J_0=10^8$ sec^{-1}, $r_{EX}=4$ Å, $|U(d)|=5k_BT/(1+\kappa d)$.

[b] From general numerical solutions. Subscript u refers to uncharged radicals.

[c] $k=10^8$ sec^{-1}.

[d] f^* calculated from Eq. (3.17) by numerical integration.

[e] $k=10^{18}$.

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TABLE VI. Reencounter probabilities in the presence of shielded Coulombic interactions.[a,b]

	Attraction				Repulsion			
κd	$r_I = 6$ Å		$r_I = 10$ Å		$r_I = 6$ Å		$r_I = 10$ Å	
0.25	0.956	(0.959)	0.812	(0.817)	0.196	(0.208)	0.0549	(0.0559)
0.50	0.935	(0.940)	0.744	(0.749)	0.226	(0.237)	0.0793	(0.0786)
1.0	0.892	(0.898)	0.636	(0.642)	0.302	(0.312)	0.139	(0.136)
2.0	0.822	(0.831)	0.526	(0.526)	0.429	(0.434)	0.238	(0.238)

[a] Table entries are those obtained from general numerical solutions; those in parentheses are obtained from Eq. (3.19).

[b] Parameters used: $d = 4$ Å, $\Delta r = 0.25$ Å, $f = 100$, $M = 200$, $N = 400$, $r_N = 5054$ Å, $|U(d)| = 5k_BT/(1+\kappa d)$, $k = 10^{18}$.

laxation. Also, for computational convenience, an irreversible "reaction" rate constant $k(r)$ is placed at $r = d$ to remove singlets that have been trapped in the binding potential well. One may, in a sense, think of this k as a crude means of adjusting for momentum relaxation, etc.

The results for EFP may be summarized by noting that Eqs. (3.3) and (3.5) do apply provided, however, $\Lambda \geq 10^{-3}$. This is because, for $\Lambda < 10^{-3}$, effects of the relative diffusion of singlets vs triplets (RDM[3]) are able to play a role compared to the weak reactivity of the system. This restriction is thus akin to that for the CIDEP expression, Eq. (3.6); one similarly notes, from Eqs. (3.11), that $\Lambda < 10^{-3}$ is the regime where $\Delta\mathfrak{F}$ is typically too small to be experimentally observable.

Furthermore, we have found that Eqs. (3.8) and (3.9) with the modification Eq. (3.16) do apply rigorously except when $|\hbar J_0/kT| > 10$. This breakdown is closely connected with the nature of the EFP model as described above and in II. That is, for $\hbar J_0/kT \gg 1$, the radical trapping effects become so large as to overwhelm any effects of k for smaller k values ($k \leq 10^{-8}$ sec). This point indicates, of course, that a more detailed description of the reaction dynamics will yield a somewhat different approach to expressing Λ than that which we have found in this work and which relates simply and directly to the familiar theories of reaction kinetics in solution.[7,9]

When Eqs. (3.8), (3.9), and (3.16) apply, then one finds that Eq. (3.18) applies with $\epsilon \simeq 0$, as we expect for very short range interactions. Typical results illustrating these matters are found in Table VII. It is seen that the effect of f^* in Eq. (3.18)[12b] is to enhance $\mathfrak{F}^*$, which is opposite to the "exchange volume" effect tending to reduce $\mathfrak{F}^*$ (cf. Table IV). Finally, we find that Eqs. (3.11) continue to apply (for $\Lambda \geq 10^{-3}$).

Also, we wish to note the following points that emerge within the context of the EFP model: (1) Since substantial CIDNP polarizations require nonnegligible values of Λ, which is a function of the magnitude of J_0, values of $\hbar J_0/kT > 1$ are needed and this implies the importance of corrections for the finite range and magnitude of $J(r)$ as discussed in this work; (2) When $J(\mathbf{r}_i, \mathbf{r}_j)$ is not spherically symmetric, one expects that the primary effect on the analysis is to cause a reduction in the magnitude of Λ over that for a spherically symmetric $J(r)$, i.e., only that fraction of reencounters for which $\hbar J(\mathbf{r}_i, \mathbf{r}_j)/kT > 1$ are important and their description involves correction for the finite magnitude of J. Thus, the role played by nonspherically symmetric $J(\mathbf{r}_i, \mathbf{r}_j)$ is different in CIDNP than in CIDEP.[3]

