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Electron transfer mechanism in the reaction center of photosynthetic bacteria

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The structure of the photosynthetic reaction center recently resolved by Deisenhofer *et al.* is discussed in relation to design principles for energy-storing systems. The rates of the primary electron transfer reactions are deduced by taking the electronic structure of the chromophores and their geometrical arrangement explicitly into account, while the protein portion is considered as a dielectric continuum which is rigid to an extent that the free-energy loss by solvent reorganization can be neglected. The values of the different rate constants thus obtained are in good agreement with experimental data. Each chromophore component in the reaction center appears to be positioned optimally for the purpose of energy storage in electron transfer. This can be shown by repeating the calculations for various arrangements that differ somewhat from the arrangement obtained by Deisenhofer *et al.* The device can only operate as an energy-storing system if each functional component molecule is exactly adjusted to each other sterically and energetically. It is shown by proposing a reasonable evolutionary pathway that the emergence of the specific arrangement of chromophores and proteins in the reaction center can be made plausible.

I. GENERAL CONSIDERATIONS

The primary process in photosynthesis, as known for many years,[1] is a photoinduced transmembrane electron transfer carrying the electron from a low to a high energy level. Attempts to find a mechanism for that process and to construct corresponding arrangements with the goal of developing future energy-storing systems have stimulated work on electron transfer in monolayer assemblies.[2–12]

Assemblies were constructed based on the idea that for energy storage by photoinduced vectorial charge separation the electron should be removed from the excited dye D fast enough to avoid deactivation and it should be kept at a high energy level. It should be transferred from D to an acceptor A where it could remain for, e.g., a millisecond to allow subsequent dark reactions then taking place without appreciable loss of free energy. D^+ should recover to D in a time short compared to a millisecond by transferring an electron from a donor D' to D^+. Here D, D', and A are considered to be extended π-electron systems.

To discover constructional details of such a molecular device the rates of electron transfer between π-electron systems in solid matrices should be known. Such rates have been measured in monolayer assemblies where the distance between donor and acceptor can be systematically varied. There is a discrepancy between the result of these measurements and of theoretical results on electron transfer in the reaction center (see Appendix), which is critical in discussing design principles for energy-storing devices since the chromophores are arranged very specifically. It will be shown that the discrepancy can be removed by taking the electronic structure of the chromophores and their geometrical arrangement explicitly into account and by assuming that the solvent reorganization energy is very small. This assumption seems quite obvious since the chromophores in an efficient system for energy storage must be in a rigid environment to keep the loss of free energy by solvent reorganization as low as possible. It is reasonable to assume that such a rigid system has developed in the course of evolution.

Before going into the details of the calculations we discuss the results as far as their importance in seeing some essential features of energy-storing devices.

It is found that acceptor A, in order to avoid back transfer in less than milliseconds, must be at a distance of about 30 Å from D^+ if the medium is a σ-electron portion (such as the hydrocarbon portion in the model experiments with monolayers or the protein portion in the case of the reaction center [Fig. 1(a)]), acting as an energy barrier for the electron. The electron tunnels through such a barrier with a certain probability decreasing exponentially with the barrier thickness.

The electron transfer from excited D (symbolized by D^*) to A must be fast compared to the deactivation of D^* from the excited singlet state into the ground state or the triplet state. This is not possible in the case of a σ-electron portion because this portion is acting as an energy barrier. It is necessary to have an appropriate molecule W (molecular wire) in the near neighborhood of D. This molecule W is a π-electron system that can accept the electron from D^* and transmit it to A where it is trapped at a lower energy level. The idea of a molecular wire was realized in monolayer assemblies.[3,5–7] The electron in A is at a lower level than the conduction band of W. In this particular case W acts as an energy barrier (not as a conductor) allowing tunneling from A^- to D^+. This energy barrier is not as high as the barrier of the σ-electron portion. If W would be on the line connecting D and A the back transfer by tunneling through the π-electron portion would be much faster than through a σ-electron portion. To avoid back transfer faster than in the millisecond

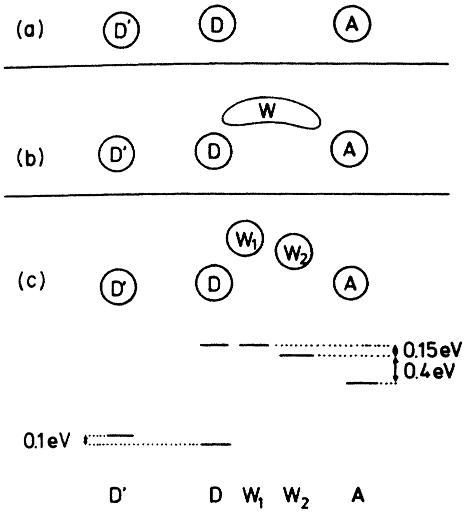

FIG. 1. Design principle for electron transport system. (a) donor D', photocatalyst D, acceptor A; (b) molecular wire W between D and A; (c) W_1 and W_2 between D and A.

range the molecular wire must be "banana shaped" [Fig. 1(b)], or A would have to be in an even larger distance, and an optimized system should be as compact as possible. In the case of a "banana shaped" W the direct back transfer by tunneling through the σ-electron portion is practically unchanged by W and tunneling through the "banana-shaped" π-electron portion has a smaller probability than tunneling through the σ-electron portion since the tunneling path is longer. The increased length of the tunneling path is more effective in lowering the rate than the decreased barrier height.

