Mechanisms of the Early Steps in Bacterial Photosynthesis and Their Implications for Experiment*

RUDOLPH A. MARCUS
Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, CA 91125, USA

(Received 5 September 1988; revised 29 September 1988)

Abstract. The current situation on experiment and theory as regards the early electron transfer steps in bacterial photosynthesis is discussed. Recent experiments have limited the mechanistic possibilities, while an internal consistency test has limited the values of some parameters in the superexchange mechanism. The partitioning method has provided a useful and unified way of treating superexchange and other properties in these systems. The alternative reaction mechanisms have a number of consequences, and various experimental tests are considered or suggested.

1. INTRODUCTION

Bacterial photosynthetic reaction centers have been the subject of intense experimental and theoretical investigation in recent years.[1,2] Much has been measured and much has been learned. Yet a number of puzzles exist, and a variety of theoretical interpretations have been advanced to treat them, though each has some degree of uncertainty. In the present article, we review several aspects of this situation and some of the approaches which have been used to treat it. We consider some implications and possible experiments to test some of the ideas which have been introduced.

2. DATA INVOLVING THE MATRIX ELEMENTS H_f, H_{rp}, AND H_{ST}

Three pieces of data which are central to the present discussion involve the electron transfer matrix elements and the mechanism of the first electron transfer steps in the reaction center. The data are: (1) the very high rate constant k_f for the formation of $BChl_2^+ BPh^-$ from $^1BChl_2^* BPh$,[3,4] (2) the slower rate constant k_T for the activationless[5a] recombination of the triplet radical ion pair, $BChl_2^+ BPh^-$,[5] and (3) the extremely small singlet–triplet energy difference ΔE_{ST} of that pair.[5–7] We shall first consider each of these in turn. Other significant relevant data concern the extent of depletion of a nearby BChl monomer,[3,4] the effects of electric fields on fluorescence,[8] and a number of other aspects considered in section 5.

2.1. H_f and k_f

A k_f^{-1} value equal to 2.8 ps at room temperature has been determined for both *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides*, the respective k_f^{-1} values at 10 K being 0.7 ps and 1.2 ps.[3] The room temperature results for k_f imply a value of about 25 cm^{-1} for the effective matrix element H for a nonadiabatic reaction, such as that indicated above, using the standard expression at room temperature[9]

$$k = \frac{2\pi}{\hbar} \frac{1}{(4\pi\lambda kT)^{1/2}} |H|^2 \exp[-(\Delta G^0 + \lambda)^2/4\lambda k_B T]. \quad (1)$$

The value of 25 cm^{-1} is based on noting that ΔG^0, the standard free energy of reaction for this $^1BChl_2^* \rightarrow BPh$ electron transfer, is –0.26 eV[10,11] and that $-\Delta G^0 \cong \lambda$ (barrierless reaction), where λ is the reorganization energy of the reaction.

The corresponding quantum low-temperature expression, for the case of $-\Delta G^0 > 0$, is[12]

$$k = \frac{2\pi}{\hbar} \frac{1}{(2\pi |\Delta G^0| \hbar\omega)} |H|^2 (\lambda/|\Delta G^0|)^{|\Delta G^0/\hbar\omega|} \times \exp[-(\Delta G^0 + \lambda)/\hbar\omega], \quad (2)$$

with $\hbar\omega \cong 100$ cm^{-1} (the commonly used value for the relevant vibrational frequency in these systems).[3,13]

*Contribution No. 7734 from the California Institute of Technology, Pasadena, CA, USA.

Abbreviations: BChl = bacteriochlorophyll; BPh = bacteriopheophytin.

Again setting $-\Delta G^0 \cong \lambda$, we obtain $H \cong 25$ cm^{-1} for *Rb. sphaeroides* and $H \cong 35$ cm^{-1} for *Rps. viridis* from the low-temperature data. The discrepancy for H in *Rps. viridis* (more precisely the temperature profile of its k_f) has been the subject of some discussion.[3] We shall use the symbol H_f to distinguish the matrix element for k_f from two other matrix elements, H_{rp} and H_{ST}, introduced below. We set $H_f \cong 25$ cm^{-1}.

2.2. H_{rp} and k_T

A second rate constant involving an electron transfer matrix element is that associated with the recombination in the triplet state of the radical ion pair $BChl_2^+ BPh^-$ to form BPh plus the triplet state $^3BChl_2^*$ of the special pair $BChl_2$. The rate constant of this reaction, k_T, is about 5×10^8 s^{-1} at room temperature.[5,14] The current data indicate a minor[6,7,14] if somewhat negative[14] temperature dependence of k_T in a quinone-free system. These results for k_T are based on a fitting of several parameters to magnetic field data, so as to treat the singlet → triplet radical ion pair step which precedes the recombination to form $^3BChl_2^*$ BPh. The matrix element obtained from k_T and Eq. (1) or (2) will be denoted by H_{rp} to distinguish it from H_f.

Given a value for k_T, some insight into the resulting extent of uncertainty in λ and H_{rp} for this reaction step can be seen in Fig. 1. For a given H_{rp} and a given $-\Delta G^0 = 0.17$ eV for this step,[10,15] Fig. 1 depicts how k_T depends on λ at room temperature (Eq. (1)) and at low temperature (Eq. (2)). Use of room temperature data is seen to make k_T for this reaction less dependent on λ and, correspondingly, to make the value inferred for H_{rp} from a given k_T less dependent on the value of the unknown λ. For $-\Delta G^0 = 0.17$ eV, the existing value of k_T would appear to be consistent with a λ as large as 0.26 eV (or perhaps even larger), as well as a λ as small as 0.10 eV (or perhaps even smaller) (cf. Fig. 1). If k_T has a significant negative temperature dependence, however, one may infer from Fig. 1 that λ will be closer to 0.17 eV than to either of these two values.

If $\lambda = 0.26$ eV, a k_T value of 5×10^8 s^{-1} yields from Eq. (1) an $H_{rp} = 1.2$ cm^{-1}, while if $\lambda = 0.10$ eV or 0.17 eV, one finds from the same equation that $H_{rp} \cong 1.3$ cm^{-1} or 1.0 cm^{-1}, respectively. We shall simply set $H_{rp} \cong 1$ cm^{-1}, which agrees with the value obtained by others and by us using similar experimental data.[5a,16,17]

In the following section, we shall need an estimate of $\Delta G^0 + \lambda$ for this step, a quantity which also represents[18] the vertical energy difference $H_{11}^T - H_{33}^T$ for the triplet radical ion pair state at its equilibrium nuclear configuration. Using the above ΔG_{13}^0 and range of λ's, its value is seen to be perhaps between 700 cm^{-1} (~0.09 eV) and −600 cm^{-1} (~ −0.07 eV) (cf. also Ref. 16b). We shall introduce these values into Eq. (7) below.

