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Spin Dynamics of Radical Pairs with Restricted Geometries and Strong Exchange Coupling: The Role of Hyperfine Coupling

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Ⓢ *Supporting Information*

ABSTRACT: Subnanosecond radical pair (RP) formation by electron transfer from an excited singlet state or by bond breaking produces two correlated spins coupled by their spin−spin exchange (J) and magnetic dipole (D) interactions. In the high magnetic field limit, the two-spin system can be described by a singlet state (S) and three triplet states (T_0, T_{+1}, T_{-1}). When J is small relative to the electron Zeeman interaction, $|T_0\rangle$ is the only triplet state that is populated by coherent spin mixing with the $|S\rangle$ state because the $|T_{+1}\rangle$ and $|T_{-1}\rangle$ states are well-separated from $|S\rangle$ by a large energy gap. Herein, we describe the spin dynamics for RPs having restricted geometries in which J is similar in magnitude to the electron Zeeman interaction and does not fluctuate significantly. Under these circumstances, depending on the sign of J, the energies of $|T_{+1}\rangle$ or $|T_{-1}\rangle$ are close to that of $|S\rangle$ so that weak isotropic electron−nuclear hyperfine coupling leads to population of $|T_{+1}\rangle$ or $|T_{-1}\rangle$. An approximate relationship for the triplet quantum yield is developed for a RP in the large J regime, where one or both electrons interact with nearby spin-1/2 nuclei. This relationship also yields the net spin polarization transfer to the nuclear spins.
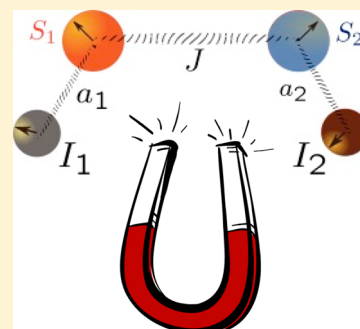
INTRODUCTION

Electron transfer following photoexcitation of a donor−bridge−acceptor (D−B−A) system can produce a long-lived radical ion pair (RP) state comprising a correlated pair of electron spins. The two spins of the RP interact with each other by the spin−spin exchange (J) and dipolar (D) interactions and are also coupled to the surrounding nuclei by hyperfine (HF) interactions. RP recombination is spin-selective and generally leads to the singlet ground state and/or the lowest excited triplet state of the D−B−A system. The complex spin dynamics of these processes have generated significant interest in quantum chemistry and biochemistry and are important for understanding natural phenomena such as photosynthesis and bird magnetoreception.[1−11] For example, the observation of these events in the photosynthetic reaction center protein led to the development of the spin-correlated radical pair (SCRP) model,[2,3,12] which describes two weakly coupled spins in which mixing occurs between the initial singlet (S) state and one of the three triplet state spin sublevels (T_0) in the high-field limit. Until recently, most studies have been conducted on SCRPs in which J and D are much smaller than the Zeeman interaction. However, when J is comparable to or larger than the Zeeman interaction in the high-field limit, spin state mixing may then involve one of the other two triplet sublevels, $T_{\pm1}$, depending on the sign of J.[13−20]

In the high magnetic field limit, when J is small, $|T_0\rangle$ is the only triplet state that is populated by coherent spin mixing because the $|T_{+1}\rangle$ and $|T_{-1}\rangle$ states are well-separated from $|S\rangle$ by a large energy gap. As a result, the EPR spectrum for transitions between the S−T_0 mixed states and the initially

unpopulated $T_{\pm1}$ states shows a pair of symmetric antiphase doublets (e.g., e,a,e,a, where e = emission and a = absorption). However, when J increases, the intensities of the EPR transitions diminishes with $\sim1/J^2$.[2,3,12] The subsequent charge recombination process is also spin-selective, that is, $^1(D^{+\bullet}−B−A^{-\bullet})$ recombines to the singlet ground state, while $^3(D^{+\bullet}−B−A^{-\bullet})$ recombines to yield the neutral triplet $^3*(D−B−A)$, which acquires the non-Boltzmann spin population of the triplet RP state.[1,9,20] The spin polarization pattern of the six EPR transitions of $^3*(D−B−A)$ at the canonical (x,y,z) orientations relative to the applied magnetic field can be used to differentiate its formation mechanism from the ordinary spin−orbit intersystem crossing mechanism. For example, when a RP undergoes intersystem crossing by S−T_n mixing, where the degree of mixing is in the order $T_{+1} > T_0 \gg T_{-1}$, the subsequent charge recombination to the neutral triplet yields a (e,e,e,e,e,e) polarization pattern (low-field to high-field), while S−T_0 mixing alone yields an (a,e,e,a,a,e) pattern.[1,9,20] The spin-polarized neutral molecular triplet state resulting from RP recombination may be observable even when J is too large to observe the RP signal itself.[20]