Assuming the electron in A is at a sufficiently low energy level its back transfer by thermal activation to the conducting level of W can also be neglected. If the level of A^- is by 0.7 eV below the level of D^* the probability of this thermally activated back transfer within a millisecond is still small at room temperature.

An appropriate "banana-shaped" π-electron system extending over 30 Å seems difficult to achieve. In a more reasonable device two molecules with π-electron systems (W_1 and W_2) are required to bridge that distance [Fig. 1(c)]. D, W_1, and W_2 must be at close contact to remove the electron from D^* within some picoseconds, i.e., within a time small compared to the lifetime of D^*. The contact of W_2 with A can be looser since the time to transfer the electron from W_2 to A must be short only in comparison with the time for returning the electron from W_2^- to D^+ (by tunneling or by thermal activation and tunneling via W_1). The need for the transient trapping of the electron in W_2 requires that its energy level in W_2 is by 0.1 to 0.2 eV below its level in W_1. On the other hand, in an optimized device, W_1^- should be at the energy level of D^*. If W_1^- would be at a higher level the required fast electron transfer would not be possible; being at a lower level would result in a unnecessary loss of free energy.

While the optimum level of W_1^- coincides with the level of D^*, the optimum energy difference between W_1^- and W_2^- is given by the condition of minimum energy loss at room temperature. If the energy difference is made smaller than in the optimum the energy loss is increased due to the increasing probability of back transfer instead of transfer to A. If it is made larger the energy loss is increased due to the lowering of the energy level. This optimization procedure leads to an energy difference between W_1^- and W_2^- of 0.15 eV. An additional requirement leads to the value of 0.17 eV [fast electron transfer from W_1^- to W_2 is only possible in the case of energetic match of the initial vibrationless state and the vibronic state reached by electron transfer (vibrational energy 0.17 eV, see Appendix)].

The optimal energy level of A^- is given by determining the minimum free-energy loss as indicated above in the case of the level of W_2^-. The optimization procedure leads to an energy difference of 0.4 eV between W_2^- and A^-.

An optimal arrangement of chromophores D, W_1, W_2, A [Fig. 1(c)] then is worked out as follows. In all arrangements taken into consideration the line connecting D and W_2 and the line connecting D and A are restricted to σ-electron portions. Such systems suppress efficiently tunneling in the backward direction. The arrangement $D\,W_1\,W_2$ then is determined by the following two conditions.

(1) The electron transfer from D^* to W_2 via W_1 is fast compared with the deactivation of D^*.

(2) The back transfer from W_2^- to D^+ by tunneling is as slow as possible under restriction (1).

The position of A follows in an analogous manner.

(1) The electron transfer from W_2^- to A must be fast compared with the back transfer from W_2^- to D^+ (direct or via W_1).

(2) The back transfer from A^- to D^+ must be as slow as possible under restriction (1).

An energy barrier separating donor D' from photocatalyst D (a σ-electron portion) is required to prevent the electron in the excited dye D from moving to another acceptor than W_1. On the other hand, this same barrier should be transparent to an electron to move from donor D' to D^+ in a slower process. The way out of this dilemma (to prevent processes that would compete with the fast transfer from D to W_1 and to allow a slow transfer from D' to D^+) is a thin barrier (20 Å center to center, 14 Å edge-to-edge distance), i.e., a barrier sufficiently thin to allow quantum-mechanical tunneling of electrons within a time short compared to the time for dark reactions regenerating D' (short compared to milliseconds under reasonable conditions), but to be not too thin in order to avoid tunneling of the photoexcited electron through the barrier instead of moving to W_1. Electron tunneling is generally assumed to take place in the reaction center[13] but the processes were not considered in the light of the above design principles. The importance of a π-electron system serving as a molecular wire to remove the electron from the excited photocatalyst should be emphasized since a σ-electron portion is often used as distance keeper between photocatalyst and acceptor in simulating photosynthesis.

II. COMPARISON WITH THE SITUATION IN THE REACTION CENTER

The photosynthetic reaction center is a device to store energy by vectorial electron transfer. A certain dye D (the special pair) is excited by trapping an exciton from an antenna system. The excited electron in D moves to an acceptor A (a quinone) which is located at a certain distance from D, thus being shielded from deactivation and back reaction. Oxidized dye D is later recovered by accepting an electron from donor D' (cytochrome).[13–15]

According to the recent x-ray analysis by Deisenhofer *et al.*[16] in the case of *Rhodopseudomonas viridis,* the heme groups belonging to cytochrome are arranged in a row in close contact allowing fast electron hopping from one group to the other. A larger distance between the last heme group and the special pair is observed. Thus indeed the predicted barrier between donor D' and photocatalyst D appears to be realized in the reaction center. In close contact with the special pair is a bacteriochlorophyll molecule (W_1) and then in a close contact with W_1 a bacteriopheophytin molecule (W_2) and at the end a quinone, the electron acceptor A. The chromophores and the phytyl chains are interlocking in the way that phytyl chains contribute significantly to the contact between bacteriochlorophyll and bacteriopheophytin. The proposed molecular wire connecting donor D and acceptor A is indeed realized by nature.