2.3. H_{ST} and ΔE_{ST}

Matrix elements also play a role in the singlet–triplet splitting ΔE_{ST} of the radical ion pair. It is frequently as-

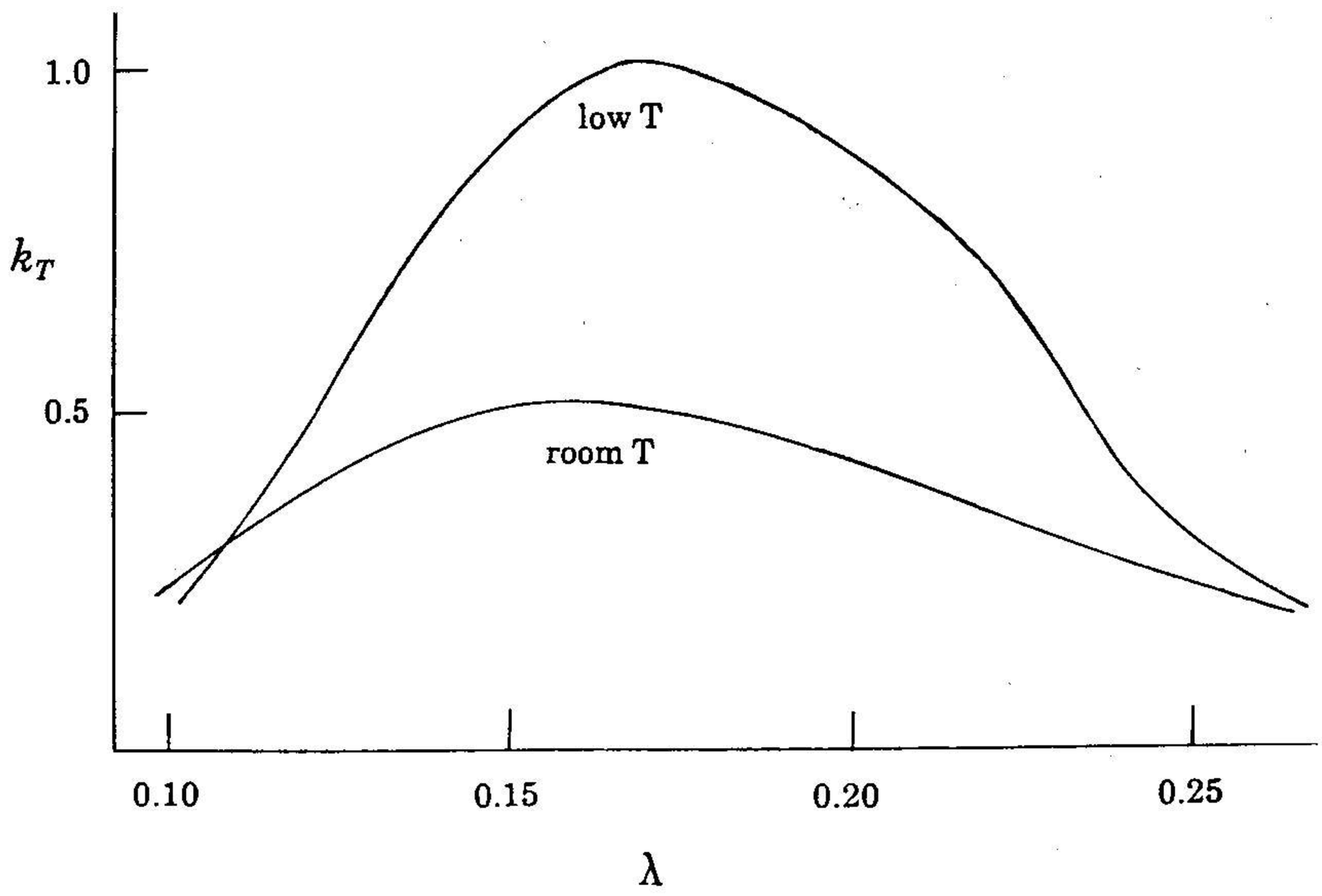

Fig. 1. Plot of k_T (in ns^{-1}) vs. λ (in eV) for $\Delta G_{13}^{0T} = 0.17$ eV. The upper curve is the low-temperature result (Eq. (2)) and the lower curve is the result for 293 K (Eq. (1)).

sumed that the singlet and triplet states of the pair are each perturbed by the singlet and triplet states of $BChl_2^*$ via their interaction with the BChl monomer ("superexchange"). (Hypotheses, given later, using other or additional states have also been proposed.) To introduce the relevant electron transfer matrix elements, we consider a mechanism for the singlet–triplet splitting of the radical ion pair based on its perturbation by the $^1BChl_2^*$ and $^3BChl_2^*$ states.

We first consider a 3×3 Hamiltonian matrix associated with the three electronic configurations $BChl_2^*$ BChl BPh (configuration 1), $BChl_2^+$ $BChl^-$ BPh (configuration 2) and $BChl_2^+$ BChl BPh^- (configuration 3). In Refs. 17, 19, 20 we used a partitioning method (Löwdin, Larsson, cited in Ref. 20) to reduce this matrix to a 2×2 one, containing an effective matrix element $\bar{H}_{13}$ for the interaction between configurations 1 and 3. We shall have occasion to use two such elements,[17,19,20] denoted here by $\bar{H}_{13}^{\mathrm{TP}}$ and $\bar{H}_{13}^{\mathrm{f}}$:

$$\bar{H}_{13}^{\mathrm{TP}} = H_{12}H_{23}/(H_{22} - H_{33}) + H_{13}, \qquad (3)$$

$$\bar{H}_{13}^{\mathrm{f}} = H_{12}H_{23}/(H_{22} - H_{11}) + H_{13}, \qquad (4)$$

where $\bar{H}_{13}^{\mathrm{TP}}$ is used in Eq. (5) below to describe the perturbation of the energy of electronic configuration 3 due to interaction with configuration 1 via an interaction with configuration 2 (also known as superexchange). $\bar{H}_{13}^{\mathrm{f}}$ describes, instead, the perturbation of the energy of configuration 1 by interaction with configuration 3 via configuration 2 (superexchange). In Eqs. (3) and (4), H_{ij} ($i \neq j$) is the electron transfer matrix element for configuration interaction between the electronic configurations i and j, and H_{ii} is the energy of configuration i before it is modified by interaction with the other configurations. (The modified value of H_{ii} for $i = 3$ is given by E in Eq. (5) below.)[17,19,20] The diagonal matrix elements, particularly, vary with the nuclear configuration. In our applications of these expressions, we shall usually need to evaluate $\bar{H}_{13}^{\mathrm{f}}$ at the equilibrium nuclear configuration of $^1BChl_2^*$ BPh and $\bar{H}_{13}^{\mathrm{TP}}$ at that of the radical ion pair $BChl_2^+$ BPh^-.