IV. CIDNP INTENSITIES AND ENHANCEMENT

In this section, we wish to relate the $\mathfrak{F}$'s calculated in the previous section with the intensities as observed in a CIDNP experiment. Several works[5,13,14] have to some extent dealt with this connection, but they all use unnecessary assumptions (e.g., a steady state or constant precursor assumption), which limit the range of applicability. We wish to point out that within the usual assumption of negligible cross relaxation, one can easily obtain exact relations for the time dependent intensities. Such relations are of importance both for obtaining rate constants as well as determining the $\mathfrak{F}$'s by a CIDNP experiment. The present approach is similar to that used by one of us[15] for the CIDEP case, and that work gives the proper modifications needed if one is interested in a high accuracy for times smaller than or of the order of the spin lattice relaxation time. Here we neglect these complications, i.e., we assume the intensity is described by the z component of the magnetization, as is indeed the case for $t > T_1$.

The following simple reaction scheme is considered for illustration:

$$\begin{tikzcd}
S \arrow[r] & \overline{R_a^\cdot + R_b^\cdot} \arrow[r] \arrow[dr] & R_{ab} \\
& & R_a^\cdot + R_b^\cdot \, .
\end{tikzcd}$$

The precursor S decomposes into a radical pair $\overline{R_a^\cdot + R_b^\cdot}$, where the bar indicates that the radicals are initially close together. This initialization process is assumed to be a first order or pseudo-first order reaction with reaction constant k_0. $R_a^\cdot$ means radical A in a specific nuclear state a. The two radicals initially together may diffuse apart into $R_a^\cdot + R_b^\cdot$, never to meet again, in which case the radicals end up in scavenging products or they may, after a diffusive excursion, recombine to give a recombination product R_{ab}. In the following, $S(t)$ and $R(t)$ are the total concentration at time t, respectively, of the precursor and of the recombination products, irrespective of the nuclear states, while $R_{ab}(t)$ is the concentration at time t of recombination product in a specific nuclear state specified by the subscript.

If we assume that the recombination product R is dif-

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TABLE VII. Effect of exchange forces upon τ_1 and $\mathfrak{F}^*$.[a]

J_0	τ_1/τ_{1u} [b,c]	$(f^*)^{-1}e^{J_0/k_BT}$ [d]	$\mathfrak{F}^*/\mathfrak{F}^*_u$ [b,e]	f^* [d]
10^{12}	1.023	1.023	1.0021	1.0020
10^{13}	1.262	1.261	1.0190	1.0183
10^{14}	10.81	10.83	1.1310	1.1249
10^{15}	5.8×10^{11}	5.4×10^{10}	1.3460	1.330

[a] EFP model. Parameters used: $d=4$ Å, $\Delta r=0.05$ Å, $f=100$, $M=200$, $N=400$, $r_N=1014$ Å, $r_{\mathrm{EX}}=4$ Å, $Q=10^8$ sec^{-1}, $D=10^{-5}$ cm^2/sec.

[b] From general numerical solutions. Subscript u refers to case of absence of exchange forces (EFA).

[c] $k=10^8$ sec^{-1}.

[d] f^* calculated from Eq. (3.17) by numerical integration.

[e] $k=10^{18}$ sec^{-1}.

ferent from precursor S, then the rate equation for S yields

$$S(t)=S(0)\exp(-k_0t)\,. \tag{4.1}$$

The rate of formation of a specific radical pair $\overline{R_a^\cdot+R_b^\cdot}$ is $k_0X_s^{-1}\,S(t)$, where it is assumed that all nuclear states of the precursor are equally populated. X_s is the nuclear degeneracy of S. The fraction of radical pairs $\overline{R_a^\cdot+R_b^\cdot}$ that recombine to give recombination product R_{ab} is $\mathfrak{F}_{ab}$ (where the subscripts serve to define the Q value when the g values and hyperfine splittings are known). The rate equation for $R_{ab}(t)$ is therefore

$$\frac{d}{dt}\,R_{ab}(t)=k_0X_s^{-1}\,\mathfrak{F}_{ab}S(t)-T_1^{-1}[R_{ab}(t)-R_{ab}^{eq}(t)]\,, \tag{4.2}$$

where the last term gives the nuclear spin lattice relaxation. A single averaged relaxation time T_1 is assumed, and cross relaxation between different nuclear states is neglected. This may be a rather crude approximation and is assumed here for ease in the presentation. $R_{ab}^{eq}(t)$ is defined as

$$R_{ab}^{eq}(t)=P_{ab}^{eq}\,R(t)\,, \tag{4.3}$$

where P_{ab}^{eq} is the Boltzmann population of product state ab. The rate equation for $R(t)$ is obtained by summing Eq. (4.2) over all states a and b:

