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Line-shape analysis of polarized electron paramagnetic resonance spectra of the primary reactants of bacterial photosynthesis

P.J. Hore [a,*], E.T. Watson [a], J. Boiden Pedersen [b] and A.J. Hoff [c]

[a] Physical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ (U.K.), [b] Department of Physics, Odense University, 5230 Odense M (Denmark) and [c] Department of Biophysics, Huygens Laboratory, State University, Leiden (The Netherlands)

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A simple analytical method is described for calculating transient EPR spectra of the primary reactants of photosynthesis. Polarization is generated in the primary radical pair P^+I^- and passed to the acceptor X^- by electron transfer. Satisfactory agreement between theoretical and experimental spectra is obtained by including a dipolar interaction between P^+ and I^- and an anisotropic g tensor for X^-.

Introduction

The primary steps of photosynthesis, the process that converts the energy of light into chemical energy, may be written:

$$\mathrm{PIX} \xrightarrow{h\nu} \mathrm{P^*IX} \rightarrow \mathrm{P^+I^-X} \rightarrow \mathrm{P^+IX^-} \rightarrow \ldots \qquad (1)$$

P is the primary electron donor, I an early transient electron acceptor and X the first stable acceptor. P* is an excited singlet state of P. This reaction scheme is appropriate for the two plant photosystems and for all known photosynthetic bacteria. P^+, I^- and X^- are radicals that can be trapped and have well-characterized electron paramagnetic resonance (EPR) spectra. When observed shortly after flash photolysis, anomalous EPR intensities are found in both plant and bacterial photosystems. These effects, known as chemically induced dynamic electron polarization (CIDEP) [1] or simply electron spin polarization, arise from the combined action of spin exchange and/or dipolar interactions and Zeeman and/or hyperfine interactions within a pair of radicals. Analysis of such transient EPR spectra therefore yields information on the disposition of the components of the reaction centres and on the magnetic interactions between them [2].

Polarization is generated predominantly in the radical pair intermediate P^+I^- which undergoes rapid (approx. 200 ps) electron transfer to form P^+IX^-. This step conserves the electron spin state, and consequently gives quantitative transfer of polarization from I^- to X^-. P^+ and X^- are far enough apart to have a negligibly small magnetic interaction which prevents the production of further polarization. Unlike P^+I^-X, P^+IX^- lives long enough to be easily observable by EPR. Indeed time domain EPR can detect the polarization of this state before it is diminished by relaxation or by further electron transfer reactions. We shall be concerned here solely with these 'maximum polarized' spectra.

In the following paragraphs we describe a particularly straightforward yet accurate method for calculating the polarized EPR spectra of P^+IX^-.

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[*] To whom correspondence should be addressed.

Abbreviation: CIDEP, chemically induced dynamic electron polarization.

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This treatment is an extension of the theory suggested by Pedersen [3]. Specifically we introduce a dipolar interaction between P^+ and I^- and allow the g tensor of X^- to be anisotropic. Both inclusions appear to be essential to account satisfactorily for the CIDEP spectra of randomly oriented reaction centres of *Rhodopseudomonas sphaeroides*. It is inferred (a) that the principal axis of the P^+I^- dipolar interaction is approximately perpendicular to the plane of the semiquinone part of X^-; (b) that the singlet electronic state of P^+I^- lies lower in energy than the triplet; and (c) that the dipolar interaction between P^+ and I^- is about 60-times larger than their exchange interaction.

Theory

To expedite matters a few innocuous simplifications can be introduced. It is assumed that the high-field approximation is valid, i.e., that the Zeeman interaction of the electrons with the applied magnetic field is much larger than any of the other interactions (hyperfine, exchange and dipolar) within or between the radicals involved. In this limit the T_{+1} and T_{-1} states of the P^+I^- radical pair do not participate, and attention can be restricted to the S and T_0 states. Hyperfine interactions between the unpaired electrons and the various nuclei in the three radicals are not included individually, but are dealt with collectively by means of isotropic continuous (gaussian) distributions of hyperfine fields in each radical. Since hyperfine couplings are not resolved in the EPR spectra of reaction centre preparations, this seems a reasonable approximation. At least in bacterial photosystems, although perhaps not in plants (about which less is known) the g tensors of P^+ and I^- are nearly isotropic and are treated here as perfectly so. This approximation however is not made for the g tensor of X^- which is appreciably anisotropic in bacteria. P^+ and X^- (which are separated by approx. 20 nm in the bacterium *Rhodopseudomonas viridis* [4]) are are assumed to have no exchange or dipolar interaction.

