Chemically Induced Dynamic Nuclear Polarization

VI. Kinetic Formulation of the Radical Pair Mechanism[1]

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NMR emission and enhanced absorption of products of radical reactions (CIDNP) is explained by nuclear spin dependent adiabatic transitions between singlet and triplet states of transient radical pairs. In magnetic fields larger than about 1 kG only $S-T_0$-transitions contribute to nuclear polarization. From a kinetic formulation of the pair mechanism equations for quantitative calculations of CIDNP patterns are derived.

1. Introduction

After the discovery[1a, 2a] of NMR emission and enhanced absorption of reaction products during radical reactions, the so-called chemically induced dynamic nuclear polarization (CIDNP) phenomenon evidence against its explanation by dynamic polarization in free radicals[1b, 2b] was soon accumulating. The experimental observations[1–12] and chemical arguments[13] strongly indicate that the effects are caused by interactions in radical pairs which appear in free radical formation and destruction steps. On this basis quantitative theories explaining CIDNP have first been developed by CLOSS[5] and by KAPTEIN and OOSTERHOFF[14]. They have been applied successfully for the interpretation of CIDNP spectra[5], and can in fact also explain polarizations during aroyl peroxide decompositions[15] which were hitherto thought to support the original model[1]. Modifications and extensions of the Closs-Kaptein radical pair mechanism have also been proposed[16–18].

In this paper a simple kinetic formulation of the radical pair mechanism is presented. An accompanying paper applies the results to CIDNP of reaction products of some independently generated alkyl radicals[1f]. We attribute nuclear polarizations to

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adiabatic transitions between the non-adiabatic singlet and triplet states of radical pairs caused by pair geometry fluctuations. Our treatment differs from previous ones [5, 14, 16, 17] only in a formal sense, since these may also be regarded as descriptions of adiabatic models, some of our equations we think however particularly useful for quantitative CIDNP explanations. Many of our results agree with Glarum's recent theory [18].

2. Adiabatic Transitions and Rate Equations

Two radicals of distance R interact by coulomb, exchange (J) and magnetic dipole forces between the unpaired electrons. The electronic states of the pair are pure singlet (S) and triplet (T_σ, $\sigma = +, 0, -$) states for small R, for instance if $R < 5$ Å for a pair of hydrogen atoms [19]. For larger values of R the triplet states T_σ are mixed by the magnetic electron dipole interactions (D), S and T-states are mixed by the electron-nuclear hyperfine interactions within the individual radicals (a) and by the difference of the electron Zeeman interactions (ω_S) of the radical electrons in magnetic fields. Since the hyperfine interaction energies depend on the nuclear spin configurations of the radicals the mixing will be nuclear spin dependent and provides selective state populations. In general, the mixing becomes important in regions of R where the pure states cross or approach one another. In Fig. 1 the energies of the states of a radical pair in a magnetic field are sketched very schematically for a hypothetical nuclear spin state. Mixing within the T-manifold is neglected; analogous to the pair $H\cdot\ \cdot H$ the energy of S shall be lower than the energies of T_σ for small R [19]. For $J \approx \omega_\mathrm{S}$ the pure states S and T_- (dotted curves) cross and for $J \leqq a$ S and T_0 approach.

For a radical pair in solution (CIDNP has so far been observed in solutions only) R varies with time. If $\mathrm{d}R/\mathrm{d}t = \dot{R} \approx 0$ the pair states are the eigenstates of the complete Hamiltonian for all times and can be calculated from this Hamiltonian [17a, 19]. In Fig. 1a pair prepared in S for small R then transforms with increasing R to a pair with state $\beta\beta \triangleq \mathrm{T}_-$ by adiabatic transitions in the region $J \approx \omega_\mathrm{S}$ [20]. The transition probability for these adiabatic transitions is $P_{ij_\sigma} = 1$, where i, j_σ denote the electron-nuclear spin states. On the other hand, if $\dot{R} \approx \infty$ a prepared state is conserved ($P_{ij_\sigma} = 0$). In a real system we will have $0 < P_{ij_\sigma} \ll 1$ and we may calculate P_{ij_σ} from the matrix-element describing the mixing and from the time which is spent in the mixing region (see below).

