CONTRIBUTIONS OF SPIN–SPIN INTERACTIONS TO THE MAGNETIC FIELD DEPENDENCE OF THE TRIPLET QUANTUM YIELD IN PHOTOSYNTHETIC REACTION CENTERS

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Calculations are presented which show that dipolar coupling in the primary radical ion pair of quinone-depleted photosynthetic reaction centers substantially affects the magnetic field dependence of the triplet quantum yield, as does exchange coupling to the semiquinone–Fe(II) complex, when quinone is present. Inclusion of these interactions resolves significant discrepancies between theory and experiment.

1. Introduction

The observation in photosynthetic reaction centers (RCs) that the quantum yield of triplets, Φ_T, depends on the magnitude of an applied magnetic field has provided important insight into the origin of the triplet. As shown schematically in fig 1, the singlet photoexcited electron donor, ^1P, transfers an electron to the primary acceptor, I, with a nearly 100% quantum efficiency [1]. As a consequence, the molecular triplet state of the donor, ^3P, cannot be formed in appre-
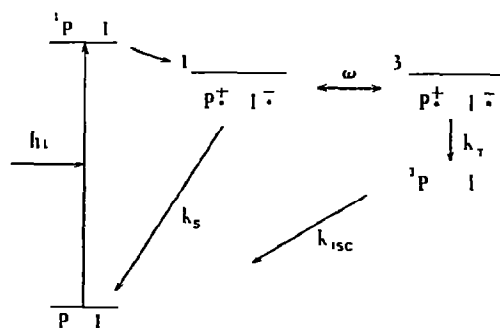

Fig. 1. A simplified scheme for the primary events in quinone-depleted RCs. k_S and k_T are the singlet and triplet radical pair recombination rate constants; ω is the singlet–triplet mixing frequency. The bar above $P^{\pm}I^{\mp}$ denotes a spin-correlated radical pair.

ciable yield by conventional intersystem crossing and is thought to be produced by ion-pair recombination [2]. In order to conserve angular momentum in the recombination, the spin multiplicity of the radical ion pair must evolve from the singlet to the triplet state before ^3P can be formed, and magnetic field effects are manifested because the singlet–triplet mixing in the radical pair, $^1[P^{\pm}I^{\mp}] \overset{\omega}{\rightleftharpoons} {}^3[P^{\pm}I^{\mp}]$, depends on magnetic interactions. Although the effects of small magnetic fields (0–1000 G) are qualitatively quite simple, there has been no satisfactory quantitative analysis of these effects in RCs. The purpose of this paper is to demonstrate that electron–electron dipolar coupling in the primary radical pair, $P^{\pm}I^{\mp}$, which has been previously ignored, may be the key to a quantitative understanding of the magnetic field effects at low field for quinone-depleted RCs. Furthermore, an improved treatment of the effects of spin coupling with other paramagnetic centers is presented to rationalize the magnetic field effects for RCs containing semiquinone radicals.

Φ_T in RCs at room temperature is observed to decrease when a magnetic field is applied, reaching a minimum at ≈ 1000 G [3–5]. Φ_T increases at higher field, reaching a value in excess of that at zero field, and levels off at fields greater than 50 kG [6,7]. At low field ($0 \leqslant H \leqslant 1000$ G) there are four experimental characteristics of the field dependence: the absolute quantum yield at zero field, $\Phi_T(0)$; the ratio of the

quantum yields at 1000 and 0 G, $\Phi_T(1000)/\Phi_T(0)$, the field at which $\Phi_T(H) = \frac{1}{2}[\Phi_T(1000) + \Phi_T(0)]$, the so-called $B_{1/2}$ value; and the shape of the field dependence, in particular the observation that $\Phi_T(H)$ decreases monotonically from its value at zero field. At high field ($H \geqslant 1000$ G) there are two experimental characteristics of the field dependence the upward curvature of $\Phi_T(H)$, which is primarily determined by the g-factor difference between P^+ and I^- [6], and the limiting quantum yield, which is obtained when ω greatly exceeds the recombination rates, $\Phi_T(\infty) = k_T/(k_S + k_T)$ [7]. A further experimental characteristic is the optically determined lifetime of the radical pair (10–20 ns).

