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EARLY STEPS IN BACTERIAL PHOTOSYNTHESIS. COMPARISON OF THREE MECHANISMS

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ABSTRACT

Mechanisms for the early electron transfer steps in the bacterial photosynthetic reaction center are discussed. An internal consistency test is described which places a real constraint on the unknown parameters. A resulting possible paradox is described, together with proposed electric field measurements and an alternate mechanism.

INTRODUCTION

The increasingly detailed level of experimental data on the bacterial photosynthetic reaction center is abundantly documented in this conference. In principle there are many unknowns, such as the λ's and $\Delta G°$'s of the individual electron transfer steps (using current notation[1]), and the electron transfer matrix elements of these steps. The apparent presence of both an "unrelaxed" and a "relaxed" state (proposed by Parson and coworkers[2]) of the radical pair that is formed also adds to the complexity. [2]

One puzzle which has arisen, and which we have addressed earlier,[3] concerns the apparent discrepancy between the fast forward rate of electron transfer[4] to form a radical pair $BChl_2^+BPh^-$ and the small singlet-triplet splitting of that pair.[5-7] Here, $BChl_2$ denotes the bacteriochlorophyll dimer and BPh a bacteriopheophytin. A slow recombination of the pair to form a triplet $BChl_2^*$ and BPh is also pertinent.[5-7] This situation has been discussed by several authors recently.[3,7,8] In the present article I would like to describe an internal consistency test[9] which addresses directly the question of whether or not there is a paradox between the fast forward electron transfer rate and these other observations.

The work presented by Martin *et al.*[10] at this conference provides rather compelling evidence against the chemical intermediate mechanism ($BChl^-$ or $BChl^+$). This evidence will be taken for granted in the following and it will be used to develop the internal consistency test. A third possible mechanism for the early electron transfer steps in these photosynthetic reaction centers will also be suggested and explored (cf. ref. 9). Experiments which may distinguish between the mechanisms are considered.[9]

We first consider two alternative mechanisms for the role of the accessory bacteriochlorophyll monomer BChl in the initial electron transfer from $BChl_2^*$ to BPh. Three electronic states are particularly relevant to the discussion:

State 1. $BChl_2^*$ BChl BPh
State 2. $BChl_2^+$ BChl $^-$ BPh
State 3. $BChl_2^+$ BChl BPh^- ,

where the asterisk denotes an electronically-excited state.

The free energy curves for these three electronic states are plotted *vs* a reaction coordinate in Fig. 1 for two postulated mechanisms. In the case of a superexchange mechanism the free energy curve for state 2 is relatively high, as in Fig. 1a. In contrast, curve 2 is lower for the case of the $BChl^-$ chemical intermediate mechanism, as in Fig. 1b. We shall frequently refer to the electron