For the sake of clarity we first set out the basic framework with isotropic g tensors in the absence of dipolar interactions. We consider initially the radical pair P^+I^-, formed in a singlet electronic state, in a strong magnetic field. P^+ and I^- have nuclear spin states such that they resonate at fields B and B_I, respectively. The electron polarization in P^+ at time t after the creation of the pair is [5]:

$$\Pi_P(B, B_I, t) = -\frac{2JQ(B)}{\omega^2}\sin^2\omega t \tag{2}$$

J is the magnitude of the exchange interaction between the radicals, $Q(B)$ is half the difference in Larmor precession frequencies of the two unpaired electrons in a field of strength B, and

$$\omega^2 = J^2 + Q^2(B) \tag{3}$$

If the electron-transfer step forming P^+IX^- is first order with a rate constant $1/\tau$, then averaging Eqn. 2 over the time t at which the electron transfer takes place gives the polarization of P^+ at times long compared to τ, but short compared to the spin-lattice relaxation time:

$$\Pi_P(B, B_I) = -4JQ(B)\tau^2 \tag{4}$$

provided $4\omega^2\tau^2 \ll 1$, which seems reasonable given the rapidity of the electron transfer ($\tau \approx 200$ ps) and the likely magnitude of ω. $Q(B)$ is defined in terms of the g values (g_P and g_I) and hyperfine couplings (A_j^P and A_k^I of the two radicals in the usual way:

$$Q(B) = \tfrac{1}{2}(g_P - g_I)\mu_B\hbar^{-1}B + \tfrac{1}{2}\sum_j A_j^P M_j^P - \tfrac{1}{2}\sum_k A_k^I M_k^I \tag{5}$$

M_j^P and M_k^I are the magnetic quantum numbers of nuclei j and k in radicals P^+ and I^- respectively, and μ_B is the Bohr magneton. Using the resonance conditions

$$2\pi\nu = g_P\mu_B\hbar^{-1}B + \sum_j A_j^P M_j^P = g_I\mu_B\hbar^{-1}B_I + \sum_k A_k^I M_k^I \tag{6}$$

(ν is the microwave frequency), $Q(B)$ can be written in the more convenient form:

$$Q(B) = -\tfrac{1}{2}g_I\mu_B\hbar^{-1}(B - B_I) \simeq -\mu_B\hbar^{-1}(B - B_I) \tag{7}$$

so that

$$\Pi_P(B, B_I) = bJ(B - B_I) \tag{8}$$

with

$$b = 4\mu_B\hbar^{-1}\tau^2 \tag{9}$$

To get the total polarization of P^+, $\Pi_P(B)$, one must average over all possible nuclear spin states of I^-, i.e., over all values of B_I, thus:

$$\Pi_P(B) = \int_{-\infty}^{+\infty} \mathrm{d}B_I\, \Pi_P(B, B_I) L_I(B_I)$$

$$= bJ(B_P^0 - B_I^0) + bJ(B - B_P^0) \qquad (10)$$

$L_I(B_I)$ is the normalized, unpolarized EPR line-shape and B_I^0 the average resonance field of I^-:

$$B_I^0 = \int_{-\infty}^{+\infty} \mathrm{d}B_I\, B_I L_I(B_I) \qquad (11)$$

If the lineshape function $L_I(B)$ is symmetric then B_I^0 is simply the centre field of the I^- spectrum and is related to the g value of I^- by $B_I^0 = h\nu/\mu_B g_I$. As shown in Eqn. 10, $\Pi_P(B)$ can be written as the sum of two terms: one independent of the off-set of B from B_P^0 (the net polarization) and the other linear in this off-set (the multiplet polarization). The phases of polarization predicted by Eqn. 10 (negative for emission, positive for absorption) agree with the sign rules for net and multiplet CIDEP effects [1], as expected.

Now we turn to X^- formed from I^- by electron transfer. Since there is no correlation between the nuclear spin orientations of the two radicals, the polarization received by X^-, Π_X, is the polarization of I^- averaged over all possible nuclear spin states of that radical. That is, Π_X (using an expression for $\Pi_I(B)$ analogous to Eqn. 10) is given by:

$$\Pi_X = \int_{-\infty}^{+\infty} \mathrm{d}B\, \Pi_I(B) L_I(B) = bJ(B_I^0 - B_P^0) \qquad (12)$$

Thus only the net polarization of I^- survives the electron transfer to X^-.

