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On the viability of the superexchange mechanism in the primary charge separation step of bacterial photosynthesis

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We investigate the feasibility of participation of the intermediate bacteriochlorophyll of the reaction center via a superexchange mechanism in the primary charge separation process of bacterial photosynthesis. When an internal charge transfer state of the special pair is incorporated into the theoretical model, an adequate rate of electron transfer can be attained without creating a discrepancy in the calculated singlet-triplet splitting of the charge-separated radical pair state, in contrast to results obtained by R.A. Marcus (Chem. Phys. Lett. 133 (1988) 471–477) without the internal charge transfer state.

Introduction

The mechanism of primary charge separation in bacterial photosynthesis is presently a subject of intense theoretical [1–3] and experimental [4–7] interest. Despite the availability of the X-ray crystal structures of the *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* reaction centers [8–11], accurate first principles calculations of the electronic and vibronic interactions required to solve the problem unambiguously are out of range of current theoretical methods. Consequently, one must resort to the construction of approximate model Hamiltonians and rely upon comparison with (or better, prediction of) experimental results to establish the validity of any proposed mechanism.

From a phenomenological kinetic standpoint, the first process that can clearly be observed experimentally upon light excitation is the reaction $P^* \rightarrow P^+H^-$, where P is the primary donor (a BChl dimer), H is a pheophytin acceptor, and P^* here explicitly refers to the lowest energy exciton component of the special pair dimer. This reaction has been shown to proceed with a 2.8 ps time constant at room temperature [6,7]; the rate increases by approximately a factor of 2 at 4 K (Breton, J., personal communication). Electron transport apparently proceeds down only one side of the approximate C_2 symmetry axis of the reaction center [10]; the pheophytin H referred to above designates specifically the molecule on the dynamically active branch. (L and M subscripts

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Abbreviations: P, primary donor (special pair); BChl, bacteriochlorophyll; H, pheophytin acceptor; P^*, lowest-energy exciton component of special pair; B, intermediate BChl; S-T, singlet-triplet; Δ_{PH}, S-T splitting in P^+H^-; ET, electron transfer; CT, charge transfer; P_{CT}, charge-transfer state of $P_L^+P_M^-$ dimer; ZPL, zero phonon line; RC, reaction center; PW, Parson and Warshel; SF, Scherer and Fischer.

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denoting the branch (light-weight; medium-weight) have been suppressed except when necessary in the interest of avoiding cluttered notation.) The role of the 'intermediate' or 'spectator' BChl between P and H, henceforth labeled B, is not understood at present; attempts to detect the participation of this molecule as a kinetic intermediate have thus far failed, despite the utilization of femtosecond laser pulses and the attainment of excellent signal-to-noise ratios in these experiments [6,7].

Four basic mechanisms have been proposed as the dominant pathway for the initial charge separation. These are: (1) direct transfer between P^* and H, with no role for B; (2) the participation of P^+B^- as a kinetic intermediate which is converted so rapidly to P^+H^- that it cannot be observed [1]; (3) involvement of some state of B via a superexchange mechanism [2]; (4) excitation transfer from P^* to the state B^+H^-, followed by transfer of the hole on B to P [3]. The first of these can probably by ruled out because of the large P to H separation and the rapidity of the reaction; indeed, most calculations to date neglect the direct interaction entirely. The task is then to choose between the three remaining possibilities, each of which has certain attractive features and certain difficulties.

The principal purpose of this paper is to address the chief difficulty of the superexchange mechanism, which is certainly the obvious choice on grounds of simplicity, i.e., no intermediate is observed because the participating state of the B molecule is at a higher energy than the P^* state. Marcus [1] has recently argued that the singlet-triplet (S-T) splitting in the radical pair P^+H^- (henceforth designated Δ_{PH}) can be used to estimate the magnitude of the relevant superexchange matrix element, and that the extremely small magnitude of the former (about $1.9 \cdot 10^{-7}$ eV) leads to a correspondingly small value of the latter, rendering the electron transfer (ET) rate constant calculated from the superexchange mechanism three orders of magnitude lower than the experimental one. While the calculations in Ref. 1 are rather simplistic (e.g., vibronic surfaces are included only in a rough manner), the size of the discrepancy demonstrated requires that they be taken seriously.

The present paper considers the superexchange mechanism and its consequences for Δ_{PH} using a model that differs in one crucial respect from that employed in Ref. 1. In the new model, the singlet state of P^* is strongly mixed with a close lying internal charge transfer (CT) state of the dimer, $P_L^+P_M^-$, henceforth designated P_{CT}. The arguments for the existence of this state and its coupling and energetics are reviewed. It is then shown that introduction of P_{CT} can substantially increase the superexchange coupling without markedly perturbing Δ_{PH}. A brief discussion of the comparative merits of the proposed ET pathways in light of this calculation is then given.

