# Net and Multiplet CIDEP of the Observer Spin in Recombination of Radical-Biradical Pair

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Net and multiplet chemically induced dynamic electron polarization (CIDEP) of the observer/catalyst spin formed in recombination of the radical-biradical pair is studied theoretically. We obtained analytical expressions for the observer spin CIDEP in the high magnetic field and for the multiplet polarization in zero magnetic field. Polarization in the vicinity of the so-called *J* resonance and its magnetic field dependence are investigated numerically. The observer spin methodology can be useful for probing magnetic interactions in the short-lived spin triads.

## 1. Introduction

Singlet−triplet intersystem crossing is the limiting stage of many photoreactions involving radical species. Frequently light-induced radical pairs are formed in the spin-correlated state (singlet or triplet), whereas their recombination to stable products is spin-selective and usually is allowed only from their singlet state. As a consequence, the transitions between the electronic spin states often play the key role in the kinetics of radical reactions, giving rise to various magnetic field and spin effects in chemical reactions. The phenomenon of electron spin catalysis[1−4] has drawn much attention during the past decade. In the heart of the spin catalysis methodology is a spin triad,[3,4] the system of three electron spins $R_1^\bullet$, $R_2^\bullet$, $R_3^\bullet$, where $R_1^\bullet$ and $R_2^\bullet$ constitute a spin-correlated radical pair and $R_3^\bullet$ is a spin catalyst sometimes[5] referred to as an "observer" spin. Typically, recombination of $R_1^\bullet$ and $R_2^\bullet$ radicals selectively proceeds from their collective singlet state, whereas the triplet states are nonreactive. If the inter-system crossing is the limiting stage of the radical pair recombination, then the exchange interaction between the catalyst and $R_1^\bullet$ (or $R_2^\bullet$) facilitates the reaction $R_1^\bullet + R_2^\bullet \rightarrow$ "product" by altering the spin state of the radical pair $[R_1^\bullet \ldots R_2^\bullet]$. This is the reason the stable spin center can be considered as a catalyst: just as any other catalyst $R_3^\bullet$ is not a reactive species but it facilitates the radical reaction. The catalyzing effect of paramagnetic species on recombination of spin-correlated radical pairs has been observed experimentally a number of times.[6−10] More examples of paramagnetic spin catalytic effects are surveyed in a review by Buchachenko and Berdinsky.[3]

It is remarkable that catalyzing radical reactions, the observer spin may acquire significant nonequilibrium polarization referred to as the chemically induced dynamic electron polarization (CIDEP),[5,11−16] thereby, the CIDEP may serve as an indication of the catalytic activity of paramagnetic catalysts. The CIDEP of the observer spin in prereduced bacterial reaction centers has been studied experimentally by Hoff et al.[11] As has been shown later, the methodology of the observer spin can be utilized for probing reaction and spin dynamics of the spin triad.[5,12−15] Since the temporal resolution of the EPR technique is limited to tens of nanoseconds, it does not allow one to directly detect the intermediates with shorter lifetimes. At the same time, spin and reaction dynamics of the triad may significantly affect the EPR spectra of long-lived paramagnetic reaction products ($R_3^\bullet$ spin in the case under study). By measuring their CIDEP patterns the information on the entire 3-spin system can be deciphered. Thus, the catalyst spin $R_3^\bullet$ plays the role of an observer: being nonreactive, it is involved into the spin dynamics of the entire three-spin system, whereas its CIDEP spectra carry the information on magneto-resonance parameters of the spin triad. In prereduced bacterial reaction centers the phase of the CIDEP spectra of the observer spin can be used to determine the sign and value of exchange interactions between $R_1^\bullet$ (or $R_2^\bullet$) and $R_3^\bullet$ spins.[5,13,17] In essence, the observer spin CIDEP resembles the chemically induced dynamic nuclear polarization (CIDNP) phenomenon often observed as the anomalous NMR spectra of diamagnetic products of radical reaction.[18] Stable radicals can also acquire spin polarization in the presence of triplet excited molecules[19−24] that can be accounted for by the radical-triplet pair mechanism[21] described in detail in ref 25. In the radical-triplet pair mechanism, net or multiplet CIDEP are created via the nonadiabatic transitions between quartet and reactive doublet states in triplet-radical pairs. This mechanism of the CIDEP formation is to a certain extent similar to that in spin triads although the latter case involves three unpaired electrons instead of a pair of radical and triplet molecule.

In polar solutions spin triads can be formed in reaction of excited electron donor molecule D* and a molecule A−Sp−C$^\bullet$ containing a stable radical center C$^\bullet$ and an electron acceptor A, where Sp denotes a spacer.[7] Electron transfer from excited donor D* to A leads to the formation of radical-biradical pair (RBP) $D^{\bullet+} + A^{\bullet-}-Sp-C^\bullet$. In nonpolar solutions, three-spin systems of this kind can be generated radiolytically.[26,27] Initially $D^{\bullet+}$ and $A^{\bullet-}$ are in spin-correlated state (either singlet or triplet depending on the multiplicity of the precursor D*) and are allowed to selectively recombine from their singlet state yielding stable paramagnetic product with radical center C$^\bullet$.[28] In RBP, the C$^\bullet$ spin center plays a role of a catalyst spin (or an "observer" spin), since it "survives" in RBP recombination and its exchange interaction with $A^{\bullet-}$ spin affects spin dynamics of the triad altering $[D^{\bullet+} + A^{\bullet-}]$ pair spin state. The effects of the external magnetic field on recombination efficiency of the RBP have

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been studied in detail in recent theoretical work.[29] It has been shown that the magnetic field effect (MFE) on recombination efficiency of RBP is a useful technique for probing exchange interaction $J$ between spin centers in biradical. Characteristic sharp resonances in magnetic field dependence of recombination yield in zero field and in magnetic field equal to $J$ have been predicted. Similar behavior of the MFEs has later been reported in the theoretical work of Magin et al.[30]

In the present work, we shall study theoretically the CIDEP formed in recombination of RBPs in liquid solution. This treatment is aimed at examining the potential of the CIDEP technique for determination of magneto-resonance parameters of elusive spin triads that are beyond the reach of the conventional EPR methods. In liquid solution, all anisotropic magnetic interactions that significantly affect the observer spin CIDEP spectra in photosynthetic centers[5,11−16] are averaged out making our theoretical treatment simpler. On the other hand, here we also perform a theoretical study of the CIDEP in RBP recombination products at variable magnetic field strength paying special attention to the CIDEP in zero field, high magnetic fields, and polarization in the vicinity of $J$ resonance. We assume that the observer spin is coupled to its magnetic nuclei by hyperfine interactions (HFI). This may give rise to the CIDEP dependent on the nuclear spin state of the observer spin, that is, to the multiplet electron−nuclear polarization. A detailed study of the observer spin CIDEP can be useful for determination of the $J$ couplings in biradicals directly related to the catalytic activity of the spin catalyst from the CIDEP spectra of RBP recombination products.