The polarized EPR spectrum of a radical is the polarization Π_j ($j = \mathrm{P,X}$) multiplied by the corresponding unpolarized line-shape L_j. The complete spectrum of P^+ and X^- is simply:

$$L(B) = \Pi_P(B) L_P(B) + \Pi_X L_X(B)$$

$$= bJ(B_P^0 - B_I^0) L_P(B) + bJ(B - B_P^0) L_P(B)$$

$$+ bJ(B_I^0 - B_P^0) L_X(B) \qquad (13)$$

Typically, $L_P(B)$ and $L_X(B)$ would be gaussian line-shape functions representing unresolved hyperfine couplings:

$$L_j(B) = \left(\frac{2}{\pi}\right)^{1/2} \frac{1}{\Delta B_j} \exp\frac{-2\left(B - B_j^0\right)^2}{\Delta B_j^2}; \quad j = \mathrm{P,X}, \qquad (14)$$

where ΔB_j is the linewidth at the points of maximum slope and B_j^0 is the centre field of the spectrum ($B_j^0 = h\nu/\mu_B g_j$).

This treatment is easily extended to include an axially symmetric dipolar interaction (dipolar parameter, D) between P^+ and I^-. Inspection of the high-field hamiltonian in the ST_0 basis reveals that J and D only affect the polarization through their influence on the energy difference between the S and T_0 states:

$$E_S - E_T = 2J + \frac{D}{3}(3\cos^2\xi - 1) \qquad (15)$$

where ξ is the angle between the dipolar axis of the P^+I^- triplet and the field direction. The correct way therefore to include the dipolar interaction is the replace J in all three terms of Eqn. 13 by:

$$J + \frac{D}{6}(3\cos^2\xi - 1) \qquad (16)$$

It is only slightly more complicated to introduce an anisotropic g tensor for X^- (g_X). The isotropic lineshape function $L_X(B)$ should be replaced by $L_X(B, \theta, \phi)$, where the Euler angles θ and ϕ define the orientation of the principal axes of g_X with respect to the field direction. If, for every orientation (θ, ϕ), X^- has a gaussian lineshape with width ΔB_X then [6]

$$L_X(B, \theta, \phi) = C \exp\frac{-2\left\{B - B_X^0(\theta, \phi)\right\}^2}{\Delta B_X^2} \qquad (17)$$

$$B_X^0(\theta, \phi) = \frac{h\nu}{\mu_B g_X(\theta, \phi)} \qquad (18)$$

$$g_X^2(\theta, \phi) = g_X(x)^2 \sin^2\theta \cos^2\phi$$

$$+ g_X(y)^2 \sin^2\theta \sin^2\phi + g_X(z)^2 \cos^2\theta \qquad (19)$$

C is a normalization constant such that

$$\int_{-\infty}^{+\infty} \mathrm{d}B \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta\, L_X(B, \theta, \phi) \sin\theta = 1 \qquad (20)$$

The isotropic lineshape of P^+ (as given by Eqn. 14) should be scaled by $1/4\pi$ to ensure a similar normalization.

The revised form of Eqn. 13 is now

$$\begin{aligned} L(B,\theta,\phi) = {} & \frac{b}{4\pi}\left\{J+\frac{D}{6}(3\cos^2\xi-1)\right\} \\ & \times\left\{\left(B_\mathrm{P}^0-B_\mathrm{I}^0\right)L_\mathrm{P}(B)+\left(B-B_\mathrm{P}^0\right)L_\mathrm{P}(B)\right\} \\ & +b\left\{J+\frac{D}{6}(3\cos^2\xi-1)\right\} \\ & \times\left(B_\mathrm{I}^0-B_\mathrm{P}^0\right)L_\mathrm{X}(B,\theta,\phi) \end{aligned} \tag{21}$$