$$\frac{dR(t)}{dt}=k_0X_s^{-1}\,\mathfrak{F}S(t)\,, \tag{4.4}$$

where

$$\mathfrak{F}\equiv\sum_{a,b}\mathfrak{F}_{ab}\,. \tag{4.5}$$

Equations (4.4) and (4.1) give

$$R(t)=X_s^{-1}\,\mathfrak{F}S(0)\,(1-e^{-k_0t})\,. \tag{4.6}$$

Equation (4.2) may be solved, using Eqs. (4.1), (4.3), and (4.6), to give

$$\begin{aligned}R_{ab}(t)={}&P_{ab}^{eq}X_s^{-1}\,\mathfrak{F}S(0)\,(1-e^{-t/T_1})\\&+X_s^{-1}\,S(0)\mathfrak{F}(k_0\mathfrak{F}_{ab}/\mathfrak{F}-T_1^{-1}\,P_{ab}^{eq})\\&\times(T_1^{-1}-k_0)^{-1}(e^{-k_0t}-e^{-t/T_1})\quad\text{for } T_1^{-1}\neq k_0\,,\end{aligned} \tag{4.7a}$$

and

$$\begin{aligned}R_{ab}(t)={}&P_{ab}^{eq}X_s^{-1}\,\mathfrak{F}S(0)\,(1-e^{-t/T_1})\\&+X_s^{-1}S(0)\,\mathfrak{F}(k_0\mathfrak{F}_{ab}/\mathfrak{F}-T_1^{-1}\,P_{ab}^{eq})\,t\quad\text{for } T_1^{-1}=k_0\,.\end{aligned} \tag{4.7b}$$

Equations (4.7) give the exact time dependence of $R_{ab}(t)$ without any simplifying assumption of steady-state and/or constant precursor concentrations.

Use of these equations permits a clearer interpretation of the experimental results. We shall, however, only consider a slow reaction as a specific example.

Slow reaction: i.e., $T_1^{-1}\gg k_0$, then $(T_1^{-1}-k_0)^{-1}\simeq T_1$ and Eq. (4.7a) is approximated by

$$\begin{aligned}R_{ab}(t)={}&S(0)X_s^{-1}\,\mathfrak{F}P_{ab}^{eq}(1-e^{-k_0t})\\&+S(0)X_s^{-1}\,\mathfrak{F}_{ab}\,k_0T_1(e^{-k_0t}-e^{-t/T_1})\,.\end{aligned} \tag{4.8}$$

Consider an NMR transition $ab\rightarrow a+1b$; then the intensity of this line is proportional to

$$\begin{aligned}I_{ab,a+1b}(t)={}&R_{ab}(t)-R_{a+1b}(t)\\={}&S(0)X_s^{-1}\,\mathfrak{F}(1-e^{-k_0t})(P_{ab}^{eq}-P_{a+1b}^{eq})\\&+S(0)X_s^{-1}\,k_0T_1(e^{-k_0t}-e^{-t/T_1})\,(\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b}),\end{aligned} \tag{4.9}$$

which has exactly the same form as Eq. (4.8).

If one had used the full Eqs. (4.7), a very similar result would have been obtained with the obvious changes in it of

$$\mathfrak{F}_{ab}\rightarrow\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b}=(\mathfrak{F}_{ab}-\mathfrak{F}_0)-(\mathfrak{F}_{a+1b}-\mathfrak{F}_0)\,, \tag{4.10a}$$

$$P_{ab}^{eq}\rightarrow P_{ab}^{eq}-P_{a+1b}^{eq}\,. \tag{4.10b}$$

Equation (4.9) can be rewritten as

$$\begin{aligned}I_{ab,a+1b}(t)={}&S(0)X_s^{-1}\,(\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b})\,k_0T_1\,(1-e^{-t/T_1})\\&+S(0)X_s^{-1}(\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b})k_0T_1\\&\times\left(\frac{P_{ab}^{eq}-P_{a+1b}^{eq}}{\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b}}\,\frac{\mathfrak{F}}{k_0T_1}-1\right)(1-e^{-k_0t}).\end{aligned}$$

The maximum intensity $I_{ab,a+1b}(\max)$ is seen to occur for $t\gtrsim T_1$ and is equal to

$$I_{ab,a+1b}(\max)=S(0)X_s^{-1}\,(\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b})\,k_0T_1\,. \tag{4.12a}$$

