NORTH-HOLLAND
PHYSICS
PUBLISHING

SUPEREXCHANGE VERSUS AN INTERMEDIATE BChl$^-$ MECHANISM IN REACTION CENTERS OF PHOTOSYNTHETIC BACTERIA

R.A. MARCUS

Noyes Laboratory of Chemical Physics [1], *California Institute of Technology, Pasadena, CA 91125, USA*

Received 15 October 1986, in final form 18 December 1986

Kinetic and singlet–triplet data are used to treat the mechanism of electron transfer for BChl$_2^*$–BChl–BPh in bacterial photosynthetic reaction centers. The data favor a two-step transfer rather than a superexchange single step.

Reprinted from CHEMICAL PHYSICS LETTERS

SUPEREXCHANGE VERSUS AN INTERMEDIATE $BChl^-$ MECHANISM IN REACTION CENTERS OF PHOTOSYNTHETIC BACTERIA

R.A. MARCUS
Noyes Laboratory of Chemical Physics [1], *California Institute of Technology, Pasadena, CA 91125, USA*

Received 15 October 1986, in final form 18 December 1986

Kinetic and singlet–triplet data are used to treat the mechanism of electron transfer for $BChl_2^*$–BChl–BPh in bacterial photosynthetic reaction centers. The data favor a two-step transfer rather than a superexchange single step.

1. Introduction

The early reaction steps in bacterial photosynthetic reaction centers have been a matter of considerable current interest, e.g., reviews in refs. [1–6], not only in their own right but also for possible implications for the design of efficient solar energy conversion schemes. The recent crystal structural determination of a particular reaction center [7] shows that the bacteriochlorophyll dimer $(BChl)_2$ is a neighbor of the monomer BChl, which has the pheophtytin BPh as another neighbor, and the latter is near a quinone Q.

In the scheme for transfer of an electron from a photoexcited molecule $(BChl)_2^*$ to Q [1–6],

$$\underset{\text{I}}{(BChl)_2^*} \xrightarrow{e} \underset{\text{II}}{BChl} \xrightarrow{e} \underset{\text{III}}{BPh} \xrightarrow{e} \underset{\text{IV}}{Q}, \qquad (1)$$

the loss of the electron from I occurs in about 2.8 ps [8], and the loss of the electron from III to IV in about 200 ps at room temperature [1]. A principal remaining question concerns the role of II in the former. Two alternative possibilities are that (a) $BChl^-$ is formed as an actual intermediate [9,10], or that (b) BChl serves to assist the transfer from $(BChl)_2^*$ to BPh (a superexchange mechanism) [8,11,12]. In the latter case no $BChl^-$ intermediate would be detected, whereas in the former the detectability would depend on the ratio of the rate constants for formation and destruction of $BChl^-$. (A critique of the evidence of ref. [9] is given in ref. [13].) In a recent experiment, $BChl^-$ was not detected spectroscopically, the limits of detectability being perhaps 15–20% of the neighboring population, and this evidence was interpreted as offering support for the superexchange mechanism [8].

To distinguish between the two mechanisms we make use of some magnetic data. The latter indicate a very weak exchange interaction between the $(BChl)_2^+$ and BPh^- [3,14], a result which is in marked contrast with the extremely rapid electron transfer from I. A virtue of the chemical intermediate mechanism is that it decouples these two pieces of data. The present paper extends in a variety of ways some results in ref. [10], including, among others, use of more general matrix elements and expressions, treatment of new data, and an alternative interpretation of the magnetic data.

2. Theory

2.1. Matrix elements and energies

We consider the following zeroth-order electronic configurations:

$$\begin{array}{llll} 1. & (BChl)_2^* & BChl & BPh, \\ 2. & (BChl)_2^+ & BChl^- & BPh, \\ 3. & (BChl)_2^+ & BChl & BPh^-, \end{array} \qquad (2)$$

---

[1] Contribution No. 7492.

0 009-2614/87/$ 03.50

designated by the symbols 1 to 3. The energies of these zeroth-order configurations will be denoted by H_{ii} and the electron exchange integrals coupling i and j by H_{ij} ($i, j = 1$ to $3, i \neq j$). For any given nuclear configuration the electronic energy E for this three-state system is then the solution of the secular equation

$$\begin{vmatrix} H_{11} - E & H_{12} & 0 \\ H_{12} & H_{22} - E & H_{23} \\ 0 & H_{23} & H_{33} - E \end{vmatrix} = 0. \tag{3}$$

The direct electron transfer matrix element H_{13} between configurations 1 and 3 is neglected in eq. (3), since the electron in 3 is now twice removed from that in 1. In eq. (3) the off-diagonal elements are written as real, for notational simplicity. The H_{ii}, but not in the "Condon approximation" the H_{12} and H_{23}, vary with the configuration of the nuclei. Thereby, the H_{ii} form potential energy surfaces for motion of all the nuclei.