The outline of the paper is as follows: in the following section, we present theoretical formalism employed for the CIDEP calculations. In section III, we study the high-field and zero-field CIDEP, the polarization at $J$ resonance, and the CIDEP dependence on the external magnetic field strength. Conclusions (section IV) summarize the main results of the paper.

## 2. Theory

In the liquid solution, the two radicals do not separate immediately by escaping to the bulk but stay close to each other in the solvent "cage" during the characteristic time $\tau_d = R^2/D$.[18] Here $R$ is the distance of the closest approach between the radicals, which is equal to the sum of reactant radii, $D$ is the coefficient of their relative diffusion. Singlet−triplet conversion during the time $\tau_d$ allows the radical pair to react forming in-cage products (geminate termination). Here we shall assume that the reactivity of the singlet radical pair is very high in comparison with the inverse time of its diffusional displacement; therefore, for the triplet-born radical pair, the inter-system crossing is the limiting stage of the geminate radical termination. The intersystem crossing rate is different in different spin sub-ensembles of the radical pairs giving rise to nonequilibrium population of the spin states of the recombination reaction products. In the case under study, these states are the collective spin states of the observer spin and its nuclear spins. Consequently, spin-selective recombination may give rise to nonequilibrium populations of the electron−nuclear spin states of the observer spin, i.e., to the net and multiplet CIDEP of the observer spin. The CIDEP can be detected as anomalous EPR spectra of the observer spin after RBP recombination.

The way of calculating the effects of CIDEP in geminate recombination of RBP follows closely the approach that was employed earlier to calculate CIDNP in the multinuclear radical pairs;[31,32] therefore, we shall here only summarize the essential steps for the convenience of the reader. The method is based on analytical solution of the stochastic Liouville equation (SLE) for the electron−nuclear spin density matrix of RBP by using the Green function technique in the so-called kinematic approximation.[33] Despite this approximation, the solution is still relatively complicated. To go on further, we shall employ the low-viscosity approximation[34,35] which implies that the frequencies of electronic singlet−triplet mixing in the radical pair [$D^{\bullet+}$... $A^{\bullet-}$], $\nu$, are relatively small in all spin sub-ensembles. That is, the spin density matrix of RBP changes only slightly during the time $\tau_d$ that is characteristic for the diffusional displacement of two particles in the solvent

$$\nu\tau_d \ll 1, \quad \text{where } \tau_d = R^2/D \tag{1}$$

This approximation is fulfilled for solvents with normal viscosity and moderate values of the HFI constants and exchange integrals, for example, for $\nu = 1$ mT, $R = 5$ Å, and $D = 10^{-5}$ cm$^2$/s, we obtain $\nu\tau_d \approx 4.4 \times 10^{-2} \ll 1$. Within this approximation, the Green function solution of the SLE[33] becomes much simpler as well as the result for the elements $\sigma_{ij}$ of the reaction product density matrix $\hat{\sigma}$.

In RBP the radical centers $D^{\bullet+}$ and $A^{\bullet-}$ are assumed to be born in spin-correlated state, either singlet or triplet. Unless otherwise stated, hereafter the terms spin-correlated, singlet- and triplet-born will refer to the initial state of the sub-ensemble [$D^{\bullet+}$... $A^{\bullet-}$]. In the case of a RBP born in its triplet state, the elements $\hat{\sigma}_{ij}$ at $t \rightarrow \infty$ are as follows:[34,35]

$$\sigma_{ij} = \frac{k_r/k_D}{1 + k_r/k_D} \sum_{\gamma,k} G_{Si,Sj;T_\gamma k,T_\gamma k} n_{T_\gamma k} \tag{2}$$

Here indices S and $T_\gamma$ denote the singlet and triplet ($T_+$, $T_0$, $T_-$) collective spin states of $D^{\bullet+}$ and $A^{\bullet-}$ pair, respectively, and $i$, $j$, and $k$ denote the electron−nuclear states of a stable reaction product, $n_{T_\gamma k}$ is the initial population of the RBP state $|T_\gamma k\rangle$ (all $n_{T_\gamma k}$ are equal to each other and their sum over $\gamma$, $k$ is equal to 1), $k_r$ is the kinetic rate constant of RBP recombination, $k_D = 4\pi RD$, and $\hat{\hat{G}}$ is the stationary value of the Green function of the RBP. Notwithstanding the low viscosity condition (1) the CIDEP of the reaction products can be much larger than their equilibrium (Boltzmann) polarization. It is noteworthy, that in the low viscosity approximation the result for $\hat{\sigma}$ (2) does not depend on the exchange interaction of $D^{\bullet+}$ spin center with $A^{\bullet-}$ and $C^{\bullet}$.[34] In principle, the present consideration can easily be extended to the singlet-born RBPs as well;[34,35] however, for the sake of clarity, here we shall always consider a triplet-born RBP. That is, the present consideration will be addressed to the following reaction scheme:

$$\begin{array}{l} {}^3D^* + A - Sp - C^\bullet \rightarrow {}^3[D^{\bullet+} + A^{\bullet-}] - Sp - C^\bullet \\ \qquad\qquad\qquad\qquad \updownarrow \\ \qquad\qquad\qquad {}^1[D^{\bullet+} + A^{\bullet-}] - Sp - C^\bullet \rightarrow D + A - Sp - C^\bullet. \end{array} \tag{3}$$

The singlet−triplet mixing of the spin states of the sub-ensemble [$D^{\bullet+}$... $A^{\bullet-}$] is a limiting stage of the RBP recombination to the stable products D + A −Sp−C$^\bullet$. The case of the singlet-born RBP can be considered in the framework of the present formalism as well. In general, the values of polarizations formed from the singlet $P_S$ and triplet $P_T$ precursors are bound by the relation[34,35]

$$P_S = -\frac{3}{1 + k_r/k_D} P_T \tag{4}$$

The assumption that the RBP recombines only from the singlet state of the sub-ensemble $[D^{\bullet +} ... A^{\bullet -}]$ is not generally valid and triplet recombination plays an important in many situations, e.g., in bacterial reaction centers. In fact, the necessary condition for the CIDEP formation is the difference in recombination rates from the singlet and triplet states of $[D^{\bullet +} ... A^{\bullet -}]$. Here we shall restrict ourselves only to the situation of the zero rate of triplet state recombination.