We consider now ΔE_{ST}, the singlet–triplet splitting of the radical ion pair, $BChl_2^+$ BChl BPh^-. This splitting is extremely small (10^{-3} cm^{-1})[6] (cf. Refs. 5, 7) and temperature-independent in a quinone-depleted reaction center.[6,7,14] The energy E of a singlet or triplet state of the radical ion pair can be written, using the above three-state partitioning formalism and the effective matrix element $\bar{H}_{13}^{\mathrm{TP}}$, as[17,19,20]

$$E = H_{33} - |\bar{H}_{13}^{\mathrm{TP}}|^2/(H_{11} - H_{33}). \qquad (5)$$

More precisely, what is obtained from Eq. (5), applied separately to the states S and T of the radical ion pair, is the energy difference between the singlet state and the center of gravity of the three triplet states. (The three triplet states may be further split by spin dipolar interaction terms, D and E.) For E_{T}, one should add in Eq. (5) a symbol T to $\bar{H}_{13}^{\mathrm{TP}}$ and H_{11}, while for E_{S} an S symbol is used. H_{33} in the *denominator* in Eq. (5) can be taken to be the same for both S and T states.

Any neglect of the direct exchange interaction between the two radicals would be equivalent to assuming that the other H_{33} in Eq. (5) is the same for the singlet and triplet radical pair states. The singlet–triplet splitting $E_{\mathrm{S}} - E_{\mathrm{T}}$, denoted by ΔE_{ST}, will then arise from any difference in $|\bar{H}_{13}^{\mathrm{TP}}|$ values and from the difference in the denominators $H_{11} - H_{33}$ in Eq. (5) for these two radical ion pair states. Each $H_{11} - H_{33}$ is evaluated at the equilibrium nuclear configuration of the radical pair.

In the triplet case, $H_{11}^{\mathrm{T}} - H_{33}$ is perhaps in the region -600 to $+700$ cm^{-1}, as noted in the previous section. The $H_{11}^{\mathrm{S}} - H_{33}$ value for the singlet state is substantially larger, about 4200 cm^{-1}, seen as follows: The denominator $H_{11}^{\mathrm{S}} - H_{33}$ in Eq. (5) for the singlet state equals $\Delta G_{31}^0 + \lambda_{13}$,[18] where $\Delta G_{31}^0 = -\Delta G_{13}^0$ and ΔG_{13}^0 is the free energy of formation of the radical ion pair state from $^1BChl_2^*$ BPh, about -0.26 eV;[10] λ_{13} is roughly about the same magnitude as this $-\Delta G_{13}^0$, since the rate constant k_{f} of the reaction of $^1BChl_2^*$ BPh has a negative temperature coefficient.[3] (Compare Eqs. (1) and (2) and a plot for k_{f} vs. λ similar to Fig. 1.) Since $-\Delta G_{13}^0 \cong 2100$ cm^{-1},[10] we thus have $H_{11}^{\mathrm{S}} - H_{33} \cong 4200$ cm^{-1}.

Eq. (5) yields

$$\Delta E_{\mathrm{ST}} \equiv E_{\mathrm{S}} - E_{\mathrm{T}} \cong \frac{|\bar{H}_{13}^{\mathrm{TP,T}}|^2}{H_{11}^{\mathrm{T}} - H_{33}} - \frac{|\bar{H}_{13}^{\mathrm{TP,S}}|^2}{H_{11}^{\mathrm{S}} - H_{33}}, \qquad (6)$$

if any difference between H_{33}^{S} and H_{33}^{T} in Eq. (5) is neglected.

One approximation, which we shall explore to see where it leads, is to assume in Eq. (3) that $H_{12}^{\mathrm{S}} \cong H_{12}^{\mathrm{T}}$ and $H_{13} \cong 0$. Thereby, $\bar{H}_{13}^{\mathrm{TP,S}} \cong \bar{H}_{13}^{\mathrm{TP,T}}$. The common value of these $\bar{H}_{13}^{\mathrm{TP}}$,s will be denoted by H_{ST}, and Eq. (6) becomes

$$\Delta E_{\mathrm{ST}} \cong |H_{\mathrm{ST}}|^2 \left(\frac{1}{H_{11}^{\mathrm{T}} - H_{33}} - \frac{1}{H_{11}^{\mathrm{S}} - H_{33}} \right). \qquad (7)$$

For a magnitude of about 10 gauss (10^{-3} cm^{-1}) of the splitting ΔE_{ST},[6] and using the above value of $H_{11}^{\mathrm{S}} - H_{33}$, $|H_{\mathrm{ST}}|$ is seen from Eq. (7) to equal[21] about 0.9 cm^{-1} or 0.7 cm^{-1}, if the value of $H_{11}^{\mathrm{T}} - H_{33}$ at the equilibrium nuclear configuration of the radical pair is (as discussed above) $+700$ cm^{-1} or -600 cm^{-1}, respectively.

The matrix element H_{rp} introduced earlier for k_T is the same as $\bar{H}_{13}^{rp,T}$,

$$H_{rp} \equiv \bar{H}_{13}^{rp,T}. \quad (8)$$

H_{rp} was found from k_T in section 2.2 to be about 1 cm^{-1}. Considering the various approximations introduced, this value is close to that found above for H_{ST} (0.9 to 0.7 cm^{-1}). Should the energy denominator $H_{11}^T - H_{33}$ have a value closer to 0 than the two values explored in section 2.2, there would be a larger difference between H_{rp} and H_{ST}, and then some of the approximations introduced might have to be reexamined. They include: $H_{33}^S \cong H_{33}^T$, $\bar{H}_{13}^{rp,S} \cong \bar{H}_{13}^{rp,T}$, a value of +700 or –600 cm^{-1} for $H_{11}^T - H_{33}$, and the use of a three-state model.

3. COMPARISON OF H_f, H_{rp}, AND H_{ST}

3.1. Relationship of H_f to H_{rp}

The relationship between H_f, H_{rp}, and H_{ST}, if any, depends on the mechanism of the $^1BChl_2^*$ BPh $\rightarrow$ $BChl_2^+$ BPh^- reaction. For example, if this reaction occurred via a superexchange mechanism, Eq. (4) would be the appropriate one for calculating H_f (H_f then equals $\bar{H}_{13}^f$). We consider next its consequences for the relationship between H_f and H_{rp}.