If the reaction centres are randomly oriented, then the observed line-shape will be the spherical average of $L(B,\theta,\phi)$, namely:

$$\begin{aligned} L(B) = {} & \int_0^{2\pi} d\phi \int_0^{\pi} d\theta\, L(B,\theta,\phi)\sin\theta \\ = {} & bJ\left(B_\mathrm{P}^0-B_\mathrm{I}^0\right)L_\mathrm{P}(B)+bJ\left(B-B_\mathrm{P}^0\right)L_\mathrm{P}(B) \\ & +bJ\left(B_\mathrm{I}^0-B_\mathrm{P}^0\right)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\mathrm{d}\theta\, L_\mathrm{X}(B,\theta,\phi)\sin\theta \\ & +\frac{bD}{6}\left(B_\mathrm{I}^0-B_\mathrm{P}^0\right)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\mathrm{d}\theta\, L_\mathrm{X}(B,\theta,\phi) \\ & \times(3\cos^2\xi-1)\sin\theta \end{aligned} \tag{22}$$

with

$$\begin{aligned} \cos\xi = {} & \sin\theta\cos\phi\sin\alpha\cos\beta+\sin\theta\sin\phi\sin\alpha\sin\beta \\ & +\cos\theta\cos\alpha \end{aligned} \tag{23}$$

where the colatitude α and azimuth β define the direction of the dipolar axis relative to the principal axes of g_X.

The first two terms of Eqn. 22 are identical to those in Eqn. 13. The third is again the net polarization of X^- with $L_\mathrm{X}(B)$ replaced by $L_\mathrm{X}(B,\theta,\phi)$. The final term, which also refers to X^-, is all that remains of the polarization formed in P^+I^- by the dipolar interaction. Because the P^+ line-shape is isotropic and the spherical average of $(3\cos^2\xi-1)$ zero, none of this extra polarization appears in the spectrum of P^+.

For partially oriented systems the polarized line-shape will be the appropriately averaged form of Eqn. 21.

Results

Fig. 1 shows a spectrum of randomly oriented reaction centres of *Rhodopseudomonas sphaeroides* (a purple bacterium) measured by Gast at 6 K [7]. These particles were prepared by alkali-urea-Triton-sodium dodecyl sulphate treatment, a procedure which destroys the magnetic coupling between X^- and the nearby Fe^{2+} [2]. Recorded 100 μs after flash photolysis using an X-band EPR spectrometer with 100 kHz field modulation, this spectrum is presented in the customary first derivative mode. It is indistinguishable from the first derivative of a spectrum obtained without field modulation (Hoff, A.J. and Proskuryakov, I.I., unpublished results); this excludes the possibility of rapid passage distortions.

Initial attempts [2,7] to reproduce this spectrum using Eqn. 13 with isotropic g tensors, no dipolar interactions and gaussian line-shapes for P^+ and X^- were encouraging. It proved possible to match the experimental line-shape quite closely by a judicious choice of g_P, g_I, g_X, ΔB_P and ΔB_X. Although the values of g_P, g_X and ΔB_X so obtained (2.0026, 2.0049 and 0.80 mT) were similar to those observed for stable P^+ and X^- (2.0026 0.0002,

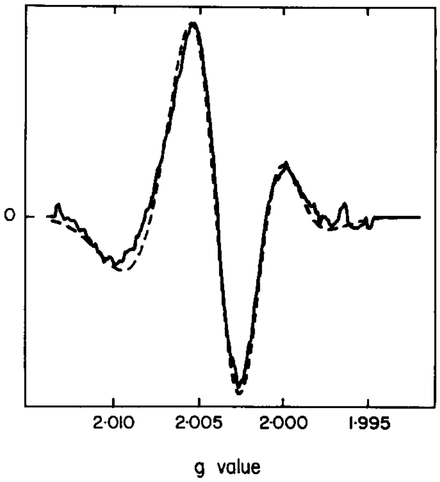

Fig. 1. Polarized EPR spectrum of *Rhodopseudomonas sphaeroides* reaction centres at ambient redox potential and a temperature of 5 K [7]. The ordinate is $d\chi''/dB$, the first derivative of the imaginary part of the magnetic susceptibility. The simulated spectrum described in the text is shown as a dashed line.

2.0046 ± 0.0002 and 0.81 ± 0.05 mT) [8], g_I and ΔB_P were more eccentric (2.0007 and 0.53 mT from the simulation compared to 2.0035 ± 0.0002 and 0.97 ± 0.02 mT). Such large discrepancies are a serious problem. Indeed even the ordering of the g values from the simulation ($g_P > g_I$) differed from that found for the isolated radicals.