Thus, Eq. (11) may be written as

$$\begin{aligned}I_{ab,a+1b}(t)={}&I_{ab,a+1b}(\max)\\&\times\left[(1-e^{-t/T_1})+\left(\frac{P_{ab}^{eq}-P_{a+1b}^{eq}}{\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b}}\,\frac{\mathfrak{F}}{k_0T_1}-1\right)\right.\\&\left.\times1-e^{-k_0t})\right].\end{aligned} \tag{4.12b}$$

The intensity goes to a maximum value during a time of order T_1 and then decays exponentially with time constant k_0 to a limiting value $I_{ab,a+1b}(\infty)$. This behavior is commonly seen,[16] but does not appear to have been given a proper expression such as that of Eq. (4.12b);

$$I_{ab,a+1b}(\infty)=S(0)X_s^{-1}\,(P_{ab}^{eq}-P_{a+1b}^{eq})\,\mathfrak{F}\,, \tag{4.13}$$

which is seen to be just the equilibrium intensity of the product when the reaction has gone to completion.

The intensity enhancement, i.e., the actual intensity at time t as given by Eq. (4.12b) divided by the intensity the product at time t would have had if the nuclear state

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population was given by a Boltzmann distribution, is easily calculated by Eq. (4.12b). However, such a quantity is not always experimentally convenient to obtain. Instead, in cases where one can measure I(∞) of Eq. 4.13 (e.g., when the product disappears at a slower rate than it is formed, as is assumed in the above example), one may define a useful experimental enhancement $V^{\exp}$ as

$$V^{\exp}_{ab,a+1b}=\frac{I_{ab,a+1b}(\max)}{I_{ab,a+1b}(\infty)}\,, \tag{4.14a}$$

which by use of Eqs. (4.12a) and (4.13) becomes

$$V^{\exp}_{ab,a+1b}=\frac{(\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b})k_0T_1}{(P^{eq}_{ab}-P^{eq}_{a+1b})\mathfrak{F}}\,. \tag{4.14b}$$

The maximum real enhancement $V^{\max}_{ab,a+1b}$ that occurs for $t\simeq T_1$ is easily seen from Eq. (4.11) to be

$$V^{\max}_{ab,a+1b}=1+\frac{(\mathfrak{F}_{ab}-\mathfrak{F}_{a+1b})}{\mathfrak{F}(P^{eq}_{ab}-P^{eq}_{a+1b})}\,, \tag{4.14c}$$

where the 1 is usually negligible.

If the nuclear states ab and $a+1b$ consist of independent states a and b, then the intensity and the enhancement of the line $a\rightarrow a+1$ is obtained in the usual manner by summing Eqs. (4.12), (4.13), and (4.14) over states b.

The experimental enhancement (or the real enhancement) for a specific precursor (S, T_0, or R.I.) may be obtained from Eq. (4.14b) and the earlier expressions for $\mathfrak{F}$. The result for a triplet precursor is

$$V^{\exp}_{ab,a+1b}=k_0T_1\,\frac{\mathfrak{F}^*_{ab}[1+\mathfrak{F}^*_{ab}(1-\Lambda)]^{-1}-\mathfrak{F}^*_{a+1b}[1+\mathfrak{F}_{a+1b}(1-\Lambda)]^{-1}}{(P^{eq}_{ab}-P^{eq}_{a+1b})\sum_{cd}\mathfrak{F}^*_{cd}[1+\mathfrak{F}^*_{cd}(1-\Lambda)]^{-1}}\,. \tag{4.15a}$$

This expression shows a very weak dependence on Λ, i.e., of the reactivity of the radicals. For a singlet precursor we have

$$V^{\exp}_{ab,a+1b}=\frac{-(1-\Lambda)k_0T_1}{(P^{eq}_{ab}-P^{eq}_{a+1b})}\,\frac{\mathfrak{F}^*_{ab}[1+\mathfrak{F}^*_{ab}(1-\Lambda)]^{-1}-\mathfrak{F}^*_{a+1b}[1+\mathfrak{F}^*{}_{a+1b}(1-\Lambda)]^{-1}}{1-(1-\Lambda)\sum_{cd}\mathfrak{F}^*_{cd}[1+\mathfrak{F}^*_{cd}(1-\Lambda)]^{-1}}\,. \tag{4.15b}$$

The enhancement [which has an opposite sign to that of the triplet (and R.I.) case] goes to zero for $\Lambda\rightarrow 1$ (high reactivity of the radicals), but note that this need not be true if the radicals were created with a large kinetic energy so that $r_0\neq d$ (c.f. Sec. III and Eq. 3.14, which is to be used to modify Eq. 4.12). The enhancement is maximum for $\Lambda=0$, but then all radicals end up in scavenging products and no signal due to a recombination product is observed. The optimal experimental condition will then be for $\Lambda\simeq\frac{1}{2}$.