For the superexchange mechanism, the H_f obtained from k_f using Eq. (1) or (2) is given by $\bar{H}_{13}^f$ in Eq. (4). That is,

$$H_f \equiv \bar{H}_{13}^f \text{ (superexchange mechanism for initial step).} \quad (9)$$

We next compare H_{rp} and H_f using Eq. (8) and also Eq. (9) (assuming a superexchange mechanism for k_f). H_{rp} and H_f should, of course, first be put on the same basis as far as the energy denominators $H_{22} - H_{33}$ in Eqs. (3) and (4) are concerned. The exact position of H_{22} is not really known at present[9] (and the lack of its detailed knowledge is one source of the many theoretical conjectures in this field!). Here, we make use of a consistency test.[19]

The test is based on noting that if the reaction $^1BChl_2^*$ BChl BPh $\rightarrow$ $BChl_2^+$ BChl BPh^- is assumed to proceed via a superexchange mechanism and is to be faster than a competitive sequential two-step mechanism involving $BChl_2^+$ $BChl^-$ BPh as an intermediate, the value of $H_{22} - H_{11}$ at the equilibrium nuclear configuration for the $^1BChl_2^*$ BChl BPh state is no longer arbitrary. It has to be larger than some amount which depends on the value assumed for λ_{12}. For a λ_{12} of 850 cm^{-1}, one had $H_{22} - H_{11} \geq 1700$ cm^{-1}.[19,22] In contrast, the vertical $H_{22} - H_{33}$ for the radical ion pair is at least 2100 cm^{-1} (if $\Delta G_{12}^0 > 0$, as assumed in the superexchange mechanism for k_f), since ΔG_{13}^0 is –2100 cm^{-1}.[10] This $H_{22} - H_{33}$ is then about 3000 cm^{-1} to 4000 cm^{-1}. If we use the latter figure as a maximum, the smallest value of $|\bar{H}_{13}^{rp}|$ that would be estimated from H_f on this basis using Eqs. (3) and (4) is about (25 cm^{-1}) (1700/4000), or about 10 cm^{-1}.

Thus, for the superexchange mechanism there is an apparent discrepancy between this $\bar{H}_{13}^{rp}$ value (10 cm^{-1}) inferred from H_f, based on k_f, and that inferred from k_T (1 cm^{-1}). We note, too, that a tenfold difference in $\bar{H}_{13}^{rp}$ corresponds to a 100-fold discrepancy in the rate constant k_T. The discrepancy is discussed below.

3.2. Relationship between H_f and ΔE_{ST}

As discussed in the next section, the mechanisms also differ in the relationship expected between H_f and ΔE_{ST}. No such relationship would be expected in the case of the superexchange mechanism. However, in the case of a nonadiabatic/adiabatic mechanism described in the next section, a relation between H_f and H_{rp}, and indeed also H_{ST} and hence ΔE_{ST}, can occur, as is seen with certain assumptions in sections 5.1 and 5.2.

4. MECHANISMS

We consider some of the mechanisms used to treat the above results on H_f, H_{rp}, and ΔE_{ST}: mechanism I (superexchange), mechanism II (intermediate $BChl^-$), mechanism III ($BChl^-$ nonadiabatic/adiabatic), mechanism IV (intermediate $BChl^+$), mechanism V ($BChl^+$ nonadiabatic/adiabatic), and mechanism VI (charge-transfer-modified I). All of these mechanisms use superexchange to treat k_T; they differ in their treatment of k_f.

Mechanism I

In this case, k_f is interpreted considering a superexchange mechanism involving the orbitals of an existing BChl monomer as an intermediate, e.g., Refs. 16, 20, 22, using, for example, the partitioning formalism in Ref. 20. One can try to make mechanism I consistent with the data in the following way:

In the previous section, it was seen that in mechanism I there is a discrepancy factor of 10 in the energy denominator corrected H_T and H_f, namely, $\bar{H}_{13}^{rp,S} \cong 10\,\bar{H}_{13}^{rp,T}$. Either mechanism I is incorrect, or to remove this discrepancy in mechanism I, it is necessary to postulate either that there is a marked protein relaxation when the radical pair is formed, so as to reduce H_{12} (and thereby $\bar{H}_{13}^{rp,T}$) considerably, or that $H_{12}^T << H_{12}^S$, or both.[22]

We next consider ΔE_{ST} using Eq. (6). The above values for $\bar{H}_{13}^{rp,T}$ ($\equiv H_{rp}$) and $\bar{H}_{13}^{rp,S}$ are next introduced into Eq. (6) for ΔE_{ST}, with[16] or without[16,17,19,20] a factor multiplying $\bar{H}_{13}^{rp,S}$ to allow for any protein relaxation accompanying formation of the radical ion pair. One finds in this way that the perturbation of the E_S and E_T of

$BChl_2^+ BPh^-$ by a configuration interaction is so large[20] that the smallness of the observed ΔE_{ST} would have to be due to a large cancellation,[16b] if this three-state superexchange mechanism for k_f were correct.

Mechanisms II and III

An alternative possibility is that k_f entails a different mechanism, so that H_f can be considerably larger than H_{rp} or H_{ST}, without a large cancellation being required to obtain a small ΔE_{ST}. Two of the mechanisms which have been considered for the $^1BChl_2^* BPh \rightarrow BChl_2^+ BPh^-$ reaction are: mechanism II, a sequential mechanism[20] having the rate constants k_1 and k_2, $^1BChl_2^* BChl BPh \xrightarrow{-k_1} BChl_2^+ BChl^- BPh \xrightarrow{-k_2} BChl_2^+ BChl BPh^-$ ($k_2 >> k_1$, $k_1 = k_f$); and mechanism III,[17,19] a reaction in which there is a very strong electronic coupling of the electronic configurations 2 and 3, such that after leaving the electronic configuration $^1BChl_2^* BChl BPh$ the system goes rapidly downhill on the adiabatic potential surface constructed from these two surfaces (configurations 2 and 3).[23] In the latter case, there is no intermediate $BChl^-$ as such. Mechanism III has been termed a nonadiabatic/adiabatic mechanism.[17,19] It is presently consistent with the above data and, apparently, with the absence of measurable BChl depletion, as discussed later in section 5.2. It could encounter a problem noted later in section 5.5. Mechanisms I and III differ mainly in the position of the energy of $BChl_2^+ BChl^- BPh$ vs. $^1BChl_2^* BChl BPh$.

Mechanisms IV and V

Mechanism IV is one in which there are two sequential steps,[24,25] i.e., $^1BChl_2^* BChl BPh \xrightarrow{-k_1} BChl_2 BChl^+ BPh^- \xrightarrow{-k_2} BChl_2^+ BChl BPh^-$, with $k_2 >> k_1$ and $k_1 = k_f$. In mechanism V, which we include as a possibility here by analogy with mechanism III, $BChl_2$ and $BChl^+$ are so strongly coupled electronically that after leaving the $^1BChl_2^* BChl BPh$ state the system goes rapidly downhill on an adiabatic surface. While this particular nonadiabatic/adiabatic mechanism has not yet been postulated in the literature, and in the only theoretical calculation thus far the second matrix element is only 2.5 times the first,[25] it represents a possibility, but it will require a larger second matrix element than that estimated in Ref. 25.