More satisfactory results were obtained using Eqn. 22 with Eqns. 14 and 17 for the lineshapes of P^+ and I^-, respectively. To reduce the number of unknown parameters, the dipolar axis of P^+I^- was set parallel to one of the principal axes (x, y or z) of g_X, i.e.,

(i) x: $\alpha = \frac{\pi}{2}$, $\beta = 0$
(ii) y: $\alpha = \frac{\pi}{2}$ $\beta = \frac{\pi}{2}$
(iii) z: $\alpha = 0$

Similarly, the g values of stable P^+, I^- and X^-, namely $g_P = 2.0026$, $g_I = 2.0035$, $g_X(x) = 2.0067$, $g_X(y) = 2.0056$ and $g_X(z) = 2.0024$, were assumed to be appropriate. The two line-width parameters ΔB_P and ΔB_X, the ratio D/J and a scaling factor were treated as free variables. No attempt was made at this stage to obtain absolute values for D and J.

Respectable agreement between $\mathrm{d}L(B)/\mathrm{d}B$ from Eqn. 22 and the spectrum of Fig. 1 was found for arrangements (i) and (ii) with $J < 0$ and $D > 0$ and for arrangement (iii) with $J < 0$ and $D < 0$. Since a negative dipolar parameter has been inferred from reaction yield-detected magnetic resonance experiments [9,10] and also corresponds to simple predictions based on the likely distribution of electron density in a radical pair, attention is henceforth restricted to arrangement (iii).

The 'best' simulated spectrum was sought by least squares optimization with the following results: $D/J = 57$, $\Delta B_P = 0.52$ mT and $\Delta B_X = 0.78$ mT (see Fig. 1). No other combination of these three parameters could account for the experimental spectrum nearly so convincingly. It is encouraging that even the weak negative feature between $g = 1.995$ and 1.998 is predicted by the simulation. The origin of this composite line-shape is indicated in Fig. 2 where the four components of Eqn. 22 are drawn separately. The phase of each component (absorption, A, or emission, E) is easily seen from Eqn. 22. With $J < 0$ and $B_P^0 > B_I^0$ the first term (net polarization of P^+) is negative, i.e., E. The second term is positive for $B < B_P^0$ and negative for $B > B_P^0$ giving AE (absorption at low field, emission at high field) for the multiplet effect of P^+. The third term (the spin-exchange component for X^-) has the sign of $J(B_I^0 - B_P^0)$, i.e., A. The final term, which represents the dipolar contribution to the polarization of X^-, is a little more subtle. For case (iii) with $D < 0$ it predicts absorption when $\xi = 0$ (when $3\cos^2\xi - 1 > 0$) and emission when $\xi = \frac{1}{2}\pi$(when $3\cos^2\xi - 1 < 0$). The resonance position is near $g_X(z)$ for $\xi \simeq 0$ and between $g_X(x)$ and $g_X(y)$ for $\xi \simeq \frac{1}{2}\pi$ so that an emission–absorption pattern is predicted as shown in Fig. 2.

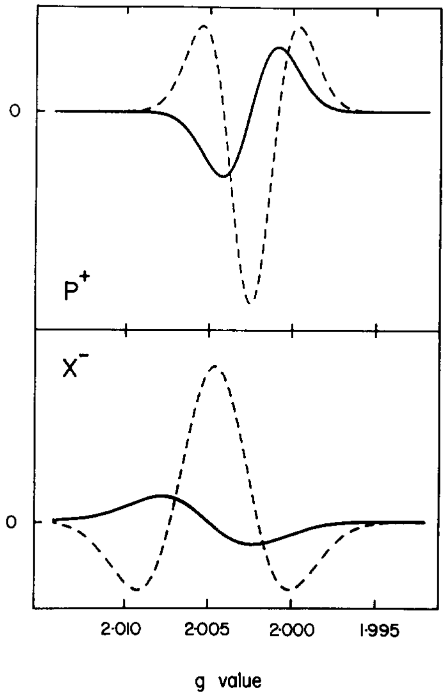

Fig. 2. The four contributions to the simulated spectrum of Fig. 1 corresponding to the four terms in Eqn 22. Above: net (solid line) and multiplet (dashed line) ESP of P^+. Below: spin exchange (solid line) and dipolar (dashed line) components of the X^- spectrum.

Interestingly, Thurnauer and Gast [11] have recently observed mixed emission/absorption polarization for A_I^- in spinach Photosystem I particles. This radical, which appears to be the plant analogue of X^-, has appreciable g anisotropy so that at least part of its ESP could arise from the dipolar interaction of P^+ with an earlier intermediate analogous to I^- (dashed line in the lower part of Fig. 2).

Discussion

The line-widths and the value of D/J found by simulation deserve comment.