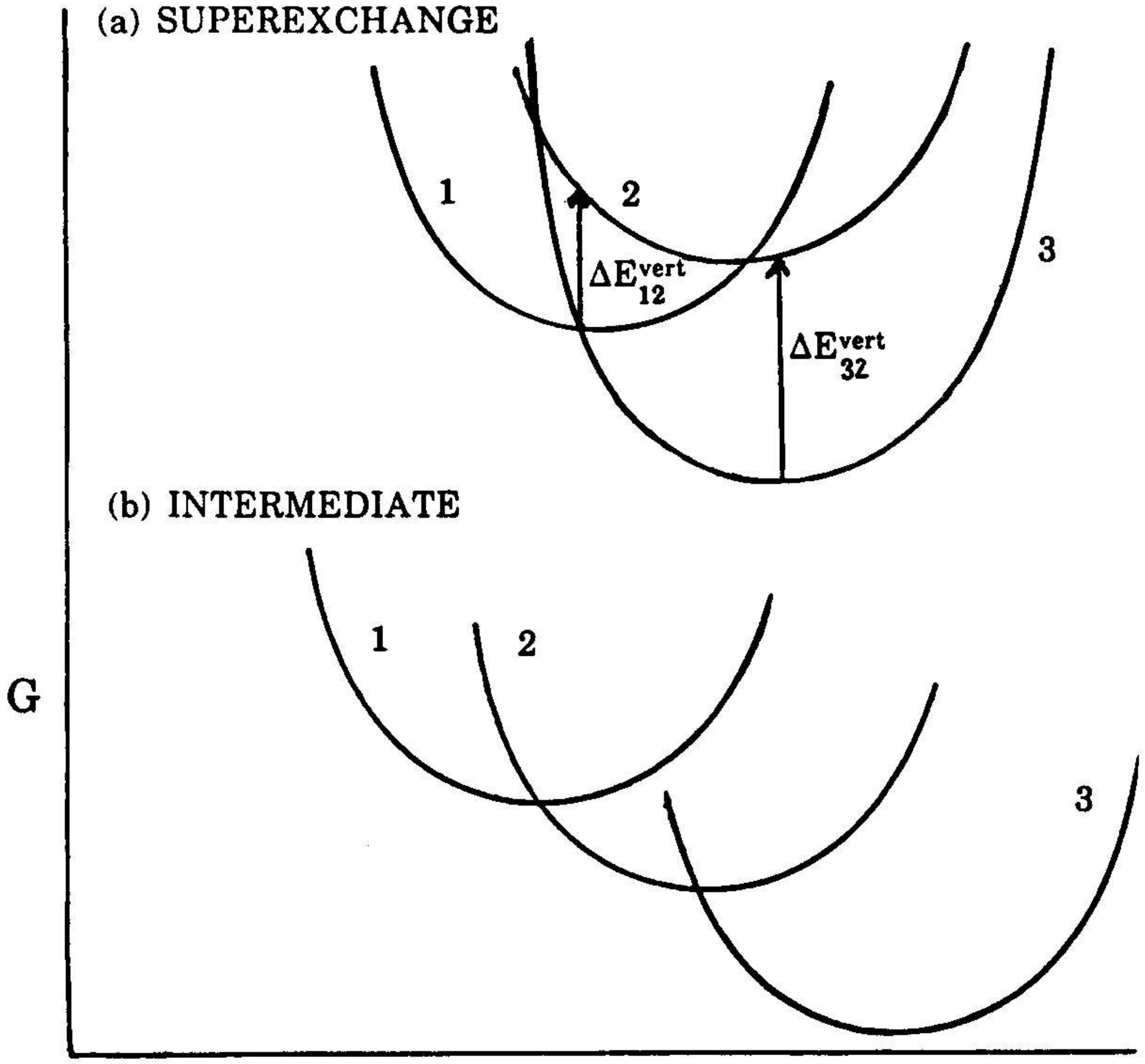

Fig. 1. Plot of free energy *G vs* the reaction coordinate for the various electronic configurations and for two mechanisms, (a) and (b). Curves 1, 2 and 3 refer to the $BChl_2^*$-BChl-BPh, $BChl_2^+$-$BChl^-$-BPh and $BChl_2^+$-BChl-BPh^- electronic states of the system, respectively. Figure (a) is appropriate to a superexchange mechanism and (b) to a chemical intermediate mechanism ($BChl^-$). The reaction coordinate in fig. 1a may differ from that in fig. 1b. Further, in fig. 1a the minimum for curve 2 is not necessarily a global minimum in the space of all reaction coordinates.

transfer steps $1 \rightarrow 2$, $1 \rightarrow 3$, $3 \rightarrow 1$, etc. We first consider the rate expressions for these two mechanisms, before addressing a third possible mechanism described later in Fig. 2.

Using a classical expression for the rate constant of an electron transfer reaction, eq. (1) can be written for the rate constant k_{13}^{super} of formation of $BChl_2^+ BPh^-$ (state 3) from $BChl_2^* BPh$ (state 1) at room temperature T for a superexchange mechanism. When, as is the case here, the reaction is activationless we have[1,3]

$$k_{13}^{super} = \frac{2\pi}{\hbar} \frac{|\overline{H}_{13}|^2}{(4\pi\lambda_{13} RT)^{\frac{1}{2}}} \quad . \tag{1}$$

Here, $\overline{H}_{13}$ is the effective (superexchange) electron transfer matrix element and λ_{13} is the reorganizational parameter for this $1 \rightarrow 3$ step.

In a chemical intermediate mechanism the rate constant k_{12} for the formation of $BChl_2^+ BChl^-$ from $BChl_2^* BChl$, where $BChl^-$ is the intermediate, is given by[1]

$$k_{12} = \frac{2\pi}{\hbar} \frac{|H_{12}|^2}{(4\pi\lambda_{12} RT)^{\frac{1}{2}}} e^{-\Delta G_{12}^*/RT} \quad , \tag{2}$$

where H_{12} is the electron transfer matrix element, λ_{12} the reorganization parameter and ΔG_{12}^* the activation free energy, for this $1 \rightarrow 2$ step. The ΔG_{12}^* can be written in terms of λ_{12} and ΔG_{12}°, the standard free energy of reaction for that step[1]:

$$\Delta G_{12}^* = (\lambda_{12} + \Delta G_{12}^\circ)^2 / 4\lambda_{12} \quad , \tag{3}$$

The internal consistency test[9] arises because the $\lambda_{12} + \Delta G_{12}^\circ$ in eq. (3) also occurs as an energy denominator in an expression for $\overline{H}_{13}$. Using the arguments given in Appendix A, $\overline{H}_{13}$ for the superexchange mechanism $1 \rightarrow 3$ can be approximated by

$$\overline{H}_{13} = H_{12} H_{23} / \Delta E_{12}^{vert} \quad , \tag{4}$$

where

$$\Delta E_{12}^{vert} = \lambda_{12} + \Delta G_{12}^o \quad . \tag{5}$$

ΔE_{12}^{vert} is depicted in Fig. 1a. In eq. (4) H_{12} and H_{23} are the matrix elements for the electron transfers $BChl_2^* BChl\, BPh \rightarrow BChl_2^+ BChl^- BPh$ and $BChl_2^+ BChl^- BPh \rightarrow BChl_2^+ BChl\, BPh^-$, respectively.