There is enormous variability in reports of magnetic field effects in RCs from different laboratories. Triplets are formed in RCs only when electron transfer from I^- to a secondary acceptor is blocked [8]. As they are normally isolated, RCs contain one molecule of tightly bound ubiquinone, Q [9]. Secondary electron transfer from I^- to Q can be blocked in one of three ways; removal of Q, one-electron reduction of Q to Q^-, or two-electron reduction of Q to Q^{2-}. The complete removal of Q provides the simplest scheme and will be discussed first. If Q^- is present, spin–spin interactions with I^- are possible and with Q^{2-} present, there may be electrostatic interactions with I^-. A further complication is the presence of a paramagnetic Fe(II) in the RC. In the absence of Q there is no evidence for a strong magnetic interaction between $[P^+ I^-]$ and Fe(II), however, the effect may be subtle. If both Q^- and Fe(II) are present, they are strongly spin coupled, and their *combined* effect on the spin dynamics in $[P^+ I^-]$ must be considered.

Theoretical treatments of the triplet quantum yield *at low field* were developed by Werner et al. [10] and Haberkorn and Michel-Beyerle [11]. Both groups had been previously concerned with calculating the quantum yield of ion-pair recombination products *in solution* where radical intermediates are free to diffuse. As such, these treatments are an extension of the well-known radical pair theory of CIDNP [2]. Both groups transferred the formalism to the RC problem, with the additional assertion that the isotropic electron exchange interaction between P^+ and I^- (singlet–triplet splitting, J) should be non-zero and constant in time, as the radicals are not free to diffuse in the RC. Both treatments lead to the important qualitative conclusions that a

radical pair is the precursor to ^3P and that J must be small (of the order of or less than the total hyperfine energy).

In the following we show that there are very significant discrepancies if these treatments are used to quantitatively explain $\Phi_T(H)$ at low field for the simplest case of Q-depleted RCs. The presence of anisotropic dipolar coupling in Q-depleted RCs has recently been demonstrated in the reaction yield detected magnetic resonance (RYDMR) spectrum of $[P^+ I^-]$ [13]. We have shown recently that $\Phi_T(H > 0)$ depends on the *orientation* of the RC in a field and that both the sign and magnitude of this anisotropy depend on field strength [14]. A more subtle fact is that the average yield (average of the yield over equally weighted orientations) should also depend on anisotropic interactions. For example, the anisotropic dipolar coupling between P^+ and I^- produces a zero-field splitting in the radical pair energy levels. As a field is applied, the energy levels mix depending on the orientation of the dipolar tensor relative to the field. Thus, an appropriate average of triplet yields over orientation must be taken, and neither the magnitude nor the field dependence of this average is the same as that obtained assuming that the dipolar interaction is zero. It is demonstrated below that the substantial dipolar coupling masks the expected effects of deuteration of $[P^+ I^-]$ on the low-field characteristics. In addition, we show that for Q^--containing RCs, spin exchange between I^- and Q^-Fe(II) is expected to *increase* $B_{1/2}$, contrary to previous predictions and in agreement with experiment.

2. Calculations

The numerical treatment introduced by Werner et al. [10] was modified for inclusion of the dipolar interaction. This two-proton model was chosen because it is the simplest model in which both electron spins are affected by hyperfine fields, and the number of nuclear states is sufficient to avoid anomalous hyperfine resonances in the calculated $\Phi_T(H)$. Furthermore, when J and the dipolar coupling are zero, the two-proton model gives yields which are within 2% of an even more accurate four-proton model. The standard dipolar hamiltonian, parameterized in terms of the zero-field splittings D and E, was added to the isotropic hamiltonian and the yield was computed for orientations specified by

the polar angles θ and ϕ. Sufficiently accurate results for the average yield were obtained by numerical integration of the yield using Simpson's rule with twenty-five orientations, comprising five equally spaced values of ϕ between $\phi = 0$ and $90°$ and five equally spaced values of $\cos\theta$ between $\cos\theta = 0$ and 1. This calculation was performed for $H = 0, 10, 20, 40, 70, 100,$ and 1000 G. The yields at higher fields were obtained using expressions we have presented elsewhere [6,14].