For a R.I. (or F^5) precursor (note that the initialization step, i.e., the first encounter, is assumed to be described by a pseudo-first order reaction), the enhancement is given by

$$V^{\exp}_{ab,a+1b}=\frac{\Lambda k_0T_1}{(P^{eq}_{ab}-P^{eq}_{a+1b})}\,\frac{\mathfrak{F}^*_{ab}[1+\mathfrak{F}^*_{ab}(1-\Lambda)]^{-1}-\mathfrak{F}^*_{a+1b}[1+\mathfrak{F}^*_{a+1}(1-\Lambda)]^{-1}}{1+\Lambda\sum_{cd}\mathfrak{F}^*_{cd}[1+\mathfrak{F}^*_{cd}(1-\Lambda)]^{-1}}\,. \tag{4.15c}$$

The enhancement is maximum for $\Lambda=1$ and goes to zero as Λ goes to zero.

Results similar to those in Eqs. (4.15) may be obtained in a similar manner for other reaction schemes, e.g., for scavenging products, or for identical precursor and recombination products. Modifications needed for $t<T_1$ may also be incorporated.[15] Inclusion of cross relaxation would, however, require the solution of more complex matrix equations.

V. SUMMARY AND CONCLUSIONS

As anticipated, our rigorous results largely confirm the basic reencounter mechanism first proposed by Adrian and discussed as well by Kaptein. It is shown for a variety of physical models that the CIDNP polarizations may be expressed in terms of just two parameters—Λ, the fractional probability of radical pairs reacting for the *complete collision* including *all* reencounters, and $\mathfrak{F}^*$, the probability that triplets are converted to singlets and then react per collision with $\Lambda=1$. This interpretation of Λ, which is unequivocal from our analysis, was not appreciated in the earlier work. Expressions have been obtained for Λ for (a) a simple contact reaction mechanism (EFA); (b) the same as (a), but diffusion under exchange forces (EFP), and (c) for ionic interactions. These results bear a close relation to the well-known theories for reaction kinetics and diffusion unlike the result of Evans *et al.*, who neglected to consider the usual boundary conditions. Furthermore, our results give a precise meaning to the "reaction volume", which is at best unclear in the familiar treatments.

Our results for $\mathfrak{F}^*$ in case (a) are very similar to those obtained by Adrian, Kaptein, and Evans *et al.*, provided $Qd^2/D\ll 1$ and $J_0r_{EX}d/D\ll 10$. We have provided the corrections when those strong inequalities no longer apply. In the absence of the former inequality, (i) a "renormalized" $\mathfrak{F}^*$ which depends upon Λ is required, and (ii) the role of reencounters is reduced. In the absence of the latter, there is a finite "exchange region" in which a large $J(r)$ precludes singlet–triplet mixing due to Q, thus reducing $\mathfrak{F}^*$. Our results for (b) show that the short-range exchange forces do enhance $\mathfrak{F}^*$ essentially because the effective distance of closest

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approach f^*d replaces d. The quantity Λ is also enhanced. The analysis of EFP underscores the fact that a consistent treatment of exchange in both the reactive-diffusive trajectories and the spin Hamiltonian require large values of J_0 for substantial reactivities, hence the corrections to $\mathfrak{F}^*$ for large J_0 and finite range of $J(r)$ discussed here are relevant. Our results for case (c) show that the ionic interactions also exhibit an enhancement for attraction (and a diminution for repulsion) which is largely attributable to the replacement of d by f^*d. However, for these longer-range forces, there is further correction, which depends upon the magnitude of Q, that represents the effects of the modified encounter dynamics on the Q mixing.

We have obtained a simple expression for the first encounter probability t_f when interactions between the radicals are present. We note that our results for the different initial spin conditions show that those of Adrian and Kaptein were not entirely correct but those of Evans *et al.* have the correct interrelationship. Also, the effects of initial $r_I \neq d$ are found to be closely related to t_f.

Finally, our expressions for CIDNP intensities and enhancement factors for a typical reaction scheme show how the intensities vary with time, and they furthermore show the important roles played by the "renormalized" $\mathfrak{F}^*$ and Λ. The role of Λ is strongly dependent upon the precursor spin multiplicities.