Theory

Charge transfer states of the special pair

We first review the experimental and theoretical basis for the introduction of a strongly interacting CT state of P into the model for primary charge separation. The most direct experimental evidence for CT character in the long wavelength P^* absorption band (at 980 nm in *Rps. viridis*) is recent Stark effect measurements by several groups [12,13]. These measurements clearly indicate that the difference between the dipole moment of this excited state and that of the ground state of P is substantially larger than the analogous values for a BChl monomer in solution, or for the other reaction center (RC) pigments. While one could certainly devise other explanations for this effect, admixture of the lowest Q_y exciton component of the dimer with a CT state is the most straightforward hypothesis available.

More indirect, but still powerful, evidence comes from holeburning experiments on this same band carried out by two experimental groups several years ago [14–16]. In contrast to results for chlorin in glassy media [17], or for chlorophyllide introduced into apomyoglobin [18] (both of which yield a sharp zero-phonon hole), a broad, featureless hole of width approx. 400 cm^{-1} is observed. These spectra have recently been simulated with a realistic vibronic coupling model which simultaneously reproduces many RC optical properties (absorption, circular dichroism, polarized absorption, temperature dependence) and quantitative details of the hole spectra (burn wavelength dependence of the width and position) with a relatively small number of adjustable parameters [19,20]. Strong coupling of the Q_y manifold of P* with a state lying fairly close in energy (no further than 2000 cm^{-1}) was shown to produce a transition to a chaotic spectrum in which the zero phonon line (ZPL) was destroyed without damaging the agreement of other computed spectral properties. In contrast, an alternate explanation [21] in which such coupling was not assumed yields an incorrect, symmetrical bandshape for the low temperature absorption [22].

The conclusion that the perturbing state is a CT state provides at once a simple explanation of both the Stark and holeburning results. The question of the identity of this CT state is more difficult to address, and the arguments to be made here are less well grounded in experiment. The QCFF-PI calculations of Warshel and Parson [23,24] predict a very strong coupled internal CT state of the P_{CT} type. INDO calculations of Plato and co-workers [25] on the P dimer employ a supermolecule formalism in which CT configurations are not included as separate configurations. These calculations nevertheless predict substantial CT character in the lowest excited state of the dimer; furthermore, the inclusion of some of the protein residues apparently leads to this CT character being asymmetric, i.e., there is a higher density of the excited electron on the P_M molecule. [26] Finally, the failure to observe an instantaneous bleaching of the B absorption band in femtosecond transient absorption spectra argues against identifying the strongly coupled, quasiresonant CT state as P^+B^- (as suggested in Ref. 27), although a further investigation of this point is desirable. In fact, it is a feature of the present model (and all superexchange models) that the latter state has a finite admixture with states on P; it is not clear what classes of such models will quantitatively satisfy the constraints imposed by experiments to date.

With the forgoing assumptions, our model will explicitly include four electronic states; P*, P^+B^-, and P^+H^-, and P_{CT}, henceforth labeled 1, 2, 3 and 4 (the first three states are thus consistent with the notation of Ref. 1). Note that P_{CT} will have a triplet analog, just as do all of the other states. An important assumption in what follows is that the S-T splitting of P_{CT} is much smaller than that of P*, due to the significantly larger spatial separation of the two relevant electrons in the former state. This assumption is along the same lines as those already made in previous treatments of the S-T splitting in various charge separated states [1].

Theory

We will focus here upon calculation of Δ_{PH} and evaluation of superexchange matrix elements, as opposed to a complete determination of electron transfer rates. While it is not entirely clear what the correct formalism is for describing the ET reaction (e.g., is the reaction adiabatic of nonadiabatic), and there are issues concerning the temperature dependence, these considerations affect the rate predicted from the superexchange mechanism much less dramatically than the magnitude of the effective coupling between states 1 and 3. At present we are concerned with qualitative estimations; a subsequent paper will examine these other dynamical issues.