To calculate the CIDEP, one has to evaluate the elements of the Green function determined by the spin evolution of RBP during the time $\tau_d$. As usual, we completely neglect the paramagnetic spin relaxation that is typically inefficient during the lifetime of the RBP and consider only dynamic spin evolution of RBP. Hence, the RBP spin evolution is merely due to the Zeeman, hyperfine, and exchange interactions. With these assumptions in the case of diffusive motion of the radicals the elements of $\hat{\hat{G}}$ are as follows:[33]

$$G_{ij,kl} = \sum_{m,n} Q_{im} Q_{ln} Q^{-1}_{mk}\, Q^{-1}_{nj} \mathcal{G}(\mathcal{E}_m - \mathcal{E}_n) \tag{5}$$

Here $\mathcal{E}_i$ are the eigenvalues of the RBP spin Hamiltonian $\hat{\mathcal{H}}$ (RBP energy levels) and $\hat{\hat{G}}$ is the matrix of its eigenvectors

$$\mathcal{G}(x) = \frac{1}{1 + \sqrt{\iota x \tau_\mathrm{d}}} \approx 1 - \sqrt{\iota x \tau_\mathrm{d}} \quad \text{at } x\tau_\mathrm{d} \ll 1$$

and $\iota$ is the imaginary unit.

Expression 5 gives the relationship between the Green function $\hat{G}$ and the Hamiltonian of the RBP $\hat{\mathcal{H}}$ that has the following form:

$$\hat{\mathcal{H}} = \omega_\mathrm{A}\hat{S}_\mathrm{Az} + \omega_D\hat{S}_\mathrm{Dz} + \omega_\mathrm{C}\hat{S}_\mathrm{Cz} + J(\hat{\mathbf{S}}_\mathrm{A}\cdot\hat{\mathbf{S}}_\mathrm{C}) + \sum_j a_j(\hat{\mathbf{S}}_\mathrm{C}\cdot\hat{\mathbf{I}}_j) \tag{6}$$

Here $\omega_{\mathrm{A,D,C}} = g_{\mathrm{A,D,C}}B/g_\mathrm{e}$ represent the electronic Zeeman interactions of the radical centers ($B$ is the external magnetic field strength, $g_\mathrm{A}$, $g_\mathrm{D}$, and $g_\mathrm{C}$ are the $g$ factors of radical centers $A^{\bullet -}$, $D^{\bullet +}$, and $C^{\bullet}$, respectively, $g_\mathrm{e}$ is the $g$ factor of a free electron), $J$ is the strength of exchange interaction between $A^{\bullet -}$ and $C^{\bullet}$ spins, $a_j$ is the HFI constant of the catalyst spin with its $j$th magnetic nucleus, $\hat{\mathbf{S}}_\mathrm{A}$, $\hat{\mathbf{S}}_\mathrm{D}$, and $\hat{\mathbf{S}}_\mathrm{C}$ are the operators of the electron spins, and $\hat{\mathbf{I}}_j$ is the operator of the $j$th magnetic nucleus spin. For simplicity, we assume that the radical centers $A^{\bullet -}$ and $D^{\bullet +}$ have no magnetic nuclei. The Hamiltonian $\hat{\mathcal{H}}$ (eq 6) is written in the units of the magnetic field to make the theoretical treatment of the CIDEP field dependence more convenient. As usual, we neglect the nuclear Zeeman interactions with external magnetic field that are evanescent as compared to the electronic ones.

## 3. Results and Discussion

Following the work of Lukzen et al.[29] dedicated to MFE on the RBP recombination efficiency, we consider three main regions of magnetic fields where the RBP spin dynamics exhibits qualitatively different behavior: (i) high magnetic fields far from $J$ resonance; (ii) very weak magnetic fields; (iii) fields close to the value of $|J|$. In all cases, we consider a triplet-born RBP and assume that its recombination to a stable product is diffusion controlled, that is, $k_\mathrm{r} \gg k_\mathrm{D}$.

**3.1. CIDEP in High Magnetic Fields.** First we consider high magnetic fields far from $J$ resonance, i.e., $B \gg a_j$ and $|B - J| \gg a_j$. This means that flip-flop electron–nuclear transitions involving $C^{\bullet}$ spin and its nuclear spins are forbidden.[29] As a consequence, secular approximation for HFI can be applied and in the $M$th nuclear spin sub-ensemble characterized by certain projections $M_j$ of all nuclei: $\{M\} = \{M_1, M_2, ..., M_j, ...\}$ the RBP Hamiltonian of the form:

$$\hat{\mathcal{H}} = \omega_A\hat{S}_\mathrm{Az} + \omega_\mathrm{D}\hat{S}_\mathrm{Dz} + \omega_\mathrm{CM}\hat{S}_\mathrm{Cz} + J(\hat{\mathbf{S}}_\mathrm{A}\cdot\hat{\mathbf{S}}_\mathrm{C}) \tag{7}$$

where

$$\omega_\mathrm{CM} = \omega_\mathrm{C} + \sum_j a_j M_j \tag{8}$$

$\omega_\mathrm{CM}$ is the precession frequency of the observer spin in the $M$th nuclear sub-ensemble. The value of $\omega_\mathrm{CM}$ is varied by varying the nuclear configuration $\{M\}$. In prereduced reaction centers where the $g$-tensor anisotropy is not averaged out, the observer spin precession frequency is varied due to the different orientations of the sample thus giving rise to the anomalous observer spin EPR spectra[5,13] that can be used to determine the $J$ couplings in the spin triad.[5,13,17] In the case under study, the CIDEP formation is due to different rates of sinlget-triplet conversion in RBPs with $+^1/_2$ and $-^1/_2$ projections of the observer spin on the $Z$ axis.

