

# Theory of chemically induced dynamic electron polarization. III. Initial triplet polarizations

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An analysis of dynamical aspects of the CIDEP mechanism proposed by Wong *et al.* is given. This mechanism is based upon the formation of an excited triplet by intersystem crossing that populates the three triplet levels unequally. The subsequent rotational averaging of the initial population distribution coupled with the orientational effects of the zero field splitting is carefully treated in this work utilizing the stochastic Liouville equation in a manner closely analogous to that recently given for ESR line shapes and relaxation of slow-tumbling triplets. It is shown that the predicted CIDEP polarizations can indeed be very substantial, in agreement with Wong *et al.*, but they will depend in general on the relative magnitudes of not only the zero field ( $D$  and  $E$ ) and Zeeman terms ( $\omega_0$ ) but also the relevant reaction rates and the rotational tumbling times ( $\tau_R$ ). A useful perturbation expression valid for  $D^2 \lesssim (1/2)[\omega_0^2 + \tau_R^{-2}]$  is obtained which shows these details. Typical complete solutions, obtained numerically, are given for cases when this inequality does not hold.

## I. INTRODUCTION

In Papers I<sup>1</sup> and II<sup>2</sup> we have presented a detailed analysis of CIDEP in terms of the radical pair model, which should be important for some recent experimental observations.<sup>1-3</sup> Recently Wong *et al.*<sup>4</sup> presented a theory for CIDEP polarization for some photochemical processes in liquid solution. The model adopted by Wong *et al.* is based upon polarizations generated by the intersystem crossing of a photoexcited singlet state to a triplet state such that one (or more) of the molecular frame triplet states  $T_x$ ,  $T_y$ , or  $T_z$ , is initially populated preferentially. This, in itself, is a commonly observed phenomenon in the solid state, as they point out. They showed that this preferential population, coupled with the effect of the zero-field splitting term in modifying the high-field triplet states, can lead to a rotationally invariant term causing a net initial polarization of the radical pair which emanates from the reaction (or decomposition) of the triplet molecule. The crucial requirement then appears to be that the triplet lifetime be short compared to the triplet spin-lattice relaxation time  $T_1$ , so that this initial polarization is not relaxed before the radical pair forms.

This mechanism has now been invoked in several experimental CIDEP studies of photolytically generated radicals to explain pure emission spectra as well as cases where both radicals are observed in emission.<sup>5,6</sup> An important feature of this mechanism is that it is essentially independent of the hyperfine terms. The likelihood of having both the triplet polarization mechanism of Wong *et al.* and the radical-pair mechanism contributing to the CIDEP polarization in such cases has been suggested by Atkins *et al.*<sup>6</sup>

The theoretical treatment of Wong *et al.*<sup>4</sup> clearly demonstrates the potential importance of this photolytic triplet mechanism for systems where the rate of triplet decomposition into radical pair is rapid. However, they did not explicitly consider the dynamics of the

problem, i. e., the dynamical competition between the rotational reorientation, the various triplet decay processes, and the  $T_1$  process. In particular, the  $T_1$  process is itself expected to be generated by the rotational modulation of the zero-field splitting. This is, in fact, a well-known mechanism, and the relevant expressions exist for it.<sup>7,8</sup> However, when the zero field splitting becomes comparable to or larger than the tumbling rate, then the usual motional narrowing predictions break down, since one is in the "slow-motional" region. In this region there need no longer be a simple  $T_1$  behavior. Instead the nonequilibrium polarizations will decay with several decay constants representing a more complex solution of the coupling of the spin-degrees of freedom to the reorientational process.<sup>3</sup> Despite the complexity of the problem, a thorough analysis may be given in terms of the stochastic Liouville equation. In fact, what will be seen to be a closely analogous problem, that of ESR spectra from slow tumbling triplets, has been analyzed in this manner.<sup>7</sup> It should be noted that the slow-tumbling condition affects not only the meaning of a  $T_1$  process (and hence the competition between it and the triplet decomposition process), but also the way in which an orientation-dependent initial polarization (due to the orientation of the molecular  $T_x$ ,  $T_y$ , and  $T_z$  states relative to the lab frame) is averaged by the rotational reorientation.

We present in this work a dynamical analysis of these aspects of the triplet polarization mechanism.