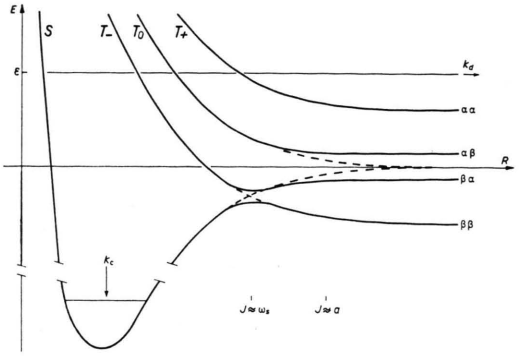

Fig. 1. Schematic representation of the energies of the electron states of a radical pair for a hypothetical nuclear spin configuration. k_c denotes internal conversion to a discrete product state, k_d escape from the region of interaction.

The diffusive behaviour of reactive molecular pairs has been treated by several authors [21]. We shall use their results in the following simplified manner: It seems probable that a pair starting at small R undergoes several transitions ($n_\mathrm{c} \approx 1 \dots 10^2$) [21c] through the mixing regions before the final steps of reaction or escape from the regions of interaction occur. From this picture of pair librations in a solvent cage the probability of finding a pair in a prepared initial state after n_c librations becomes

$$P^{\mathrm{tot}}_{ij_\sigma} = 1 - 2\, n_\mathrm{c}\, P_{ij_\sigma}\, (1 - P_{ij_\sigma}) \approx 1 - 2\, n_\mathrm{c}\, P_{ij_\sigma}\, .$$

The kinetic formulation of the radical pair mechanism easily arises from these considerations. A radical pair $R\cdot\ \cdot R'$ with Λ nuclear spins λ belonging

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to $R\cdot$ and Λ' nuclear spins λ' belonging to $\cdot R'$ has

$$n = \prod_{\lambda}^{\Lambda} (2\,I_\lambda + 1) \prod_{\lambda'}^{\Lambda'} (2\,I_{\lambda'} + 1)$$

singlet states $i = |\,S, m_1 \ldots m_\lambda \ldots, m_{1'} \ldots m_{\lambda'} \ldots >$ and an equal number of triplet states

$$j_\sigma = |\,T_\sigma, m_1 \ldots m_\lambda \ldots, m_{1'} \ldots m_{\lambda'} \ldots > .$$

Adiabatic transitions between i and j_σ occur with rate constants $k_{ij_\sigma} = -\dot{P}^{\text{tot}}_{ij_\sigma}$ and $k_{j_\sigma i}$ respectively, during the lifetime of the pair. Escape is described by a common formal rate constant $k_\text{d} = k_{\text{d}i} = k_{\text{d}j_\sigma}$, reaction to a product by a formal rate constant k_c. Reaction shall be possible only from S-states, thus $k_{\text{c}i} = k_\text{c}$, $k_{\text{c}j_\sigma} = 0$. Transitions within the triplet manifold are neglected. As will be seen below, this approximation restricts our treatment to high magnetic fields. The rate equations for the populations of the pure states then become

$$\dot{N}_i = r_i - \Big(k_\text{c} + k_\text{d} + \sum_\sigma \sum_j k_{ij_\sigma}\Big) N_i + \sum_\sigma \sum_j k_{j_\sigma i} N_{j_\sigma}, \tag{1}$$

$$\dot{N}_{j_\sigma} = r_{j_\sigma} - \Big(k_\text{d} + \sum_i k_{j_\sigma i}\Big) N_{j_\sigma} + \sum_i k_{ij_\sigma} N_i \tag{2}$$

where r_i and r_{j_σ} are the pair production rates. From the pairs the products are formed in nuclear spin states i with

$$\dot{M}_i = k_\text{c} N_i\,, \tag{3}$$

pairs of free radicals with the same nuclear spin states by

$$\dot{R}_{\text{p}i} = k_\text{d} \Big(N_i + \sum_\sigma N_{i_\sigma}\Big). \tag{4}$$