In what follows, we adopt the approach of Marcus [1], which we believe is a reasonable way of obtaining an order of magnitude level of accuracy. In the formalism of Ref. 1, all electronic matrix elements (diagonal and off-diagonal) needed for calculation of Δ_{PH} are to be evaluated at the equilibrium geometry of the radical pair, while those needed for the superexchange matrix element relevant to ET (henceforth referred to as H_{ET}) must be computed at the crossing point of the potential curves for states 1 and 3. In Ref. 1, differences in matrix elements as a function of nuclear coordinates are neglected. This is probably acceptable for the off-diagonal elements (where it is equivalent to the Condon approximation, a standard assumption in molecular spectroscopy and electron transfer theory), but it is more problematic with regard to the diagonal energies. This difficulty has already been pointed out in Ref. 2, and invoked to predict a much larger H_{ET} than that estimated by Marcus. Our analysis below will emerge with an effect intermediate between these two extremes. The Condon approximation will be retained in what follows; we will also assume that all off-diagonal elements are identical for the corresponding singlet and triplet states.

We will not repeat here a derivation of the matrix partitioning method presented in Ref. 1; readers should consult this paper for details. Our notation closely follows that of Ref. 1, so that the arguments below should be easily followed given an understanding of the results therein. The one significant notational difference is that we will assume in advance that the direct coupling of any state of P with state 3 is zero. Hence, the matrix element of any such state i with state 3 will be written as H_{i3}, i.e., we drop the bar over H used by Marcus to denote renormalized quantities. As pointed out in Ref. 1, renormalization of the diagonal matrix elements is quantitatively unimportant; we therefore suppress the bar on these parameters as well.

The effect of the intermediate state 2 on both quantities of interest (Δ_{PH} and H_{ET}) is mediated by the effective coupling

$$H_{i3} = H_{i2}H_{23}/(H_{22}(Q) - H_{33}(Q)) \tag{1}$$

Here Q represents the entire nuclear potential surface, H_{i2} is the interaction of any electronic state i on P with state 2, H_{23} is the exchange coupling of states 2 and 3, and H_{22} and H_{33} are the energies of these states at nuclear configuration Q. We can define

$$K_{23}(Q) = H_{23}/(H_{22}(Q) - H_{33}(Q)) \tag{2}$$

a dimensionless transmission factor which is independent of the initial state on P and hence is relevant to models with and without a $\mathrm{P_{CT}}$ state. Because of the different nuclear configurations relevant to each observable, K_{23} will in principle differ for calculation of Δ_{PH} and H_{ET}, due to different values of the denominator (recall that we assume that the off-diagonal electronic matrix elements are unaltered as a function of Q). To proceed further we must approximate K_{23} for each case of interest; note that it will be identical for the singlet and triplet states, as only states 2 and 3 (whose S-T splitting is neglected by hypothesis) are involved. To simplify notation, we will henceforth designate all quantities used in the Δ_{PH} calculation by an 'a' superscript (e.g., $K_{23}^{(\mathrm{a})}$) and all those used in the H_{ET} calculation with a 'b' superscript.

The $\mathrm{P_{CT}}$ state is easily incorporated into the matrix partitioning method as follows. We first exactly diagonalize the 2 × 2 matrix consisting of the $\mathrm{P_{CT}}$ and $\mathrm{P^*}$ states to obtain two new P eigenstates, $\mathrm{P_U}$ and $\mathrm{P_L}$ (U and L designate the upper and lower energy states emerging from the diagonalization) with E_{U} and E_{L}. The couplings of $\mathrm{P_U}$ and $\mathrm{P_L}$ with state 3 via state 2 are now calculated via Eqns. 1 and 2, leading to the values $H_{\mathrm{U3}}^{(z)}$ and $H_{\mathrm{L3}}^{(z)}$, where $z = \mathrm{a}$ or b. More explicitly,

$$H_{\mathrm{K}3} = (C_{1\boldsymbol{K}}H_{12} + C_{4\mathrm{K}}H_{24})K_{23} \tag{3}$$

where $C_{i\boldsymbol{K}}$ is the coefficient of basis function i in eigenvector $\boldsymbol{K}$ and H_{24} is the coupling of the $\mathrm{P_{CT}}$ state with state 2. The signs of the two terms in parentheses in Eqn. 3 cannot be determined in any reliable way at present. We will assume that they add constructively, as this will lead to larger superexchange matrix elements.