From these equations the ratio of rate constants k_{13}^{super} / k_{12} is given, after some cancellation, by[9]

$$\frac{k_{13}^{super}}{k_{12}} = \frac{|\overline{H}_{13}|\, r\, e^{\Delta G_{12}^*/RT}}{2(\lambda_{13} \Delta G_{12}^*)^{\frac{1}{2}}} \quad , \tag{6}$$

where

$$r = |H_{23}/H_{12}| \quad . \tag{7}$$

(A main feature of eq.(6) is the manipulation which eliminated the explicit presence in eq. (6) of an additional unknown, the λ_{12} present in eq. (2).)

The $\bar{H}_{13}$ in eq. (6) can be calculated, assuming a superexchange mechanism, by equating the expression in eq. (1) to the observed rate constant for the formation of the radical pair, $BChl_2^+BPh^-$, from $BChl_2^*BPh$. The latter is 3.6 10^{11} s^{-1} at room temperature, taken as 20°C.[4] The value of λ_{13} is about 0.15 eV using the activationless property of the reaction ($\lambda_{13} \simeq -\Delta G_{13}^\circ$)[1] and using a ΔG_{13}° of −0.15 eV for the formation of the (initial) unrelaxed state of the radical pair.[2b] With these values, and assuming a superexchange mechanism, $\bar{H}_{13}$ is found from eq. (1) to be about 25 cm^{-1}.

In order that the contribution of the superexchange mechanism dominate that of the chemical intermediate mechanism, so that the $BChl^-$ concentration at room temperature is small, the ratio k_{13}^{super}/k_{12} should be fairly large. If the ratio is assumed to be larger than some particular value, and if for the r in eq. (7) a value (following Jortner's suggestion)[11] equal to the ratio of the corresponding electronic overlap integrals is used ($\simeq 7$ in the calculation of Plato in this volume), eq. (6) can be solved for ΔG_{12}^*. It is found that ΔG_{12}^* must be equal to or larger than 850 cm^{-1}, if $k_{13}^{super}/k_{12} \geq 5$.

An infinite set of values of the $(\lambda_{12}, \Delta G_{12}^\circ)$ pairs can be found from eq. (3), each pair consistent with this value of ΔG_{12}^*. Examples are (1200 cm^{-1}, 800 cm^{-1}), (850, 850) and (300, 710), the first being in the region where $\lambda_{12} > |\Delta G_{12}^\circ|$ (the "normal" region for the $1 \rightarrow 2$ electron transfer) and the last being in the region where $\lambda_{12} < |\Delta G_{12}^\circ|$ (the "inverted region"). In turn, the corresponding values of H_{23} obtained with these values and eqs. (4), (5) and (7) are 590, 545 and 420 cm^{-1}, respectively. All are rather large and are a consequence of assuming a dominant superexchange mechanism. Before this introduction of an internal consistency test, values of H_{23} and the ΔE_{12}^{vert} in eq. (4) that had been employed were adjustable parameters, without any constraining equation.

SINGLET-TRIPLET SPLITTING

We next consider the implications of the foregoing arguments for the magnitude of the singlet-triplet splitting of the $BChl_2^+BPh^-$ radical pair in the relaxed state of the system. We use for this analysis the three electronic configurations described earlier. The energy of state 3, for the case of a singlet state of the radical pair, is influenced by configuration interaction with states 1 and 2, as in eq. (2) below. The energy of the radical pair triplet state is influenced by a configuration interaction with the corresponding triplet states of 1 and 2. The difference of these interactions gives, in this three-configuration model, a difference in singlet and triplet energies for the radical pair.