For times corresponding to negligible thermal polarizations of the product the enhancement factor of a NMR-transition $i \to i'$ $(E_{i'} > E_i)$ of the product is given by [5]

$$V_{ii'} = \frac{\dot{M}_i - \dot{M}_{i'}}{\dot{M}_i + \dot{M}_{i'}} \cdot \frac{1}{\langle I_{ii'} \rangle_0} \tag{5}$$

where $\langle I_{ii'} \rangle_0$ is the relative population difference of i and i' in thermal equilibrium. Similarly enhancement factors can be defined for the NMR-transitions of the products of reactions of the escaping radicals. For k_{ij_σ}, $k_{j_\sigma i} \ll k_\text{d}$, k_c approximate solutions of (1) and (2) are easily derived. We shall, however, treat here the complete solutions for a simple illustrative and important case. The state populations of the pairs shall be time independent, and one singlet state i shall mix with only one triplet state j_ϱ. Then

$$N_i = \frac{1}{k_\text{c} + k_\text{d}} \left\{ r_i + r_{j_\varrho} \cdot \frac{W_{j_\varrho i}}{1 + W_{j_\varrho i}} \right\} \cdot \left\{ 1 + \frac{k_\text{d}}{k_\text{c} + k_\text{d}} \cdot \frac{W_{ij_\varrho}}{1 + W_{j_\varrho i}} \right\}^{-1} \tag{6}$$

$$N_{j_\varrho} = \frac{1}{k_\text{d}} \left(r_i + r_{j_\varrho i} - (k_\text{c} + k_\text{d}) N_i \right) \tag{7}$$

where $W_{j_\varrho i} = k_{j_\sigma i}/k_\text{d}$.

For subcase $\underline{A}$ we will further assume a conservation of the nuclear spin configuration during a transition, i.e. $j = i$ and the operator mixing S and T to be hermitian, i.e. $k_{j_\sigma i} = k_{ij_\sigma}$. This case corresponds to S-T$_0$-transitions when anisotropic interactions are neglected (Section 3).

The pairs may now be formed a) from the decomposition of singlet precursor molecules, b) from triplet precursor molecules, and c) from diffusive encounters of free radicals. To specify (6) for these modes of pair formation we introduce r as total pair production rate, neglect the small initial nuclear polarizations of the precursor molecules [a), b)] and initial nuclear polarizations of the free radicals [c)], thus

$r_i = r/n$, $r_{i_\varrho} = 0$ for mode a),
$r_i = 0$; $r_{i_\varrho} = r/3\,n$ for mode b),
$r_i = r_{i_\varrho} = r/4\,n$ for mode c),

and arrive at

$$N_i = \frac{r/n}{k_\text{c} + k_\text{d}} \, \frac{1}{1 + \dfrac{k_\text{d}}{k_\text{d} + k_\text{c}} \, \dfrac{W_{ii_\varrho}}{1 + W_{ii_\varrho}}} \tag{8}$$

(singlet precursor),

$$N_i = \frac{r/3n}{k_\text{c} + k_\text{d}} \, \frac{\dfrac{W_{ii_\varrho}}{1 + W_{ii_\varrho}}}{1 + \dfrac{k_\text{d}}{k_\text{d} + k_\text{c}} \cdot \dfrac{W_{ii_\varrho}}{1 + W_{ii_\varrho}}} \tag{9}$$

(triplet precursor),

$$N_i = \frac{r/4n}{k_\text{c} + k_\text{d}} \left\{ 1 + \frac{k_\text{c}}{k_\text{c} + k_\text{d}} \, \frac{\dfrac{W_{ii_\varrho}}{1 + W_{ii_\varrho}}}{1 + \dfrac{k_\text{d}}{k_\text{c} + k_\text{d}} \, \dfrac{W_{ii_\varrho}}{1 + W_{ii_\varrho}}} \right\}$$

(radical encounter). (10)

From (4) we further obtain

$$\dot{R}_{pi} = r_i + \sum_\sigma r_{i_\sigma} - \dot{M}_i\,. \tag{11}$$

Equations (8) to (11), (3) and (5) immediately give the following rules for CIDNP in subcase A:

A) 1. The enhancement factor of a NMR transition of a pair reaction product and the enhancement factor of the corresponding transition of a product derived from the radicals escaping that cage are of opposite signs.

A) 2. The enhancement factor of a NMR transition of a reaction product derived from a pair with singlet precursor and the enhancement factor of the same transition of the same reaction product derived from pairs with triplet precursors or free radical precursors are of opposite signs.

A) 3. For equal product formation rates the amplitude of the enhancement factor of a NMR transition is smaller for products derived from free radical encounters than for products derived from triplet precursor pairs.