Here, we describe the spin dynamics for nondiffusing RPs having restricted geometries and a large J coupling in the high magnetic field limit. For example, at high magnetic fields, when the energy of $|T_{+1}\rangle$ is close to that of $|S\rangle$, even a small isotropic HF coupling leads to the population of $|T_{+1}\rangle$. We present an

exact calculation of the triplet quantum yield (QY) in the large J regime, where one or both electrons interact with a nearby spin-1/2 nucleus. These simple cases give insights into the RP spin dynamics when more than one nucleus is involved. An approximate relationship for the triplet QY is then presented for a singlet born RP, which can be used for realistic models of the RP. This relationship takes into account the individual singlet and triplet RP recombination rates and includes all relevant nuclear configurations that are involved in singlet–triplet mixing. The approximation becomes more accurate as the ratio of HF to exchange coupling becomes smaller. Our result is not perturbative,[21−23] and in particular, it can also be used near S−T$_{+1}$ resonance, where the energy gap between these two levels becomes smaller than the energies represented by the recombination rates and HF coupling.

The conservation of total spin along the magnetic field direction implies that populating the $|T_{+1}\rangle$ state is accompanied by net spin polarization transfer to the nuclei. Chemically induced dynamic nuclear polarization (CIDNP) has been discussed intensively in the literature;[3,10,13,14,18,22−28] however, these models assume a time-dependent fluctuating J, which results from the diffusive motion of the RP spins or conformational fluctuations in the compound bearing both spins. Consequently, the coherence between quantum states is suppressed, and the singlet and triplet RP states interconvert incoherently. Diffusion also introduces asymmetry in the EPR line shape, deviating from the antiphase doublet pattern predicted by simple theory.[29−31] In contrast, we consider the case in which the two spins comprising the RP are constrained to a highly restricted distance and geometry within a single molecule and experience a large, but constant J. Therefore, the mixing between singlet and triplet RP states is coherent; dephasing and relaxation are introduced into the model only by spin-selective singlet and triplet RP recombination.

■ THEORY

RP in a Magnetic Field Interacting with Nearby Nuclear Spins. The general spin Hamiltonian of the RP with its surrounding nuclei is

$$H = H_Z + H_{exc} + H_I \tag{1}$$

$$H_Z = \mu_B B \cdot g_1 \cdot S_1 + \mu_B B \cdot g_2 \cdot S_2 \tag{2}$$

$$H_{exc} = S_1 \cdot J \cdot S_2 + S_1 \cdot D \cdot S_2 \tag{3}$$

$$H_I = \sum_i I_1^i \cdot A_1^i \cdot S_1 + \sum_j I_2^j \cdot A_2^j \cdot S_2 \tag{4}$$

where H_Z is the Zeeman splitting term, H_{exc} is the exchange interaction, H_D is the dipolar interaction, and H_I is the HF coupling term (see Figure 1). The interaction with the magnetic field is given by the Zeeman term H_Z, where g_1 and g_2 are tensors. The spin−orbit interaction contributes to g anisotropy in the first order and to the dipolar interaction in the

second order. The interaction of each electron spin with its nearby nuclear spins is incorporated in the HF term H_I where A_1^i, A_2^i are generally anisotropic. For simplicity, the RP is studied in solution, where we assume that fast molecular tumbling averages all anisotropies. As a result, the total Hamiltonian is

$$H = \omega_1 S_1^z + \omega_2 S_2^z - J S_1 \cdot S_2 + \sum_i a_1^i S_1 \cdot I_1^i + \sum_j a_2^j S_2 \cdot I_2^j + \frac{J}{4} \tag{5}$$

where J is the isotropic part of the spin exchange, $\omega_1 = g_1 \mu_B B$ and $\omega_2 = g_2 \mu_B B$ are the isotropic Zeeman energies, and a_1^i and a_2^i are isotropic HF couplings.

We first define the quantum system and its environment (the bath). The singlet and triplet RP states are considered the quantum system, while the singlet ground state and the lowest excited triplet state resulting from spin-selective charge recombination as well as the nuclear spin states are considered as part of the bath. The bath causes dephasing and relaxation of the quantum system. RP recombination to the singlet ground state occurs with the rate constant $k_S = 1/\tau_S$, while recombination to the triplet state occurs with $k_T = 1/\tau_T$, where τ_S and τ_T are the singlet and triplet RP lifetimes, respectively.