## II. ANALYSIS

We develop our analysis in terms of the excited triplet spin distribution represented by the spin-density matrix  $\rho$ . We first make the fundamental assumption, essentially equivalent to that of Wong *et al.*,<sup>4</sup> that a radical pair formed at time  $t$  either from the decomposition of an excited triplet molecule, or from a reaction [e.g., abstraction of an electron (or an H atom) from a

solvent molecule<sup>5,6</sup>] will still be characterized by the same triplet spin-density distribution  $\rho(t)$ , although the orbital electronic distribution has been altered. This appears reasonable for a decomposition process. For an abstraction process, e. g., of a hydrogen atom, the electron spin ( $k_1$ ) of the H atom must pair up with one of the original electrons ( $e_1$ ) forming the triplet, so the other electron ( $k_2$ ) of the pair bond for the H atom in its original solvent molecule will have the same spin character as  $e_1$ .<sup>5</sup> Once we adopt this point of view, then we note that the polarization of each radical product is given by<sup>1</sup>

$$P = \rho_{T_-,T_-} - \rho_{T_+,T_+}, \quad (1)$$

where  $\rho_{T_-,T_-}$  and  $\rho_{T_+,T_+}$  are the diagonal density-matrix elements for the  $T_-$  and  $T_+$  states (and we have set  $\rho_{S,T_0} = 0$ , since we have assumed that the excited state from which the reaction takes place is a simple triplet state). The states  $T_+$ ,  $T_0$  correspond to the  $M = \pm 1$  and 0 high field states in the laboratory frame. Actually, one needs the polarization achieved after the process is completed by which the initially excited triplet molecules have formed a radical pair, or relaxed to a stable ground state or else decomposed to yield other products. The polarization of the radical products in this limit is given by

$$P^\infty \equiv \lim_{t \rightarrow \infty} P(t) = \int_0^\infty [\rho_{T_-,T_-}(t) - \rho_{T_+,T_+}(t)] k_1 dt \quad (2)$$

or alternatively

$$P^\infty = k_1 [\rho_{T_-,T_-}(s=0) - \rho_{T_+,T_+}(s=0)], \quad (3)$$

where  $\rho(s)$  is the Laplace transform of  $\rho(t)$ , and  $k_1$  is the pseudo-first order rate constant for formation of the radical pair from the triplet states. The simplification of utilizing the  $t \rightarrow \infty$  limit was also used in I and II. It may be justified here in a similar manner; viz., the polarization generating process is much faster than any subsequent rate processes of the separated radical pair, e. g., their spin relaxation and their further reactivity.

The spin-density matrix  $\rho$  obeys the stochastic Liouville equation (SLE):

$$\partial \rho / \partial t = -i\mathcal{H}\rho - \Gamma(\rho - \rho_{\text{eq}}) - (k_1 + k_2)\rho, \quad (4)$$

where  $\mathcal{H}$  is the spin-Hamiltonian super operator,  $k_2$  is the quasi-first order rate constant for all other processes which deplete the triplets, and  $\Gamma$  is the Markoffian operator for the classical molecular diffusive processes. Also,  $\rho_{\text{eq}}$  is the equilibrium density matrix given by

$$\rho_{\text{eq}} = \frac{\sigma \exp(-\hbar\mathcal{H}/k_B T)}{\text{Tr} \exp(-\hbar\mathcal{H}/k_B T)} \cong \frac{1}{3}\sigma \left(1 - \frac{\hbar\mathcal{H}}{k_B T}\right), \quad (5)$$

where the approximate equality is the usual high temperature approximation and  $\sigma$  is discussed below. The inclusion of  $\rho_{\text{eq}}$  in Eq. (4) guarantees that the spins relax to the thermal equilibrium.<sup>2,3</sup> As a result of the dissociation and decay processes (assumed spin-independent),  $\rho_{\text{eq}}$  obeys the simple rate equation

$$\partial \rho_{\text{eq}} / \partial t = -(k_1 + k_2)\rho_{\text{eq}}. \quad (6)$$

It is convenient, at this stage, to introduce the variable  $\chi$  which is the deviation of  $\rho$  from its equilibrium value:

$$\chi \equiv \rho - \rho_{\text{eq}}. \quad (7)$$

It then follows from Eqs. (4) and (6) that  $\chi$  obeys

$$\partial \chi / \partial t = -(i\mathcal{H}\chi + \Gamma + k)\chi, \quad (8a)$$

where we have let

$$k \equiv k_1 + k_2. \quad (8b)$$

Equations (6)–(8) are seen to yield the formal solution

$$\rho(t) = e^{-kt} [\exp(-i\mathcal{H}t + \Gamma t) \chi(t=0) + \rho_{\text{eq}}(t=0)]. \quad (9)$$

We now normalize  $\rho(t=0) \equiv \rho(0)$  and  $\rho_{\text{eq}}(t=0) \equiv \rho_{\text{eq}}(0)$ , so that

$$\text{Tr} \rho(0) = \text{Tr} \rho_{\text{eq}}(0) = 1 \quad (10a)$$

and, more generally,

$$\text{Tr} \rho_{\text{eq}}(t) = \text{Tr} \rho(t) \equiv \sigma(t) \quad (10b)$$

and

$$\text{Tr} \chi(t) = 0, \quad (10c)$$

where  $\sigma(t)$  obeys the same rate equation as  $\rho_{\text{eq}}$  in Eq. (6), i. e., it measures the fraction of excited triplet molecules which remain at time  $t$ .