The solution of the eigenproblem of the Hamiltonian (eq 7) required to obtain the expression for density matrix $\hat{\sigma}$ is relatively simple and can be done analytically by making use of the computer algebra software (e.g., Mathematica or Maple). To calculate the CIDEP in the $M$th nuclear sub-ensemble, $P_M$, one has only to calculate the populations of $|\alpha_\mathrm{C}\rangle$ and $|\beta_\mathrm{C}\rangle$ states, i.e., the following two elements of the product spin density matrix: $\sigma_{\alpha_\mathrm{C}\alpha_\mathrm{C}}$ and $\sigma_{\beta_\mathrm{C}\beta_\mathrm{C}}$. As usual, hereafter $|\alpha\rangle$ and $|\beta\rangle$ denote the states of $^1/_2$ spin with $+^1/_2$ and $-^1/_2$ projections of the $Z$ axis. The value of the CIDEP, $P_M$, is then as follows:[18]

$$P_M = \frac{\sigma_{\alpha_\mathrm{C}\alpha_\mathrm{C}} - \sigma_{\beta_\mathrm{C}\beta_\mathrm{C}}}{2} \tag{9}$$

It is equal to the product of the polarization formation efficiency at given $\omega_\mathrm{CM}$, $P(\omega_\mathrm{CM})$, and initial population of $|T_\gamma M\rangle$ state of RBP, $n_M$. Analytical expression for CIDEP which can be obtained from eq 9 by using the general formula (eq 2) is as follows:

$$P_M = P(\omega_{CM})n_M = \frac{n_M}{48}\left(1 - \frac{\delta}{\psi}\right)\{g(J - \omega - \psi) - g(J + \omega + \psi)\} + \frac{n_M}{48}\left(1 + \frac{\delta}{\psi}\right)\{g(J - \omega + \psi) - g(J + \omega - \psi)\} \tag{10}$$

where

$$g(x) = \frac{\mathcal{G}(x\tau_\mathrm{d}/2) + \mathcal{G}(-x\tau_\mathrm{d}/2)}{2}, \quad \delta = \omega_\mathrm{CM} - \omega_\mathrm{A},$$
$$\psi = \sqrt{\delta^2 + J^2},$$
$$\omega = \omega_\mathrm{A} + \omega_\mathrm{CM} - 2\omega_\mathrm{D} = \delta + 2(\omega_\mathrm{A} - \omega_\mathrm{D}) \tag{11}$$

In the framework of the low viscosity approximation (eq 1) $x\tau_\mathrm{d} \ll 1$ and $g(x) \approx 1 - \sqrt{|x|\tau_\mathrm{d}/2}$. As a consequence, the expression for the CIDEP can be recast as follows:

$$P_M = \frac{\sqrt{\tau_d}}{96}\left(1 - \frac{\delta}{\psi}\right)(\sqrt{|J + \omega + \psi|} - \sqrt{|J - \omega - \psi|})n_M + \frac{\sqrt{\tau_d}}{96}\left(1 + \frac{\delta}{\psi}\right)(\sqrt{|J + \omega - \psi|} - \sqrt{|J - \omega + \psi|})n_M \tag{12}$$

Since $P_M$ depends on $\omega_{CM}$ (i.e., on the nuclear spin configuration $\{M\}$), the CIDEP value, that is the electron spin magnetization, is different in different nuclear subensembles. This means that the multiplet electron−nuclear CIDEP is formed.

Now let us consider the CIDEP patterns and CIDEP signs in different cases.

**Case 1: $\boldsymbol{\delta \gg J}$.** In this case secular approximation for the exchange interaction can be applied because the mutual flip-flop transitions of $A^{\bullet-}$ and $C^{\bullet}$ spins are forbidden. Consequently, the CIDEP is due to different rates of singlet−triplet conversion in the states with $\alpha_C$ and $\beta_C$ $Z$ projections of the observer spin that are conserved since $[\hat{S}_{Cz}, \hat{\mathscr{H}}] \approx 0$. This physical situation formally coincides with the CIDNP formation in high external magnetic field. As a consequence, the expression for the CIDEP takes the form

$$\mathrm{CIDEP} \propto \sqrt{|2(\omega_A - \omega_D) + J|} - \sqrt{|2(\omega_A - \omega_D) - J|} \quad (13)$$

The rule for the CIDEP sign, $\Gamma$, is as follows:

$$\Gamma = \mu \Gamma_J \Gamma_{\omega_A - \omega_D} = \mu \Gamma_J \Gamma_{g_A - g_D} \quad (14)$$

Hereafter, $\Gamma_x = \mathrm{sgn}(x)$ and $\mu$ is determined by the initial multiplicity of the spin-correlated pair

$$\mu = \begin{cases} +1, \text{ triplet} - \text{born pair} \\ -1, \text{ singlet} - \text{born pair} \end{cases} \quad (15)$$

The rule (eq 14) exactly coincides with the famous Kaptein rules[18,36] for the CIDNP sign in high magnetic fields where the HFI constant is replaced by $J$ and $\Delta g$ is replaced by $g_A - g_D$. According to eq 4, the polarization sign changes with changing the multiplicity of the precursor.

**Case 2: $\boldsymbol{\delta \ll J}$.** The expression for the CIDEP is as follows:

$$\mathrm{CIDEP} \propto \sqrt{|2J + \omega|} - \sqrt{|2J - \omega|} \quad (16)$$

and its sign is given by the rule

$$\Gamma = \mu \Gamma_J \Gamma_{\omega} \quad (17)$$

**Case 3: $\boldsymbol{\omega_A \approx \omega_D \neq \omega_{CM}}$.** This case resembles the CIDNP formation in low magnetic fields. The value of $\omega$ is equal to $\delta$ and the CIDEP is as follows:

$$\mathrm{CIDEP} \propto \left(1 - \frac{\delta}{\psi}\right)\left(\sqrt{|J + \delta + \psi|} - \sqrt{|J - \delta - \psi|}\right) + \left(1 + \frac{\delta}{\psi}\right)\left(\sqrt{|J + \delta - \psi|} - \sqrt{|J - \delta + \psi|}\right) \quad (18)$$

and its sign is the following:[18]

$$\Gamma = -\mu \Gamma_J \Gamma_{\delta} \quad (19)$$

In the case under study the values of $\delta$ and $\omega$ are varied and different CIDEP regimes are reached by varying the nuclear state $\{M\}$ of $C^{\bullet}$. As a consequence, at different regions of $C^{\bullet}$ EPR spectrum (corresponding to different nuclear states), the CIDEP formation efficiency and sign may differ and the CIDEP value depends on the observer spin nuclear state. That is, not only the net but also the multiplet CIDEP is formed in RBP recombination.