Quantum Behavior. Upon irradiation, the RP is generated in its singlet state. We assume that formation of the RP is sufficiently fast so that its formation is complete prior to coherent spin state mixing. Thus, the initial quantum state of the system is

$$|\Psi_0\rangle = |S, \psi_n\rangle \tag{6}$$

with $|\psi_n\rangle$ being the nuclear spin state. The RP density matrix is obtained by taking the trace over the nuclear states, for example, the density of the singlet state is $\rho_{ss} = \sum_n \langle S, \psi_n | \rho | S, \psi_n \rangle$. A convenient quantity that simplifies the description of the system is the QY of the singlet or triplet states that result from RP recombination. The singlet QY is defined as

$$QY_S = k_S \int_0^\infty \rho_{ss}(t)\, dt \tag{7}$$

with a similar expression for the triplet QY. The RP EPR spectrum line shape depends on the QY of different triplet sublevels.

To calculate QY, it is not necessary to find the time-dependent density matrix $\rho(t)$. An exact expression for the QY was derived by Hore and Timmel[5,32] which is valid either in the absence of the exchange ($J = 0$) or in the absence of the HF coupling ($a = 0$) and when motional dephasing is neglected. The model presented here consists of four spin states coupled to each other via the HF and large J interaction in the presence of the magnetic field. Nevertheless, the QY can still be calculated without solving for the time-dependent density matrix. This can be done either by calculating the inverse of the Liouvillian matrix or by solving for the stationary solution of the master equation.

Treatment for One RP Spin Interacting with Nearby Nuclear Spins. In the simplest model of the HF interaction, one RP spin is coupled to a single nearby nucleus I, that is

$$H_I = a S_2 \cdot I \tag{8}$$

The axial symmetry implies that the total spin along the magnetic field $S_{total}^z = S_1^z + S_2^z + I_2^z$ is a conserved quantity. Therefore, states with different S_{total}^z cannot be coupled to each other; therefore, the Hamiltonian is block-diagonal. The singlet
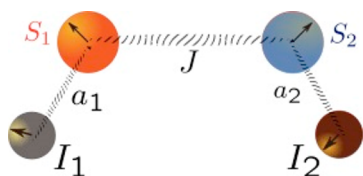

Figure 1. Radical pair spins S_1 and S_2 are coupled to the nearby nuclei I_1 and I_2 and interact with each other with the exchange coupling J.
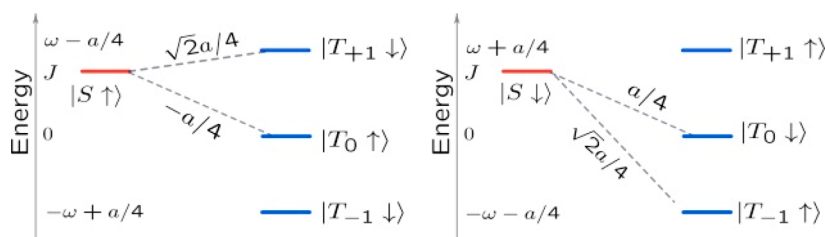
Figure 2. Energy levels of a RP in the presence of exchange, HF, and a magnetic field. One of the RP spins is coupled to a nearby spin-1/2 nucleus. Conservation of S_{total}^z implies that $|S\uparrow\rangle$ couples to $|T_{+1}\rangle$ (left) and $|S\downarrow\rangle$ couples to $|T_{-1}\rangle$.

state is generated in any of $|S;I,m\rangle$ states, where the notation means that the RP forms a singlet and the nuclear state is $|\psi_n = |I,m\rangle$, with $\hat{I}^2|I,m\rangle = I(I+1)|I,m\rangle$ and $\hat{I}^z|I,m\rangle = m|I,m\rangle$. The

conservation of total spin S_{total}^z implies that for a given $|S;I,m\rangle$, only four states ($|S;I,m\rangle$, $|T_0;I,m\rangle$, $|T_{+1};I,m-1\rangle$, and $|T_{-1};I,m+1\rangle$) are coupled to each other. In this basis, the Hamiltonian is

$$H_{I,m} = \frac{1}{4}\begin{pmatrix} 4J & -2ma+\delta\omega & \sqrt{2}\,aA_m^- & -\sqrt{2}\,aA_m^+ \\ -2ma+\delta\omega & 0 & \sqrt{2}\,aA_m^- & \sqrt{2}\,aA_m^+ \\ \sqrt{2}\,aA_m^- & \sqrt{2}\,aA_m^- & 2(m-1)a+4\omega & 0 \\ -\sqrt{2}\,aA_m^+ & \sqrt{2}\,aA_m^+ & 0 & -2(m+1)a-4\omega \end{pmatrix}$$