For the purposes of modeling the data, we will take as given the two hyperfine coupling constants, $A_{p\pm}/g_e\beta = -9.5$ G and $A_{I\mp}/g_e\beta = 13$ G, which are consistent

Table 1

The calculated effects of various parameters on the triplet quantum yield, low-field modulation of the yield, $B_{1/2}$ value, and curvature at low field ($H < 1000$ G). The curvature is described by the presence or absence of a resonance, an initial rise in $\Phi_T(H)$ due to level crossing. The calculations were performed using a two-proton model with $Ap\pm/g_e\beta = -9.5$ G and $A_{I\mp}/g_e\beta = 13$ G. For comparison, experimental results are: $\Phi_T(0) = 0.21 \pm 0.07$; $\Phi_T(1000)/\Phi_T(0) = 0.49 \pm 0.02$, $B_{1/2} = 42 \pm 5$ G; no resonances

$10^{-7} k_S$ (s^{-1})	$10^{-7} k_T$ (s^{-1})	$J/g_e\beta$ (G)	$D/g_e\beta$ (G)	$E/g_e\beta$ (G)	$\Phi_T(H=0)$	$\Phi_T(1000)/\Phi_T(0)$	$B_{1/2}$ (G)	Resonances
2	10	0	0	0	0.74	0.71	18	no
5					0.57	0.62	18	no
10					0.41	0.54	18	no
20					0.25	0.47	20	no
50					0.10	0.40	30	no
10	5	0	0	0	0.34	0.51	18	no
	10				0.41	0.54	18	no
	20				0.42	0.56	21	no
	50				0.38	0.51	30	no
	100				0.30	0.45	41	no
20	10	−10	0	0	0.20	0.40	30	slight [a]
		0			0.25	0.47	20	no
		10			0.22	0.36	26	no
		20			0.14	0.30	39	yes
20	10	0	−40	0	0.13	0.60	47	yes
			−30		0.17	0.55	34	no
			−25		0.18	0.52	30	no
			0		0.25	0.47	20	no
			25		0.20	0.48	28	no
10	10	−20	−45	0	0.16	0.46	28	no
		−15			0.13	0.72	35	no
		−10			0.13	0.91	100	yes
		0			0.17	0.70	64	yes
		10			0.31	0.44	25	no
		20			0.34	0.26	26	no
10	5	0	−45	10	0.18	0.53	43	yes
10	10	0	−45	10	0.23	0.55	40	slight [a]
			−45	15	0.26	0.50	34	no
			−60	15	0.21	0.49	46	slight [a]
			−60	20	0.24	0.43	38	no
10	20	0	−45	10	0.26	0.56	39	no
			−60	15	0.24	0.52	46	no

[a] Slight means that an initial increase in $\Phi_T(H)$ is predicted, but it is less than the 2% experimental uncertainty.

with the known EPR data for P^+ [15] and I^- [16] [*]. For fully deuterated RCs, $A_{P^+}/g_e\beta = -3.9$ G and $A_{I^-}/g_e\beta = 8.8$ G are used. The variables to be considered are $k_S, k_T, J, D,$ and E. Each variable will be tested against the four characteristics of the low-field data,

[*] The negative sign for A_{P^+} is used to avoid a physically unreasonable model in which the singlet states are only coupled to triplet states with small or negative hyperfine energies, but not to triplet states with large positive hyperfine energies.