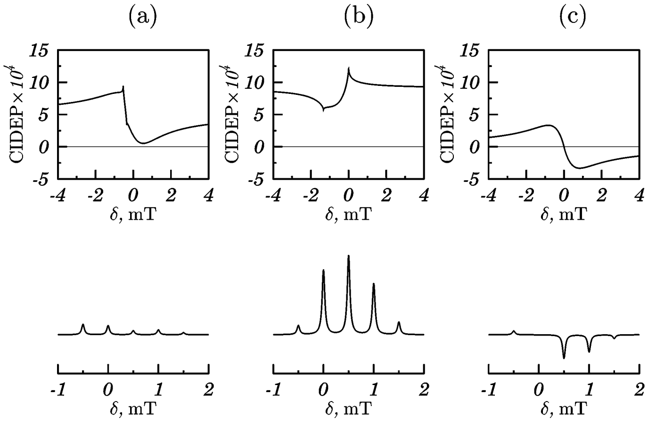

**Figure 1.** Dependencies of the high field CIDEP on the parameter $\delta = \omega_{CM} - \omega_A$ (top graphs) and the corresponding CIDEP spectra of the observer spin having 4 equivalent nuclei with HFI constants $a = 0.5$ mT (bottom graphs). The RBP parameters are as follows: $J = 1$ mT, $\omega_A - \omega_D = 0.2$ mT (a); $J = 1$ mT, $\omega_A - \omega_D = 1$ mT (b); $J = 1$ mT, $\omega_A - \omega_D = 0$ (c) and $\omega_C - \omega_A = 0.5$ mT, $\tau_d = 0.2$ ns.

The CIDEP dependencies on $\omega_{CM}$ frequency and the corresponding CIDEP spectra of the observer spin are shown in Figure 1. In all of the cases, the CIDEP value is a relatively complicated function of all three frequencies ($\omega_A$,$\omega_D$,$\omega_{CM}$) and the exchange integral $J$. Varying the nuclear state of the observer spin one may substantially change the CIDEP value. Thereby, the CIDEP patterns carry the information about the interactions in the spin triad. To illustrate the CIDEP effects we have taken $C^{\bullet}$ radical center having 4 equivalent nuclei and with the HFI constants $a = 0.5$ mT. At thermal equilibrium the EPR spectrum of $C^{\bullet}$ consists of 5 equally spaced lines (with splittings equal to $a$) with the intensities (proportional to the statistical weights of the corresponding hyperfine structure components) being in the ratio 1:4:6:4:1. To calculate the intensity of the line with certain frequency $\omega_{CM}$ in the observer spin CIDEP spectra, one has to take the product of the statistical weight of the corresponding hyperfine structure component and the polarization formation efficiency at this frequency $P(\omega_{CM})$ from eq 12. The $C^{\bullet}$ CIDEP patterns formed in the course of the triad recombination differ drastically from the equilibrium EPR spectra: some of the lines are in absorption and some are in emission and their relative intensities obviously deviate from 1:4:6:4:1 ratio. Inasmuch as the EPR line intensities are dependent on the parameters $\omega_A$, $\omega_D$, and $J$, the shape of the CIDEP patterns can be used for probing magnetic interactions in the spin triad (the frequencies $\omega_{A,D}$ and exchange coupling $J$).

**3.2. CIDEP in Zero Magnetic Field.** Since in the zero magnetic field there is no preferred axis of quantization, no net zero-field CIDEP is expected at $B = 0$. Nevertheless, if $C^{\bullet}$ has magnetic nuclei, one may expect the formation of the multiplet electron−nuclear polarization. Although the spins do not acquire net magnetizations the populations of $C^{\bullet}$ electron−nuclear states may differ from those at thermal equilibrium. As usual,[31,32,37−39] one should expect that $C^{\bullet}$ electron−nuclear states of the same multiplicity (same total momentum) are equally populated: due to the symmetry of space, the electron−nuclear state populations are independent of the total spin projections in this state. At the same time, the states with different multiplicity acquire different populations because of the different singlet−triplet conversion rates in RBP in these states. To check this expectation, we have calculated the spin state populations of the stable paramagnetic product of RBP recombination for $C^{\bullet}$ having one magnetic nuclei with spin $^1/_2$ and HFI constant $a$. The Hamiltonian of RBP can be written as follows:

$$\hat{\mathscr{H}} = J(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_C) + a(\hat{\mathbf{S}}_C \cdot \hat{\mathbf{I}}) \quad (20)$$

In zero field, the spin states of the stable radical center $C^{\bullet}$ can

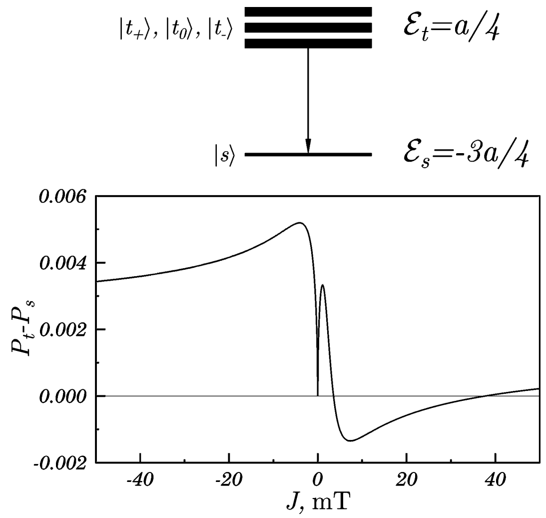

**Figure 2.** Dependence of the zero-field CIDEP $P_t - P_s$ on $J$-coupling and scheme of the electron−nuclear state populations at $B = 0$. Here $a = 3$ mT, $\tau_d = 0.2$ ns. The EPR transition is shown by the arrow.