(9)

where $A_m^\pm = (I(I+1) - m(m\pm1))^{1/2}$ and the Zeeman energy difference is $\delta\omega = 2(\omega_1 - \omega_2)$ and $\omega = (\omega_1 + \omega_2)/2$. Note that while isotropic Zeeman splitting $\delta\omega$ contributes only to S–T$_0$ mixing, the isotropic HF interaction contributes to the mixing of the singlet to all three triplet sublevels. This difference stems from the fact that in the Zeeman term, the magnetic field appears as a classical vector, while in the HF term, the nuclear spin I is a quantum operator. Therefore, while the former can be written as a single term $H \propto B^z S^z$, all components of the spin operator always contribute to the HF term $H \propto I^z S^z + I^y S^y + I^x S^x$.

The advantage of using the conservation of S_{total}^z is that the Hamiltonian is written as 4×4 exact blocks. Given the above Hamiltonian and including the singlet/triplet recombination processes, one can calculate the QY of each of these four states for a given $S_{total}^z = m$, taking the trace over m results in the total QY. The final result depends on J, a, and ω. Equation 9 also indicates that the energy difference between S and T$_0$ is fixed by J, while the S–T$_{\pm1}$ energy gap can be tuned by the magnetic field. When the Zeeman splitting is near the S–T$_{+1}$ resonance, the energies of the T$_0$ and T$_{-1}$ levels are very far from the singlet energy. Therefore, it is expected that the QY of T$_0$ and T$_{-1}$ are small and can be neglected. The QY of T$_{+1}$ is approximately given by

$$QY_{T_+} \approx \frac{k_T(k_T + k_S)}{2I + 1}$$
$$\times \sum_m \frac{(aA_m^-)^2}{((aA_m^-)^2 + 2k_Tk_S)(k_T + k_S)^2 + 8\Delta_m^2 k_T k_S}$$

(10)

where $\Delta_m = J - \omega - (m-1)a/2$ is the energy gap between S and T$_{+1}$ near the resonance point. The above calculation is based on the coherent dynamics of the singlet and triplet RP states; the exchange coupling J is time-independent, and the relaxation is introduced into the model only by RP recombination with rates k_S and k_T. Note that the triplet yield goes to zero when $k_T \to 0$, where the states eventually relax to the singlet ground state. The quantum dynamics of the

above model differs from that of diffusive RP models,[3,10,13,14,22–24,26–31,33,34] where a fluctuating time-dependent J causes incoherent singlet–triplet conversion.

It is interesting to consider two opposite limits of the above QY. When the HF coupling is very small compared to the energy gap or the rate constants, that is, $(aA_m^-)^2 \ll \Delta_m^2, (aA_m^-)^2 \ll k_S k_T$, the QY in eq 10 reduces to

$$QY_{T_+} \approx \frac{2}{3} \frac{(k_T + k_S)a^2 I(I+1)}{k_S(k_T + k_S)^2 + 8\Delta_0^2 k_S}$$

(11)

In the opposite limit, that is, at the resonance and when the rates k_S and k_T are very small, we get

$$QY_{T_+} \propto \frac{k_T}{k_T + k_S} \frac{2I}{2I + 1}$$

(12)

which defines the upper limit of QY of the T$_{+1}$ state. Note that normal perturbation theory cannot be applied at resonance.

As a function of ω, the QY of the T$_{+1}$ state is the sum of Lorentzian (homogeneous) curves resulting from each nuclear spin configuration. Generally, the sum of the large number of Lorentzian curves is an inhomogeneous (Gaussian) function. However, in the above case, the final result retains its Lorentzian shape. This is because the distance between different Lorentzian peaks is always less than the width of each peak. The distance between adjacent peaks is on the order of HF coupling $\Delta_m - \Delta_{m-1} \approx a/2$, while the width of the peak is $w \approx (k_T + k_S)[(a^2/8k_Tk_S) + (1/4)]^{1/2} > a/2$. Even for a large HF constant a, the minimum width (which is realized when $k_T = k_S$) is still greater than $a/2$.