From spectroscopic evidence it is known that the time of electron transfer from the special pair to the bacteriopheophytin is 5 ps.[17] A transient first building up in about 100 fs was tentatively interpreted as reduced bacteriochlorophyll (W_1^-). The time to transfer the electron from D^* via W_1 to W_2 is indeed short in comparison with the time for deactivating the excited special pair which seems to be about 20 ps.[18] The time of electron transfer from bacteriophephytin to quinone is 230 ps (Ref. 19) (this is indeed short compared with the time to transfer the electron from reduced bacteriopheophytin to oxidized special pair [15 ns (Ref. 19)]). The time of electron transfer from cytochrome to oxidized special pair is 270 ns in the present case (*Rhodopseudomonas viridis*).[19] This is short compared to the time of electron transfer from reduced quinone to oxidized special pair [9 ms (Ref. 20)]. The midpoint potential (oxidized special pair/photoexcited special pair) is about $E = -0.83$ V, the midpoint potential of quinone $E = -0.165$ V, the level difference then about 0.7 eV.[20] The level of W_2^- is about 0.2 eV below the level of photoexcited special pair D^*.[21–27] The level difference of W_2^- to quinone then is about 0.5 eV. All values are consistent with the design principles considered above, and a more detailed analysis is of interest.

The reaction center has another equivalent molecular wire contacting the special pair, but the quinone is missing at the end. It cannot be excluded that one quinone was lost during preparation of the crystals.[16] An iron is found to be present between the quinone and the proposed position of the second quinone. Based on spectroscopic work it was suggested[20,28] that a primary and a secondary quinone are bound to an iron ion. The primary quinone is reduced by the light-generated reduced bacteriopheophytin to form the semiquinone, and the electron is transferred from the primary to the secondary quinone in 6 μs. The secondary quinone is bound less tightly to the reaction center, but nevertheless also seems to be associated with the Fe.[20] The situation is similar in plant photosynthesis where Witt *et al.* identified the first stable acceptor as a quinone and where it was shown that the electron is transferred from Q_A to Q_B and that Q_B is released not before being reduced to hydroquinone by accepting two electrons.[29]

III. SPECIAL PAIR D. IS ARRANGEMENT OF CHROMOPHORES OPTIMIZED TO ACT AS AN EXCITON TRAP?

Dye D can act as an exciton trap only if it absorbs at sufficiently long wavelengths, i.e., if its absorption band overlaps with the emission band of the antenna system. As shown below this can be reached by arranging the dye chromophores such that the chromophore planes are parallel and shifted along each other. Such an arrangement in the special pair is indeed observed by Deisenhofer *et al.* Based on the geometrical parameters given by Deisenhofer *et al.*[16] (3 Å distance between the molecular planes, 7 Å distance between the two magnesium atoms) a strong band shifted by 60 nm to long waves and a weak band shifted by 60 nm to short waves are expected (oscillator strengths 0.85 and 0.11, respectively; see following details). The transition moment of the strong band has the direction of the long axis of the special pair, the transition moment of the weak band is directed perpendicular to this axis and parallel to the molecular planes. Bands related to the special pair of the predicted intensities and polarizations separated by 110 nm are actually observed[30,31] (960 and 850 nm, respectively; intensities in ratio 8:1 (see Ref. 30, Fig. 2) as compared to 0.85:0.11 =7.6:1. The monomer band seems to be shifted to 910 nm by environmental influences and to be split into the 850 nm and 960 nm band by dimer formation. The arrangement of the two molecules in the dimer appears to be optimized for maximum split (maximum bathochromic shift ΔE of the strong band).

This shift was obtained by assuming the smallest possible distance between molecular planes, and by looking for the arrangement with the largest negative value calculated

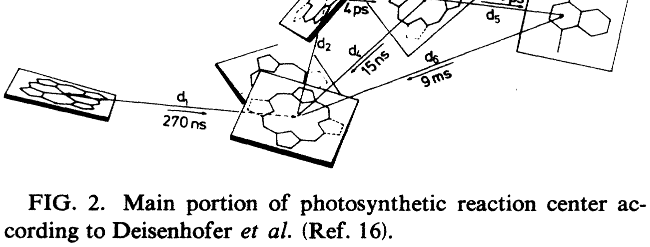

FIG. 2. Main portion of photosynthetic reaction center according to Deisenhofer *et al.* (Ref. 16).