be separated separated into two manifolds, one with the total spin (which is $\hat{\mathbf{S}}_C + \hat{\mathbf{I}}$) equal to 1 (triplet) and one with the total spin equal to 0 (singlet). Our analytical calculations have shown that three electron−nuclear eigenstates of the stable product within the triplet manifold have equal populations $P_t$ which differ from that $P_s$ of the singlet state

$$P_t = \sigma_{t_+t_+} = \sigma_{t_0t_0} = \sigma_{t\_t\_} \neq \sigma_{ss} = P_s \qquad (21)$$

Here

$$|t_+\rangle = |\alpha_C\alpha_N\rangle, \quad |t_0\rangle = \frac{|\alpha_C\beta_N\rangle + |\beta_C\alpha_N\rangle}{\sqrt{2}}, \quad |t_-\rangle = |\beta_C\beta_N\rangle \qquad (22)$$

are the electron−nuclear triplet states and

$$|s\rangle = \frac{|\alpha_C\beta_N\rangle - |\beta_C\alpha_N\rangle}{\sqrt{2}} \qquad (23)$$

is the electron−nuclear singlet state where $\alpha_N$ and $\beta_N$ stand for the $Z$ projection of the nuclear spin. The multiplet polarization value is then equal to the difference in population of any of the triplet states and that of the singlet state, e.g.

$$P = \sigma_{t_+t_+} - \sigma_{ss} = P_t - P_s$$
$$= \{4\theta^2 + 3J^2(g(2\theta) - 1) - \theta(2\theta - 2a + J)g(a + J + \theta) - \theta(2\theta + 2a - J)g(a + J - \theta)\}/108\,\theta^2 \qquad (24)$$

Here we introduce $\theta = \sqrt{a^2 - aJ + J^2}$ and $g(x)$ is given by eq 11. Taking the values of $g(x)$ from eq 11, we obtain the following expression for $P$:

$$P = \sqrt{\tau_d}\{\theta(2\theta - 2a + J)\sqrt{|a + J + \theta|} + \theta(2\theta + 2a - J)\sqrt{|a + J - \theta|} - 3J^2\sqrt{2\theta}\}/216\,\theta^2\sqrt{\tau_d} \qquad (25)$$

In zero magnetic field, all triplet sublevels are degenerate and the splitting between the singlet and any of the triplet states is equal to $a$. Therefore, at $B = 0$ there are three EPR transitions: $|s\rangle \rightleftharpoons |t_+\rangle$, $|s\rangle \rightleftharpoons |t_0\rangle$, and $|s\rangle \rightleftharpoons |t_-\rangle$ of the same frequencies and the CIDEP spectrum consists of only one line at a frequency equal to $a$. Our calculations (Figure 2) show that depending on $J$ and $a$ values the difference $P_t - P_s$ can be either positive or negative. The energies of the triplet and the singlet states, $\mathcal{E}_t$ and $\mathcal{E}_s$, are the following: $\mathcal{E}_t = \mathcal{E}_{t_+} = \mathcal{E}_{t_0} = \mathcal{E}_{t_-} = a/4$, $\mathcal{E}_s = -3a/4$. If $a$ is positive and $P_t > P_s$, then the enriched triplet states will lie higher in energy than depleted singlet state and in the EPR spectrum there will be one emissive line. On the contrary, at $a < 0$ and $P_t > P_s$, there will be one absorptive line in the zero-field EPR spectrum. As usual, the CIDEP sign changes with the change of the precursor multiplicity. As a consequence, the CIDEP spectrum phase is either absorptive or emissive depending on the values of $J$ and $a$ and the signs of $a$ and $\mu$. The dependence of the difference $P_t - P_s$ responsible for the zero-field CIDEP formation on $a$ and $J$ is depicted in Figure 2.

It is important to note that zero-field multiplet electron−nuclear polarization can be formed not only in recombination of RBPs but also in transient radicals.[39] Although the mechanisms of the CIDEP formation are different in both cases, the main peculiarities of the CIDEP patterns are the same: in zero field the states are always selected with respect to their total momentum. This zero-field CIDEP spectra can be detected by applying oscillating magnetic fields.[39] Studies of the zero-field multiplet polarization are very useful and allow one to measure the electron−nuclear relaxation times in zero magnetic field.[39] This law of selecting the spin states with respect to their momenta is very general and holds not only for the zero-field CIDEP but for the zero-field CIDNP[31,32,37,38] as well.

If $C^\bullet$ has only one nucleus with spin $^1/_2$ the zero-field CIDEP can be calculated analytically. Unfortunately, if the hyperfine structure of the observer spin is more complex, the analytical solution of the problem becomes problematic. Nevertheless, one may expect that the main peculiarities of the zero field polarization remain the same. We anticipate that for an arbitrary hyperfine structure of the observer spin, the electron−nuclear spin states having the same multiplicity are equally populated, whereas the populations of states with different momenta have different populations. This gives rise to significant multiplet electron−nuclear polarization that can be detected[39] by means of the EPR technique.

**3.3. CIDEP in the Vicinity of *J* Resonance and Its Field Dependence.** Here we shall study the polarization in the vicinity of $J$-resonance and its dependence on the external magnetic field strength. To make it feasible, we restrict ourselves to spin triad with only one magnetic nucleus on $C^\bullet$ radical center with spin $^1/_2$ and the HFI constant $a$.