The Laplace transforms of Eqs. (6) and (8) are

$$[s+k]\rho_{\text{eq}}(s) = \rho_{\text{eq}}(0) \quad (11a)$$

and

$$[s+k+i\mathcal{H} + \Gamma]\chi(s) = \chi(0), \quad (11b)$$

and we have

$$\rho(s) = \chi(s) + \rho_{\text{eq}}(s). \quad (12)$$

Then in the limit  $s \rightarrow 0$  required for Eq. (3), we have

$$\lim_{s' \rightarrow k} \rho(s') = \lim_{s' \rightarrow k} \chi(s') + \rho_{\text{eq}}(0)/k, \quad (13)$$

where  $s' = s+k$ . Thus we may solve for  $\chi(s')$  and add to it the second term of Eq. (13).

In the present problem  $\mathcal{H}(\Omega)$  is the orientation-dependent triplet spin Hamiltonian<sup>7</sup>

$$\mathcal{H} = \omega_0 S_x + \sum_{m'} \{6^{-1/2} D_{0,m'}^2(\Omega) + \frac{1}{2} E [D_{2,m'}^2(\Omega) + D_{-2,m'}^2(\Omega)]\} A^{2,m'}, \quad (14)$$

where

$$A^{2,0} = \sqrt{6}(S_x^2 - \frac{1}{3}S^2), \quad (15a)$$

$$A^{2,\pm 1} = \mp(S_x S_{\pm} + S_{\pm} S_x), \quad (15b)$$

$$A^{2,\pm 2} = S_x^2.$$

Here  $D$  and  $E$  are the standard zero-field splitting parameters,  $\omega_0$  is the Larmor frequency for the triplet,  $\Omega$  represents the Euler angles for the transformation between molecular axes  $x', y', z'$  and space fixed axes  $(x, y, z)$ ,  $D_{lm}^L(\Omega)$  are the generalized spherical harmonics, and  $\Gamma_\Omega$  is the Markoffian operator for the rotational reorientation process. For isotropic reorientation, the eigenfunctions of  $\Gamma_\Omega$  and the  $D_{lm}^L(\Omega)$  with eigenvalues

$$E_{L,\kappa,M} = R B_L L(L+1), \quad (16)$$

with  $R$  the isotropic rotational diffusion coefficient and

$B_L$  a "model parameter," which is unity for Brownian reorientation, and at the other limit of strong jumps (leading to randomization of orientation with each molecular collision) one has  $B_L = R/E_{L,K,M}$  for  $L \neq 0$ . A whole range of jump models between these two cases may be treated in terms of the proper  $B_L$  as discussed elsewhere.<sup>3,9</sup>

The method of solution of Eq. (11b) is to expand  $\chi(s')$  in the complete orthogonal set  $\mathcal{D}_{KM}^L(\Omega)$  as

$$\chi(s') = -i \sum_{LKM} C_{KM}^L(s') \mathcal{D}_{KM}^L(\Omega). \quad (17)$$

Also, one can expand the initial condition (see below) as

$$\chi(t=0) = -i \sum_{LKM} d_{KM}^L \mathcal{D}_{KM}^L(\Omega). \quad (18)$$

One can rewrite Eq. (11b) as a matrix equation<sup>7</sup> by the use of Eqs. (17) and (18), and by taking spin matrix elements of  $C_{KM}^L$  and  $d_{KM}^L$  as described below. One has

$$\mathcal{A}\mathbf{C} = \mathbf{d}, \quad (19)$$

where  $\mathbf{C}$  is an  $n$ -dimensional column vector consisting of the expansion coefficients  $C_{KM}^L(i)$ , while  $\mathbf{d}$  is the  $n$ -dimensional column vector of  $d_{KM}^L(i)$ 's (see below) and  $\mathcal{A}$  is an  $n \times n$ -dimensional complex matrix, obtained from evaluating the operator coefficient of  $\chi(s')$  in Eq. (11b) in the standard manner.<sup>7,10</sup>

At this stage we note that for the  $\mathcal{H}(\Omega)$  of Eq. (10) and the  $\Gamma_\Omega$  with eigenvalues of Eq. (16),  $\mathcal{A}$  is formally *identical* to the matrix required to solve triplet slow-tumbling spectra when rf and dc fields are parallel, and this has already been given by Freed *et al.*<sup>7</sup> (one only requires  $i\omega \rightarrow s'$ ).

Next we note that for isotropic liquids, one wants the average  $\bar{\rho}(s')$  given by

$$\bar{\rho}(s') = \frac{1}{8\pi^2} \int d\Omega \rho(s') = -i C_{0,0}^0(s') + \frac{\frac{1}{2}(1 - \hbar\omega_0 S_z / k_B T)}{s'}, \quad (20)$$

where the second equality follows from Eqs. (12), (18), (11a), (5), and (14).