The ΔE_{ST} for mechanism IV has been estimated[25] to be too high (5×10^{-3} cm^{-1}). Protein relaxation of the radical pair was postulated as a possible reason for the discrepancy.[25]

Mechanism VI

To explain the smallness of ΔE_{ST}, mechanism I has been modified by introducing a fourth state: an internal $BChl_2$ charge transfer state, both as singlet and triplet $BChl^+$ and $BChl^-$ states.[26] In this case, a form of cancellation in ΔE_{ST} different from that postulated for mechanism I arises, as in a recent four-state treatment of the singlet–triplet splitting.[25] With the energy of the charge transfer triplet state of $BChl_2$ assumed to be above that of the radical pair $BChl_2^+ BPh^-$ and the usual $^3BChl_2^*$ state known to be below it, for example, there are opposing tendencies which reduce the triplet perturbation and its contribution to ΔE_{ST}.

We consider next some consequences and further tests of some of these mechanisms. Two miscellaneous implications are discussed in the Appendix.

5. IMPLICATIONS AND EXPERIMENTAL TESTS

5.1. Relationship of H_{ST} and H_{rp}

If the superexchange mechanism I is correct, a meaningful H_{ST} cannot be calculated from ΔE_{ST} using Eq. (7). In this case, the moderately close agreement found in section 2.3 between the H_{ST} inferred from ΔE_{ST} and the H_{rp} inferred from k_T is treated as accidental. Only one reaction center has been studied thus far. This possibility of an accidental agreement can be tested when other quinone-depleted reaction centers having different ΔE_{ST} and k_T values are studied, the use of quinone-depleted centers serving to simplify the interpretation of the data. Conversely, any continued closeness in the values of $|H_{ST}|$ and $|H_{rp}|$ for these other reaction centers would argue against the cancellation required in the current form of mechanism I to explain the smallness of ΔE_{ST}.

If there were many virtual states, rather than merely one, participating in the superexchange mechanism, and if they had randomly distributed positive and negative contributions to ΔE_{ST}, the chance would be larger for the existence of some cancellation, and hence for a small averaged ΔE_{ST} in such a modification of mechanism I.

5.2. Relationship of H_f and H_{rp}

We had $H_{rp} = H_{12}^T H_{23}/(H_{22} - H_{33})$ (cf. Eqs. (3) and (5)). In mechanism III, the values of H_f and H_{rp} are related, $H_f = H_{12}^S$, and we assume for the present that $H_{12}^S \cong H_{12}^T$. H_{23} is about 6 H_{12} in the calculations of Plato,[27] and $H_{22} - H_{33}$ is $\Delta G_{23}^0 + \lambda_{23}$.[18] Using a set of parameters employed in the quantum dynamical calculations[28,29] for this mechanism, with $\Delta G_{12}^0 = -350$ cm^{-1}, we have $H_{22} - H_{33}$ ($=\Delta G_{23}^0 + \lambda_{23}$) ~4000 cm^{-1}. One then finds that the H_{rp} calculated from the above H_f is $6(25)^2/4000 \cong 0.9$ cm^{-1}, which is fortuitously close to the value found from k_T (~1 cm^{-1}) in section 2.2 and to the $\overline{H}_{13}^{rp}$ (calculated as H_{ST}) in section 2.3.

5.3. BChl Depletion

Experimentally, the transient depletion of BChl dur-

ing the reaction is estimated to be no more than 2% (Ref. 3) or, more conservatively, 4% (Ref. 4). (The interpretation of the spectral data to assess the depletion is the subject of some difference of opinion; the details depend on the nature of the radical ion-pair induced Stark effect on the BChl absorption spectrum, the role of charge transfer states in the absorption spectrum of $BChl_2$, etc.)[30]

Taken at face value, the apparently negligible depletion requires, using Eq. (13) of Ref. 20, that the second step of the two-step sequential mechanism II or IV be faster than the adiabatic value $\omega/2\pi$ ($= 3 \times 10^{12}$ s^{-1} if $\hbar\omega \cong 100$ cm^{-1}) by a factor of 5 to 10 depending on the assumed detection limit for the depletion. In this case, mechanisms II or IV would be inappropriate, unless some way can be found for assuming a higher frequency vibration for $\omega/2\pi$. We shall return to this point later.

Simplified one-dimensional quantum-mechanical dynamical ("fast Fourier transform") calculations of the BChl depletion for the nonadiabatic/adiabatic mechanism III yield a value of about 2% for a $-\Delta G^0_{12}$ value of 350 cm^{-1} and also for a value of 150 cm^{-1}.[28,29] The treatment of mechanism III is being extended to higher dimensions, in part analytically.[28]) Simply by changing labels, the same remarks may apply to the nonadiabatic/adiabatic mechanism V, if similar energetics are assumed.

5.4. Field-free Absorption Spectrum of $BChl_2$ and the Stark Effect

The perturbation of the energy of the excited state $^1BChl_2^*$ by a directly coupled charge transfer or another zeroth state i (wave function ψ_i) is given by

$$E = H_{11} - |H_{1i}|^2 (H_{ii} - H_{11}) \qquad (10)$$

(e.g., for $i = 2$, cf. Refs. 17, 19, 20).

Here, $H_{ii} - H_{11}$ is the vertical energy difference, evaluated at the equilibrium configuration of $^1BChl_2^*$. The perturbed wavefunction of $^1BChl_2^*$ is $\psi_1 - \psi_i H_{1i}/(H_{ii} - H_{11})$, from which a dipole moment of the excited state could be estimated. In mechanism I, if $H_{12} \sim 80$ cm^{-1} and $H_{22} - H_{11} \sim 800$ cm^{-1} (cf. Ref. 22), this perturbation, $E - H_{11}$ in Eq. (10), would be small (about -8 cm^{-1}). For mechanism III, if $H_{12} \sim 25$ cm^{-1} and $\Delta G^0_{12} \sim -350$ cm^{-1}, then $\lambda_{12} \cong 600$ cm^{-1} and $H_{22} - H^S_{11} \sim 250$ cm^{-1}.[28] The perturbation in this case is again small, about -2.5 cm^{-1}. From the estimated electric field effect on $H_{22} - H_{11}$, the contribution to the Stark effect on $^1BChl_2^*$ could be calculated. The oscillator strength is presumed here to be carried only by ψ_1.

In order to prepare by optical excitation a "pure" $^1BChl_2^*$ state, free from a contribution by ψ_i, it would be necessary to use an optical pulse with an energy width of about $|H_{ii} - H_{11}|$, which in many cases would be much larger than that usually used in optical excitation.

5.5. Electric Field Effect on Fluorescence

The prompt fluorescence of $^1BChl_2^*$ is in competition with the forward electron transfer rate, k_f. The effect of the electric field[8,22,31] on k_f, and thereby on the fluorescence yield, differs for some of the different mechanisms. A calculation for the sequential mechanism (mechanism II) appears to lead to a too large electric field effect on the fluorescence yield.[16b] For the nonadiabatic/adiabatic mechanism III, the appropriate range of permitted $-\Delta G^0_{12}$ values for the hypothetical process $1 \rightarrow 2$ has not yet been determined (cf. section 5.8 below), and appropriate electric field calculations remain to be made.