The electronic configurations 1,2,3 in a configuration interaction scheme yield a 3×3 Hamiltonian matrix with elements H_{ij}.[3] Using a partitioning argument[3], the corresponding secular determinant for the energy of a state 3 that is modified by the configuration interaction can be easily solved approximately. In this way the energy E of the radical pair is given by[3*]

$$E \simeq \bar{H}_{33} - \frac{|\bar{H}_{13}|^2}{\bar{H}_{11} - \bar{H}_{33}}, \tag{8}$$

when $|\bar{H}_{13}| << |\bar{H}_{11} - \bar{H}_{33}|$ (as it is in our case) and where values of the barred matrix elements are given in Appendix A. The $\bar{H}_{13}$ in eq. (8) refers to the effective matrix element for the radical pair in its equilibrium nuclear

*In eq. (7) of ref. 3 the sign of the last term, and in eq. (10) that of the rhs, should be changed. The discussion there is unaffected, since only absolute values were considered.

configuration and differs from the H_{13} in eq. (4), which is evaluated instead at the equilibrium nuclear configuration of state 1. We denote the $\overline{H}_{13}$ for the radical pair by $\overline{H}_{13}{}^{rp}$ and the $\overline{H}_{13}$ in eq. (4) by $\overline{H}_{13}{}^{super}$. Using the argument in Appendix A and assuming that $H_{12}\,H_{23}$ in the radical pair's "relaxed state" is the same as in the initial equilibrium configuration for state 1, we have

$$\frac{\overline{H}_{13}^{rp}}{\overline{H}_{13}^{super}} = \frac{\Delta E_{12}^{vert}}{\Delta E_{32}^{vert}} \tag{9}$$

for the case of the singlet states. In Appendix A we estimate $\Delta E_{32}{}^{vert} \simeq 4000$ cm^{-1}. From the range of values of the $(\Delta G_{12}{}^{\circ}, \lambda_{12})$ pairs, the $\Delta E_{12}{}^{vert}$ in eq. (5) would appear to be in the vicinity of 1000 to 2000 cm^{-1}. We shall use a value of 1500 cm^{-1}. $\overline{H}_{13}{}^{rp}$ can now be calculated from $\overline{H}_{13}{}^{super}$ and eq. (9) to be about 65 cm^{-1}.

In estimating the last term in eq. (8) for the energy of the radical pair singlet state, a value for $\overline{H}_{11} - \overline{H}_{33}$ is needed at the equilibrium nuclear configuration for state 3. Now, λ_{13} is about 0.16 eV (an average of the 0.15 eV given earlier and the 0.17 eV deduced from the activationless formation of the triplet state of state 1 from the radical pair, state 3[7,12,13]), and $\Delta G_{13}{}^{\circ}$ is -0.26 eV.[12-14] Since this $\overline{H}_{11} - \overline{H}_{33} = \Delta G_{31}{}^{\circ} + \lambda_{13} = -\Delta G_{13}{}^{\circ} + \lambda_{13}$, $\overline{H}_{11} - \overline{H}_{33}$ is approximately 0.4 eV.

The last term in eq. (8) can now be estimated from the above values to be about 0.03 cm^{-1} for the singlet state. Had we used an $r = 2$ for the ratio H_{23}/H_{12} instead of $r = 7$, the corresponding value would have been 0.05 cm^{-1}.[9]

To calculate the singlet-triplet splitting it is necessary to make a similar calculation for the last term in eq. (8) for the triplet state and to calculate the first term on the right hand side of eq. (8), $\overline{H}_{33}$, for both states. This $\overline{H}_{33}$ is discussed in Appendix B. The singlet-triplet splitting thus consists of several terms, one of which is 0.03 cm^{-1} (or 0.05 cm^{-1} if $r = 2$). If we discount the likelihood of cancellation of any large terms (the terms have quite different contributions and there is no reason why there should be such a cancellation) there is seen to be a factor of about 30 discrepancy with the observed (10^{-3} cm^{-1})[5-7]singlet-triplet splitting of the $BChl_2{}^{+}$ BPh^{-} radical pair. When the ΔE^{vert}'s in eq. (9) become better known an improved estimate of $\overline{H}_{13}{}^{rp}$ can be made.

It is seen that the above calculated value of $\overline{H}_{13}{}^{rp}$ rests on the superexchange assumption and on the use of the internal consistency test to narrow the estimates of the ΔE^{vert}'s. The above calculation of a major contribution to the singlet-triplet splitting rests only on this $\overline{H}_{13}{}^{rp}$ and on the reasonably well known estimate of the denominator $\overline{H}_{11} - \overline{H}_{33}$ in eq. (8).

An important question is whether the value of $H_{12}\,H_{23}$ in eq. (4) for $H_{13}{}^{super}$ is different from its value in the expression for $\overline{H}_{13}{}^{rp}$. The effect of energy on H_{12} and H_{23} is very minor.[3] Thus, only if $H_{12}\,H_{23}$ were different for the "unrelaxed" and "relaxed" configurations of the radical pair would there be a difference in $\overline{H}_{13}{}^{rp}$ and $\overline{H}_{13}{}^{super}$ due to this source.