The effect of the P manifold on the energy of state 3 is now given by

$$E_3 = H_{33}^{(\mathrm{a})} + \{H_{\mathrm{U3}}^{(\mathrm{a})}\}^2/(E_{\mathrm{U}} - H_{33}^{(\mathrm{a})}) + \{H_{\mathrm{L3}}^{(\mathrm{a})}\}^2 /(E_{\mathrm{L}} - H_{33}^{(\mathrm{a})}) \tag{4}$$

This equation is valid for both the singlet and triplet state. For the superexchange coupling matrix element relevant for ET, we assume that relaxation processes mandate that ET occurs primarily out of the lower eigenstate $\mathrm{P_L}$, so that the relevant quantity is $H_{\mathrm{L3}}^{(\mathrm{b})}$. Defining H_{ET} and ΔP_{H} explicitly, we now have

$$\Delta_{\mathrm{PH}} = E_3^{(\mathrm{S})} - E_3^{(\mathrm{T})} \tag{5}$$

where the superscripts of E_3 on the right-hand side indicate that Eqn. 4 is to be evaluated with parameters appropriate to the singlet or triplet, respectively;

$$H_{\mathrm{ET}} = H_{\mathrm{L3}}^{(\mathrm{b})} \tag{6}$$

where the right-hand side is defined in Eqn. 3.

Model parameters

The S-T splitting of the P* state has been established as 0.4 eV [28]. As in Ref. 1, we assume that the S-T splitting of the charge-separated states 2 and 3 is negligible, because of the physical separation of the relevant electrons. This argument applies to the P_{CT} state as well, although perhaps not as rigorously, as the special pair molecules are in closer proximity than any other pair of chromophores. Below we set the S-T splitting of P_{CT} equal to zero for most cases, but examine one case where it is put to 50 cm^{-1} to check the robustness of the results to such a perturbation.

Delayed fluorescence measurements place the free energy of the relaxed radical pair state 3 at roughly 1500 cm^{-1} below the singlet P^* state [2] (the small disagreements of various experimental measurements are not relevant to our objectives here). We will use this value for the energy separation $H_{11}^{S} - H_{33}^{(a)}$ as well, in the absence of a reliable breakdown of the energetic and entropic contributions; no particularly convincing arguments in Ref. 1 are presented for the assumed energetic component of 400 cm^{-1}. Use of the smaller value would not change the qualitative arguments below.

We must next choose a value for H_{22}, which we will assume is minimally affected by motion along the reaction coordinate (this principally alters the energy of state 3 in the simple picture adopted, for the moment, in this paper). Ref. 2 proposes that this energy be taken as 500 cm^{-1} above H_{11}^{S}. For lack a better estimate, we utilize this value; again, precise quantitative considerations are not crucial. These assumptions yield the result $H_{22}^{(a)} - H_{33}^{(a)} = 2000$ cm^{-1}. At the transition state of the activationless ET reaction, the energy of the initial and final states are nearly equal; we therefore set $H_{33}^{(b)} = H_{11}^{S}$, whereupon $H_{22}^{(b)} - H_{33}^{(b)} = 500$ cm^{-1}.

The central physical hypothesis of this paper is that coupling to P_{CT} has little effect on the S-T splitting of state 3, because the S-T splitting of P_{CT} itself is small. We therefore will estimate H_{23} using the experimental value of Δ_{PH} of about $1.9 \cdot 10^{-7}$ eV. From Eqns. 3 and 4 with any coupling to P_{CT} neglected ($H_{14} = H_{24} = 0$) we find that $H_{13}^{(a)}$ must be equal to 1.1 cm^{-1} to reproduce the experimental result (the discrepancy with the value of 0.7 cm^{-1} in Ref. 1 arises from the differing assumptions concerning $H_{33}^{(a)}$).

The remaining unknowns in Eqn. 1 (with $i = 1$) are H_{12} and H_{23}. The character of the states suggests that $H_{23} > H_{12}$ (both 2 and 3 are charge separated states, unlike 1). For definiteness, we will take $H_{23} = 2H_{12}$; this ratio is in rough agreement with various electronic structure calculations [3]. This leads to the results $H_{12} = 33$ cm^{-1}, $H_{23} = 66$ cm^{-1}.

Finally, we can evaluate the two required K_{23} parameters, obtaining $K_{23}^{(a)} = 0.033$, $K_{23}^{(b)} = 0.132$. The factor of 4 difference in these coefficients can increase the ET rate (with no P_{CT} state) by a factor of 16 as compared to the estimates of Ref. 1. A two order of magnitude discrepancy for the ET rate predicted by the superexchange model still remains.

The remaining parameters of interest are those defining the energy of the CT state and its coupling to P^* and to P^+B^-. These quantities (H_{44}, H_{14}, and H_{24}, respectively) will be explicitly varied in what follows.

The numerical values of the off-diagonal exchange matrix elements H_{ij} which enter into the model are obviously important in determining the resultant predictions of electron transfer rates. Before proceeding to next section, it will therefore be useful to compare the estimates made above with the calculations of other workers.