It is hoped that the more precise distinctions and relationships given here for the several models should facilitate the interpretation of CIDNP in terms of reaction dynamics.

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[7] (a) See, for example, I. Amdur and G. G. Hammes, *Chemical Kinetics* (McGraw-Hill, New York, 1966), Chap. 2; (b) This point is readily confirmed by our general method of solution by varying the location of r_N, the outer absorbing wall. It may alternatively be seen from the following simple example. Consider a radical pair $A-B$ which react with rate k to form C, but separate permanently at rate τ^{-1}. The rate equations for $[A-B]$ and $[C]$ (where the bracketed quantities are probabilities) are just $d[A-B]/dt = -(\tau^{-1}+k)[A-B]$ and $d[C]/dt = k[A-B]$. Thus, the solution for $[C]_{t\to\infty}$ subject to the initial condition $[A-B]_{t=0}=1$ is easily found to be $k\tau/[1+k\tau]$. This simple case neglects reencounters, so τ may be regarded as the lifetime of a single encounter. Since reencounters are definitely important in the diffusion process, and Eq. (3.8) included *all* reencounters, for which the total reaction probability is greater than that for a single encounter, it then follows that $\tau_1 > \tau$. One can generalize the above simple model to include one or more steps of (diffusive) separation to readily show that $\tau_1 > \tau$ and the general *form* of Eq. (3.8) remains unchanged.

[8] By comparison with typical treatments of diffusive effects on reaction-rate constants (cf. Noyes[9], and Amdur and Hammes[7]), one easily finds that $\hat{k}$ (which is k in Noyes' notation), the normal second order rate constant for equilibrium distributions, is given for Eq. (3.9) by $k\tau_1 \times 2k_2(d)$, where $2k_2(d) = 4\pi dD$, the rate of new bimolecular encounters, i.e., $\hat{k} = k4\pi d^2(\Delta r/2) = k\Delta V$; and the experimentally observed rate constant[7] k_f (k in Noyes' notation) including the effect of diffusion is $k_f = 2k_2(d)/[1+(k\tau_1)^{-1}] = \hat{k}[1+k\tau_1]^{-1} = 2k_2(d)\Lambda$, assuming steady-state fluxes.

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[11] However, if $r_I \gg d$ such that Q mixing is fully effective before an encounter, then the value obtained for $\mathfrak{F}$ is independent of the initial spin conditions going over into that of $\mathfrak{F}$ (R.I., r_I) given by Eqs. (3.12) and (3.11c).

[12] (a) The result [Eq. (3.19] may be anticipated from the discussion of Eqs. (31) and (32) of II, when the expression $k_2(d) = 2\pi f^*D$ (cf. Refs. 7 and 9) is used for $k_2(d)$, the rate of new bimolecular collision producing either S or T_0 states; (b) Note that for $\lambda d \gg 1$, one can approximate f^{*-1} by the asymptotic form $\{1+(\lambda d)^{-1}\sum_{n=1}^{\infty}(A^n/nn!)[1-(2/n\lambda d)+0(n\lambda d)^{-3}]\}$, where $A = -\hbar|J_0|/kT$. If one retains only the first type of term under the summation, then one has $f^{*-1} \simeq \{1-(\lambda d)^{-1}\times[\mathrm{Ei}(A) - C - \ln(-A)]\}$, where $C = 0.577215$ and $\mathrm{Ei}(A)$ is the exponential integral [cf. Gradshteyn and Ryzhik, *Table of Integrals, Series and Products*, Academic, New York, 1965)]. For $|A| > 1$, one can employ the further asymptotic form $\mathrm{Ei}(A) = e^A \sum_{R=1}(P-1)!/A^P$. These forms illustrate (1) that for very short range forces, i.e., $\lambda d \to \infty$, then $f^* \to 1$, and (2) the essentially logarithmic dependence of f^* on J_0 for large $|A| \gg 1$.

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Erratum: Some theoretical aspects of chemically-induced dynamic nuclear polarization [J. Chem. Phys. 61, 1517 (1974)]

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Printer's errors were made in Eq. (3.8) and (3.6). They should read

$$P^{\infty}(\mathrm{R.I.})/\mathfrak{F}(\mathrm{R.I.}) = -P_{k=0}^{\infty}(S) = +P_{k=0}^{\infty}(T) \ .$$

$$\Lambda = k\tau_1/(1 + k\tau_1) \ .$$

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