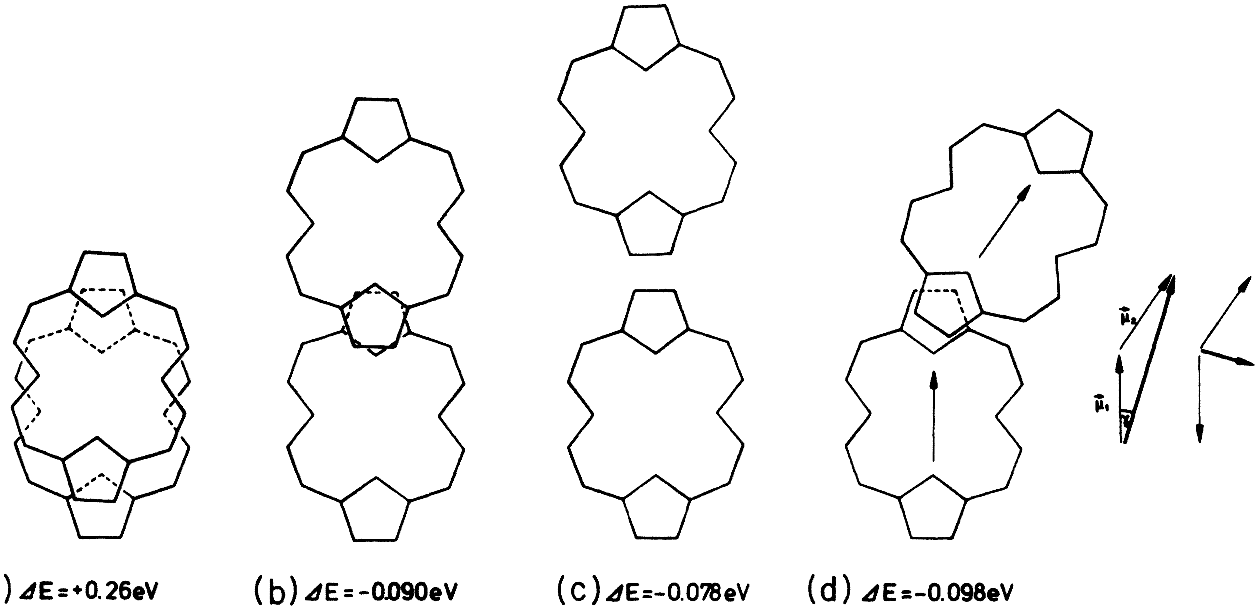

FIG. 3. Some arrangements of two molecules of bacteriochlorophyll and the corresponding shift ΔE of the strong absorption band. Distance between molecular planes 3 Å. Transition moments $\mu_1\mu_2$. In (a) the shift is hypsochromic, in (b) to (d) bathochromic, in (d) (arrangement in the special pair) the bathochromic shift is largest.

for ΔE. In Fig. 3 ΔE is given for some arrangements *a* to *d*. Arrangement *d* is observed in the reaction center.

For calculating these band shifts and oscillator strengths a simple procedure known to be reliable and useful in predicting shifts of absorption bands in dye aggregate formation was applied.[32] The electronic wave functions of the two molecules (1 and 2) were described by the free electron wave functions given explicitly in Ref. 33. The energetic shift is

$$\Delta E = \pm 2\langle \psi_1'\psi_2 \,|\, V \,|\, \psi_1\psi_2' \rangle \ , \qquad (1)$$

where $\psi_1, \psi_2, \psi_1', \psi_2'$ are the wave functions of the two interacting electrons in molecules 1 and 2 in ground state and excited state, V is the Coulomb energy between the two electrons. Following the procedure in Refs. 32 and 33 it was assumed in evaluating the Coulomb energy between electrons 1 and 2 that the medium between the two chromophores (σ-electron portion) is a dielectric of the relative permittivity of a hydrocarbon.

The transition moments of individual molecules 1 and 2 (μ_1 and μ_2) have the directions of the axes indicated in Fig. 3. In the aggregate of molecules 1 and 2 the bands at long and short waves have the transition moments

$$\frac{1}{\sqrt{2}}\,|\mu_1+\mu_2| = \frac{1}{\sqrt{2}}2\mu\cos\gamma$$

and

$$\frac{1}{\sqrt{2}}\,|\mu_1-\mu_2| = \frac{1}{\sqrt{2}}2\mu\sin\gamma \ ,$$

respectively, where γ is the angle between the direction of μ_1 (or μ_2) and the direction of the long axis of the special pair ($\gamma = 20°$, see Fig. 3). The oscillator strength is proportional to the square of the transition moment. Since the oscillator strength of the band in the isolated molecule is 0.48 the oscillator strengths of the aggregate bands are $0.48 \times 2\cos^2\gamma = 0.85$ and $0.48 \times 2\sin^2\gamma = 0.11$, respectively.

In conclusion we can say that the arrangement observed seems to constitute the arrangement with the maximum possible bathochromic shift of the strong absorption band. This shift is necessary for the special pair to act as an exciton trap.