To our knowledge, there is no experimental result other than the ST splitting which allows one to derive values for H_{12} and H_{23}. The analysis of Marcus [1] never explicitly determines these matrix elements individually. However, as pointed out above, our results are consistent with his calculations. One could obtain different results by using altered values for the energy gap in the denominators of Eqn. 4; this sort of exercise seems unproductive at the present time, particularly as the existing calculations already vary several other matrix elements.

Several groups have now carried out electronic structure calculations on the reaction center chromophores, using semiempirical methods of various types [3,23–26]. Of these, Plato and co-workers [26] report only relative matrix element estimates (they are primarily interested in the directionality of charge separation). Scherer and Fischer (SF) obtain values of 41 cm^{-1} and 121 cm^{-1} for H_{12} and H_{23}, respectively, while Parson and Warshel (PW) report 5.9 cm^{-1} and 15 cm^{-1} for these same two quantities.

In view of the significant discrepancies between the reported electronic structure results and (more importantly) the many uncontrolled approximations that have been made in all of the above calculations in the electronic structure methodology and treatment of the protein environment, it appears as though one can rely upon these numbers only as a qualitative guide to what is reasonable; in other words, their status is not very different from those obtained by the empirical fits to experiment described above. A sensible approach is to examine the consequences of assuming that any given set of parameters is correct; this will not allow one to choose definitively between them (an impossible goal at present, in our view), but will illuminate the compatibility of the parameter sets with the proposed charge separation mechanisms.

First, consider the PW results, which are a factor of 5–10 smaller than our empirical estimates or than the results of SF. If these are correct, then the ST splitting can be fit only by assuming a very small energy gap. This near degeneracy between states 2 and 3 would then throw into question the use of a superexchange model, leading again to the issue of detectability intermediate state 2. The analysis of the femtosecond experiments vis-à-vis detailed simulations of electron transfer dynamics is far from definitive; thus, this picture could turn out to be the appropriate one.

If the larger matrix element values are correct, the superexchange picture becomes reasonable, subject to the previously mentioned arguments of Marcus [1]. The principal purpose of the calculations below is to demonstrate that these arguments lose their force if one introduces the P_{CT} state along with appropriate coupling strengths. The question of whether the requisite coupling strengths exist in the actual system cannot be established rigorously at present. Our purpose is rather to clarify the assumptions and conditions that are necessary for the superexchange model to be viable.

Results

Our mode of presentation will be to display numerically computed values of $H_{ET} = H_{L3}$ and the S-T splitting of state 3, Δ_{PH}, (evaluated from Eqns. 3 and 4, respectively) for several sets of P_{CT} parameters. Note that a precise reproduction of the estimated experimental Δ_{PH} is not essential here; rather, we will show that the order of magnitude arguments of Ref. 1 relating H_{ET} to this quantity are not valid if P_{CT} is included in the calculations.

We begin by considering the case where H_{14} and H_{24} are set equal to zero, i.e., P_{CT} is decoupled from the remaining manifold of states. In this case, our model becomes equivalent to that of Marcus. With $K_{23}^{(a)}$ specified above and $H_{12} = 33$ cm^{-1}, the expected value of $1.9 \cdot 10^{-7}$ eV is obtained for the S-T splitting (note that Eqn. 4 for this simple case reduces to Eqn. 7 of the first paper listed under Ref. 1). Fig. 1 displays the effect of increasing H_{12} and holding all other parameters constant. As expected, the S-T splitting increases to an unacceptable value if one tries

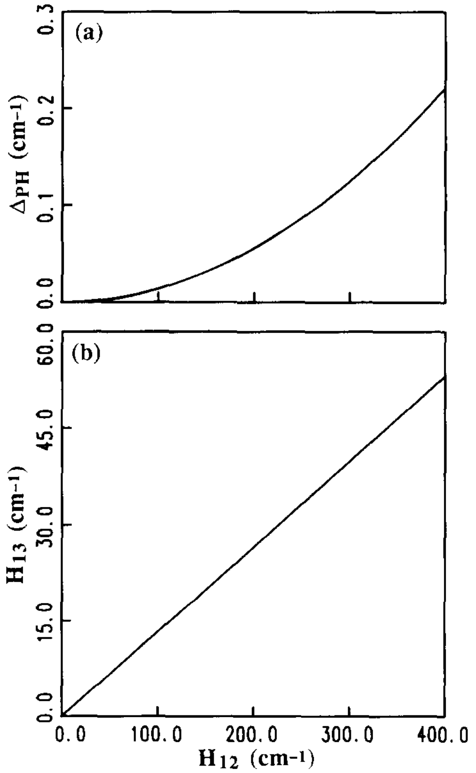

Fig. 1. (a) The S-T splitting Δ_{PH} and (b) the superexchange matrix element, H_{13}, as a function of H_{12}. The P_{CT} state is decoupled in this example. The values of all remaining parameters are given in the text.

to make H_{ET} sufficiently large by this mechanism (a value of H_{ET} of roughly 17 cm^{-1} is required to yield a reasonable rate constant if the ET model employed in Ref. 1 is utilized to estimate the ET rate).