The study of the electric-field-induced fluorescence *anisotropy*,[18c] in which one finds, largely, the angle between the transition dipole and the donor–acceptor vector, is more consistent with mechanism I than with mechanism II.[18c] Calculations are being made for mechanism III.[28] A donor–acceptor vector might result for mechanism III between those of mechanisms I and IV. An alternative nonadiabatic/adiabatic model, mechanism V, might be acceptable, since its donor–acceptor vector could be along the $BChl^+ BPh^-$ direction and so close to that inferred from the fluorescence anisotropy study.[18c]

5.6. Electric Field Effect on ΔE_{ST} and k_T

For most of the mechanisms, a substantial effect of the electric field on small energy denominators, such as that in Eq. (3) for $\bar{H}^{P,T}_{13}$, is predicted to occur. Existing arguments can be used to estimate an electric effect on ΔE_{ST}. The effect on k_T itself is estimated to be small (cf. Fig. 1).

5.7. Effect of Electric Field on BChl Depletion

In the presence of a suitable electric field in an oriented reaction center, the level of BPh^- might be raised sufficiently that an actual BChl depletion might be observed.[19,20] (The extent of raising depends upon whether BPh^- is first formed in a reported transient configuration with a $-\Delta G^0_{13}$ of about 0.17 eV, or whether no such transient configuration exists.[11])

5.8. Electric Field Effects on k_f

These effects, measured directly and preferably in oriented reaction centers, may help identify better the actual value of $-\Delta G^0_{12}$, and thereby, the energy of electronic configuration 2 relative to that of configuration 1. When appropriate calculations are made, they might distinguish between mechanism I on one hand and mechanisms III and V on the other. The experiments on field ef-

fects in randomly oriented systems mentioned in section 5.5 have yielded valuable information.

5.9. Effect of Temperature on ΔE_{ST}

In the case of mechanism II, the lack of a temperature effect[5–7] on ΔE_{ST} for quinone-depleted reaction centers has been used to place some lower limit on ΔG^0_{32},[6,32] the standard free energy of reaction for forming electronic configuration 2 from configuration 3. The limit is based on the following assumptions: (1) there exists a species $BChl_2^+$ $BChl^-$ BPh; (2) its singlet–triplet splitting is assumed to be 1 cm^{-1}; and (3) this transient species is in thermal equilibrium with the radical ion pair.

If the uncertainty in the value of ΔE_{ST} were about 1 gauss (10^{-4} cm^{-1}), the result that ΔE_{ST} is temperature-independent between 160 K and 295 K shows that there is a lower limit of 1850 cm^{-1} for ΔG^0_{32}, in agreement with the similarly estimated value in Ref. 32. Since the value of $-\Delta G^0_{12}$ is 0.26 eV,[10] it follows that $-\Delta G^0_{12} \leq 250$ cm^{-1}. (The same remarks might apply to mechanism IV.) If, however, the potential energy surfaces are those assumed in the nonadiabatic/adiabatic mechanism, an equilibrated species $BChl_2^+$ $BChl^-$ BPh no longer exists, and then the above calculation does not apply. A new type of calculation would be needed for mechanism III or V.

5.10. Possible Charge Transfer Band for $BPh^- \rightarrow BChl^-$

The implications of mechanism I lead to a predicted[17,19] charge transfer absorption BChl BPh^- $\rightarrow$ $BChl^-$ BPh if that mechanism is applicable. The $h\nu_{CT}$ equals $H_{22} - H_{33}$, evaluated at the equilibrium configuration of the radical pair, and this in turn equals[18] $\Delta G^0_{32} + \lambda_{23}$. The intensity could be appreciable, assuming the large matrix element H_{23} required[17,19,27] if mechanism I prevails.

* * *

We return finally to the point discussed in section 5.3 regarding BChl depletion. One new fact is that there are indeed some very fast processes in this system, faster than an $\omega/2\pi = 100$ cm^{-1} would indicate. In particular, when the Q_y transitions of BChl and BPh were excited by an optical pulse, a transfer of the excitation to $BChl_2$ occurred within the time-resolution of the apparatus, about 100 fs.[33] While this process is an excitation transfer, the principles of excitation transfers and electron transfers have much in common.[34] Perhaps some high frequency motion is available, at least for the excitation transfer, or perhaps considerations of coherency vs. incoherency arise. A better understanding of that rapid excitation transfer may await an improved time-resolution, so as to determine the phenomenological kinetics associated with the transfer.

6. SUMMARY

We have seen that there are strengths and drawbacks to the various mechanisms of the early steps in bacterial photosynthesis. In one way or another, all the mechanisms use superexchange for k_T. They differ in their treatment of k_f, in part because of their different guesses for the energy of $BChl^-$ (or $BChl^+$). The advantage of mechanism I (superexchange) for k_f is that it "seems reasonable", is consistent with the absence of BChl depletion and, thus far, is more or less consistent with the electric field effect on the fluorescence including the field-induced anisotropy. Its drawbacks are that it requires a large cancellation to yield a small singlet–triplet splitting ΔE_{ST} and also requires that the type of agreement noted among the data summarized in sections 5.1 and 5.2 should be accidental.

Mechanism II (sequential, $BChl^-$) is eliminated by two new experiments, namely the absence of BChl depletion (see, however, qualification in section 5.3 and at the end of section 5) and the electric-field-induced fluorescence anisotropy.

Mechanism III (nonadiabatic/adiabatic, $BChl^-$) has led to a current agreement between the k_f, k_T, and ΔE_{ST} values (cf. sections 2.3, 5.1 and 5.2). Thus far, in a one-dimensional calculation, mechanism III is also consistent with the absence of BChl depletion. Its possible drawback, when the calculations are made, may be in explaining the electric-field-induced fluorescence anisotropy data. Other calculations (fluorescence yield effect, temperature independence of ΔE_{ST}) also remain to be made. Mechanism III explains the fast forward rate, as contrasted with the slow triplet recombination and the small singlet–triplet splitting, by assigning a superexchange mechanism to the latter two processes and, in contrast to mechanism I, a direct mechanism for the fast forward reaction.

Mechanism IV (sequential, $BChl^+$) suffers from the same drawback as mechanism II with respect to BChl depletion. It is consistent, however, with the electric-field-induced fluorescence anisotropy. Its consistency with the remaining data might need to be examined more fully.

Mechanism V (nonadiabatic/adiabatic, $BChl^+$) is, by analogy with mechanism III, consistent with the absence of BChl depletion, and also with the current electric-field-induced fluorescence anisotropy. Its consistency with the other measurements remains to be investigated, perhaps using arguments similar to those we have described for mechanisms I to III. At present, the principal comparison of the data with mechanism IV (and thereby, indirectly, with mechanism V) has been via calculation of the numerous diagonal and off-diagonal matrix ele-

ments of the six-pigment "supermolecule".[24,25] With the latter procedure, more experimental quantities, such as the absorption spectrum, can be calculated; however, the individual comparisons with the experimental data depend heavily on the accuracy of the details in those calculations. A search for internal relationships, such as those described in this paper for mechanisms I–III, could be a useful complement to these other detailed calculations.