IV. ELECTRON TRANSFER FROM D' TO D^+

Electron transfer in solid matrices is a controversial subject. Current theories predict a rate of electron transfer from D' to D^+ which is smaller by 4 orders of magnitude than the measured rate (for details, see Appendix). In the following, in contrast to these theories, the electronic structure of donor and acceptor is explicitly taken into account, and the protein matrix surrounding the chromophore is assumed to be rigid to an extent that the solvent reorganization energy can be neglected which is reasonable, as mentioned in Sec. I. The medium is considered as a dielectric continuum (since the relevant states in the σ-electron portion are at much higher levels than those in the π-electron systems), neglecting specific interactions (the question of in-bond or in-space tunneling is not addressed). An excellent agreement between calculated and measured rates in all electron transfer steps in the reaction center is thus obtained (see Appendix). In our opinion the explicit use of π-electron wave functions is crucial, but it is sufficient for an essential understanding to use the very crude wave functions given by the free electron model.

It is safe to assume that the protein portion between D' and D acts as the required barrier for electrons on the excited dye level in the picosecond range (since it contains no large π-electron system).

However, an electron can tunnel through the barrier. This effect is only important for an electron localized near the barrier for a sufficiently long time. For estimating the time required for an electron in D' to tunnel to D^+ it must be taken into account that the barrier is lower than it would be in the case of vacuum between D' and D^+, since the protein is a polarizable material. Ionization of D' by transferring the electron into vacuum requires the energy $\varphi_0=4.5$ eV + Ee ($E=0.33$ V midpoint potential of the donor against normal hydrogen electrode) according to a widely used approximation. To transfer the electron into a medium of relative permittivity D the energy is approximately

$$\begin{aligned}\varphi&=\varphi_0-3.8\ \text{eV}(1-1/D)\\&=4.5\ \text{eV}+Ee-3.8\ \text{eV}(1-1/D)\ .\end{aligned}\tag{2}$$

This equation is obtained by assuming that a Fermi hole of 1.8 Å radius is produced in the medium. In the case of $D=2.5$ (permittivity of the hydrocarbon portion of a fatty acid) the last term is -2.3 eV. This value is obtained from tunneling through a fatty acid layer sandwiched between metal electrodes.[8] In the present case ($E=0.33$ V) $\varphi_0=4.83$ eV and with $D=4$, $\varphi=2.0$ eV. Values $D=4$–6 are widely used for proteins in molecular mechanics computations[34] and $D=4$ corresponds to the value measured for nylon at high frequency.[35] We use the value $D=4$ throughout the paper. With $D=3$–6 the results are only slightly changed (see Sec. V).

The rate of electron transfer (k) from donor D to acceptor A depends on the electronic perturbation energy (ε) and on the vibronic excitation of donor and acceptor during electron transfer (S) (for details see Appendix):

$$k=\frac{2\pi}{\hbar}\varepsilon^2 S \tag{3}$$

where $\hbar=h/2\pi$ and h is Planck's constant. ε depends on the overlap of the wave functions of the electron before and after the transfer. This overlap depends on the geometrical arrangement of donor and acceptor, decreasing exponentially with distance. It is larger for smaller ionization energy, i.e., it increases with increasing polarizability of the medium. S depends on the change in bond lengths in the π-electron systems of donor and acceptor. This change is related to the change in the electron distribution caused by the removal of an electron from the donor and its transfer to the acceptor. Both factors can be evaluated (see Appendix). In the present case of the transfer from D' to D^+ the values $S=2.4\ \text{eV}^{-1}$, $\varepsilon=10^{-5}$ eV [for $d_1=18$ Å (d_1=distance between Fe of heme and Mg of special pair)], $\varepsilon=10^{-6}$ eV (for $d_1=21$ Å), and $\varepsilon=10^{-7}$ eV (for $d_1=24$ Å). This gives $k^{-1}=5\times10^{-7}$ s (for $d_1=18$ Å); $k^{-1}=5\times10^{-5}$ s (for $d_1=21$ Å), and $k^{-1}=5\times10^{-3}$ s (for $d_1=24$ Å); see Table I. Rate k is seen to be strongly dependent on d_1. The measured halftime (270 ns, i.e., $k^{-1}=4\times10^{-7}$ s) gives the value $d_1=18$ Å. The actual distance according to Deisenhofer *et al.* is $d_1=21$ Å.

Is the level of D' not higher than expected for an optimal design? The reaction $D'\xrightarrow{e}D^+$ is downhill ($\Delta G^0=-0.13$ eV) and thus the reverse reaction is slower (by a factor of 150). In a functioning device the rate of the back transfer should not be more than a few percent of the rate of the forward reaction, and thus $-\Delta G^0$ cannot be much smaller than 0.13 eV.

In the present case the solvent reorganization is neglected. The electron transfer is considered as being accompanied by the vibronic excitation of the donor or acceptor (vibrational energy $\hbar\omega_D$ or $\hbar\omega_A$ of 0.17 eV). The electron transfer then requires an activation energy of $0.17-0.13$ eV$=0.04$ eV, corresponding to a moderate decrease of the rate with lowering temperature.

The possibility must also be considered that the vibrationless states before and after electron transfer energetically coincide, and that the 0.13 eV loss of free energy is due to a subsequent environmental reorganization. In this case of activationless electron transfer, the Franck-Condon factor S (and thus the rate) is about ten times larger than in the first case. The measured halftime gives the value $d=19.5$ Å almost in agreement with the actual distance. In this case the rate should slightly increase with decreasing temperature (see Appendix). In both cases a moderate temperature dependence of the rate of electron transfer from the Cytochrom to the special pair is expected for *Rhodopseudomonas viridis*, in contrast to the strong temperature dependence observed in *Chromatium*.[13] For further analysis and as a crucial test of the present theory it would be important to measure the temperature dependence of this rate in the case of *Rhodopseudomonas viridis* under conditions where the structure is retained.