We consider first the use of eq. (3) to treat the superexchange behavior of electronic configurations 1 and 3. Using a partitioning technique [15,16] the problem in eq. (3) is reduced to a 2 × 2 secular determinant. We have [16]

$$\begin{vmatrix} \bar{H}_{11} - E & \bar{H}_{13} \\ \bar{H}_{13} & \bar{H}_{33} - E \end{vmatrix} = 0, \tag{4}$$

where

$$\bar{H}_{ii} = H_{ii} + H_{i2}^2/(H_{22} - E) \qquad (i = 1, 3), \tag{5a}$$

$$\bar{H}_{13} = H_{12}H_{23}/(H_{22} - E). \tag{6a}$$

In the case of a superexchange mechanism for electron transfer the latter can occur when the system crosses the intersection of the $\bar{H}_{11}$ and $\bar{H}_{33}$ surfaces, i.e. where $\bar{H}_{11} = \bar{H}_{33}$ in nuclear configuration space, as in fig. 1, and the relevant electron transfer matrix element is $\bar{H}_{13}$. We can thereby approximate the E in eqs. (5a) and (6a) by $\bar{H}_{33}$ ($=\bar{H}_{11}$), thus yielding

$$\bar{H}_{ii} \approx H_{ii} + H_{i2}^2/(H_{22} - \bar{H}_{33}) \qquad (i = 1, 3) \tag{5b}$$

and

$$\bar{H}_{13} \approx H_{12}H_{23}/(H_{22} - \bar{H}_{33}). \tag{6b}$$

(Numerically, using the values of the quantities in eq. (5b) estimated later, $\bar{H}_{11}$ and H_{11} differ only by less than 1 cm^{-1}, and $\bar{H}_{33}$ and H_{33} differ only by about 1 cm^{-1}. Accordingly, one need not really distinguish between them.)

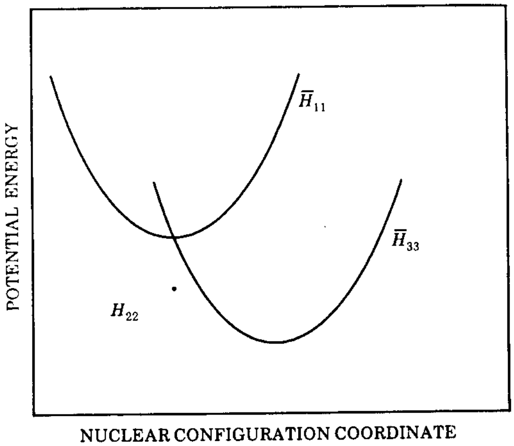

Fig. 1. Superexchange mechanism: profile of $\bar{H}_{11}$ and $\bar{H}_{33}$ potential energy surfaces in many-dimensional nuclear configuration space for an activationless transfer (no energy barrier). The H_{22} may have its minimum, when plotted along this coordinate, to the left or to the right of the intersection of $\bar{H}_{11}$ and $\bar{H}_{33}$, and only a possible value of H_{22} at the intersection is indicated. The nuclear configuration space involves the vibrational coordinates of the reactants and the coordinates of the atoms of the surrounding protein. There is actually a vertical splitting of $2\bar{H}_{13}$ at the intersection of the two surfaces (too small to be indicated).

In the case of the calculation of the energies E of the singlet and triplet states of the $BChl_2^+BPh^-$ radical pair when their interaction is due to a superexchange, the E in eqs. (5a) and (6a) is again approximated by $\bar{H}_{33}$, but now the relevant nuclear configurations are those appropriate to this modified electronic configuration 3 rather than those where $\bar{H}_{11} = \bar{H}_{33}$, namely at the minimum of the $\bar{H}_{33}$ surface in fig. 1. Thus, eqs. (5b) and (6b) again apply, but with different nuclear configurations involved. To obtain a perturbation expression for the energy E of the singlet or triplet state of the separated radical pair using eq. (4), the first E in the latter is approximated by $\bar{H}_{33}$, thereby yielding

$$E \approx \bar{H}_{33} + \bar{H}_{13}^2/(\bar{H}_{11} - \bar{H}_{33}) \qquad \text{(config. 3 perturbed by superexchange).} \tag{7}$$

In contrast, the energy $E^\dagger$ of the transition state for a superexchange electron transfer mechanism for I → III is obtained by setting $\bar{H}_{11} = \bar{H}_{33}$ in eq. (4), whence $E^\dagger = \bar{H}_{11} - |\bar{H}_{13}|$.