A) 4. No CIDNP effects can be observed if there is no product formation from the pair ($k_c = 0$) or if there is no pair escape ($k_d = 0$), Further, no CIDNP arises if $k_{ii_\varrho} = 0$ (a trivial result) or if $k_{ii_\varrho} \gg k_d$.

These rules have, at least in part, been formulated previously [5, 14, 16–18]. They are strongly supported by the experimental results [1–12].

Similar rules can be stated for a second subcase $\underline{B}$ in which the nuclear spin configuration is *not* conserved ($j \neq i$). For simplicity one singlet state i shall mix with only one triplet state j_σ, the corresponding triplet state i_σ shall not mix with singlet states. Glarum has shown [18] that this case corresponds to S-T₋-transitions caused by isotropic hyperfine interaction of a single nucleus. From (4)

$$\dot{R}p_i = \sum_\sigma r_{i_\varrho} + (k_d/k_c)\,\dot{M}_i \tag{12}$$

and, in contrast to subcase $\underline{A}$:

B) 1. The enhancement factor of a NMR transition of a pair reaction product and the enhancement factor of the corresponding transition of a product derived from the radicals escaping that cage are of like signs.

The relative signs and amplitudes of the enhancement factors of products derived from pairs with singlet, triplet or free radical precursors are given by A) 2. and A) 3. in this case also, but the rule corresponding to A) 4. now reads:

B) 4. No CIDNP effects are observed if $k_d = 0$, $k_{ij_\sigma} = 0$, but there is a maximum polarization if no product formation occurs ($k_c = 0$).

Rules for subcase $\underline{B}$ have also been derived by Glarum [18], however, we are not aware of any CIDNP result which has to be explained by these rules.

3. The Rate Constants k_{ij_σ}

The results of the last section were obtained without detailed consideration of the rate constants k_{ij_σ} for intersystem crossing and follow from the rate equations as consequence of spin balancing. The absolute signs and amplitudes of the CIDNP effects are determined by k_{ij_σ}, however, therefore this quantity has to be discussed now.

We do not aim at a rigorous derivation. This will be difficult because it requires a complete analytical description of the diffusive behaviour of the pair $R(t)$. Instead we apply an approximation based on the transition probability between continuum states obtained by Coulson and Zalewski [22] who used a quasi-classical description of translational motions.

$$2\,P_{ij_\sigma} = 1 - \exp\left\{ - \frac{2/v^2\,|\int \Omega_{ij_\sigma}\,\mathrm{d}R|^2}{1 + \frac{1}{v^2}\,|\Omega_{ij_\sigma}\,\mathrm{d}R|^2} \right\}. \tag{13}$$

Ω_{ij_σ} is the matrix element of the electronic part of the Hamiltonian between states i and j_σ in angular frequency units and $v_i \approx v_{j_\sigma} \approx v$ are the classical velocities $\dot{R}$ in these states. Since the adiabatic transitions will occur in specific regions of R of width ΔR we approximate

$$|\int \Omega_{ij_\sigma}\,\mathrm{d}R|^2 \approx |\Omega_{ij_\sigma}|^2\,\Delta R^2.$$

For typical hydrocarbon radicals $|\Omega_{ij_\sigma}| \approx |a| \approx 10^8$ rad/sec [23]. For thermal velocities $v \approx 10^{11}$ to 10^{12} Å/sec and a width ΔR of the order of one Ångstrom, we notice from (13) $P_{ij_\sigma} \ll 1$, and arrive at the rather crude approximation for k_{ij_σ}

$$\begin{aligned} k_{ij_\sigma} = \dot{P}^{\mathrm{tot}}_{ij_\sigma} &\approx (k_c + k_d)\cdot 2\,n_c \cdot P_{ij_\sigma} \\ &= 2\,n_c\,(k_c + k_d)\,\frac{\Delta R^2}{v^2}\,|\Omega_{ij_\sigma}|^2 \end{aligned} \tag{14}$$

where $\tau^{-1} \approx k_c + k_d$ is the total lifetime of the pair and $\Delta R/v$ is the time the system spends in the mixing region during one transition. (14) is very similar to the formulas used by others [5, 14, 16, 18] for the quantity driving the singlet triplet transitions. It is proportional to the square of the matrix element and to a dynamic factor which depends on

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the model used for $R(t)$ or $J(t)$. In KAPTEIN's treatment[14] $\Delta R/v$ is identified with the total lifetime of the pair.