TRIPLET RECOMBINATION

The value of $\overline{H}_{13}{}^{rp}$ estimated from the superexchange mechanism for the 1 $\rightarrow$ 3 electron transfer and the internal consistency test was seen to yield too high a value of the singlet-triplet radical pair splitting. The value needed for $\overline{H}_{13}{}^{rp}$ to be consistent with the observed splitting is roughly about $[10^{-3}\,(\overline{H}_{11} - \overline{H}_{33})]^{\ddagger}$, where $\overline{H}_{11} - \overline{H}_{33}$ is evaluated at the equilibrium configuration of the radical pair

and was determined in the previous section to be about 0.4 eV. Thereby, this $\overline{H}_{13}{}^{rp}$ is about 2 cm^{-1} (1.8 cm^{-1}). It is useful compare this value with a value of $\overline{H}_{13}{}^{rp}$ for the corresponding triplet recombination 3 → 1 step, determined using the rate constant $k_{31}{}^{T}$ for the latter.

The rate constant $k_{31}{}^{T}$ is about 6 10^8 s^{-1}, and is activationless.[7] The theoretical value of $k_{31}{}^{T}$ is given by eq. (1), but now the $\overline{H}_{13}$ refers to its value $\overline{H}_{13}{}^{rp,T}$ for the triplet system, at the equilibrium nuclear configuration of the radical pair. Calculated from $k_{31}{}^{T}$ using eq. (1) $\overline{H}_{13}{}^{rp,T}$ is found to be about 1.4 cm^{-1}. This value is close to that found above for $\overline{H}_{13}{}^{rp}$. The orbitals of the $BChl_2{}^*$ singlet differ somewhat in the asymmetry of the charge distribution from those of the $BChl_2{}^*$ triplet, and so some difference in the $\overline{H}_{13}{}^{rp}$ and $\overline{H}_{13}{}^{rp,T}$ is expected.

THE ONE-STEP NONADIABATIC/ADIABATIC MECHANISM

It certainly appears, as already noted, that on the basis of the data of Breton *et al.*[10] the chemical intermediate mechanism can be discarded. We have also seen that using the consistency test the superexchange mechanism encounters problems of a factor of 30 or so. While some other way might possibly be found of avoiding this difficulty it seems appropriate to consider possible alternative mechanisms, such as the one depicted in Fig. 2.

In Fig. 2 the only real barrier to reaction involves the transition 1 → 2 which is a nonadiabatic one. Its matrix element H_{12} is chosen to be 25 cm^{-1}, using the observed rate constant and eq. (2). It is postulated that the system then flows (in Fig. 2) on a new adiabatic curve — the lower curve there, constructed from the original 2 and 3 curves that are split quantum