Also we note that the  $L, K, M$ th element of  $\mathbf{d}$  is given by

$$i \int d\Omega \rho(0) \mathcal{D}_{KM}^{L*}(\Omega) = d_{KM}^L. \quad (21)$$

Note that  $C_{KM}^L(s')$  is still a spin operator, and following the notation of Freed *et al.*<sup>7</sup> we let

$$\begin{aligned} \langle -|C|0 \rangle &= C(1), \quad \langle 0|C|-\rangle = C(-1), \quad \langle -1|C|-\rangle = C(a), \\ \langle 0|C|1 \rangle &= C(2), \quad \langle 1|C|0 \rangle = C(-2), \quad \langle 0|C|0 \rangle = C(b), \\ \langle -1|C|1 \rangle &= C(3), \quad \langle 1|C|-\rangle = C(-3), \quad \langle 1|C|1 \rangle = C(c), \end{aligned} \quad (22)$$

where we let  $C_{KM}^L(s', j) = C(j)$  for convenience. We may write equivalent expressions for the  $d_{KM}^L(i)$  or  $d(i)$ . Thus from Eqs. (3), (20), and (22) we must solve for

$$-i [C_{0,0}^0(a) - C_{0,0}^0(a)] + P_{\text{eq}}/k \quad (23a)$$

with

$$P_{\text{eq}} = \frac{2}{3} \hbar\omega_0 / k_B T. \quad (23b)$$

It is easy to show from the general properties of the expansion coefficients (cf. Ref. 7) that  $C_{0,0}^0(c)$  and  $C_{0,0}^0(a)$  are pure imaginary. Thus we obtain

$$P^\infty - (k_1/k) P_{\text{eq}} = k_1 \lim_{s \rightarrow h} \text{Im} [C_{0,0}^0(s, a) - C_{0,0}^0(s, c)]. \quad (24)$$

### A. Initial conditions

We now wish to evaluate the  $n$ -dimensional vector  $\mathbf{d}$  with elements given by Eq. (21). We note that just after a preferential intersystem crossing,  $\rho(0)$  is most conveniently described in the molecular frame. In general, we may write

$$\rho(0) = w_x |X'\rangle \langle X'| + w_y |Y'\rangle \langle Y'| + w_z |Z'\rangle \langle Z'|, \quad (25)$$

where  $|X'\rangle$ ,  $|Y'\rangle$ , and  $|Z'\rangle$  are the zero-field kets for the triplet in the molecular frame (i. e.,  $T_x$ ,  $T_y$ , and  $T_z$ ) and  $w_x$ ,  $w_y$ ,  $w_z$  are the preferential probabilities of populating these states by the intersystem crossing, such that

$$w_x + w_y + w_z = 1. \quad (26)$$

[Equation (25) neglects any coherence between the relative probabilities of populating the three triplet states; otherwise  $\rho(0)$  would have off-diagonal elements in the  $|X'\rangle$ ,  $|Y'\rangle$ ,  $|Z'\rangle$  representation.] If we let  $|m\rangle$ , where  $m = +1, 0$ , or  $-1$ , represent the high-field kets in the molecular frame, then we have

$$|\pm 1\rangle = (\mp 1/\sqrt{2}) [ |X'\rangle \pm i |Y'\rangle ] \quad (27)$$

and these kets are the irreducible tensor components.<sup>7</sup> The high-field kets in the molecular frame are transformed into the high-field kets in the lab frame  $|k\rangle$  according to

$$|m\rangle = \sum_k |k\rangle \mathcal{D}_{mk}^1(\Omega) \quad (28)$$

with the generalized spherical harmonics already discussed. Thus

$$|m\rangle \langle m'| = \sum_{k,k'} |k\rangle \langle k'| \mathcal{D}_{mk}^1(\Omega) \mathcal{D}_{m'k'}^1(\Omega) (-1)^{m'-k'} \quad (29)$$

and one may transform Eq. (25) for  $\rho(0)$  in the  $|X'\rangle$ ,  $|Y'\rangle$ ,  $|Z'\rangle$  basis set into the  $|k\rangle$  basis set. The matrix elements  $d_{KM}^L(i)$  according to the definitions analogous to Eq. (22) appear in Table I for an axially symmetric molecule (i. e.,  $K=0$ ). This case is sufficient if  $E=0$ . It is seen that the initial conditions corresponding to  $|X'\rangle$  or  $|Y'\rangle$  give identical results, since for  $E=0$  the choice of these molecular axes is arbitrary. Also they yield values for  $d_{0M}^L(i)$  which are  $(-\frac{1}{2})$  those for the initial condition of  $|Z'\rangle$ . Thus, it is sufficient to solve for the initial case of  $\rho(0) = |Z'\rangle \langle Z'|$  and multiply the result by  $r = [w_x - \frac{1}{2}(w_x + w_y)]$  to obtain the correct  $P^\infty$  for an arbitrary initial condition. Table I does not include contributions arising from  $\rho_{\text{eq}}$  of Eq. (5) via Eq. (7). An analysis of these terms in an analogous manner to those of Table I shows that