As an example, consider the specific case of a nuclear spin $I = 1/2$, where the total spin of the RP and nucleus along the z-axis takes four possible values $S_{total}^z = \pm1/2, \pm3/2$; two states with $S_{total}^z = \pm3/2$ correspond to two isolated states $|T_{+1}\uparrow\rangle$ and $|T_{-1}\downarrow\rangle$, which are isolated and are relevant only when the RP is initially generated in the triplet state. Three states $|S\uparrow\rangle$, $|T_0\uparrow\rangle$, and $|T_{+1}\downarrow\rangle$ have $S_{total}^z = 1/2$, and their Hamiltonian block in this basis is

$$H_{1/2} = \frac{1}{4}\begin{pmatrix} 4J & -a & a\sqrt{2} \\ -a & 0 & a\sqrt{2} \\ a\sqrt{2} & a\sqrt{2} & -a + 4\omega \end{pmatrix}$$ (13)

Three states $|S\downarrow\rangle$, $|T_0\downarrow\rangle$, and $|T_{-1}\uparrow\rangle$ have $S_{total}^z = -1/2$, and their Hamiltonian block in this basis is

$$H_{1/2} = \frac{1}{4}\begin{pmatrix} 4J & a & -a\sqrt{2} \\ a & 0 & a\sqrt{2} \\ -a\sqrt{2} & a\sqrt{2} & -a - 4\omega \end{pmatrix}$$ (14)

It is also important to note that when the RP is photogenerated, the singlet can be $|S\uparrow\rangle$ or $|S\downarrow\rangle$ states with equal probability of 1/2. By changing the magnetic field, these two states can become close in energy to $|T_{+1}\downarrow\rangle$ and $|T_{+1}\uparrow\rangle$; however, the conservation of total spin forbids coupling between the singlet and $|T_{+1}\uparrow\rangle$, Figure 2. Therefore, by tuning the magnetic field, only half of the singlet population can be brought into resonance with triplet state T_{+1}.

This model can be generalized to the case where the RP spin is coupled not to one but to a few nuclei with identical HF couplings. The nuclear Hamiltonian is then $H_I = aS_2 \cdot \sum_n I_n$. Here, besides the total spin along the magnetic field, the total nuclear spin $I = \sum_n I_n$ is also a conserved quantity. Therefore, for this Hamiltonian, one has to first find the possible values of total magnetic spin I with the corresponding probabilities, and then for each I, one uses the Hamiltonian (eq 9) and calculates the QY.

Treatment for Both RP Spins Interacting with Nearby Nuclei. So far, it was assumed that only one of the RP spins interacts with its neighboring nucleus. When both spins interact with their neighboring nuclei, it is not clear whether the singlet−triplet mixing is going to be enhanced or be reduced. Recall that the difference between the Zeeman couplings contributes only to S−T_0 mixing, while the HF interaction couples the singlet to all triplet sublevels.

Consider the simplest example when each RP spin interacts with a spin-1/2 nucleus $I_1 = I_2 = 1/2$ with the same HF coupling, $a_1 = a_2$. The RP singlet can be generated in four possible states $|S,s\rangle$, $|S,t_0\rangle$, $|S,t_{+1}\rangle$, and $|S,t_{-1}\rangle$ where $|s\rangle$, $|t_0\rangle$, $|t_{+1}\rangle$, and $|t_{-1}\rangle$ represent the singlet and triplet states of the two nuclei. First, consider $|S,s\rangle$; the HF interaction couples this state to three new states $|T_0,t_0\rangle$, $|T_{+1},t_{-1}\rangle$, and $|T_{-1},t_{+1}\rangle$, and the Hamiltonian in the basis $|S,s\rangle$, $|T_0,t_0\rangle$, $|T_{+1},t_{-1}\rangle$, $|T_{-1},t_{+1}\rangle$ is

$$H = \frac{1}{4}\begin{pmatrix} 4J & 2a & -2a & -2a \\ 2a & 0 & 2a & 2a \\ -2a & 2a & 4\omega - 2a & 0 \\ -2a & 2a & 0 & -2a - 4\omega \end{pmatrix}$$ (15)

The initial RP prepared in $|S,t_{+1}\rangle$ couples to $|T_{+1},s\rangle$ with the Hamiltonian

$$H = \frac{1}{4}\begin{pmatrix} 4J & 2a \\ 2a & 4\omega \end{pmatrix}$$ (16)

The initial state $|S,t_z\rangle$ is only coupled to $|T_0,s\rangle$, and the initial pair $|S,t_{-1}\rangle$ is coupled to $|T_{-1},s\rangle$, and $|S,t_{+1}\rangle$ is coupled to $|T_+,s\rangle$. For very large J, where $J = \omega$, we do not consider $|S,t_0\rangle$ and $|T_0,s\rangle$ because only the T_{+1} state is close to resonance with the RP singlet.