There is also a sixth possible mechanism, not discussed in this paper, involving a direct protein-mediated electron transfer from $^1BChl_2^*$ to BPh. Two main facts to be explained in suggesting such a mechanism are that $k_T << k_f$ and that ΔE_{ST} is so small. Thus far, no compelling explanation appears to have been offered. Another mechanism involves BChl*.[35]

Various experiments to test some of the consequences of the several mechanisms are also suggested or considered in the present paper.

Acknowledgment. It is a pleasure to acknowledge stimulating discussions with M.E. Michel-Beyerle, J. Jortner, and S.G. Boxer. The support of this research by the National Science Foundation and the Office of Naval Research is indeed greatly appreciated.

APPENDIX
MISCELLANEOUS IMPLICATIONS

Two implications of the previous discussion are considered in this Appendix.

1. $\overline{H}_{22}^S - \overline{H}_{22}^T$

As noted in the text, a singlet–triplet splitting of about 1 cm^{-1} of the hypothetical electronic configuration 2, $BChl_2^+$ $BChl^-$ BPh, is sometimes assumed in the literature. However, the actual value of the splitting for these two large radicals in near contact does not appear to be known. It is useful, therefore, to estimate whether the splitting might be due to the fact that the S and T states of the electronic configuration 2 are each perturbed differently by configuration interaction with the states $^1BChl_2^*$ BChl and $^3BChl_2^*$ BChl of the electronic configuration 1.

The perturbation, obtained using a perturbation equation rather similar to Eq. (5), is

$$E = H_{22} - |H_{12}|^2/(H_{11} - H_{22}). \qquad \text{(A1)}$$

The value of H_{12} depends on whether mechanism I or III is correct. In the case of mechanism III, H_{12} was found from k_f to be about 25 cm^{-1}, as noted earlier. In the case of mechanism I (superexchange), H_{12} was found to be about 80 cm^{-1}.[22,27] The vertical value of $H_{11} - H_{22}$, evaluated at the equilibrium nuclear configuration of electronic configuration 2, equals $\Delta G_{12}^0 + \lambda$. For the singlet state, if $-\Delta G_{12}^0$ were 350 cm^{-1} and λ_{12} were 600 cm^{-1}, this $H_{11} - H_{22}$ would be 950 cm^{-1} and the perturbation of E_S obtained from Eq. (A1) would be about –0.7 cm^{-1}. For the triplet state, $-\Delta G_{12}^0$ would be the above minus 0.4 eV. If H_{12} were again 25 cm^{-1}, the perturbation of E_T obtained from Eq. (A1) would be +0.2 cm^{-1}. Thus, the splitting would be about 1 cm^{-1}, in agreement with the value sometimes assumed.

In the case of the superexchange mechanism for k_f, the $\Delta G_{12}^0 + \lambda_{12}$ (=$H_{11} - H_{22}$ in Eq. (A1))[17] for the singlet state has been estimated[22] to be >1600 cm^{-1}, using a value of λ_{12} = 800 cm^{-1} and the internal consistency test.[19] The perturbation of E_S calculated from Eq. (A1) then becomes –4 cm^{-1} for the singlet state and 1.3 cm^{-1} for the triplet state, giving rise to a singlet–triplet splitting of about 5 cm^{-1}. (Such values tacitly assume no structural relaxation of the radical pair, as compared with the initial state.[16b,17])

2. Direct Exchange Value of $H_{33}^S - H_{33}^T$

The direct exchange integral involved with this splitting is omitted in many discussions and has been omitted in applying Eqs. (3) and (4) in the text. It is a double electron exchange integral and it can be expected to fall off twice as rapidly with separation distance r as a single electron exchange integral [exp $-(\beta r/2)$], according to related experimental results by Closs et al. on the rate of triplet excitation transfer for a different system.[34] Thereby, $H_{33}^S - H_{33}^T$ may fall off with r as exp($-\beta r$), where $\beta \cong$ 1.1 $Å^{-1}$ for other systems.[9] The edge-to-edge distance of the $BChl_2^+$ $BChl^-$ radical pair is about 5.5 Å, while that of $BChl_2^+$ BPh^- is about 9.5 Å.[36] Neglecting, for the present rough argument, the differences between radicals, and assuming a $\beta \cong 1.1$ $Å^{-1}$ in the absence of experimental data on this particular system, the exchange integral $H_{33}^S - H_{33}^T$ for the $BChl_2^+$ BPh^- pair is then calculated, with these assumptions, to be smaller than the $BChl_2^+$ $BChl^-$ pair by a factor of about 80. Thus, if the direct exchange value of the splitting for $BChl_2^+$ $BChl^-$ were about 1 cm^{-1}, that for $BChl_2^+$ BPh^- would be about 0.01 cm^{-1}, a rather large value in comparison with ΔE_{ST} (10^{-3} cm^{-1}). Clearly, it would be useful to have direct experimental information on $H_{33}^S - H_{33}^T$.

REFERENCES AND NOTES

(1) Cf. the recent collection of articles given in *The Photosynthetic Bacterial Reaction Center–Structure and Dynamics*; NATO ASI Series A: Life Sciences, Vol. 149; Breton, J.; Vermeglio, A., Eds.; Plenum Press: New York,