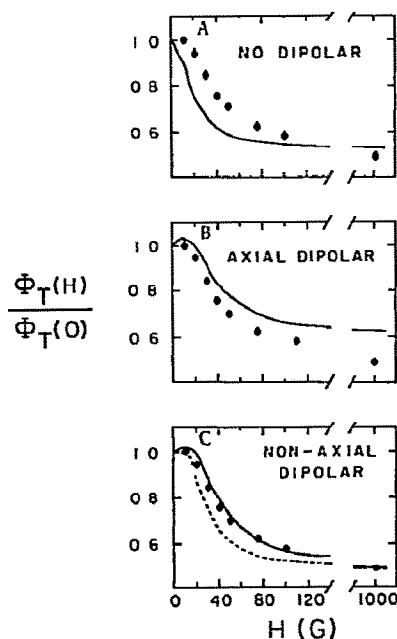
$$\frac{\Phi_T(H)}{\Phi_T(0)}$$

H (G)

Fig. 2. Comparisons of the experimentally determined effect of a magnetic field on the triplet quantum yield in Q-depleted RCs at 293 K and calculated curves for several cases from those listed in table 1. The experimental relative triplet quantum yield is shown in each panel (•); error bars are the standard deviation of five measurements ($\Phi_T(0) = 0.21 \pm 0.07$). In each panel the theoretical curve is calculated for a two-proton model with $A_{P^+}/g_e\beta = -9.5$ G (see footnote [*]) and $A_{I^-}/g_e\beta = 13$ G, and $k_S = k_T = 1 \times 10^8$ s^{-1} and $J = 0$ (J is likely to be non-zero, see table 1). (A) No dipolar coupling illustrating the basic discrepancy between theory and experiment at low field. (B) The effect of including an axial dipolar interaction between P^+ and I^- with $D = -35$ G and $E = 0$. (C) The effect of including a non-axial dipolar interaction between P^+ and I^- for the cases. $D = -60$ G, $E = 15$ G (——) and $D = -45$ G, $E = 15$ G (- - -).

the two associated with the high-field data, and the radical pair lifetime. The results are summarized in table 1.

3. Experimental and results

Q-depleted RCs were prepared as previously described [17]. The sample was held in a cuvette at 293 K in a Helmholtz coil ($0 \leq H \leq 500$ G) or a superconducting solenoid ($0 \leq H \leq 50$ kG). Quantum yields were measured as described elsewhere [18]. $\Phi_T(H)$ is shown in fig. 2. $\Phi_T(0) = 0.21 \pm 0.07$. $\Phi_T(1000)/\Phi_T(0) = 0.49 \pm 0.02$. $B_{1/2} = 42 \pm 5$ G. $\Phi_T(H)$ is independent of field for $H < 10$ G within the experimental uncertainty, then decreases as H increases for $10 < H < 1000$ G.

4. Discussion

4.1. The effects of k_S, k_T and J

The effects of k_S, k_T and J on the low-field yield have been considered previously by Werner et al. [10] and Haberkorn and co-workers [5,11]. They showed that the triplet radical pair levels are broadened by hyperfine interactions and that both the singlet and triplet levels are lifetime broadened. The value of $B_{1/2}$, in the absence of dipolar coupling, is then determined by whichever is largest: $\hbar k_S/g_e\beta$, $\hbar k_T/g_e\beta$, or the hyperfine interaction energy expressed in G. For $J = D = E = 0$, reasonable fits to $B_{1/2}$ can be obtained only with very large values of k_T ($\approx 1 \times 10^9$ s^{-1}). As a result k_S values of $\approx 2 \times 10^8$ s^{-1} are required to fit $\Phi_T(0)$. These fits are unsatisfactory for two reasons: (i)Values of k_T greater than 5×10^8 s^{-1} are totally incompatible with the yield we have measured at high field (fig 2B) for any value of the g-factor difference [6,14]. (ii) At room temperature, where the triplet quantum yield is low, the radical pair decay is determined primarily by k_S and is measured to be $\approx 9 \times 10^7$ s^{-1} [19]. To further illustrate this discrepancy, the calculated yield for the reasonable values $k_S = k_T = 1 \times 10^8$ s^{-1} and $J = 0$ is compared with the experimental data at low field in fig. 2A. Note that the absolute quantum yield at zero field is the least accurately known experimental char-