2.2. *Rate expressions*

The non-adiabatic rate constant $k_{\mathrm{I}\to\mathrm{II}}$ for the formation of an intermediate II from I is (references cited in ref. [6])

$$k_{\mathrm{I}\to\mathrm{II}} = (2\pi/\hbar) H_{12}^2 (\mathrm{FC}), \tag{8}$$

where (FC), with dimensions of energy^{-1}, is the Franck–Condon factor. The rate constant $k_{\mathrm{II}\to\mathrm{III}}$ for the formation of BPh^- from BChl^- is given by an analogous expression, with H_{12} replaced by H_{23} and with the relevant (FC). A schematic plot of the potential energy profiles is given in fig. 2.

The superexchange electron transfer rate constant $k_{\mathrm{I}\to\mathrm{III}}$ in the non-adiabatic approximation can similarly be written as

$$k_{\mathrm{I}\to\mathrm{III}} = (2\pi/\hbar) \bar{H}_{13}^2 (\mathrm{FC}) \quad \text{(superexchange)}, \tag{9}$$

where (FC) is now the Franck–Condon factor for the transition from the $\bar{H}_{11}$ to the $\bar{H}_{33}$ surface.

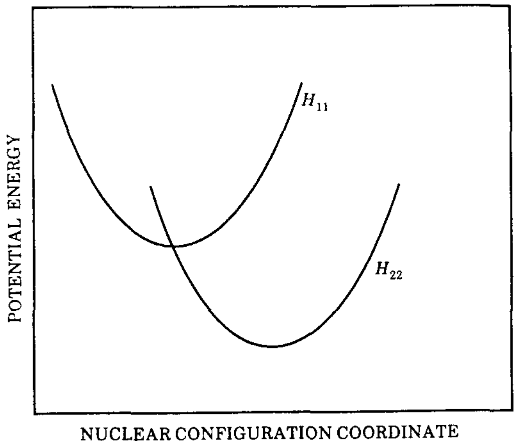

Fig. 2. Direct I → II mechanism: profile of H_{11} and H_{22} surfaces in many-dimensional space, depicted for an activationless transfer I → II. The abscissa now includes mainly changes in coordinates in and around I and II, rather than in and around I and III, and so differs from that in fig. 1. There is actually a vertical splitting of $2H_{12}$ at the intersection of the two surfaces.

2.3. *Singlet–triplet energy difference*

We next use eq. (7) to obtain an expression for the singlet–triplet splitting of the radicals $(\mathrm{BChl})_2^+$ and BPh^-. The values of $\bar{H}_{33}$ in the singlet and triplet states are essentially equal, because of the large separation distance of the two radicals. We shall suppose that the H_{22} for the two spin states are also approximately equal. (Thereby, in eq. (10) below H_{22} represents a mean.) Only in the case of electronic configuration 1 is there a large S–T energy difference, due to the singlet–triplet energy difference within $(\mathrm{BChl})_2^*$. We distinguish the corresponding two $\bar{H}_{11}$ by S and T superscripts. The neglected difference in H_{12}^{T} and H_{12}^{S} contributes only a small correction term to eq. (10) below[‡], and the H_{12} in eq. (10) (appearing via the terms for H_{11} and H_{13} in eq. (10) represents a mean.

Using eq. (7), with S and T superscripts, one obtains, upon subtracting E^{T} from E^{S},

$$E^{\mathrm{S}} - E^{\mathrm{T}} \approx \frac{(\bar{H}_{13})^2 (\bar{H}_{11}^{\mathrm{S}} - \bar{H}_{11}^{\mathrm{T}})}{(\bar{H}_{11}^{\mathrm{S}} - \bar{H}_{33})(\bar{H}_{11}^{\mathrm{T}} - \bar{H}_{33})}. \tag{10}$$

From the values of the various energy differences, one may thereby infer from eq. (10) a value for $\bar{H}_{13}$. Related expressions are given in refs. [10,18], the former containing a wayward factor of 2. An equation appropriate to a different situation is given in ref. [19].