We now consider the effect of turning on the couplings to P_{CT}. The easiest case to investigate analytically is when H_{44} is degenerate with H^{S}_{11} and H_{14} is small but non-zero. In this event, the coupling of P_{CT} to $^{3}P^{*}$ can be neglected, while the singlet splits into two completely delocalized states but nearly degenerate states. The key point is that the effect of the two delocalized singlet states of P on the singlet energy of state 3 is roughly equivalent to the effect of $^{3}P_{CT}$ on the triplet energy of state 3 even if H_{24} is large. A numerical verification of this argument is demonstrated in Fig. 2a, which plots Δ_{PH} as a function of H_{24} for several values of H_{14}. In all cases, Δ_{PH} remains quite small (note the order of magnitude in the figure abscissa, in contrast to that for Fig. 1a); the experimental value could be trivially attained by, e.g., adjustment of H_{12}.

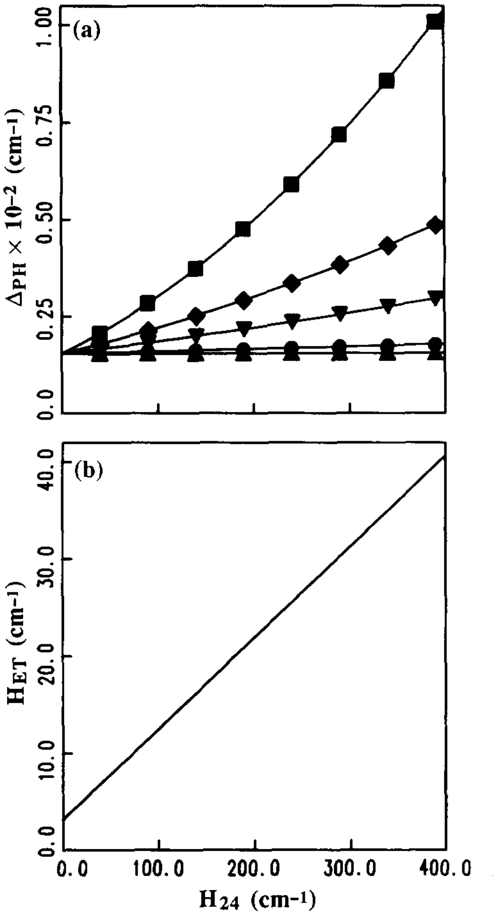

Fig. 2. (a) The S-T splitting Δ_{PH} and (b) the superexchange matrix element H_{ET} as a function of H_{24} for various CT coupling H_{14}; ▲, 1 cm^{-1}; ●, 10 cm^{-1}; ▼, 50 cm^{-1}; ◆, 100 cm^{-1}; ■, 200 cm^{-1}. The CT state is degenerate with P*, i.e., $\Delta E(P_{CT} - {}^{1}P^{*}) = 0.0$ cm^{-1}, and $\Delta E({}^{1}P_{CT} - {}^{3}P_{CT}) = 0$ cm^{-1}. Only one plot is displayed in (b) because all values of H_{14} yield the identical curves for H_{ET}.

On the other hand, H_{24} is still efficacious in increasing the superexchange coupling H_{ET} to the desired value. Thus, a substantial value of H_{24} can lead to a rapid ET rate for the superexchange mechanism while leaving Δ_{PH} quite small. This is shown in Fig. 2b, which plots H_{ET} versus H_{24} for various values of H_{14}.

Some comments should be made with regard to the range of parameter values utilized for H_{14} and H_{24} in the above plots. First, the value $H_{14} = 1$ cm^{-1} is shown only for pedagogical reasons; we do not believe that this is a reasonable value for the coupling of P_{CT} with P* (e.g., such weak coupling would be incompatible with the hole-burning experiments, as demonstrated in Ref. 20). Similarly, the maximum value of H_{24} displayed (400 cm^{-1}) is somewhat larger than what one would expect based on the range of results from electronic structure calculations (although, as noted above, the approximations made in all of these calculations to date preclude ruling out such a large coupling strength).