$$\rho_{\text{eq}}(L=2) = (D/2\omega_0) P_{\text{eq}} \rho(0; L=2, Z'), \quad (30)$$

where  $\rho(0; L=2, Z')$  gives the  $L=2$  contributions of Table I assuming the initial condition  $\rho(0) = |Z'\rangle \langle Z'|$ , while  $\rho_{\text{eq}}(L=2)$  refers only to the  $L=2$  contributions of  $\rho_{\text{eq}}$ . Also

$$\rho_{\text{eq}}(L=0) = \left[ \frac{1}{3} - \frac{1}{2} P_{\text{eq}} S_z \right] \quad (31)$$

[cf. Eq. (20)]. The effect of  $\rho_{\text{eq}}(L=2)$  can be included in a modified  $r$ , while the effect of  $\rho_{\text{eq}}(L=0)$  must be explicitly included to obtain the proper polarization effects resulting from the relaxation of the triplets to thermal equilibrium.

**B. Perturbation theory**

We now wish to solve Eq. (19) subject to the initial conditions of Table I, by a perturbation method valid for small enough  $D$ . It is clear from Eq. (24) that we only need  $C_{0,0}^0(a)$  and  $C_{0,0}^0(c)$ , which in lowest order in  $D$  are found to couple only to  $C_{0\mp 1}^2(\pm 1)$ ,  $C_{0\mp 1}^2(\pm 2)$ , and  $C_{0,\mp 2}^2(-3)$  from Eqs. (24) of Ref. 7. One can then solve the problem by conventional perturbation schemes. However, in zero order,  $C_{0,0}^0(a)$  and  $C_{0,0}^0(c)$  are "degenerate" with  $C_{0,0}^0(b)$ , so degenerate perturbation theory is called for with a van Vleck-type transformation being appropriate.<sup>10,11</sup> Furthermore, Eqs. (24) of Ref. 7 are not symmetric, but can be made so by a simple symmetrizing transformation [after first multiplying through those expressions by the factor  $(2L+1)$ ].

We can summarize the procedure by introducing three transformations:  $U$ ,  $T$ , and  $P$  such that Eq. (19) becomes

$$(PTU\alpha U^{-1}T^{-1}P^{-1})(PTUC) = (PTUd) \quad (32)$$

or

$$\alpha'''C''' = d''''.$$

Here  $U$  is the orthogonal transformation which transforms the  $C_{0,0}^0(i)$  for  $i=a, b$ , and  $c$  into their "normal modes" of relaxation. It is given by the partitioned matrix

$$U = \begin{pmatrix} \mathbf{u} & 0 \\ 0 & \mathbf{1} \end{pmatrix}, \quad (33a)$$

where

$$\mathbf{u} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{6}} & -\frac{2}{\sqrt{6}} & \frac{1}{\sqrt{6}} \end{pmatrix} \quad (33b)$$

and  $\mathbf{1}$  is the six-dimensional unit matrix in the subspace spanned by the six needed  $C_{M,0}^2(i)$  terms. The second normal mode is  $(1/\sqrt{2})[C_{0,0}^0(a) - C_{0,0}^0(c)]$ , which appears in Eq. (24).  $T$  is the symmetrizing transformation, a  $9 \times 9$  diagonal matrix with the first three elements equal to unity and the next six equal to  $\sqrt{5}$ . Then  $P$  is the van Vleck-type matrix which diagonalizes  $\alpha'' = TU\alpha U^{-1}T^{-1}$  to lowest order in  $D$ . Once this approximate diagonalization is achieved, then one solves for  $(1/\sqrt{2})[C_{0,0}^0(a) - C_{0,0}^0(c)]$ .

The final result of the perturbation analysis yields

$$\frac{P'{}^\infty}{r} = \frac{4D}{15} \left( \frac{k_1}{k} \right) \left\{ \frac{\omega_0}{\omega_0^2 + \tau_R^{-2}} \left[ \frac{k}{k + T_1^{-1}} - \frac{(k + 2\tau_R^{-1})k}{\omega_0^2 + (k + \tau_R^{-1})^2} \right] \right\}$$

$$+ \frac{4\omega_0}{4\omega_0^2 + \tau_R^{-2}} \left[ \frac{k}{k + T_1^{-1}} - \frac{(k + 2\tau_R^{-1})k}{4\omega_0^2 + (k + \tau_R^{-1})^2} \right] \Bigg\}, \quad (34)$$

where

$$r = w_x - \frac{1}{2}(w_x + w_y) - (D/2\omega_0)P_{\text{eq}}, \quad (35)$$

$$T_1^{-1} = \frac{2}{15} D^2 \left[ \frac{\tau_R^{-1}}{\omega_0^2 + \tau_R^{-2}} + \frac{4\tau_R^{-1}}{(2\omega_0)^2 + \tau_R^{-2}} \right], \quad (36)$$

and

$$P'{}^\infty = P'{}^\infty + \frac{k_1}{k} \left( \frac{T_1^{-1}}{k + T_1^{-1}} \right) P_{\text{eq}}. \quad (37)$$