V. ELECTRON TRANSFER FROM D^* TO W_1, W_1^- TO W_2, W_2^- TO A AND TO D^+, A^- TO D^+

These electron transfer rates were calculated as in Sec. IV for various distances d_2 to d_6 (see Appendix) and compared with the experimental rates given by the measured halftimes (Fig. 2). The distances d_2 to d_6 for which the calculated rate agrees with the experimental rate are given in the following table and compared with the x-ray data of Deisenhofer *et al.*[16] (the distance is given in angstroms):

	d_1	d_2	d_3	d_4	d_5	d_6
Calculated	18	$\lesssim 10$	10	17	14	25
Observed	21	10	10	17	14	28

There is excellent agreement between these values. The small value calculated for d_6 may indicate some flexibility of the quinone (the shorter distances, occasionally reached by fluctuation during the available time of milliseconds, may be determining for the tunneling).

In the case of the electron transfer from W_2^- to A it can be concluded from the temperature dependence that such a coincidence is given in the reaction center (see Appendix). It seems to be the result of an optimization process: in the case of coincidence A can be at a larger distance d_5 to fulfill the requirements for an energy storing device than in any other case.

The calculated rates are strongly changed by small changes in the assumed distances d_1 to d_6, showing that slightly changed arrangements of the chromophores cannot act anymore as energy storing systems. For instance, if d_3 is increased by 3 Å, the rate of electron transfer from W_1^- to W_2 decreases by a factor of 100 and is then much smaller than the rate of deactivation of D^* (see Appendix). Thus electron transfer cannot successfully compete anymore with deactivation. The result demonstrates that the arrangement in the reaction center is highly optimized and that energy-storing systems constructed according to these principles must be extremely well organized, each functional component molecule being exactly adjusted to the other.

No adjustable parameters are introduced in the calculation, but there is some ambiguity in the value of the dielectric constant D. All calculations are based on the value $D=4$, but the result is rather insensitive to D. [For example, in the case of $A^- \xrightarrow{e} D^+$ ($d_6=25$ Å), ε (in 10^{-8} eV) varies from 1 ($D=3$) to 3 ($D=4$) to 9 ($D=6$).] Thus the values d_1 to d_6 obtained from rate constants change slightly with D. Some remarkable features of the calculation of the rate constants shall be mentioned (for details, see Appendix).

A. Arrangement D, W_1, W_2

As mentioned in Sec. I the geometry of this arrangement should be determined by the condition that electron transfer from D^* to W_1 and to W_2 is fast compared with the deactivation of D^* (20 ps) and that the electron transfer from W_2^- to D^+ is as slow as possible under this condition.

For the arrangement given by Deisenhofer *et al.* the value $\varepsilon \simeq 10^{-2}$ eV is obtained for both the electron transfer from D^* to W_1 and from W_1^- to W_2. In the case of energetic match the time to transfer the electron from D^* to W_1 should be roughly equal to $h/2\varepsilon=0.2$ ps; and similar time should be required for the transfer from W_1 to W_2 and the back transfers from W_2 to W_1 and from W_1 to D^+ forming D^*. The electron thus moving between $D\,W_1\,W_2$ can be trapped at W_2 by vibrational relaxation. The electron may also be trapped at D by deactivation of D^*, however, this is less probable than the trapping at W_2 since the lifetime of D^* is about 20 ps as compared to the vibrational relaxation time of W_2^- of 1 ps. The relaxed state of W_2^- is lower than W_1^- and D^* and untrapping therefore requires thermal activation. Thus the electron transfer from D^* to W_2 via W_1 within a few picoseconds and the formation of a transient state W_1^- within a fraction of a picosecond[17,36] can be rationalized by assuming an intermediate where the excited electron is spread over $D\,W_1\,W_2$.

Evidence for the accessory bacteriochlorophyll being involved as a transient was obtained from 150 fs flash spectroscopy on *Rhodopseudomonas viridis*,[17] but no corresponding evidence was obtained in the case of *Rhodopseudomonas sphaeroides*.[37] It was suggested that the proposed intermediate can be excluded.[37,38] This does not seem reasonable in the present view, since the value $\varepsilon=10^{-4}$ eV obtained for the direct electron transfer from D^* to W_2 corresponds to a time of $h/2\varepsilon=20$ ps, not smaller than the 20 ps lifetime of D^*.

The electron trapped at W_2 can be transferred back to D^+ by tunneling through the space between W_2^- and D^+ or by thermal activation and back transfer via W_1.