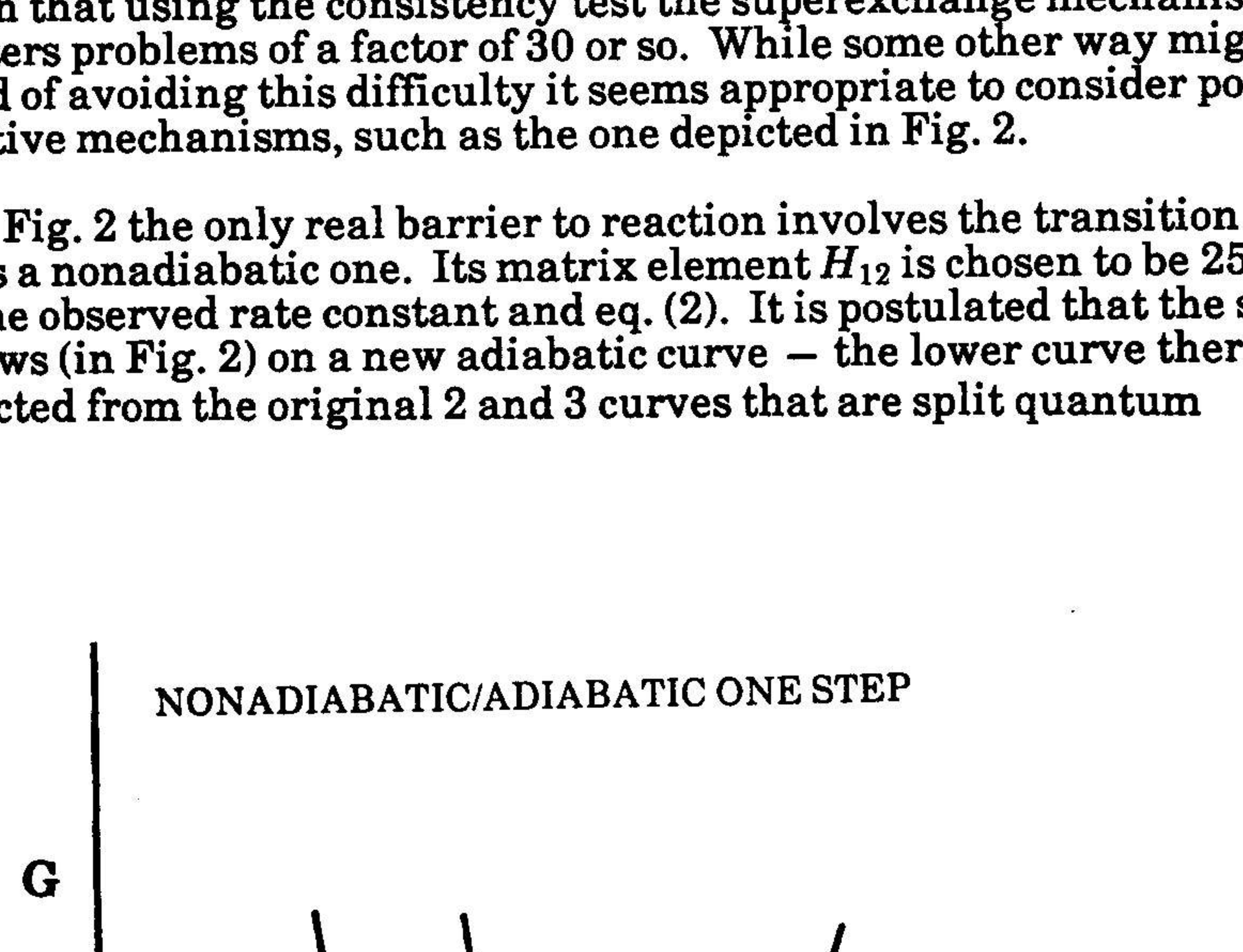

Fig. 2. Plot of free energy G *vs* the reaction coordinate for a mechanism in which there is only one step, namely a curve crossing from curve 1 to the lower solid curve. The latter is an adiabatic curve constructed from the original curves 1 and 2 that are split at their "intersection" by an amount $2H_{23}$. During the motion of the system on this lower adiabatic curve the $BChl^-$ has, in effect, negligible temporal existence.

mechanically at their "intersection" by an amount equal to $2H_{23}$. Using $r = 7$ in eq. (7) we have $H_{23} \approx 175\ cm^{-1}$. In this mechanism, state 2 in Fig. 2 doesn't even exist for a vibrational period and its concentration (and hence BChl depletion or "bleaching") during the $1 \rightarrow 3$ transition remains small throughout (about 2% or so in a preliminary quantum mechanical wave packet calculation).[15]

A next question is whether such a mechanism would also be consistent with the $10^{-3}\ cm^{-1}$ singlet-triplet energy difference of the radical pair, since this was the point where the superexchange mechanism had difficulty. ΔE_{32}^{vert} for this mechanism is ~0.4 eV (Appendix B). Using the above values for H_{12} and H_{23}, the value of $\overline{H}_{13}^{rp}$ calculated from eq. (4) with ΔE_{12}^{vert} replaced by ΔE_{32}^{vert} is about $1.5\ cm^{-1}$. Introducing this value into the last term of eq. (8) and using $\overline{H}_{11} - \overline{H}_{33} \simeq 0.4$ eV found earlier for the singlet state at the equilibrium configuration of state 3, the last term in eq. (8) is estimated as $\sim 10^{-3}\ cm^{-1}$, which is of the same magnitude as the observed singlet-triplet splitting of the radical pair, $10^{-3}\ cm^{-1}$.

Incidentally, if the situation in Fig. 2 prevails, earlier discussions [8] on the vertical position of curve 2, inferred from an absence of a temperature effect on the singlet-triplet splitting of quinone-free systems, would no longer apply, at least not in their original form.

CHARGE TRANSFER BAND

We have also considered elsewhere the implications of a superexchange mechanism for a $BPh^- \rightarrow$ BChl charge transfer band, if the large values of H_{23} required by the superexchange prevailed.[9] If, indeed, H_{23} were very large, a significant intensity would be found for this hypothetical charge transfer band, which would be located at the ΔE_{32}^{vert} in Fig. 1a, which is very roughly estimated to be around $4000\ cm^{-1}$ if the superexchange mechanism were valid (Appendix B).

ELECTRIC FIELD EFFECT

Electric field effects on quantum yields have been investigated by Dutton and coworkers[16] using Langmuir-Blodgett monolayer films of close-packed reaction centers. Fields of as much as 150 mV/nm or more were used. The effect of the electric field on the possible bleaching of the BChl monomer and on the rate of the initial electron transfer step would be of particular interest. Using the component of the distances along the C_2-axis and using an assumption regarding the dielectric properties of the system it was deduced that with an adverse field of about 150 mV/nm the energy of state 2 and that of the (unrelaxed) state 3 at their equilibrium configurations would approach each other, if the situation at no field were as depicted in Fig. 2.[9] If there were no "unrelaxed" state or if the situation were, instead, that given by Fig. 1a, the energy of state 2 would still be higher than that of state 3 and there would still be no BChl bleaching.[9]. Thus, with a sufficiently adverse field there would be the possibility of observing $BChl^-$ and a bleaching of BChl, if the mechanism in Fig. 2 prevailed. A direct measurement of the electric field effect on the initial rate, particularly at low temperatures, would also be of interest.