Equations 15 and 16 show that the isotropic and identical $a_1 = a_2$ HF couplings do mix the singlet with triplet states, while the Zeeman couplings $g_1 = g_2$ do not; the mixing depends on the difference of the Zeeman couplings and the sum of the absolute values of the HF couplings. The total QY of T_{+1} is plotted in Figure 3. This figure also compares the exact yield derived above to the approximate yield derived in the next section for a general RP interacting with several nuclear spins.
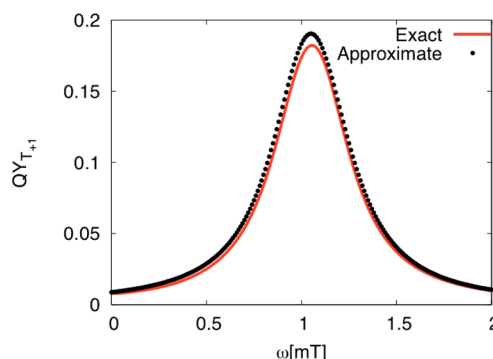

Figure 3. Exact QY of T_+ (red solid line) as a function of the (average) Zeeman energy ω when two RP spins interact with two nuclear spins $I_1 = I_2 = 1/2$. Here $J = 1$ mT, $a_1 = a_2 = 0.2$ mT, and $k_S = k_T = 2.8 \times 10^6$ s^{-1}. For comparison, the result of the approximate general method (eq 24) is shown (dotted line).

General Case of Both RP Spins Interacting with Several Nuclear Spins. The above cases are the simplest examples of RP spins interacting with nearby nuclei. In the general case for both RP spins coupled to their neighboring nuclei, the total nuclear spin is not conserved, and therefore, it is not easy to write the Hamiltonian in 4 × 4 blocks. To solve this problem numerically, one has to consider a large block of the Hamiltonian containing many different nuclear states. For example, consider the case where RP spins S_1 and S_2 interact with two nearby nuclei I_1 and I_2 with different HF couplings a_1 and a_2. The initial state of the RP is assumed to be $|S;m_1,m_2\rangle$ where the short notation $|m_1,m_2\rangle$ represents the nuclear state $|m_1,m_2\rangle = |I_1 m_1\rangle|I_2 m_2\rangle$ (represented by $|\psi_n\rangle$ in the previous section). Up to first order, this state is coupled to $|T_{+1},m_1-1,m_2\rangle$ and $|T_{+1},m_1,m_2-1\rangle$. However, this description is incomplete; in principle, $|S;m_1,m_2\rangle$ can be coupled to all states with total magnetization $S_{total}^z = m_1 + m_2$, and that includes, for example, the state $|S,m_1-1,m_2+1\rangle$. The coupling between this latter state and the initial state is to second order $\propto a_1^2, a_2^2$. When the singlet energy is not close to any of the triplet energies, one can safely disregard these latter states and find the population densities using perturbation theory.[35] However, when the singlet energy is close to the triplet T_{+1} energy, one has to include all possible states with a given total spin S_{total}^z. For large nuclear spins I_1 and I_2 or when large number of nuclear spins are considered, this block of the Hamiltonian can be very large.

Below, we present a general procedure that can be used to derive an accurate estimate of the QY of the T_{+1} state, even when the T_{+1} energy is equal to the singlet energy. To do so, the HF Hamiltonian is written as
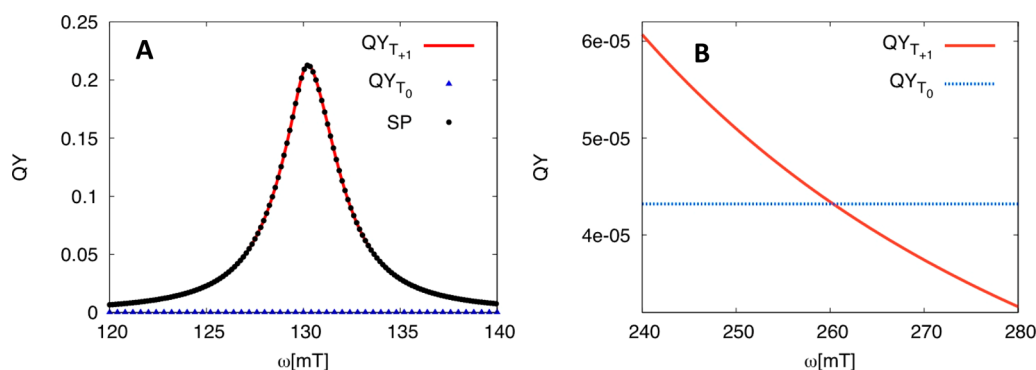
$$H_I = H_I^1 + H_I^2$$ (17)