The direct electron transfer can lead to the excited singlet, the triplet, or the ground state of D. The first case can be neglected since the reaction is uphill. In the third case the reaction is downhill by 1.1 eV and is slow due to the high vibronic excitation. Only the second case [forming triplet, reaction downhill by 0.2 eV (Ref. 40)] must be considered. It takes a time of the order of nanoseconds (see Appendix) in agreement with a recent experimental value,[41] and in addition the time required for relaxing the spin in W_2^-, which should be of the order of a few nanoseconds.[42–44]

The rate of back transfer by thermal activation depends on the energetic position of W_2^-. In the optimum case, determined according to Sec. I, the level should be by about 0.17 eV below the level of W_1^- (and D^*) and in reality by about 0.2 eV (Sec. II). Then the back transfer to W_1 requires thermal activation of about 0.2 eV; being in W_1 the electron falls back to W_2 again, or (with small probability) it moves to D^+ and is trapped by deactivation (as mentioned above this probability is $\frac{1}{20}$). The back transfer by this mechanism then requires $20e^{0.2\,\text{eV}/k_BT}=4\times10^4$ collisions or about 4×10^4 ps$=$40 ns, in reasonable agreement with a recent experimental result.[41,45] Considering these different channels the halftime should be in the 10 ns range. The measured halftime is 15 ns. This is indeed long compared to the halftime for the electron transfer from W_2^- to A (230 ps).

The optimum gap between levels W_1^- and W_2^- is obtained by maximizing the free-energy gain per absorbed quantum of light, the quantity $\Delta G^0 P$ where ΔG^0 is the free energy required to transfer the electron from D to A, and P is the probability that the excited electron is transferred from D^* to A. We write $\Delta G^0=U_0-U_1-U_2$ where U_0 is the excitation energy (1.29 eV), U_1 the energy difference of W_2^- and D^*, and U_2 the energy difference of A^- and W_2^- [$U_2=0.46$ eV, as obtained from the midpoint potentials of W_2^-/W_2 (-0.62 eV) and A^-/A (-0.165 eV) and therefore $\Delta G^0=0.83\text{ eV}-U_1$]. Furthermore

$$P=\frac{\dfrac{1}{230\text{ ps}}}{\dfrac{1}{230\text{ ps}}+\dfrac{1}{15\text{ ns}}+\dfrac{1}{20\text{ ps}}e^{-U_1/k_BT}}\,,$$

230 ps is the halftime for electron transfer from W_2^- to A, 15 ns the halftime for tunneling from W_2^- to D^+, and 20 ps is the time for thermally deactivating D^*. The

maximum of the function $\Delta G^0 P$ is obtained for $U_1/k_B T = 5.7$ or $U_1 = 0.148$ eV. In this case the thermally activated back transfer is fast in comparison with the back transfer by tunneling from W_2^- to D^+; in the case $U_1 = 0.2$ eV (which is probably given in the reaction center of *Rhodopseudomonas viridis*) the thermally activated back transfer is slow in comparison.

As mentioned above the fast transfer from W_1^- to W_2 requires an activationless process. The electron transfer is accompanied by vibronic excitation of donor or acceptor (vibrational energy $\hbar\omega_D$ or $\hbar\omega_A$ of 0.17 eV) which is later dissipated. The residual energy loss of $0.2-0.17$ eV$=0.03$ eV is considered to be due to environmental reorganization.

B. Acceptor A

The electron trapped in A can be transferred back to D^+ by tunneling through space or by thermal activation and back transfer via W_2 or via W_2 and W_1. The direct electron transfer leading to the triplet of D is uphill in this case and only the transfer to the ground state must be considered. In the thermally activated back transfer the electron in A^- is lifted to the level of W_2^-, tunnels to W_2 and is then transferred to D^+ (directly or via W_1). The halftime of this back transfer from A^- to W_2 differs from the halftime of the forward reaction (230 ps) by the Boltzmann factor (it is uphill by $\Delta G^0 = 0.465$ eV), and this gives a halftime of $(230 \text{ ps}) \times \exp(0.465 \text{ eV}/k_B T) = 10^{-2}$ s. The probability of the electron to be transferred from W_2^- to D^+ and to be trapped is 1.5% (230 ps/15 ns) and thus electron transfer from A^- to D^+ via W_2 occurs in about 1 s. If the level of A^- would be higher by 0.1 eV the corresponding time would be 5 ms. Thus the observed level of A^- seems to be almost but not fully optimized.

VI. WHAT IS THE ACTION OF THE SECOND BRANCH?

As mentioned in Sec. II a quinone seems to bind occasionally to the second branch, to accept the electron from the quinone bound to the first branch, to diffuse away, and to transfer the electron to some reactant, thus acting as a shuttle shifting electrons into a pool. Such an arrangement allows removal of the negative charge from A^- within a fraction of a millisecond. The electron transport system then has recovered by the time the next exciton arrives in the reaction center under natural conditions. The assumption that the second branch is important as a support, but takes no active part in electron transfer, is justified by the fact that the formation of W_2^- has an effect on the absorption of only one of the two extra bacteriochlorophylls besides the special pair.[30] The inactivity of the second branch could be due to the fact that W_2^- in the second branch is at a slightly higher energy level due to the changed environment. Then it does not act as a trap; the excited electron is trapped by W_2 in the first branch, even if it has been transferred primarily to the second branch.