acteristic, and small changes in k_S and k_T can generally be used to fit $\Phi_T(0)$ within the experimental uncertainty without greatly affecting the fit to other characteristics. With these qualifications we will consider cases where both k_S and k_T are in the range $(1-2) \times 10^8$ s^{-1} The effect of varying J is shown in table 1. Values of $|J|/g_e\beta$ in excess of 20 G for $k_T <$ 5×10^8 s^{-1} produce an initial rise in Φ_T due to level crossing of S with T_+ or T_- (depending on the sign of J) Such resonances are not observed experimentally

4.2 The effects of D and E

The dipolar coupling does not in itself cause S—T mixing, but modulates the rate of triplet formation by changing the energy splittings between the singlet state and the triplet sub-levels. The effect of D for E = 0 is shown in table 1 for a range of values of J For $J = 0$, an axial dipolar interaction increases $B_{1/2}$ substantially, which is physically reasonable because a dipolar interaction lifts the degeneracy of the zero-field triplet states. The Zeeman interactions have no diagonal matrix elements in the zero-field basis set {S, T_x, T_y, T_z}, and, to first order, the magnetic field does not perturb the energies of the non-degenerate triplet levels. The readjustment of the triplet energy levels upon application of a field and the resulting decrease in triplet quantum yield are not complete until $H/g_e\beta$ $\gg |D|, |E|$. For values of D sufficiently large to fit the experimental $B_{1/2}$ value of ≈ 42 G, however, a low-field resonance is predicted, and the ratio $\Phi_T(1000)/$ $\Phi_T(0)$ becomes much larger than is experimentally observed. An example is shown in fig. 2B. As seen in table 1, varying $J/g_e\beta$ from -20 to $+20$ G does not alleviate these problems without creating others. Thus, it is reasonable to assert that a dipolar interaction may be important, but, for an *axial* tensor, reasonable values of the recombination rate constants, and exchange coupling, the data cannot be fit.

As shown in the last entries of table 1, reasonable agreement with all experimental characteristics can be obtained if the dipolar tensor is *non-axial*, that is, for sizable values of E. Values of $|E|$ close to $\frac{1}{3}|D|$ increase the zero-field quantum yield by bringing one one of the triplet levels back into degeneracy with S at $H = 0$, while not substantially changing the yield at 1000 G. This brings the ratio $\Phi_T(1000)/\Phi_T(0)$ into a range compatible with experiment. The addition of E

also avoids the S—T_- resonances which occur using only D. We have not attempted to fit the data to all parameters, because this is prohibitively expensive at the present time. However, the values of the parameters near the bottom of table 1 clearly bracket values for D and E which would be obtained from a full curve fitting analysis. This is further illustrated in fig. 2C.

4.3. The effects of $Q^{\ddot{}}Fe(II)$

For RCs containing $Q^{\ddot{}}Fe(II)$ there is considerable variation in the reported $B_{1/2}$ values [3–5,13]; they are greater than that reported here for Q-depleted RCs. If $Q^{\ddot{}}Fe(II)$ had the same g factor as $I^{\ddot{}}$, then spin exchange between them would. (i) not affect $B_{1/2}$; (ii) increase the absolute triplet yield because exchange with the uncorrelated spin on $Q^{\ddot{}}Fe(II)$ provides an alternate route to the triplet radical pair state; and (iii) increase the ratio $\Phi_T(1000)/\Phi_T(0)$ because the yield of triplets produced by exchange is not affected by the applied field. These predictions were discussed by Werner et al. [10], however, this model is *not correct* because the g factor of $Q^{\ddot{}}Fe(II)$ [9,17] is substantially different from that of $I^{\ddot{}}$ [16]