With the above value of ΔB_X, the spherically averaged spectrum of X^- was approximately gaussian with a width (0.87 mT) similar to the 0.81 mT measured for stable X^-. The width of the P^+ spectrum (0.52 mT), however, is substantially smaller than that of isolated P^+ in vivo (0.97 mT). It proved impossible to reproduce the experimental spectrum using a value of ΔB_P close to 0.97 mT. This rather disturbing discrepancy may conceivably be due to the line-narrowing from a rapid electron exchange process. The most plausible candidates are an electron transfer reaction of the type, $P^+A \rightleftharpoons PA^+$ or a Heisenberg spin exchange between P^+ and another radical, say A^-, although other mechanisms are possible. If the counter radical had a similar g value to P^+ these processes would give, in the rapid exchange limit, a single resonance centred at g_P of width:

$$\Delta B'_P = \left(f_P^2 \Delta B_P^2 + f_A^2 \Delta B_A^2\right)^{1/2} \tag{24}$$

where f_P and f_A are the proportions of the two radicals ($f_P + f_A = 1$) and ΔB_P and ΔB_A are the line-widths in the absence of exchange. Provided ΔB_A is less than ΔB_P, the resulting line will be narrower than in the absence of exchange. The other obvious explanation for this difference in line-widths is that the model presented above is incomplete or invalid. In the light of the agreement obtained between theory and experiment this does not seem too likely. The assumption of isotropic hyperfine interactions for I^-, however, is perhaps questionable as the pyrrole nitrogens carry appreciable spin density.

The other interesting result described above is the value of 57 for D/J. High field reaction yield-detected magnetic resonance studies of X-depleted *Rps. sphaeroides* give values in the range 5–10 [10] while a preliminary evaluation (Hore, P.J., unpublished results) or recent low field reaction yield-detected magnetic resonance spectra [12], also of *Rps. sphaeroides* from which X has been removed, suggests that D/J is less than 3. Since J has a much stronger dependence (exponential) on the P^+I^- separation than $D(R^{-3})$, small changes in the conformation of the reaction centre protein may have a drastic effect on D/J. Conceivably, the separation of P^+ and I^- is slightly smaller in the X-depleted reaction centres than in alkali-urea-Triton-sodium dodecyl sulphate particles.

The magnitude of J can be estimated from the observation that (at 150 K) the polarized spectrum is about three times more intense than the spectrum of radicals that have completely relaxed [7]. Using Eqn. 22, the g values quoted above and 250 ps [13] for τ, one finds, $J \simeq -8$ mT. This is certainly far too large: a more reasonable value would be in the range 0 to -1 mT. The discrepancy may indicate that the electron transfer from I^- to X is slower in alkali-urea Triton-sodium dodecyl sulphate particles particles than it is for intact reaction centres.

A negative exchange interaction is as expected for a radical pair in which configuration interaction with doubly ionised singlet states ($P^{2+}I^{2-}$) depresses the energy of the singlet P^+I^- state below that of the triplet. This result disagrees with the interpretation of reaction yield-detected magnetic resonance spectra by Norris et al. [9,10] once allowance is made for their definition of J which differs in sign from that employed here. Their spectra were consistent with J and D parameters of the same sign (using our definition of J) only when D was rather larger [10]. As our analysis points to a value of D considerably greater than J and of the same sign this may be a way of reconciling the results of the two experiments. The negative sign of J also conflicts with the conclusion of Hoff and Hore [14] that the emissive ESP observed in pre-reduced ($X \rightarrow X^-$) *Rps. sphaeroides* reaction centres requires J to be positive. More extensive calculations have shown that emissive polarization is in fact consistent with a negative value of J provided J is small (0 to -0.3 mT) and the I^-X^- dipolar interaction is between about -2 mT and $+2$ mT. Such a value of J would also be consistent with the rather large value of D/J found above.

Conclusion

In the preceding paragraphs we have outlined a simple method for calculation of spin polarized EPR spectra of photosynthetic reactants. The theory has been applied successfully to a spectrum of *Rps. sphaeroides* alkali-urea-Triton-sodium dodecyl sulphate particles reaction centres with the following results: (a) the P^+I^- dipolar axis appears to be more nearly parallel than perpendicular to the z axis of the g tensor of X^-, i.e., the normal to the plane of the semiquinone ring; (b) the sign of the exchange interaction between P^+ and I^- is such that the singlet state of the radical pair is stabilised relative to the triplet, and (c) and dipolar coupling of P^+ and I^- is about 60-times larger than the exchange interaction.

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