Figure 4. (A) QY of T_+ (red solid), T_0 (black dots), and the minus polarization (blue crosses) of nuclear spins as a function of the (average) Zeeman energy ω. The peak is around the resonance point $\omega \approx J$. (B) The QY of T_0 (dotted line) exceeds the QY of T_+ (solid line) for $\omega > 2J$. The RP exchange coupling is $J = 130 \pm 10$, mT and the RP recombination rates are $k_S = 2 \times 10^6$ s^{-1} and $k_T = 1 \times 10^6$ s^{-1} at 80 K. One RP spin is coupled to four protons with $a_1 = 1.35$ mT, and the other is coupled to two protons with $a_2 = 0.5$ mT.

$$H_I^1 = \frac{1}{2}(S_1 - S_2)\cdot K$$
$$= \frac{1}{2}(S_1^z - S_2^z)K^z + \frac{1}{4}(S_1^+ - S_2^+)K^- + \frac{1}{4}(S_1^- - S_2^-)K^+ \tag{18}$$

$$H_I^2 = \frac{1}{2}(S_1 + S_2)\cdot L$$
$$= \frac{1}{2}(S_1^z + S_2^z)L^z + \frac{1}{4}(S_1^+ + S_2^+)L^- + \frac{1}{4}(S_1^- + S_2^-)L^+ \tag{19}$$

where we introduce the following nuclear spin operators

$$L = \sum_i a_{1i}I_{1i} + \sum_j a_{2j}I_{2j} \tag{20}$$

$$K = \sum_i a_{1i}I_{1i} - \sum_j a_{2j}I_{2j} \tag{21}$$

The first Hamiltonian term H_I^1 couples the singlet to triplets; the second term H_I^2 couples triplets to each other and also determines the (diagonal) energy term of each state. Suppose that J and ω are large such that the T_{+1} energy level is close to the S state while T_0 and T_{-1} are separate from S by energy gaps of J and $J + \omega$. The coupling between different triplet states, which is determined by the last two terms in H_I^2, is on the order of $a_i/\omega \ll 1$, and therefore, it can be neglected at large magnetic fields; the first term in H_I^2 contributes to the local energies, and it is retained in the calculation. Three terms in H_I^1 couple the singlet state to T_0, T_{+1}, and T_{-1}.

Equation 21 defines operator $K^+ = \sum_i a_{1i}I_{1i}^+ - \sum_j a_{2j}I_{2j}^+$ and its complex conjugate K^-, which are generalized raising and lowering spin operators. We find the (orthonormal) eigenvectors of the nuclear spin operator K^+K^-

$$K^+K^-|r_n\rangle = r_n|r_n\rangle \tag{22}$$

This process is similar to finding the eigenvectors of the total spin operator. For example, the singlet and triplet states of the sum of two proton spins $L = I_1 + I_2$ are in fact the eigenvectors of L^+L^-. The procedure is generally used for the numerical calculation of the Clebsch−Gordon coefficients (which are the components of each eigenstate). In eq 22, this process is generalized to several spins added to each other with different coefficients a_is. All eigenvalues r_ns are zero or positive. The orthonormal basis $|r_n\rangle$ has the following properties; first $|r_n\rangle$ is also an eigenvector of the total magnetization $M = \sum_i I_{1i}^z + \sum_j$

I_{2j}^z. This is expected because the magnetization is a conserved quantity, although in general $|r_n\rangle$ mixes states with different total nuclear spin. Second, when K^- acts on the $|r_n\rangle$ basis, it gives another $|l_n\rangle$ basis (i.e., $K^-|r_n\rangle = (r_n)^{1/2}|l_n\rangle$), which are eigenvectors of K^-K^+

$$K^-K^+|l_n\rangle = r_n|l_n\rangle \tag{23}$$

Finally, in the limit when all HF couplings are equal, the basis $|r_n\rangle$ goes to the well-known eigenbasis of total nuclear spins $|I,m\rangle$.