2.4. *Numerical calculations*

We next estimate the various energy differences in these equations. The value of $\bar{H}_{11}^{\mathrm{S}} - \bar{H}_{11}^{\mathrm{T}}$ is about 0.4 eV [20]. The magnetic data have been fitted in

---

[‡] We need to estimate the change of H_{12} when the $\bar{H}_{11}$ is changed from $\bar{H}_{11}^{\mathrm{S}}$ to the mean, $\frac{1}{2}(\bar{H}_{11}^{\mathrm{S}} + \bar{H}_{11}^{\mathrm{T}})$, i.e. by 0.2 eV. We use the data of Krongauz, Huddleston and Miller [17] on another system: We have H_{ij} $(i \neq j) \propto \exp(-\frac{1}{2}\beta d)$, as noted later. The β changed from 1.12 to 1.15 Å^{-1} when the binding energy of the electron in a solute relative to the intervening environment was changed from 2.0 to 2.2 eV, and changed from 1.33 to 1.34 Å^{-1} when this energy change was from 4.0 to 4.2 eV. For a d of 4 Å (discussed later) the resulting change in H_{ij} is only 6% and 2%, respectively.

ref. [14] with a magnitude of $E^S - E^T$ of about 16 G, i.e. 1.9×10^{-7} eV. A number of other results in the literature, reviewed in ref. [21], also yielded an $E^S - E^T$ of roughly this amount. (The precise value is less important than its smallness.) Both in the presence [4] and in the absence [22] of a blocking quinone Q^- the free energy difference corresponding to the energy difference $\bar{H}_{11}^S - \bar{H}_{33}$ has been estimated from the temperature behavior of delayed fluorescence to be about 0.16 eV. Data on the energy difference $\bar{H}_{11}^S - \bar{H}_{33}$ are more complicated: various values, depending on the temperature [4] and on the conditions [22,23], have been estimated. In the calculations below we shall use 0.05 eV. Using a value of $\approx$0.40 eV for $\bar{H}_{11}^S - \bar{H}_{11}^T$ the value of $\bar{H}_{33} - \bar{H}_{11}^T$ is then estimated to be about 0.35 eV. From eq. (10) one now obtains $\bar{H}_{13} \approx 0.7$ cm^{-1}, which is very small and reflects mainly the very small S–T splitting. If a value of 0.16 eV were used for $\bar{H}_{11}^S - \bar{H}_{33}$ instead of 0.05 eV, with a corresponding change of $\bar{H}_{33} - \bar{H}_{11}^T$ to 0.24 eV, $\bar{H}_{13}$ would be higher only by about 50%, while if a value of 0.015 eV [4] were used, it would be lower by 45%.

This $\bar{H}_{13}$ is next used to calculate a superexchange $k_{\mathrm{I}\to\mathrm{III}}$. While the $\bar{H}_{13}$ in eq. (10) is not quite the same as that in eq. (9) (only the latter is calculated at nuclear configurations where $\bar{H}_{11} \approx \bar{H}_{33}$), this difference should not drastically change $\bar{H}_{13}$. In order to calculate $k_{\mathrm{I}\to\mathrm{III}}$ using eq. (9), an expression for the Franck–Condon factor (FC) is needed. Expressions and references for the latter are cited in ref. [6]. Assuming for the moment a system of N vibrations of frequency ν, the vibrational overlap integral appearing in (FC) can be converted to a vibrational overlap along one coordinate. The value of (FC) is then $(h\nu)^{-1}$ times the overlap integral, weighted over all initial vibrational states, with a maximum value, therefore, of $(h\nu)^{-1}$. We introduce the quantities λ, a reorganization parameter, and ΔG^0, the standard free energy of the reaction step, appearing in the classical free energy barrier to the reaction $\Delta G^* = \frac{1}{4}\lambda(1 + \Delta G^0/\lambda)^2$ [6]. The value of (FC) for reaction from the lowest vibrational state is now (references cited in ref. [6])

$$(\mathrm{FC}) = \mathrm{e}^{-S} S^{v}/[\Gamma(v+1)h\nu]$$

$$\approx (S/v)^{v}/[(2\pi v)^{1/2}h\nu]\,\mathrm{e}^{v-S}, \qquad (11)$$

where $S = \lambda/h\nu$, $v = -\Delta G^0/h\nu$, and Γ is the gamma function. Stirling's approximation for Γ was used in the second half of eq. (11) (error 2% or less for the v given below). Using the first equality in eq. (11) the maximum value for (FC) is seen to be $(h\nu)^{-1}$, as already noted, and occurs when $v = S = 0$, i.e. when both λ and ΔG^0 are zero. The Franck–Condon overlap integral leading to eq. (11) is then unity.