If $J(R)$ is known we may express ΔR in terms of the variation ΔJ in the mixing region. An exponential dependence $J = J_0 \exp\{-R/R_0\}$ seems realistic[19], thus $|\Delta R| = R_0 |\Delta J| / J_{\mathrm{M}}$ where J_{M} is the value of J in the mixing region. Now, the energy splitting of the mixing states is $|\Delta J| \approx |\Omega_{ij_\sigma}|$[20], thus

$$|\Delta R| \approx R_0 \frac{|\Omega_{ij_\sigma}|}{J_{\mathrm{M}}} \tag{15}$$

From (14) and (15) the importance of the various transitions between S and T_0, T_+ and T_- states may be estimated: In magnetic fields satisfying $\omega_{\mathrm{S}} \gg |\Omega_{ij_\sigma}|$ S-T_0-transitions lead to much larger values of k_{ij_σ} than S-T_- or S-T_+-transitions since for S-T_0 $J_{\mathrm{M}} \approx |\Omega_{ij_\sigma}| \approx |a|$, for S-$\mathrm{T}_-$ $J_{\mathrm{M}} \approx \omega_{\mathrm{S}}$ and for S-T_+ $J_{\mathrm{M}} \approx \infty$ (see Fig. 1). Therefore, in sufficiently high magnetic fields it will be essentially the S-T_0-transitions which cause nuclear polarizations. In low magnetic fields ($\omega_{\mathrm{S}} \ll |\Omega_{ij_\sigma}|$) $J_{\mathrm{M}} \approx |\Omega_{ij_\sigma}|$ for all transitions S-T_σ. In this case mixing of S with T_-, T_0, and T_+ become of equal importance.

We will restrict our treatment to the high field case in the following. In fact, most of the experimental results[1–12] on CIDNP were obtained with high fields, though some low field results have been reported[1,2].

For the evaluation of Ω_{ij_σ} we use the spin Hamiltonian[5,14,16–18]

$$\begin{aligned}\hbar^{-1}\mathscr{H} = {} & (\omega_{\mathrm{S}} S_z + \omega_{\mathrm{S}'} S_{z'}) + J/2 \cdot (1 + 4\,S S') \\ & + S\boldsymbol{D}S' + \sum_{\lambda} a_\lambda S I_\lambda + \sum_{\lambda'} a_{\lambda'} S' I_{\lambda'} \\ & + \sum_{\lambda} S\,\boldsymbol{t}_\lambda I_\lambda + \sum_{\lambda'} S'\,\boldsymbol{t}_{\lambda'} I_{\lambda'}\end{aligned} \tag{16}$$

where $\omega_{\mathrm{S}} = \hbar^{-1} g \beta H_0$. g-factor anisotropies, nuclear Zeeman and internuclear interactions are neglected. The basis functions i and j_σ are applied. In general they are mixed by all terms in (16) except the exchange interaction operator. The dipol-dipol term $\boldsymbol{D}$ in particular mixes within the triplet manifold. We may neglect $\boldsymbol{D}$ if the elements D_{kl} are small compared to $(\omega_{\mathrm{S}} + \omega_{\mathrm{S}'})/2$ or to J. Assuming the distance of level crossings or approaches R to be $R > 5$ Å as for the pair $H\cdot \cdot H$[19] the familiar formulas for D_{kl} yield $D_{kl} \ll (\omega_{\mathrm{S}} + \omega_{\mathrm{S}'})/2$ if H_0 is larger than a few hundred gauss. Since we wish to restrict our treatment to the high field case $\boldsymbol{D}$ may in fact be neglected. In this field region the condition $\omega_{\mathrm{S}} \gg |\Omega_{ij_\sigma}|$ is also fulfilled and thus the S-T_0-transitions are the only ones important. It has to be pointed out further that for $R > 5$ Å the parameters a_λ and t_{kl_λ} may be identified without any ambiguity as the hyperfine interaction parameters of the free non-interacting radicals. This may not hold for smaller values of R[19].