In the work of Lukzen et al.,[29] it has been shown that in high fields close to the exchange coupling value $J$ spin dynamics of the triad is qualitatively different from that in fields $|B - |J|| \gg a$. Namely, for $J > 0$ at $B = J$, the product yield field dependence has a well-pronounced peak (or trough): the so-called $J$-resonance.[29] This resonance is due to the crossing of the following two spin states of a biradical $A^{\bullet-}-Sp-C^\bullet$:

$$|S'\beta_N\rangle = \frac{|\alpha_A\beta_C\rangle - |\beta_A\alpha_C\rangle}{\sqrt{2}}|\beta_N\rangle, \quad |T'_-\alpha_N\rangle = |\beta_A\beta_C\rangle|\alpha_N\rangle \qquad (26)$$

where $|S'\rangle$, $|T'_\alpha\rangle$ denote the collective states (singlet or triplet) of spins $\hat{\mathbf{S}}_A$ and $\hat{\mathbf{S}}_C$. The mixing of the states $|S'\beta_N\rangle$ and $|T'_-\alpha_N\rangle$ occurs with a matrix element $a/2\sqrt{2}$ due to flip-flop transitions involving the observer spin and the spin of magnetic nucleus. The efficiency of the flip-flop transition passes through its maximum at $B = J$, and likewise, the MFE on RBP recombination passes through an extremum.[29] If $J$ is negative, at $B = |J|$ the levels $|S'\alpha_N\rangle$ and $|T'_+\beta_N\rangle$ cross and their mixing also

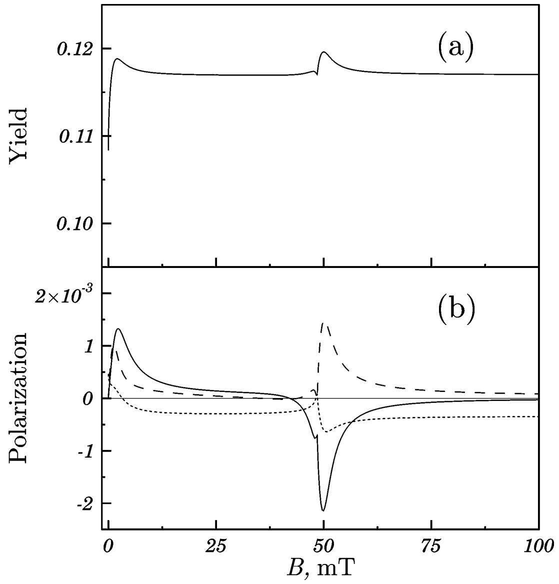

**Figure 3.** Field dependencies of the reaction yield (a) and polarization (b). Graph (b) presents the net CIDEP (solid line), CIDNP (long-dashed line) and mutliplet polarization (short-dashed line). The parameters of calculation are as follows: $J = 50$ mT, $a = 3$ mT, $g_A = g_C = g_D = 2.002$.

proceeds with a matrix element $a/2\sqrt{2}$. Spin dynamics then exhibits the behavior qualitatively similar to the case of a positive $J$.

We anticipate that the polarization field dependence exhibits qualitatively similar behavior: since "flips" of the observer spin (accompanied by the "flops" of the nuclear spin) efficiently proceed at $B \approx J$, the CIDEP field dependence should have a feature at $B = J$. To check this expectation, we shall perform numerical calculation of the polarization formed upon RBP recombination at variable magnetic field strength.

At arbitrary strength of external magnetic field the polarizations can be defined in the usual way[18] as the expectation values of the corresponding spin operators. For example, the net polarization of the electron spin is as follows:

$$\langle S_{Cz}\rangle = Tr\{\hat{S}_{Cz}\hat{\sigma}\} \tag{27}$$

Unless the RBPs have been produced by pulsed chemical excitation of very short duration, the stationary density matrix $\hat{\sigma}$ is diagonal in the basis of the eigenstates of the product Hamiltonian $\hat{\mathscr{H}}_{pr}$[40,41]

$$\sigma_{ij} = \delta_{ij}\sigma_{ii} \tag{28}$$

Here $\delta_{ij}$ is the Kronecker delta. Consequently, it is sufficient to calculate only the elements $\sigma_{ii}$ of the product spin density matrix from the formula (2). According to classification of Ernst et al.[40,41] nonequilibrium states given by the density matrix (eq 28) are called the nonequilibrium states of the first kind. In the opposite case of very rapid photo- or radiochemical excitation the nondiagonal elements become important as well and the nonequilibrium states of this kind are referred to as the nonequilibrium states of the second kind.[40,41] To make the present consideration simpler, we content ourselves with the nonequilibrium states of the first kind. The Hamiltonian $\hat{\mathscr{H}}_{pr}$ is as follows:

$$\hat{\mathscr{H}}_{pr} = \omega_C\hat{S}_{Cz} + a(\hat{\mathbf{S}}_C\cdot\hat{\mathbf{I}}) \tag{29}$$

and the $\hat{\mathscr{H}}_{pr}$ eigenstates are given by the well-known Breit-Rabi formulas[42]

$$\begin{aligned} |1\rangle &= |\alpha_C\alpha_N\rangle \\ |2\rangle &= \cos\varphi|\alpha_C\beta_N\rangle + \sin\varphi|\beta_C\alpha_N\rangle \\ |3\rangle &= -\sin\varphi|\alpha_C\beta_N\rangle + \cos\varphi|\beta_C\alpha_N\rangle \\ |4\rangle &= |\beta_C\beta_N\rangle \end{aligned} \tag{30}$$

where

$$\varphi = 2\arctan\left(\frac{a}{\omega_C}\right) \tag{31}$$

As a consequence, the net CIDEP is as follows:

$$\langle S_{Cz}\rangle = \frac{\sigma_{11} - \sigma_{44}}{2} + \cos 2\varphi\frac{\sigma_{22} - \sigma_{33}}{2} \tag{32}$$

Together with the net CIDEP, we shall define the multiplet electron−nuclear polarization (mutual spin entanglement) as an expectation value of the operator $\hat{S}_{Cz}\hat{I}_z$[18]

$$\langle S_{Cz}I_z\rangle = Tr\{\hat{S}_{Cz}\hat{I}_z\hat{\sigma}\} = \frac{\sigma_{11} - \sigma_{22} - \sigma_{33} + \sigma_{44}}{4} \tag{33}$$

and the net magnetization of the nuclear spin (that is, the net CIDNP)

$$\langle I_z\rangle = Tr\{\hat{I}_z\hat{\sigma}\} = \frac{\sigma_{11} - \sigma_{44}}{2} - \cos 2\varphi\frac{\sigma_{22} - \sigma_{33}}{2} \tag{34}$$

All of these quantities can be calculated numerically by taking the values of $\sigma_{ii}$ from eq 2. To check whether the resonant behavior of the polarization is accompanied by $J$-resonance in the MFE on reaction yield[29] we shall also calculate the product yield, $Y = Tr\{\hat{\sigma}\} = \sum_i\sigma_{ii}$.