(We will generally use  $P'{}^\infty$  to represent that part of the polarization which is independent of  $P_{\text{eq}}$  terms.) Also the validity of the analysis requires

$$D^2 \ll \omega_0^2 + \tau_R^{-2}. \quad (38)$$

Note that the  $T_1$  of Eq. (36) is the well-known result for triplets, but its validity in the present derivation requires only that Eq. (38) be fulfilled. In the limits

$$\omega_0 \gg T_R^{-1} \gg k \gg T_1^{-1} \cong \frac{4}{15} \frac{D^2}{\omega_0^2} \tau_R^{-1} \quad (39)$$

one has the simple result

$$\frac{P'{}^\infty}{r} = \frac{8D}{15\omega_0} \frac{k_1}{k}, \quad (40)$$

which is seen to be equivalent to the perturbation result of Wong *et al.* (for  $k_1 \gg k_2$ ) wherein the dynamical features are unimportant.<sup>4,12</sup> It immediately indicates that substantial polarizations can be generated in that limit. The positive (negative) sign in Eqs. (37) or (34) indicates absorptive (emissive) polarizations. Another, less restrictive, limit of Eq. (38) as well as

$$k \ll \tau_R^{-1} \quad (41)$$

leads to

$$P'{}^\infty = A \frac{k}{k + T_1^{-1}} \frac{k_1}{k}, \quad (42a)$$

$$A = \frac{4D}{15} \left( \frac{\omega_0}{\omega_0^2 + \tau_R^{-2}} + \frac{4\omega_0}{4\omega_0^2 + \tau_R^{-2}} \right) r, \quad (42b)$$

TABLE I. Coefficients  $d_{KM}^L(i)$  representing the initial triplet populations for an axially symmetric zero-field splitting.

Coefficient	$\rho(0) =  Z'\rangle\langle Z' $		$\rho(0) =  X'\rangle\langle X' $ or $ Y'\rangle\langle Y' $	
	$L=0$	$L=2$	$L=0$	$L=2$
$d_{00}^L(a)$	1/3	-1/15	1/3	1/30
$d_{00}^L(b)$	1/3	2/15	1/3	-1/15
$d_{00}^L(c)$	1/3	-1/15	1/3	1/30
$d_{0,-1}^L(1)$	0	1/5√3	0	-1/10√3
$d_{0,-1}^L(2)$	0	-1/5√3	0	+1/10√3
$d_{0,-2}^L(3)$	0	-√2/5√3	0	1/5√6
$d_{0,1}^L(-1)$	0	1/5√3	0	1/10√3
$d_{0,1}^L(-2)$	0	1/5√3	0	-1/10√3
$d_{0,2}^L(-3)$	0	-√2/5√3	0	1/5√6

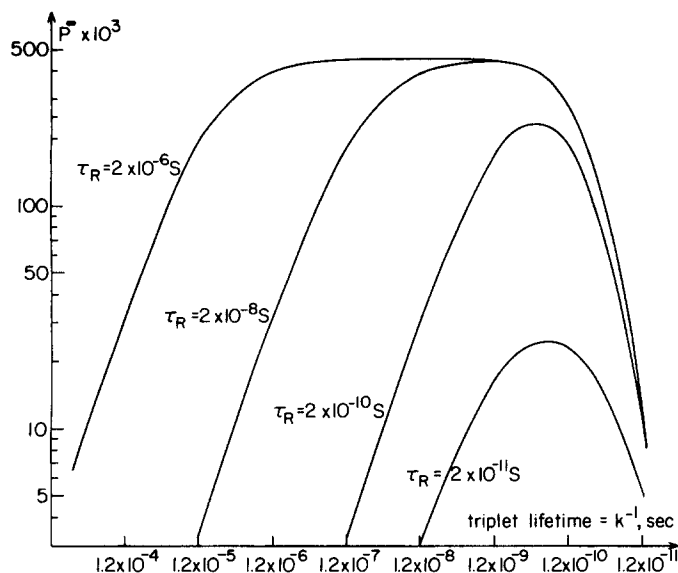


FIG. 1. Graph of  $P^\infty$  vs triplet lifetime  $= k^{-1}$  for different values of  $\tau_R$ , the rotational correlation time. The zero-field splitting  $D=3000$  G, while  $\omega_0=3000$  G. It is assumed that  $k=k_1$ ; for  $k \neq k_1$  the results for  $P^\infty$  should be multiplied by  $k_1/k$ . The initial condition  $\rho(0) = |Z\rangle\langle Z|$  is assumed, so in general the results should be multiplied with  $\gamma$  defined by Eq. (35). The results given do not include any contributions from  $P_{\text{eq}}$  [i.e., they are rigorously the  $P^\infty$  values, [e.g., Eq. (37)]]].