It is easily seen that an operator mixing S and T_0 states should have the form $(S_z - S_{z'})\,C$ where C is an operator not containing electron spin operators. Truncating $\mathscr{H}$ to this form we obtain

$$\begin{aligned}\hbar^{-1}\mathscr{H}_{\mathrm{tr}} = {} & (S_z - S_z')\tfrac{1}{2}\{\omega_{\mathrm{S}} - \omega_s' + \sum_{\lambda} a_\lambda I_{z\lambda} \\ & - \sum_{\lambda'} a_{\lambda'} I_{z\lambda'} + \sum_{\lambda} f_\lambda^z I_{z\lambda} - \sum_{\lambda'} f_{\lambda'}^z I_{z\lambda'}\} \\ & + (S_z - S_z')\tfrac{1}{2}\{\sum_{\lambda} f_\lambda^+ I_{+\lambda} - \sum_{\lambda'} f_{\lambda'}^+ I_{+\lambda'}\} \\ & + (S_z - S_z')\tfrac{1}{2}\{\sum_{\lambda} f_\lambda^- I_{-\lambda} - \sum_{\lambda'} f_{\lambda'}^- I_{-\lambda'}\}\end{aligned} \tag{17}$$

where

$$\begin{aligned} f_\lambda^z = {} & \tfrac{1}{2}\{t_{\xi\lambda}(3\cos^2\beta_\lambda - 1) \\ & - (t_{\xi\lambda} - t_{\eta\lambda})\sin^2\beta_\lambda \cos 2\gamma_\lambda\} \\ f_\lambda^+ = {} & (f_\lambda^-)^* = \tfrac{1}{4}\{(t\zeta_\lambda - t_{\eta\lambda})(\sin 2\gamma_\lambda + i\cos\beta_\lambda \cos 2\gamma_\lambda) \\ & + 3\,i\,t\zeta_\lambda \cos\sigma_\lambda\}\sin\beta_\lambda\, e^{-i\alpha_\lambda}. \end{aligned} \tag{18}$$

t_ξ, η, ζ are the principal elements of the anisotropic hyperfine interaction tensor $\boldsymbol{t}$ and α, β, γ are the Eulerian angles relating the radical frame ξ, η, ζ to the laboratory frame x, y, z.

The first term in (17) is hermitian and mixes S and T_0 states with the same nuclear spin configurations, $i \rightarrow i_0$. The other terms mix S and T_0 states with different nuclear spin configurations. It has been shown by CLOSS[5c,d] and it is our experience that matrix elements calculated from (17) under neglect of the anisotropic interactions do give most gratifying agreement between experimental and calculated CIDNP-patterns. This is not unreasonable since for typical hydrocarbon radicals ususally $|t_{\xi}, \eta, \zeta| \approx \frac{1}{2}|a|$[23]. Following this heuristic reasoning we neglect t_ξ, η, ζ and find

$$\begin{aligned} & |\Omega_{ii_0}|^2 = |\Omega_{i_0 i}|^2 \\ & = \tfrac{1}{4}\{(g - g')\beta H_0 \hbar^{-1} + \sum_{\lambda} a_\lambda m_{I\lambda} - \sum_{\lambda'} a_{\lambda'} m_{I\lambda'}\}^2 \end{aligned} \tag{19}$$

as the final result for the pertinent matrix element. Further, we see that subcase $\underline{A}$ and the corresponding equations of section 2 should give the description of CIDNP patterns at least to a fair approximation.

If the anisotropic terms are retained, different radical orientations lead to different matrix elements and a suitable averaging over the sample has to be applied in the calculation of k_{ij_σ}. In particular the nuclear polarizations will depend on the mutual orientations of the interacting radicals. We do not persue this point further though there may be radicals with anisotropic terms of higher importance.

4. Discussion

Summarizing the results of the previous sections CIDNP spectra of radical reaction products in magnetic fields larger than a few hundred gauss may be calculated from equations (3), (4), (5), (8), (9), (10), (14), and (19). If radical g-factors and hyperfine parameters are known the only unknown parameters are $k_\mathrm{d}/k_\mathrm{c} + k_\mathrm{d}$, $2\,n_\mathrm{c}\,(\Delta R^2/v^2)$ and the modes of pair formation. Usually spectra consisting of many lines contain enough information to allow unambiguous fits of these parameters. Thus CIDNP gives important information on the mechanistic aspects of product formation and on the reactive and diffusive behaviour of radical pairs. In many cases the information is also sufficient to allow g-factor and hyperfine parameter determinations. This has first been demonstrated by CLOSS [5], and further examples are given in the subsequent paper. In this discussion we wish to emphasize a few important points only. It is tempting to assume $2\,n_\mathrm{c}\,\frac{k_\mathrm{c}+k_\mathrm{d}}{k_\mathrm{d}}\,\frac{\Delta R^2}{v^2}\,|\Omega_{ij_\varrho}|^2 \ll 1$ to obtain simpler relations for the enhancement factors. For singlet precursor pairs they become