In order to see the physical consequences of this difference, consider a simplified model in which $Q^{\ddot{}}$ in the $Q^{\ddot{}}Fe(II)$ complex is treated as a spin 1/2 particle [‡]. Exchange between $I^{\ddot{}}$ and $Q^{\ddot{}}Fe(II)$ produces S—T mixing in the radical pair, but, due to the difference in the g factors of $I^{\ddot{}}$ and $Q^{\ddot{}}Fe(II)$, this mixing *does* decrease upon application of a magnetic field. For instance, the state Sα mixes with $T_0\alpha$ and $T_+\beta$ at zero field (S, T_0, T_+, and T_- refer to the radical pair, α and β to the $Q^{\ddot{}}Fe(II)$ spin state). Application of a magnetic field splits $T_+\beta$ away from Sα by a Zeeman energy difference of $\Delta g[I^{\ddot{}}-Q^{\ddot{}}Fe(II)]\beta H$, leading to a decreased triplet yield. $B_{1/2}$ for this effect should be $\approx J[I^{\ddot{}}-Q^{\ddot{}}Fe(II)]/\Delta g[I^{\ddot{}}-Q^{\ddot{}}Fe(II)]\beta$. As $\Delta g[I^{\ddot{}}-Q^{\ddot{}}Fe(II)]$ is on the order of 0.2 and $J[I^{\ddot{}}-Q^{\ddot{}}Fe(II)]/g_e\beta$ may be several tens of gauss, $B_{1/2}$ due to this effect could be several hundred gauss, much greater than predicted for hyperfine-induced mixing alone (table 1). Table 2 illustrates the effects

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[‡] Note that this is a very simplified model; a more detailed analysis requires the use of the full spin hamiltonian for $Q^{\ddot{}}Fe(II)$ described in ref. [17] and consideration of the consequences of relaxation within the $Q^{\ddot{}}Fe(II)$ complex.

Table 2
The effects of spin–spin coupling between I^- and $Q^-Fe(II)$, $J[I^- - Q^- Fe(II)]$, on the triplet quantum yield, low-field modulation of the yield and curvature at low field ($H < 1000$ G). The g factor of $Q^- Fe(II)$ was taken as 1 8 [9,17] (see footnote *). The two-proton model was used with: $Ap_z^+ /g_c\beta = -9.5$ G, $A_{I^-}/g_c\beta = 13$ G, $J = D = E = 0$; and $k_S = k_T = 1 \times 10^8$ s^{-1}

$J[I^- - Q^- Fe(II)]$ (G)	$\Phi_T(H = 0)$	$\Phi_T(1000)/\Phi_T(0)$	$B_{1/2}$ (G)
0	0 41	0 54	18
10	0.44	0.64	47
20	0.45	0.72	290

of $I^- - Q^- Fe(II)$ exchange for various coupling constants, $J[I^- - Q^- Fe(II)]$, treating $Q^- Fe(II)$ approximately as a spin $1/2$ particle and using a representative value of 1.8 for the g factor of $Q^- Fe(II)$ [9,17] (see footnote ‡). The ratio $\Phi_T(1000)/\Phi_T(0)$ increases moderately, and the $B_{1/2}$ value increases dramatically with increasing $J[I^- - Q^- Fe(II)]$. Thus, the observation of large $B_{1/2}$ values in $Q^- Fe(II)$ containing RCs is compatible with this theory. At the present time there is so much disagreement in the literature on $B_{1/2}$ values for such RCs that further quantitative analysis is not warranted.