The present reactions are barrierless [1,4,6,11] (as is the reaction from III to IV in eq. (1) [12]), i.e. have a negligible activation free energy ΔG^*, so that we have $\lambda \approx -\Delta G^0$ [6] in each case and the (FC) in eq. (11) becomes $[h\nu(2\pi v)^{1/2}]^{-1}$. More elaborate expressions than eq. (11), each well known in radiationless transitions theory and cited in ref. [6], are available but the results will not differ appreciably for the particular case examined here: $\lambda \approx -\Delta G^0, h\nu \approx 200$ cm^{-1}. One can, for example, use the form of eq. (11) that applies when reactions occur not only from the lowest vibrational state but also from thermally populated vibrationally excited states, yielding only a negligible difference in the present instance [6]. One can also use another formula which includes effects due to changes in vibration frequency. The latter has been applied to treat increases in $k_{\mathrm{III}\to\mathrm{IV}}$ of a factor of 2 when the temperature is lowered from room temperature to temperatures below 100 K [11,12]. However, we shall be concerned here with discrepancies of the order of 1000 rather than 2, and so the simple eq. (11) will suffice. We take $s \approx v$ for an activation-free superexchange reaction, I → III, thereby yielding a maximum value for (FC). Using $h\nu \approx 200$ cm^{-1} and $\Delta G^0 \approx -0.16$ eV, we have $s = v = 6.5$ and (FC) = $0.16/h\nu$. Eq. (8) and the above value for $\bar{H}_{13}$ then yield $k_{\mathrm{I}\to\mathrm{III}} \approx 5 \times 10^8$ s^{-1}. This result for $k \approx 5 \times 10^8$ s^{-1} may be contrasted with the experimental value of k for the loss of the electron from I, which was about 3.5×10^{11} s^{-1} [8] or about 1000-fold larger than the value just calculated.

We turn, therefore, to the k for the alternative mechanism $k_{\mathrm{I}\to\mathrm{II}}$, given by eq. (8), and first note, as considered later, that there is some justification for taking $H_{23} \approx 2\,H_{12}$, in the absence of more direct information. The value of $H_{22} - \bar{H}_{33}$ is presently uncertain. If a value of the order of 0.1 eV is postulated, then using the value for $\bar{H}_{13}$ found earlier ($\approx$0.7 cm^{-1}) one obtains $H_{12} \approx 17$ cm^{-1} from eq. (6b). For an activationless step I → II we take $\lambda \approx -\Delta G^0$ and so $s \approx v$. When $\Delta G^0 \approx -0.1$ eV, we have $v \approx 4$

and the (FC) given by eq. (11) becomes $0.20(h\nu)^{-1}$. Eq. (8) then yields $k_{\mathrm{I}\to\mathrm{II}} \approx 3.5 \times 10^{11}\ \mathrm{s}^{-1}$, compared with the experimental value of $3.5 \times 10^{11}\ \mathrm{s}^{-1}$. These values are, of course, much closer than one might expect, considering the various approximations.

In this latter mechanism it is still necessary, however, to explain the non-detection of BChl^- in ref. [8]. We first introduce a first-order kinetic scheme for the populations of I, II and III:

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_{\mathrm{I}\to\mathrm{II}}[\mathrm{I}],$$

$$\mathrm{d}[\mathrm{II}]/\mathrm{d}t = k_{\mathrm{I}\to\mathrm{II}}[\mathrm{I}] - k_{\mathrm{II}\to\mathrm{III}}[\mathrm{II}]. \qquad (12)$$

Using the integrated results, the *maximum* value of the transient II is found to be given by