$$V_{ii'} = -\,n_\mathrm{c}\,\frac{\Delta R^2}{v^2}\cdot\frac{a_i}{2\langle I_{ii'}\rangle_0}\cdot\left\{(g-g')\,\beta\,H_0\,\hbar^{-1} + \sum_{\lambda\neq i} a_\lambda\, m_\lambda - \sum_{\lambda'} a_{\lambda'}\, m_{\lambda'}\right\} \tag{20}$$

for a nucleus i with $I = \frac{1}{2}$ belonging to R in the product $R - R'$, and

$$V_{ii'} = n_\mathrm{c}\,\frac{\Delta R^2}{v^2}\,\frac{a_i}{2\langle I_{ii'}\rangle_0}\cdot\left\{(g-g')\,\beta\,H_0\,\hbar^{-1} + \sum_{\lambda} a_\lambda\, m_{\mathrm{I}\lambda} - \sum_{\lambda'\neq i} a_{\lambda'}\, m_{\mathrm{I}\lambda'}\right\} \tag{21}$$

for a nucleus belonging to R'.

From (20) and (21) we may estimate the amplitudes of enhancement factors. Putting $n_\mathrm{c} \approx 100$, $\Delta R \approx 1$ Å, $a \approx 3 \cdot 10^8$ rad/sec, $v \approx 10^{11}$ Å/sec and $2\langle I_{ii'}\rangle_0 \approx 10^{-5}$ we obtain $V_{ii'} \approx 100$, a value which is in the experimental range [1–12] but seems somewhat low. We believe that this is due to our crude approximations in the calculation of k_{ij_σ}. More elaborate treatments [18] do in fact allow higher values of V.

(20) and (21) and similar equations for other modes of pair formation also give insight in the structure of CIDNP patterns. The terms involving $g - g'$ cause net emission or enhanced absorption of a multiplet of $R - R'$, the other terms cause the so-called multiplet type polarizations. The signs of the net polarizations of the multiplets of R and R' are inverse and depend on the signs of a $g - g'$. The phases of the multiplet type polarizations do also depend on the internuclear coupling constants of $R - R'$.

Though (20) and (21) thus allow simple predictions on the structure of CIDNP spectra, we feel that for quantitative fits the full set of equations (3), (4), (5), (8), (9), (10), (14), and (19) should be used. For instance, (20) and (21) cannot explain the changes of multiplet phases on variation of $g - g'$ or H_0 which have been observed [1f, 5c]. Further (20), (21) and the complete equations lead to different predictions on the magnetic field dependence of enhancement factors if $g - g' \neq 0$. For $g - g' = 0$ $\Omega_{ij\sigma}$ does not contain H_0 and pure multiplet type patterns arise. Since $\langle I_{ii'}\rangle_0 \sim H_0$ $V_{ii'} \sim H_0^{-1}$ from both treatments. For $g - g' \neq 0$, however, (20) and (21) give $V_{ii'} \sim H_0^0$ for the net emissions or enhanced absorptions, whereas (8), (9), (10) indicate that $V_{ii'} \to 0$ if $H_0 \to \infty$. For singlet precursors we obtain $V_{ii'} \sim H_0^{-4}$ for very high fields, thus we may expect $V_{ii'}$ to be constant for H_0 below a critical value H_0 and to decrease for larger H_0. Perhaps the magnetic field dependence of V for p-dichlorobenzene produced by photolysis of p-chlorodibenzoylperoxide and polarized in the singlet precursor pair [15] $\mathrm{Cl}\Phi\mathrm{CO}_2 \cdots \Phi\mathrm{Cl}$ has to be explained in this way. V was found constant for $1\ \mathrm{kG} \leqq H_0 \leqq 4\ \mathrm{kG}$ and decreased continuously by a factor of 10 in the range $4\ \mathrm{kG} \leqq H_0 \leqq 14\ \mathrm{kG}$ [24].

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[24] M. LEHNIG and H. FISCHER, unpublished.