The value of H_{24} typically required to yield a suitable H_{ET} is about 150 cm^{-1}; this is not unreasonable, considering, for example, the values obtained by SF for H_{23}. The precise value should not, of course, be taken seriously; alterations of a factor of 2 could easily be produced by modifying prior assumptions or by changing parameters in the dynamical computations. Note that, like H_{23} (but in contrast to H_{12}), H_{24} represents transfer between two configurations which already are charge separated states. As noted above, all three semiempirical electronic structure methods predict that $H_{23} > H_{12}$; it seems plausible that H_{24} is similarly enhanced. Furthermore, accurate ab initio calculations (on different systems) of electron transfer matrix elements indicate that many-electron orbital relaxation effects lead to a negative ion orbital (the location of the electron to be transferred in P_{CT}) having a much better overlap with neighboring molecules than an excited state orbital (in which the relevant electron resides in the P* configuration), despite the fact that these donor orbitals are the same in a simple, one electron picture (Newton, M.D., personal communication). This argument rigorously supports the intuitive physical idea that the close lying P_{CT} state acts as a 'trigger' for rapid ET by enhancing the effective coupling over the longer distance to the intermediate BChl.

The next question is the robustness of the results with respect to the energy of the CT state (H_{44}) and its coupling to P* (H_{14}). As H_{44} deviates from H_{11}, larger values of H_{14} will be required to provide enough mixing to yield sufficiently large H_{ET} values. Note, however, that coupling of this strength is also required to explain the holeburning experiments, and hence this assumption can be viewed as having strong grounding in experiment. Fig. 3 displays a series of plots of the two quantities of interest as a function of H_{24} and H_{14} for $H_{44} - H_{11}^{S} = 200$ cm^{-1}. It is apparent that the desired behavior is observed for large enough H_{14}, and that this does not unacceptably increase the radical pair S-T splitting. We have chosen to restrict our attention in this paper to models with a relatively small P_{CT} energy gap, where the behavior described above is most easily understood. The quantitative range over which the mechanism proposed here could operate effectively is as yet undetermined.

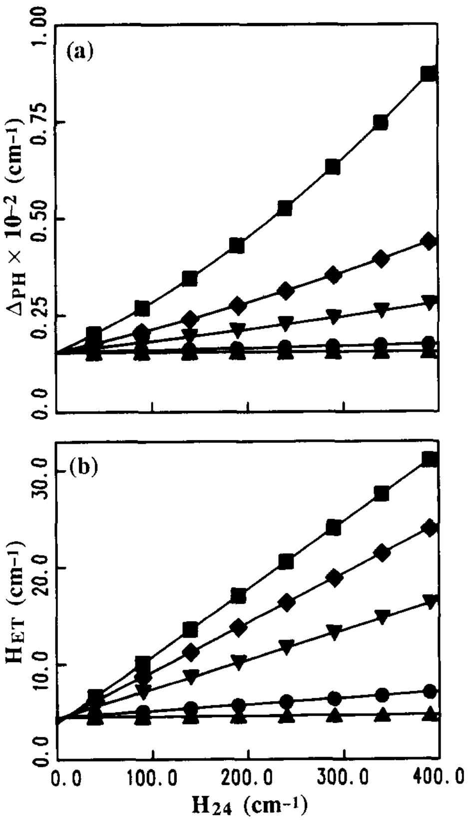

Fig. 3. (a) The S-T splitting Δ_{PH} and (b) the superexchange matrix element, H_{ET}, as a function of H_{24} for various CT coupling H_{14}; ▲, 1 cm^{-1}; ●, 10 cm^{-1}; ▼, 50 cm^{-1}; ◆, 100 cm^{-1}; ■, 200 cm^{-1}. All parameters are identical to those used in Fig. (2) except that $\Delta E(P_{CT} - {}^1P^*)$ is set to 200 cm^{-1}.