4.4. The effects of deuteration

Partial deuteration of Q^{2-}-containing RCs (which should be magnetically similar to Q-depleted RCs) has recently been reported to have no significant effect on the triplet yield [19]. As shown in table 3, complete deuteration of Q-depleted RCs is predicted to produce a 24% decrease in $\Phi_T(0)$, a 22% decrease in $B_{1/2}$, and little change in $\Phi_T(1000)/\Phi_T(0)$ if the dipolar interaction is not included and if the recombination rate constants,

k_S and k_T, are unaffected by deuteration. However, with $D/g_c\beta = -60$ G and $E/g_c\beta = 15$ G, the value of $B_{1/2}$ for deuterated Q-depleted RCs is predicted to be comparable to that in fully protonated RCs, though there is still a considerable decrease in the absolute yield The important difference is that with these large values of D and E, the $B_{1/2}$ value is not determined primarily by the strength of the hyperfine coupling, but rather by the strength of the dipolar coupling.

Finally, it was also reported that $\Phi_T(0)$ and $\Phi_T(650)/\Phi_T(0)$ are unaffected by partial deuteration of $Q^- Fe(II)$-containing RCs [19,20]; however, the radical-pair decay time is decreased by 23% at 290 K and $H = 0$ [19]. Thus, it is possible that the effect of a decrease in the rate of hyperfine-induced S–T mixing upon deuteration is cancelled by a decrease in the recombination rate constant, k_S, such as to leave the triplet yield unaffected. In Q^--containing RCs, $B_{1/2}$ may again be the same for deuterated and protonated RCs, now because secondary exchange with $Q^- Fe(II)$ may dominate the S–T mixing. In fact, if both exchange and hyperfine interactions are significant, $B_{1/2}$ for deuterated, $Q^- Fe(II)$-containing RCs could be larger than for protonated ones for the following reason. When the RCs are deuterated, a greater portion of the S–T mixing would be due to secondary exchange with $Q^- Fe(II)$ than when the RCs are protonated, and this exchange-induced S–T mixing is expected to have a larger $B_{1/2}$ than the $B_{1/2}$ due to the hyperfine interactions with or without the $P^+ I^-$ dipolar interaction (see above). Though the effect of deuteration on the $B_{1/2}$ of the triplet yield was not reported in ref. [19], deuteration was noted to cause an increase from 40 to 100 G in the $B_{1/2}$ value for another possibly related magnetic field effect, the decrease in radical pair decay time upon application of a field.

Table 3
The effects of various parameters on the triplet quantum yield, low-field modulation of the yield and curvature of low field ($H < 1000$ G) for *deuterated* RCs. The calculations were performed for a two-proton model with $Ap_z^+/G_e\beta = -3.9$ G and $A_{I^-}/g_e\beta = 8$ 8 G

$10^{-7} k_S$ (s^{-1})	$10^{-7} k_T$ (s^{-1})	$J/g_e\beta$ (G)	$D/g_e\beta$ (G)	$E/g_e\beta$ (G)	$\Phi_T(0)$	$\Phi_T(1000)/\Phi_T(0)$	$B_{1/2}$ (G)	Resonances
10	10	0	0	0	0 31	0 57	14	no
			−35		0.11	0 81	63	yes
			−60	15	0.14	0 44	40	no

5. Conclusions

By including dipolar interactions between P^+ and I^- and properly treating spin exchange between I^- and $Q^-Fe(II)$ we have been able to rationalize a number of persistent discrepancies between theory and experiment. Barring an additional magnetic interaction. substantial values of both D and E are required to rationalize $\Phi_T(H)$ for Q-depleted RCs. These values provide a further restriction on the spatial relationship between the primary donor and acceptor in RCs. Both P^+ and I^- are large aromatic radicals. To the extent that the spin density in these radicals can be viewed as lying in a circle, a highly non-axial dipole—dipole interaction suggests that the circles lie like two coins on a table. Detailed calculations of radical pair structures which are compatible with these values of D and E are in progress. The predicted absence of a significant effect of deuteration on $B_{1/2}$ in Q-depleted RCs is a further consequence of the large values of D and E. Finally. the observation that $B_{1/2}$ increases substantially when $Q^-Fe(II)$ is present can be explained by using a simple model for the $I^- - Q^-Fe(II)$ exchange interaction and a representative g factor of $Q^-Fe(II)$.

Acknowledgement

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