which is equivalent to a phenomenological expression used by Atkins *et al.*<sup>6</sup> if we let  $k=k_1$ , but they let  $A$  be purely an experimentally adjustable parameter and offer no microscopic expression. It is clear that inequality Eq. (41) [as well as Eq. (38)] must be fulfilled in order to justify their analysis. Equation (42a) again demonstrates how large polarizations may be generated provided  $k_1$  is not too much smaller than  $T_1^{-1}$ .

The dependence of  $P^\infty$  upon  $k_1$  given in Eq. (34) is an interesting one. It is seen that  $P^\infty$  goes to zero both for very small and very large values of  $k_1$ . That it goes to zero for small  $k_1$  follows because any initial polarization is quenched by the  $T_1$  process before the triplet reacts to give a radical pair. That it goes to zero for large  $k_1$  represents the fact that the initial population difference ( $\rho_{T_+T_-} - \rho_{T_+T_+}$ ) immediately after a preferential intersystem crossing is zero since only the isotropic contributions to  $\rho(0)$  are important [cf. Eq. (20)]. The polarization is generated only in times of the order of  $\tau_R$ , as the rotational averaging effectively mixes in the anisotropic contributions from  $\rho(0)$  into the polarization (which is an isotropic average over all orientations).

The contribution of  $P_{\text{eq}}$  in Eq. (37) represents the competition between the triplet decomposition process and the  $T_1$  process, going to zero for  $k \gg T_1^{-1}$  and  $(k_1/k)P_{\text{eq}}$  for  $T_1^{-1} \gg k$ .

We have compared Eq. (34) with the complete computer solutions, and we have found as a practical guide that it gives an adequate representation (to within 10% or better) provided

$$D^2 \leq \frac{1}{2} [\omega_0^2 + \tau_R^{-2}]. \quad (38')$$

We illustrate the cases for large  $D=3000$  G both for

large and small  $\omega_0$  in Figs. 1 and 2 for Brownian motion ( $B_L=1$ ). The results for  $\omega_0=3000$  G, are generally in good agreement with Eq. (34), but for  $\omega_0=1000$  G, it is found that Eq. (34) breaks down. (These results may be scaled with the dimensionless parameters:  $\omega_0/D$ ,  $\tau_R^{-1}/D$ , and  $k/D$ ). It is clearly seen from these figures that limiting values of  $P^\infty$  as high as  $450 \times 10^{-3}$  can be predicted for a range of  $k/D$  values and slow tumbling (while  $P_{\text{eq}} \sim 10^{-3}$ ). More rapid tumbling acts to decrease  $P^\infty$ . When the tumbling is slow, substantial deviations are found between the exact solution and Eq. (34) for  $\omega_0/D < 1$ . Equation (34) tends to overestimate  $P^\infty$  in this case. In the slow-tumbling limit, one does not necessarily recover results for  $P^\infty$  that are insensitive to the dynamics, since there is still competition between  $k_1$  and  $T_1$ -type processes, the latter being dependent on the rate of rotational reorientation. Of course, such conclusions will be altered if other types of processes begin to be important in  $T_1$ . [In particular, one may add these extra contributions directly to Eq. (36).]

When the tumbling is fast, Eq. (34) can even yield the wrong sign compared to the exact solution. In those cases, and when Eq. (41) applies, then Eq. (42) gives more satisfactory agreement than Eq. (34).

Note that once the radical pair is formed with initial polarization given by Eq. (24), then the radical-pair mechanism discussed in detail in I and II can become effective, so that the total final polarization  $P^\infty$ , when the radical pair separates never to reencounter, is given for radical  $a$  by

$$P_a^\infty = \lim_{t \rightarrow \infty} [\rho_{T_+T_-}(t) - \rho_{T_+T_+}(t) - 2\text{Re}\rho_{ST_0}(t)],$$

where in high fields compared to hyperfine terms the

$$\lim_{t \rightarrow \infty} (\rho_{T_+T_-} - \rho_{T_+T_+})$$

is obtained from the initial polarization, as discussed here, and  $2\text{Re}\rho_{ST_0}$  is obtained from the radical-pair