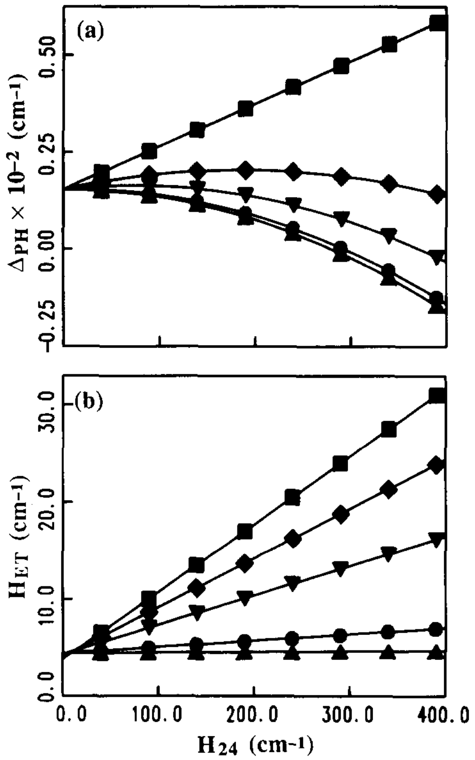

Fig. 4. (a) The S-T splitting Δ_{PH} and (b) the superexchange matrix element, H_{ET}, as a function of H_{24} for various CT coupling H_{14}; ▲, 1 cm^{-1}; ●, 10 cm^{-1}; ▼, 50 cm^{-1}; ◆, 100 cm^{-1}; ■, 200 cm^{-1}. All parameters are the same as in Fig. 3 except $\Delta E({}^1P_{CT} - {}^3P_{CT}) = 50$ cm^{-1}.

Finally, we consider the effect of introducing and S-T splitting for the P_{CT} state. Fig. 4 plots Δ_{PH} and H_{ET} for a 50 cm^{-1} S-T separation in P_{CT}

as a function of H_{24} for various values of H_{14} and using the value $H_{44} - H_{11} = 200\ \mathrm{cm}^{-1}$. The qualitative picture we have presented is still valid. Obviously, one could increase this separation to the point where our argument breaks down; a more detailed investigation of this point seems better undertaken with a more rigorous computational method.

Experimental verification

A significant difficulty with the many of the speculations concerning primary charge separation dynamics in the reaction center is the difficulty of experimental verification. The present proposal is no exception to this; it will undoubtedly be quite difficult to establish unambiguously that the above description is correct. We attempt to confront this challenge here by making an experimental prediction which is a straightforward consequence of the model.

If the hypothesis about the S-T splitting of P_{CT} (i.e., that it can be neglected) is correct, there should be triplet CT state near the energy of the singlet P* state, i.e., at an energy between 2000 and 6000 cm^{-1} above the P* triplet state. It might be possible to observe this state by measuring the triplet-triplet absorption in this spectral region. There are unfortunately substantial experimental difficulties in observing a transition which is so far into the infrared, and which is likely to possess a small oscillator strength; overcoming this problem will undoubtedly by a severe challenge for experimentalists.

The identification of such absorption as due to a CT state could be made by carrying out Stark effect measurements on the triplet-triplet absorption spectrum. The observation of a strong Stark effect in this spectral region would constitute important evidence for the validity of the model presented in this paper.

Another experiment which would be valuable in assessing the validity of our model is a resonance Raman experiment in which an excitation profile through the P* long wavelength band was obtained. An analysis of the Raman intensity of various vibrational modes as a function of excitation wavelength would, in favorable cases, prominently display effects due to vibronic mixing of a nearby electronic (CT) state. This experiment is also not easy to carry out, because of problems involving fluorescence and detection in the infrared.

Conclusion

We have argued above that a superexchange mechanism can no longer be ruled out by the small observed value of Δ_{PH}. The most recent femtosecond experiments of Martin and coworkers [6,7] impose, in the context of a simple kinetic picture of ET dynamics, demanding criteria on the two alternate mechanisms, i.e., the second step in which the proposed intermediate is depleted must be extraordinarily rapid. This is not impossible, particularly if these is strong electronic coupling between the intermediate and the final state, along the lines suggested in Ref. 27 for the interaction between P* and P^+B^-. Therefore, our conclusion is that none of the reasonable models of current interest can be definitively eliminated. As stated in the introduction, the superexchange model would appear to be most attractive at this time on the basis of simplicity.

An alternate possibility (suggested by the discussion above concerning the magnitude of the exchange coupling elements) is that a more accurate dynamical ET theory, in which the energy gaps between the various states are allowed to fluctuate in time, would resolve many of the difficult issues in a different manner. This idea meshes particularly well with the picture in which both the exchange coupling matrix elements and average energy gap between the intermediate and other states are small. A comparative critique of this approach with other alternatives is beyond the scope of the present paper, however, it should certainly be kept in mind as a feasible explanation.

What is needed are new experiments which will allow a clearer choice between the different proposals. The experiments suggested above are only concerned with establishing the existence of the internal P_{CT} state; even if this was accomplished, it would not unambiguously settle the issue of the dominant dynamical channel. Possibly measurements made in a strong electric field, which would shift the energies of the proposed charge-separated states by differing amounts, will provide a means of discrimination.

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