CONCLUSIONS

In summary, we have seen that an internal consistency test can be derived and that it has consequences for the allowed values of the parameters for the superexchange mechanism. The latter mechanism leads, in turn, to a paradox, one possible solution of which is considered in the one-step nonadiabatic/adiabatic mechanism depicted in Fig. 2. Possible experiments, such as the effect of electric fields on the depletion of BChl in the initial reaction steps, are considered and may help distinguish the various mechanisms.

Perhaps it should also be stressed that the mechanisms in Fig. 1a and Fig. 2 have some common features. Both have a substantial H_{23} , though the superexchange mechanism has a larger H_{12} and H_{23}. The main difference is in the vertical position of curve 2. Electric field experiments may shed some light (as might a charge transfer band) on this question, if the dielectric properties are not too complicated.

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APPENDIX A. H_{ij} TERMS

We have from a partitioning argument[3]

$$\overline{H}_{13} = H_{13} + H_{12} H_{23} / (H_{22} - E) \quad , \tag{A1}$$

where E is replaced by H_{11} when the H_{13} for the activationless $1 \rightarrow 3$ electron transfer is desired. All terms in eq. (A1) are then evaluated at the equilibrium nuclear configuration for state 1. Neglect of the direct interaction term H_{13} then yields eq. (4), upon approximating $H_{22} - H_{11}$ by its thermodynamic average.

When the H_{13} for the radical pair state is desired ($\bar{H}_{13} \equiv \bar{H}_{13}^{rp}$) the E in eq. (A1) is replaced, instead, by H_{33} , and all terms are now evaluated at the equilibrium nuclear configuration for state 3, the radical pair. Once again, the neglect of H_{13} and the replacement of $H_{22} - H_{33}$ by a thermodynamic average leads to eq. (4), with the ΔE_{12}^{vert} replaced by ΔE_{32}^{vert} .

From the same partitioning argument we also have for $\bar{H}_{11}$, the energy of state 1 perturbed by state 2,[3]

$$\overline{H}_{11} \simeq H_{11} - |H_{12}|^2 / (H_{22} - H_{11}) \quad . \tag{A2}$$

Here, H_{11} is the unperturbed energy of state 1, H_{22} that of state 2 and H_{12} the electron transfer matrix element for the $1 \rightarrow 2$, all evaluated at the same nuclear configuration, whichever is the one of interest. Similarly, the energy of a state 3 perturbed by state 2 is [3]

$$\overline{H}_{33} = H_{33} - |H_{32}|^2 / (H_{22} - H_{33}) \quad . \tag{A3}$$

APPENDIX B. SOME ENERGETICS

An estimate of the ΔE_{32}^{vert} in Fig. 1a can be made as follows. It is needed for the "relaxed" configuration of $BChl_2^+ BPh^-$ radical pair. ΔE_{32}^{vert} equals $\lambda_{23} + \Delta G_{32}^{\circ}$, where ΔG_{32}° is the standard free energy of reaction for the $3 \rightarrow 2$ electron transfer, all evaluated at the "relaxed" configuration of state 3. We first consider an estimate made assuming the superexchange mechanism for the $1 \rightarrow 3$ reaction.

We shall approximate λ_{23} crudely by the mean of λ_{12} and λ_{13} . The λ_{13} is estimated in the text to be about 0.16 eV, while a variety of values of λ_{12} were seen to be consistent with the ΔG_{12}^{*} of 850 cm^{-1} in the text. The ΔG_{32}° equals

$-\Delta G_{23}^{\circ}$ and the latter, in turn, equals $-\Delta G_{13}^{\circ}+\Delta G_{12}^{\circ}$. The value of ΔG_{13}° for forming the relaxed configuration of state 3 is -0.26 eV,[12-14] while various values of ΔG_{12}° consistent with $\Delta G_{12}^{*}=850\ \mathrm{cm}^{-1}$ were given in the text. When various (λ_{12}, ΔG_{12}°) pairs are considered, a value of about 4000 cm^{-1} for $\lambda_{23}+\Delta G_{32}^{\circ}$ is estimated on the superexchange assumption and used in the text as a consequence of that assumption.

If, instead, the mechanism in Fig. 2 were valid, ΔE_{32}^{vert} would be somewhat smaller, assuming $\Delta G_{12}^{\circ}\simeq 0$. $\Delta E_{32}^{vert}=\lambda_{23}+\Delta E_{32}^{\circ}=\lambda_{23}-\Delta E_{23}^{\circ}\simeq\lambda_{23}-\Delta G_{13}^{\circ}$ $\simeq 0.4$ eV i.e., 3200 cm^{-1}.