1988.
(2) Cf. recent reviews or collections of articles: (a) Kirmaier, C.; Holten, D. *Photosynth. Res.*, 1987, **13**: 225. (b) Michel-Beyerle, M.E., Ed. *Antennas and Reaction Centers of Photosynthetic Bacteria–Structures, Interactions and Dynamics*; Springer-Verlag: Berlin, 1985. (c) Biggins, J., Ed. *Progress in Photosynthesis Research*; Martinus Nijhoff Publishers: Dordrecht, 1987. (d) Hoff, A. *Photochem. Photobiol.*, 1986, **43**: 727.
(3) Martin, J.-L.; Breton, J.; Lambry, J.-C.; Fleming, G.R. Ref. 1, p. 195.
(4) Kirmaier, C.; Holten, D. *FEBS Lett.*, 1988, **239:** 211. *Isr. J. Chem.*, 1988, **28**: 79.
(5) (a) Ogrodnik, A.; Remy-Richter, N.; Michel-Beyerle, M.E.; Feick, R. *Chem. Phys. Lett.*, 1987, **135**: 576. (b) Bowman, M.K.; Budil, D.E.; Closs, G.L.; Kostka, A.G.; Wraight, C.A.; Norris, J.R. *Proc. Natl. Acad. Sci. U.S.A.*, 1981, **78**: 3305. (c) Norris, J.R.; Bowman, M.K.; Budil, D.E.; Tang, J.; Wraight, C.A.; Closs, G.L. *Proc. Natl. Acad. Sci. U.S.A.*, 1982, **79**: 5532.
(6) Hunter, D.A.; Hoff, A.J.; Hore, P.J. *Chem. Phys. Lett.*, 1987, **134**: 6.
(7) Moehl, K.W.; Lous, E.J.; Hoff, A.J. *Chem. Phys. Lett.*, 1985, **121**: 22.
(8) (a) Lockhart, D.J.; Boxer, S.G. *Chem. Phys. Lett.*, 1988, **144**: 243. Lockhart, D.J.; Boxer, S.G. *Biochemistry*, 1987, **26:** 664. *Proc. Natl. Acad. Sci. U.S.A.*, 1988, **85:** 107. (b) Losche, M.; Feher, G.; Okamura, M.Y. *Proc. Natl. Acad. Sci. U.S.A.*, 1987, **84:** 7537. (c) Lockhart, D.J.; Goldstein, R.F.; Boxer, S.G. *J. Chem. Phys.*., 1988, **89**: 1408.
(9) E.g., Marcus, R.A.; Sutin, N. *Biochim. Biophys. Acta.*, 1985, **811**: 265, and references cited therein.
(10) Goldstein, R.A.; Takiff, L.; Boxer, S.G. *Biochim. Biophys. Acta.*, 1988, **934:** 253.
(11) There is some uncertainty here. If the system first forms some unrelaxed state, this electron transfer, with a $-\Delta G^0$ of about 0.17 eV (Woodbury, N.W.; Parson, W.W.; Gunner, M.R.; Prince, R.C.; Dutton, P.L. *Biochim. Biophys. Acta.*, 1986, **851**: 6), then the corresponding λ is about 0.17 eV, instead of the 0.26 eV appropriate to the relaxed state of the radical ion pair.
(12) E.g., Ref. 9, in which the usual factorial in the standard one-frequency low-temperature expression is replaced by Stirling's approximation.
(13) (a) Warshel, A. *Proc. Natl. Acad. Sci. U.S.A.*, 1980, **77**: 3105. (b) Bixon, M.; Jortner, J. *J. Phys. Chem.*, 1980, **90**: 3795.
(14) Michel-Beyerle, M.E., private communication.
(15) Typical values range roughly from about 0.15 eV to 0.18 eV, as in Refs. 10 and 16a. The most recent value appears to be that in Ref. 10 (0.17 eV).
(16) (a) Ogrodnik, A.; Volk, M.; Michel-Beyerle, M.E. Ref. 1, p. 177. (b) Michel-Beyerle, M.E.; Bixon, M.; Jortner, J. *Chem. Phys. Lett.*, 1988, **151:** 188.
(17) Marcus, R.A., Ref. 1, p. 389.
(18) A detailed discussion of these vertical excitation energies and the free energy $\Delta G^0 + \lambda$ is given in Marcus, R.A.; Sutin, N. *Comments Inorg. Chem.*, 1986, **5**: 119.
(19) Marcus, R.A. *Chem. Phys. Lett.*, 1988, **146**: 13.
(20) Marcus, R.A. *Chem. Phys. Lett.*, 1987, **133**: 471; a sign correction is noted in Ref. 19, p. 18.
(21) Cf. Ref. 17; inadvertently, a term was omitted in the last two lines of p. 393 and the first line of p. 394, so that the value there of about 2 cm^{-1} for $\bar{H}_{13}^{TP}$ should be replaced by the present value of about 1 cm^{-1}.
(22) Bixon, M.; Jortner, J.; Plato, M.; Michel-Beyerle, M.E. Ref. 1, p. 399.
(23) This strong coupling is a consequence, in part, of the calculations in Refs. 22 and 33, which yield a value of $H_{23}/H_{12} \sim 6$, and, thereby, in mechanisms I–III lead to a high H_{23} so as to be consistent with k_f. In the case of mechanism I, the internal consistency test[19] was also invoked.
(24) Fischer, S.F.; Scherer, P.O.J. *Chem. Phys.*, 1987, **115**: 151, who use here and in Ref. 25 a many-state formalism, in effect.
(25) Scherer, P.O.J.; Fischer, S.F. *J. Phys. Chem.*; in press; Ref. 1, p. 425.
(26) Won, Y.; Freisner, R.A. *Biochim. Biophys. Acta*; in press.
(27) (a) Plato, M.; Winscom, C.J.; Ref. 1, p. 421. (b) Plato, M.; Möbius, K.; Michel-Beyerle, M.E.; Bixon, M.; Jortner, J., *J. Am. Chem. Soc.*, 1988, **110:** 7279.
(28) Almeida, R.; Marcus, R.A., to be submitted. We made the behavior at the second crossing-point even more adiabatic than that implied by Plato's[22,27] H_{23}, to reduce the possibility of reflection at that crossing in these (preliminary) one-dimensional calculations.
(29) In Ref. 28, the values used for H_{12}, λ_{13}, and λ_{23} were 25 cm^{-1}, 650 cm^{-1}, and 2115 cm^{-1}, respectively, when $\Delta G_{12}^0 = -350$ cm^{-1}. When $\Delta G_{12}^0 = -150$ cm^{-1}, λ_{12} was changed to 443 cm^{-1}.
(30) Small, G.J., private communication. Cf. Tang, D.; Janowiak, R.; Gillie, J.K.; Small, G.J.; Tiede, D.M. *J. Phys. Chem.*, 1988, **92:** 4012.
(31) (a) Boxer, S.G.; Lockhart, D.J.; Franzen, S. *Proceedings, Seventh International Conference on Photochemical Conversion and Storage of Solar Energy;* Evanston, IL.; Elsevier: New York, 1988. (b) Bixon, M.; Jortner, J. *J. Phys. Chem.*, 1988, **92:** 7148.
(32) Bixon, M.; Jortner, J.; Michel-Beyerle, M.E.; Ogrodnik, A.; Lersch, W. *Chem. Phys. Lett.*, 1987, **140**: 626.
(33) Breton, J.; Martin, J.-L.; Fleming, G.R.; Lambry, J.C. *Biochemistry*, 1988, **27:** 8276.
(34) (a) Closs, G.L.; Piotrowiak, P.; MacInnis, J.M.; Fleming, G.R. *J. Am. Chem. Soc.*, 1988, **110**: 2652. (b) Oevering, H.; Verhoeven, J.W.; Paddon-Row, M.N.; Cotsaris, E.; Hush, N.S. *Chem. Phys. Lett.*, 1988, **143**: 488.
(35) Parson, W.W.; Scherz, A.; Warshel, A. Ref. 2(b), p. 122. Cf. Norris, J.R.; Budil, D.E.; Tiede, D.M.; Tang, Y.; Kolaczkowski, S.V.; Chang, C.H.; Schiffer, M. Ref. 2(c), p. 363.
(36) Budil, D.E.; Gast, P.; Chang, C.-H.; Schiffer, M.; Norris, J.R. *Annu. Rev. Phys. Chem.*, 1987, **38**: 561, Table 2 and reference to Deisenhofer, J. and Michel, H. cited therein.