$$\max[\mathrm{II}]/[\mathrm{I}_0] = x^{1/(1-x)}, \qquad (13)$$

where $x = k_{\mathrm{I}\to\mathrm{II}}/k_{\mathrm{II}\to\mathrm{III}}$ and $[\mathrm{I}_0]$ is the initial value of [I]. Thereby, if the lhs of eq. (13) is about 0.2, the value of x given by that equation is $\frac{1}{4}$. Such a factor of 4 in the ratio of rate constants $k_{\mathrm{II}\to\mathrm{III}}/k_{\mathrm{I}\to\mathrm{II}}$ can arise from differences in H_{12} and H_{23} alone: If the excited electron in I and the hole in II were delocalized among the two BChl members of $(\mathrm{BChl})_2$, H_{12} would, other things being equal, be a factor of 2 less than H_{23}, as seen from the following argument, and we note that $k_{i\to j} \propto H_{ij}^2$. In particular, H_{12} equals $\int \Psi_{\mathrm{I}} H \Psi_{\mathrm{II}}\, \mathrm{d}\tau$ and the molecular orbital coefficients in $(\mathrm{BChl})_2^+$ in Ψ_{II} are lowered by a factor of $2^{1/2}$ due to the delocalization of the hole in $(\mathrm{BChl})_2^+$ over the two halves of the dimer, as seen from ENDOR experiments [24]. A similar remark applies to a somewhat lesser extent to the coefficients in $(\mathrm{BChl})_2^*$ in Ψ_{I}. (The electronic distribution in the latter may not be equally shared: photon echo [25] and hole burning [26] experiments suggest some event, perhaps a partial intramolecular charge transfer some 25 fs after photoexcitation of the $(\mathrm{BChl})_2$.) In H_{12} only the half of the $(\mathrm{BChl})_2$ nearest the BChl monomer contributes significantly to this matrix element. However, it should be stressed that other factors beside edge-to-edge distance can affect the relative values of $k_{\mathrm{I}\to\mathrm{II}}$ and $k_{\mathrm{II}\to\mathrm{III}}$, such as orientation and such as the (FC), which even for a barrierless reaction will depend somewhat on ΔG^0, λ and ν for the individual step [‡‡].

2.5. *Adiabatic and non-adiabatic crossing*

Finally, we turn to the question of adiabaticity and non-adiabaticity, and the significance of the magnitude found in section 2.4 for $H_{12} \approx 17\ \mathrm{cm}^{-1}$. To this end we make use of the Landau–Zener formula for the probability P of crossing from one "diabatic" potential energy surface to another per passage across the "intersection" of the two surfaces [27], as in fig. 1 or 2:

$$P \approx 1 - \exp(-2\pi\epsilon^2/\hbar \mathbf{v}|\Delta s|), \qquad (14)$$

where ϵ is the electron transfer matrix element ($\bar{H}_{13}$, H_{12} or H_{23}, depending on the process), Δs is the difference in slopes of the two surfaces at their intersection (e.g. in fig. 1 or 2) and $\mathbf{v}$ is the velocity at the crossing (not to be confused with the v in eq. (11)). In the derivation of the Landau–Zener formula it is assumed that the energy exceeds the potential energy at the crossing-point, i.e. that $\mathbf{v}$ is real. While eq. (14) was derived for a one-coordinate system, it can be used approximately for an N-coordinate one, by using average quantities for the various symbols appearing in the equation.

In the case of two approximately harmonic potential energy curves, $\frac{1}{2}kx^2$ and $\frac{1}{2}k(x-a)^2 + \Delta G^0$ for reactants and products, respectively, the difference of slopes $|\Delta s|$ at the intersection is found to be ka, independently of ΔG^0. We recall that the vertical difference of the curves at $x = 0$ is $\lambda + \Delta G^0$ [6] and, for the present model, is also $\frac{1}{2}ka^2 + \Delta G^0$, i.e. $\lambda = \frac{1}{2}ka^2$. The value of $\mathbf{v}$ in eq. (14) can be taken approximately from the average of a kinetic energy term $\frac{1}{2}m\mathbf{v}^2$, which equals $\frac{1}{2}kT$ ($\approx 100\ \mathrm{cm}^{-1}$ at room temperature) or, in the case where $\lambda \approx -\Delta G^0$ and the reactants are in their lowest vibrational state, from the zero-point energy $\frac{1}{2}h\nu$ ($\approx 100\ \mathrm{cm}^{-1}$ in the present case). Using the latter we have $v|\Delta s| \approx (2\lambda h\mathbf{v})^{1/2}\, 2\pi\nu$, where ν is the vibration frequency $(k/m)^{1/2}/2\pi$.

The reaction is approximately adiabatic when the

[‡‡] We have chosen $\nu \approx 200\ \mathrm{cm}^{-1}$ [6]. The results are, for the case examined here, namely for $\Delta G^0 \approx -\lambda$, relatively insensitive to ν. However, for a different case, namely when $|\Delta G^0/\lambda|$ is large, as in a back reaction from III to reform the ground electronic state of I in eq. (1), high vibrational frequencies can play a more important role, and should be considered then.

exponent in eq. (14) is of the order of unity, since then $P \approx 1$. Using the values employed earlier ($\lambda \approx 0.1$ eV), the value of ϵ required to make the exponent in eq. (14) approximately equal to unity is about 135 cm^{-1}.