We consider next the first term $\bar{H}_{33}$ in the RHS of eq. (8). It is given, in turn, by eq. (A3). In the latter, H_{33} is essentially the same for the singlet and triplet states of the radical pair, because the radicals are relatively far apart and configuration interaction from electronic configuration 2 doesn't affect H_{33}. The H_{22} term in (A3) will differ slightly for singlet and triplet states, while H_{23} is expected to be rather similar in the two states. Thus, $\bar{H}_{33}$ will differ somewhat for the singlet and triplet state 3. However, this difference is independent of the differences in the last term in eq. (8), and, as noted earlier, we shall discount the likelihood of a cancellation of the large last term in (8) for the singlet state by other terms, this large term being a consequence of the asumption of a superexchange mechanism for the $1\rightarrow 3$ reaction.

Configuration interaction may also occur, incidentally, due to electronic states other than 1, 2 and 3, e.g., $BChl_2$ BCl^* BPh.[18]

REFERENCES

1. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* 811:265 (1985).
2. (a) N. W. Woodbury and W. W. Parson, *Biochim. Biophys. Acta* 767:345 (1984), *ibid.* 850:197 (1986);
   (b) (quinone-free) N. W. Woodbury, W. W. Parson, M. R. Gunner, R. C. Prince and P. L. Dutton, *Biochim. Biophys. Acta* 851:6 (1986).
3. R. A. Marcus, *Chem. Phys. Letters* 133: 471 (1987).
4. J. Breton, J.-L. Martin, J. Petrich, A. Migus and A. Antonetti, *FEBS Letters* 209:37 (1986);
   J. Breton, J.-L. Martin, A. Migus, A. Antonetti and A. Orzag, *Proc. Natl. Acad. Sci. US* 83:5121 (1986);
   J. -L. Martin, J. Breton, A. J. Hoff, A. Migus and A. Antonetti, *Proc. Natl. Acad. Sci. US* 83:957 (1986).
5. K. W. Moehl, E. J. Lous and A. J. Hoff, *Chem. Phys. Letters* 121:22 (1985); D. A. Hunter, A. J. Hoff and P.J. Hore, *ibid.* 134:6 (1987).
6. J. R. Norris, C.P. Lin and D. E. Budil, *J. Chem. Soc., Faraday Trans.* I. 83:13 (1987);
   J. R. Norris, M. K. Bowman, D. E. Budil, J. Tang, C. A. Wraight and G. L. Closs, *Proc. Natl. Acad. Sci. US* 79:5532 (1982).
7. A. Ogrodnik, N. Remy-Richter, M. E.Michel-Beyerle and R. Feick, *Chem. Phys. Letters* 135:576 (1987).
8. M. Bixon, J. Jortner, M. E. Michel-Beyerle, A. Ogrodnik and W. Lersch, *Chem. Phys. Letters* 140:626 (1987).
9. R. A. Marcus, Chem. Phys. Letters (submitted).
10. J. Breton, G. R. Fleming and J. L.Martin, this volume; G.. R. Fleming, J.-L. Martin and J. Breton, submitted for publication.
11. J. Jortner, private communication;
    J. L. Katz, S. A. Rice, S. -I. Choi and J. Jortner, *J. Chem. Phys.* 39:1683 (1963);
    M. E. Michel-Beyerle, M. Plato, J. Deisenhofer, H. Michel, M. Bixon and J. Jortner, *Biochim. Biophys. Acta*, in press.

12. R. A. Goldstein, L. Takiff and S.G. Boxer, *Biochim. Biophys.Acta*, submitted;
C.E.D. Chidsey, L. Takiff, R. A. Goldstein and S. G. Boxer, *Proc. Natl. Acad. Sci. US* 82:6850 (1985).
13. M.E. Michel-Beyerle and A. Ogrodnik, this volume;
A. Ogrodnik, N. Remy-Richter, and M. E. Michel-Beyerle, *Biochim. Biophys. Act*, submitted.
14. J. K. H. Hörber, W. Göbel, A. Ogrodnik, M. E. Michel-Beyerle and R. J. Cogdell, *FEBS Letters* 198:273 (1986).
15. R. Almeida and R. A. Marcus, unpublished.
16. Z. D. Popovic, G. J. Kovacs, P. S. Vincett, G. Alegria and P. L. Dutton, *Biochim. Biophys. Acta* 851:38 (1986);
Z. D. Popovic, G. J. Kovacs, P. S. Vincett and P. L. Dutton, *Chem. Phys. Letters* 116:405 (1985).
17. J. R. Norris, D. E. Budil, D. M. Tiede, J. Tang, S. V. Kolaczkowski, C. H. Chang and M. Schiffer, *in* "Progress in Photosynthesis Research", Vol 1, ed. J. Biggins (Martinus Nijhoff, 1987), p. 363.