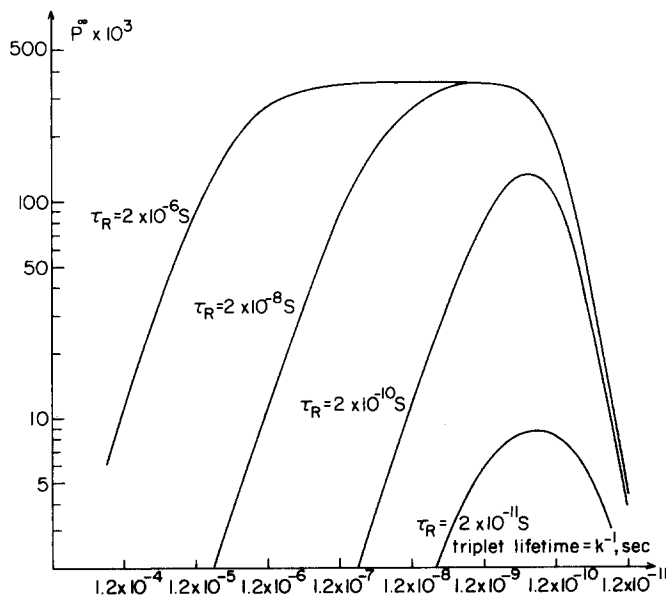


FIG. 2. Same as Fig. 1 but with  $\omega_0=1000$  G.

mechanism as discussed in I and II. The kinetic discussions of observed CIDEP intensities given in I and Ref. 13 are still applicable with  $P_a^\infty \rightarrow P_a^\infty(I)$ .<sup>14</sup>

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<sup>1</sup>J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 58, 2746 (1973). Referred to as Paper I.

<sup>2</sup>J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 59, 2869 (1973). Referred to as Paper II.

<sup>3</sup>For recent reviews see, e.g., J. H. Freed, *Ann. Rev. Phys. Chem.* 23, 265 (1972); J. K. S. Wan, S. K. Wong, and D. A. Hutchinson, *Acc. Chem. Res.* 7, 58 (1974).

<sup>4</sup>S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *J. Chem. Phys.* 58, 985 (1973).

<sup>5</sup>S. K. Wong and J. K. S. Wan, *J. Am. Chem. Soc.* 94, 7197 (1972); S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *ibid.* 95, 622 (1973); *Can. J. Chem.* 52, 251 (1974).

<sup>6</sup>P. W. Atkins *et al.*, *Mol. Phys.* 27, 769 (1974).

<sup>7</sup>J. H. Freed, G. V. Bruno, and C. Polnaszek, *J. Chem. Phys.* 55, 5270 (1971). The  $D_{KM}^{\pm}(\Omega)$  utilized are in the notation of J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* 39, 326 (1963).

<sup>8</sup>D. Kivelson, *J. Chem. Phys.* 33, 1094 (1960); A. D. McLachlan, *Proc. R. Soc. A* 280, 271 (1964).

<sup>9</sup>S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.* 56, 716 (1972).

<sup>10</sup>J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Phys. Chem.* 75, 3385 (1971).

<sup>11</sup>J. H. Freed, *J. Phys. Chem.* 78, 1155 (1974).

<sup>12</sup>This expression is consistent with Eq. (10) of Wong *et al.* for the populations of the triplet levels. There is an unwarranted factor of 2/3 in Eq. (12) of Wong *et al.* relating the spin populations of one of the radicals to those of the original triplet. The correct relationship has been given in I, and may be written as  $P_{\pm a} = \rho_{\pm a, \pm b} + \rho_{\pm a, \mp b}$  or  $P_{+a} = \rho_{T+T_0} + \frac{1}{2}(\rho_{S,S} + \rho_{T_0,T_0}) + \text{Re}\rho_{S,T_0}$ ,  $P_{-a} = \rho_{T-T_0} + \frac{1}{2}(\rho_{S,S} + \rho_{T_0,T_0}) - \text{Re}\rho_{S,T_0}$ . In the present case of a pure triplet  $\rho_{S,S} = \rho_{S,T_0} = 0$ . This unwarranted factor, however, is cancelled out in their Eq. (16). Note also that  $D$  used by Wong *et al.* is 1/3 the  $D$  used here.

<sup>13</sup>J. B. Pedersen, *J. Chem. Phys.* 59, 2656 (1973).

<sup>14</sup>Recently P. W. Atkins and G. T. Evans [*Chem. Phys. Lett.* 25, 108 (1974) and *Mol. Phys.* 27, 1633 (1974)] have worked out a solution to the dynamical problem of Wong *et al.*'s static model. Their method, which is different from that utilized here, is applicable only in the limit when "slow tumbling" effects are unimportant; whereas our complete analysis has explicitly included such effects. Thus their results are to be compared with our analytic results obtained by perturbation theory, cf. Eq. (34). This result is very similar to their result [Eq. (4.9)], but the small differences may be shown to be due to the inclusion of some incipient slow tumbling effects into our perturbation analysis, and are thus not important in the region where slow tumbling corrections are negligible. We wish to thank the referee for calling their work to our attention.