The matrix element H_{23} estimated earlier ($\approx 2H_{12} \approx 35\ \mathrm{cm}^{-1}$) is seen to be significantly less than this value of ϵ, a result which is not unexpected: If the matrix element decreases with separation distance d exponentially as $\exp(-\frac{1}{2}\beta d)$, with $\beta \approx 1.1$ Å^{-1} [6], then for each increment in d of 1 Å this quantity would be decreased by a factor of about 0.58. For an edge-to-edge separation of ≈ 4 Å [7] the factor would be ≈ 0.1. If the matrix element had its minimal adiabatic value at contact, namely $\approx 135\ \mathrm{cm}^{-1}$, then when $d \approx 4$ Å it would be $\approx 15\ \mathrm{cm}^{-1}$, which is close to the estimate of $\approx 35\ \mathrm{cm}^{-1}$ for H_{23}. (The distance at which non-adiabaticity sets in, however, is rather uncertain at present [6].)

3. Discussion

Using the available estimates we have seen that the calculated superexchange rate constant, estimated mainly from the small singlet–triplet separation, is too small by a factor of the order of 1000, whereas the direct exchange rate constant for I → II has a value of the correct magnitude. A superexchange mechanism for the loss of I would have been expected to be particularly effective, as compared with a two-step electron transfer, if the value of the energy difference $H_{22} - \bar{H}_{11}$ had been fairly large. In this case there would have been a substantial activation energy if a BChl^- intermediate had been formed. However, if $H_{22} - \bar{H}_{11}$ had indeed been large, both the calculated $k_{\mathrm{I}\to\mathrm{II}}$ and $k_{\mathrm{I}\to\mathrm{III}}$ would be much less than the experimental k in the present case.

It may also be noted that while the evidence in section 2 favors the BChl^- mechanism by a large numerical margin, the singlet–triplet splitting data were interpreted using a superexchange mechanism. Should the S–T splitting be due, instead, to an equilibrium between BPh^- and BChl^-, as assumed in ref. [10], the superexchange value of H_{13} might be even less than that calculated in section 2 and the discrepancy between the measured k for loss of I in eq. (1) and the superexchange-calculated value would become even greater than the factor of 1000.

One point that bears comment concerns the lifetime of the $(\mathrm{BChl})_2^*$ when, as depicted in fig. 2, the potential energy surface H_{22} for the products passes through or near the minimum of that of the reactants. The $(\mathrm{BChl})_2^*$ will exist, nevertheless, for a time longer than a half-vibrational period for two reasons, both evident from eq. (8): because of some non-adiabaticity H_{12} is not very large and because, even for a barrierless reaction, we have seen (FC) can be smaller than $1/h\nu$. Similar remarks apply to the corresponding situation for BChl^-: even though the $\bar{H}_{33}$ surface may pass through or near the minimum of the H_{22} surface, BChl^- can still exist for longer than a half-vibrational period, for the same reasons.

We conclude with some remarks on $\bar{H}_{13}$. Eq. (4) for the 2 × 2 matrix shows that $2\bar{H}_{13}$ is twice the splitting of the modified potential energy surfaces $\bar{H}_{11}$ and $\bar{H}_{33}$, at the intersection of the latter. It does not equal the splitting at the intersection of the unmodified surfaces H_{11} and H_{33}. The latter is instead $(H_{12}^2 + H_{23}^2)/(H_{11} - H_{22})$, which is different in an important way from $2H_{12}H_{23}/(\bar{H}_{11} - H_{22})$: Only the latter vanishes if either H_{12} or H_{23} vanishes. This point, namely that $2H_{13}$ is the splitting of the suitably modified surfaces and not of the original ones, is quite clear from an examination of the 2 × 2 Hamiltonian matrix in ref. [16] or ref. [15], though does not appear to have been specifically stressed in the literature.

Acknowledgement

It is a pleasure to acknowledge the support of this research by the National Science Foundation. The research was initiated while the author was a Leland J. Haworth Distinguished Scientist at Brookhaven National Laboratory. I am indebted to Dr. Norman Sutin and his colleagues for their gracious hospitality and many stimulating discussions. I am particularly indebted, too, to Dr. Jack Fajer of BNL, who called my attention to the experimental results in ref. [8], and to Drs. S. Boxer and W.W. Parsons for their helpful comments.

References

[1] R.E. Blankenship and W.W. Parson, in: Photosynthesis in relation to model systems, ed. J. Barber (Elsevier, Amsterdam, 1979) ch. 3.

[2] R.K. Clayton, Photosynthesis: physical mechanisms and chemical patterns (Cambridge Univ. Press, Cambridge, 1980);
T.L. Netzel, in: Biological events probed by ultrafast laser spectroscopy, ed. R.R. Alfano (Academic Press, New York, 1982) ch. 4.