Field dependencies of the net CIDEP, CIDNP and mutiplet polarization as well as that of the product yield are shown in Figure 3. As is clearly seen, $J$ resonance appears not only in the product yield field dependence but in the polarization field dependence as well. It is important to emphasize that the behavior of the CIDEP and CIDNP is different in the vicinity of $J$ resonance: although in the CIDEP field dependence a trough exists at $B \approx J$, a well-pronounced peak in the CIDNP field dependence appears (or vice versa). This is because the flip-flop transitions $|S'\beta_N\rangle \rightleftharpoons |T'_-\alpha_N\rangle$ involve the observer spin and the nuclear spins with opposite projections on the $Z$ axis. As a consequence, at $B = J$, the observer spin and the nuclear spins acquire opposite sign polarizations in the product of RBP recombination. Since the flip-flop transitions involve the catalyst spin and the nuclear spin simultaneously significant multiplet CIDEP is formed in the vicinity of $J$ resonance.

Since the polarizations are intricate combinations of magnetoresonance parameters of the spin triad, we did not manage to establish the rules for polarization signs at $B \approx |J|$ and calculated the polarization only numerically. Our simulations show that changing signs of $a$ and $J$ the signs of the CIDEP, CIDNP and multiplet polarization may change (see Figures 3b and 4a,b). In all cases, the net CIDEP and CIDNP always have opposite signs and the multiplet polarization is efficiently formed in the vicinity of $J$ resonance.

It is important to emphasize that the feature at $B = |J|$ in the CIDEP field dependence exists even at relatively small values

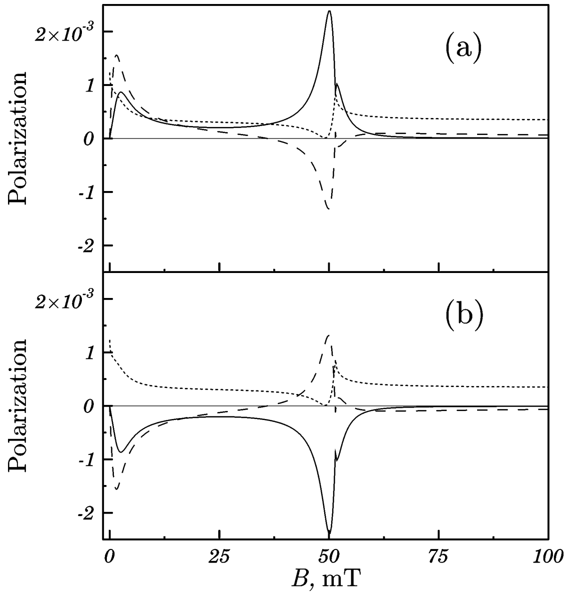

**Figure 4.** Field dependencies of the net CIDEP (solid line), CIDNP (long-dashed line) and mutliplet polarization (short-dashed line) at different values of $J$ and $a$. Here $J = -50$ mT, $a = 3$ mT (a); $J = 50$ mT, $a = -3$ mT (b) and $g_A = g_C = g_D = 2.002$.

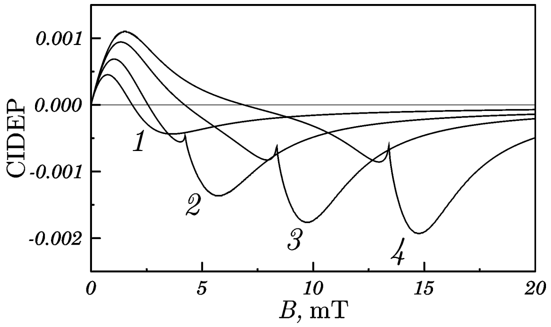

**Figure 5.** Field dependencies of the net CIDEP (solid line) at different strengths of exchange interaction $J$ equal to 3 mT (1); 6 mT (2); 10 mT (3); 15 mT (4). Here $a = 3$ mT and $g_A = g_C = g_D = 2.002$.

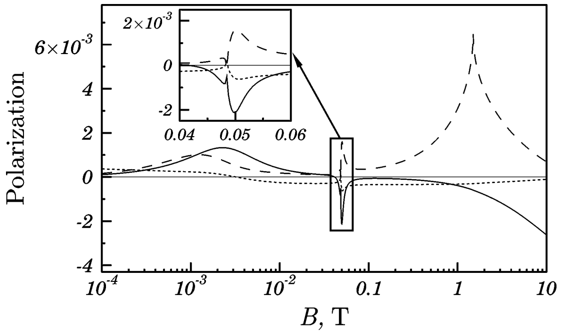

**Figure 6.** Field dependence of the net CIDEP (solid line), CIDNP (long-dashed line) and mutliplet polarization (short-dashed line) at $J = 50$ mT, $a = 3$ mT (a) and $g_A = g_D = 2.002$, $g_C = 2.004$. Insert shows the region of field dependence near $J$-resonance.

of $J$ as compared to the HFI constant $a$ (Figure 5). $J$ resonance is seen even at $J = a$, and with increasing $J$, it becomes sharper (Figure 5).

In the polarization field dependence, there are several different regions (Figure 6). At $B = 0$ (or $B \ll a$, $J$), spin evolution of the triad is governed only by $J$ coupling and HFI and only multiplet polarization is formed. At $B \approx a$, the net CIDEP and CIDNP are formed as well. Their field dependencies have extrema at $B$ of the same order of magnitude as $a$. At $B = |J|$ the polarization field dependencies have well-pronounced sharp resonant features discussed above. At $B \gg a$ and $B - |J| \gg a$, the CIDEP is completely described by formula 12.

## 4. Conclusions

In general, the observer spin CIDEP can be used as an efficient tool for probing the catalytic activity of paramagnetic particles and magnetic interactions in short-lived intermediate spin triads. Investigation of the high-field CIDEP spectra of the observer spin allows one to determine the $J$-couplings responsible for the spin catalysis efficiency and $g$-factors of short-lived radical centers. Investigations of the CIDEP at variable magnetic field strength extend the capability of the method, for instance, detection of $J$ resonance in the CIDEP field dependence allows one to unambiguously determine the exchange interaction value.

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