The above basis can be used to calculate the QY of the T_+ state. The singlet state is $|S,l_n\rangle$, which then is coupled to $|T_{+1},r_n\rangle$, whose energy is approximately $E_+ = \omega + \langle r_n|L^z|r_n\rangle/2$. The QY of the T_{+1} state is given approximately by

$$QY_{T_+} \approx \frac{k_T(k_T + k_S)}{\prod_i (2I_i + 1)}$$
$$\times \sum_n \frac{r_n}{(r_n + 2k_Tk_S)(k_T + k_S)^2 + 8\Delta_n^2 k_Tk_S} \tag{24}$$

where $\Delta_n = J - \omega - \langle r_n|L^z|r_n\rangle/2$. When all of the HF couplings are equal, we find that $r_n = (aA_{m=n})^2$, and we get the result of eq 10. Figure 3 compares the result of this calculation with the exact result for the simple case of $a_1 = a_2 = a$, when $a/J = 0.2$.

QY of the T_{+1} State in D−B−A Molecule 1.
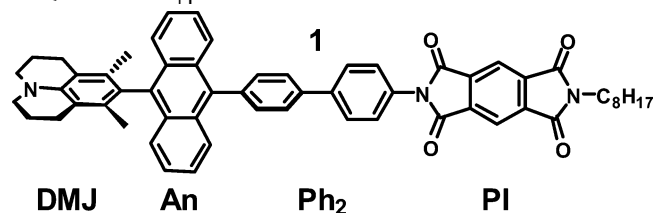
We recently presented experimental results on D−B−A molecule **1** in which photoexcitation of the charge-transfer state of the DMJ−An electron donor leads to rapid intramolecular charge separation to produce DMJ$^{+\bullet}$−An−Ph$_2$−PI$^{-\bullet}$.[20] The RP exchange coupling is $J = 130 \pm 10$ mT, and the RP recombination rates are $k_S = 2 \times 10^6$ s^{-1} and $k_T = 1 \times 10^6$ s^{-1} at 80 K. If we assume that one of the RP spins interacts with four protons having $a_1 = 1.35$ mT and the other spin interacts with two protons having $a_2 = 0.5$ mT, Figure 4A shows that the dependence of QY_{T_+} on magnetic field strength exhibits a Lorentzian peak around the resonance point. Note that because increasing the magnetic field closes the energy gap

between the S and T$_+$, the QY is quite high despite the fact that $J \gg a$. Having a large J only reduces the QY of the other two triplets T$_0$ and T$_{-1}$. Upon increasing the magnetic field beyond the resonance $\omega > J$, the energy gap between the singlet and T$_{+1}$ increases. When $\omega > 2J$, the T$_{+1}$−S and T$_0$−S energy gaps are equal, and therefore, the their QYs become equal (Figure 4B).

Polarization Transfer to Nuclear Spins. The RP spins are generated in the singlet state with total zero spin along the z-axis. The transverse (nonsecular) parts of the nuclear spin couplings (a_x, a_y) couple this state to T$_{\pm 1}$. When the T$_{+1}$ energy is close to that of the singlet state, some initial RP spins convert to T$_{+1}$, and their spin increases by one. The conservation of total spin along the magnetic field implies that the magnetization has transferred to the nuclear spins.[36−39] In Figure 4A, we also show the polarization transfer to nuclear spins. In this particular case, because the QY of other triplet states is negligible, the nuclear polarization is almost equal to the QY of T$_{+1}$ with opposite sign.

CONCLUSION

We have shown that when the exchange coupling between two RP spins is large, the overall QY of singlet−triplet mixing is very small. However, application of a strong magnetic field can close the gap between the singlet and triplet T$_{+1}$ states, so that in the presence of the HF coupling, this triplet state can be populated significantly, leading to preferential population of the T$_{+1}$ sublevel of the neutral triplet state upon RP recombination. The Zeeman splitting causes a very small population of the T$_0$ state but not of the T$_{\pm 1}$ states. Moreover, when the two RP spins are surrounded by identical environments, the Zeeman splitting does not couple the singlet state to any of the triplet states, but the HF interaction does. The theory presented here is limited to isotropic interactions. However, because the presence of the magnetic field breaks the spherical symmetry in any case, one can also apply these results to the case where only rotational (axial) symmetry around the magnetic field is preserved. The total magnetization along the magnetic field is conserved. Therefore, the QY of the T$_{+1}$ state also represents the QY of polarization transfer to the nuclear spins.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Details on calculation of the quantum yield. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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