[3] S.G. Boxer, C.E.D. Chidsey and M.G. Roelofs, Ann. Rev. Phys. Chem. 34 (1983) 389.

[4] N.W.T. Woodbury and W.W. Parson, Biochim. Biophys. Acta 767 (1984) 345; 850 (1986) 197.

[5] M.E. Michel-Beyerle, ed., Antennas and reaction centers of photosynthetic bacteria (Springer, Berlin, 1985).

[6] R.A. Marcus and N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.

[7] J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, J. Mol. Biol. 180 (1984) 385;
J. Deisenhofer and H. Michel, in: Antennas and reaction centers of photosynthetic bacteria, ed. M.E. Michel-Beyerle (Springer, Berlin, 1985) p. 94.

[8] J.-L. Martin, J. Breton, A.J. Hoff, A. Migus and A. Antonetti, Proc. Natl. Acad. Sci. US 83 (1986) 957.

[9] V.A. Shuvalov, A.V. Klevanik, A.V. Sharkov, Y.A. Matveetz and P.G. Kryukov, FEBS Letters 91 (1978) 135.

[10] R. Haberkorn, M.E. Michel-Beyerle and R.A. Marcus, Proc. Natl. Acad. Sci. US 76 (1979) 4185.

[11] C. Kirmaier, D. Holten and W.W. Parson, Biochim. Biophys. Acta 810 (1985) 33.

[12] N.W. Woodbury, M. Becker, D. Middendorf and W.W. Parson, Biochemistry 24 (1985) 7516.

[13] D. Holten, C. Hoganson, M.W. Windsor, C.C. Schenck, W.W. Parson, A. Migus, R.L. Fork and C.V. Shank, Biochim. Biophys. Acta 592 (1980) 461.

[14] A. Ogrodnik, W. Lersch and M.E. Michel-Beyerle, in: Antennas and reaction centers of photosynthetic bacteria, ed. M.E. Michel-Beyerle (Springer, Berlin, 1985) p. 198.

[15] P.O. Löwdin, in: Perturbation theory and its applications to quantum mechanics, ed. C.H. Wilcox (Wiley, New York, 1966) p. 255.

[16] S. Larsson, J. Am. Chem. Soc. 103 (1981) 4034.

[17] V. Krongauz, R.D. Huddleston and J.R. Miller, to be published.

[18] H.A. Kramers, Physica 1 (1934) 182;
P.W. Anderson, Phys. Rev. 79 (1950) 350;
R. Kubo and T. Nagamiya, Solid state physics (McGraw-Hill, New York, 1969) p. 583.

[19] J.J. Hopfield, in: Electrical phenomena at the biological membrane level, ed. E. Roux (Elsevier, Amsterdam, 1977) p. 471;
M.Y. Okamura, R.A. Isaacson and G. Feher, Biochim. Biophys. Acta 546 (1979) 394.

[20] V.A. Shuvalov and W.W. Parson, Proc. Natl. Acad. Sci. US 78 (1981) 1957.

[21] A.J. Hoff, Photochem. Photobiol. 43 (1986) 727.

[22] N.W. Woodbury, W.W. Parson, M.R. Gunner, R.C. Prince and P.L. Dutton, Biochim. Biophys. Acta 851 (1986) 6.

[23] C.E.D. Chidsey, L. Takiff, R.A. Goldstein and S.G. Boxer, Proc. Natl. Acad. Sci. US 82 (1985) 6850.

[24] J.R. Norris, M.E. Druyan and J.J. Katz, J. Am. Chem. Soc. 95 (1973) 1680;
G. Feher, A.J. Hoff, R.A. Isaacson and J.D. McElroy, Biophys. Soc. Abstr. 13 (1973) 61;
G. Feher, A.J. Hoff, R.A. Isaacson and L.C. Akerson, Ann. NY Acad. Sci. 244 (1975) 239.

[25] S.R. Meech, A.J. Hoff and D.A. Wiersma, Chem. Phys. Letters 121 (1985) 287.

[26] S.G. Boxer, D.J. Lockhart and T.R. Middendorf, Chem. Phys. Letters 123 (1986) 476;
S.G. Boxer, T.R. Middendorf and D.J. Lockhart, FEBS Letters 200 (1986) 237.

[27] S. Glasstone, K.J. Laidler and H. Eyring, The theory of rate processes (McGraw-Hill, New York, 1941) pp. 149, 150.