It can be imagined that the second branch took an active part in electron transfer at an earlier evolutionary stage. Assuming for such a stage that both quinones are loosely bound and only part of the time present, photoreduction takes place if at least one of the two quinones is bound. The electron is transferred to the quinone in either case, if it is bound to the first or the second branch. Therefore, the quantum yield is increased by the action of the second branch as conducting element.

A further increase in yield is given by tightly binding quinone Q_A and loosely binding quinone Q_B. In this case quinone Q_A is always present and ready to accept the electron (except for the short time of 6 μs needed to

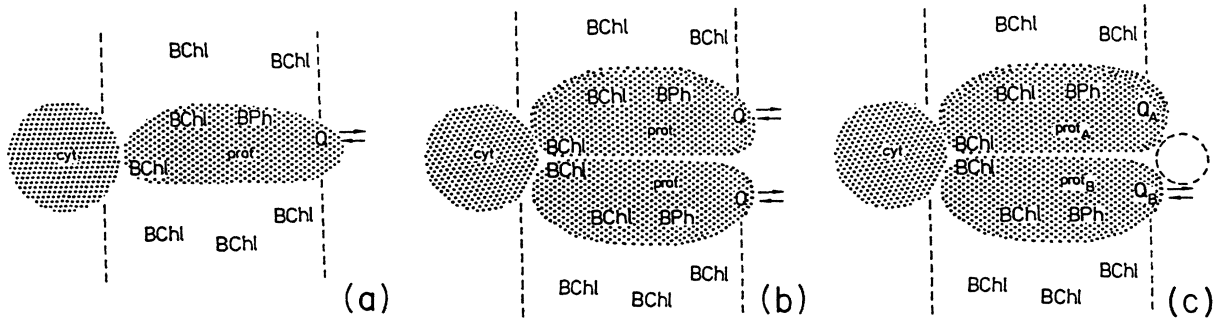

FIG. 4. Possible steps in evolution of bacterial photosynthesis. (a) Membrane bound antenna molecules (bacteriochlorophyll or precursor) and protein (prot) that binds such molecules and loosely binds quinone Q. Chromophores bound to prot act as weak exciton trap and as pump of electrons from photoexcited chromophore to quinone. The chromophore is regenerated by accepting an electron from membrane bound donor cytochrome (cyt). (b) Two electron transfer systems of the type shown in (a) have joined forming special pair of bacteriochlorophyll molecules. The pair is a better exciton trap than the single molecule (bathochromic band shift). By evolution of prot an arrangement of bacteriochlorophyll, bacteriopheophytine, and quinone develops that is optimized for efficient energy storage by electron transfer. (c) Loss of symmetry by functional division: Photoinduced electron transfer from cyt to Q_B via Q_A; Q_A binds more strongly. $Q_{B'}$ as before, carries electrons into pool. Functional division by evolution of prot into prot_A and prot_B. The specific interaction with the proteins determines energy levels of chromophores. Increase in efficiency by keeping cytochrom in fixed position.

transfer the electron from Q_A to Q_B). Then the development of such an asymmetrical arrangement (with only one branch acting as electron transport system) has a selectional advantage and the present system can have developed in this way in the course of evolution. It permits the separation of the device for photoinduced electron transfer and the device for carrying the electron into the pool where it is delivered at some acceptor. The proposed separation of an originally symmetric arrangement into two cooperating devices corresponds to a general pattern of evolutionary processes.

The originally symmetric arrangement is assumed to have evolved from a simple electron transfer system obtained by binding two bacteriochlorophylls and a bacteriopheophytin or some ancestors to a protein. It is assumed that two such systems joined forming the special pair. The arrangement then had a strong selectional advantage, since a better exciton trap now was present. This hypothesis predicts the involvement of two proteins in the fixation of the chromophores forming the two branches.[12] These proteins having evolved from the same ancestor must be genetically related (Fig. 4). Thus the puzzling complexity of the structure of the reaction center, which first appears unnecessary and useless, is considered to be a logical result of an evolutionary process.

As recently found by Deisenhofer *et al.*[46] the proposed arrangement of proteins is indeed present in the reaction center. A third protein H, bound to the ends of the two branches, adds to the rigidity of the assembly [dashed circle in Fig. 4(c)]. Q_A is bound to a portion of prot$_B$ interlocking prot$_A$. This finding does not contradict the given argumentation, since the strong binding of Q_A is considered as a late evolutionary step.

The results indicate that the arrangement of the chromophores in the reaction center is optimized by nature in an astonishing fashion. Surprisingly the protein seems to be acting essentially as a spacer allowing a very specific arrangement of the chromophores.

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APPENDIX: EVALUATION OF RATE CONSTANTS OF ELECTRON TRANSFER REACTIONS

$$D' \xrightarrow{e} D^+,\ D \xrightarrow{e} D'^+,\ D^* \xrightarrow{e} W_1,\ W_1^- \xrightarrow{e} D^+,$$
$$W_1^- \xrightarrow{e} W_2,\ W_2^- \xrightarrow{e} W_1,\ W_2^- \xrightarrow{e} D^+,\ W_2^- \xrightarrow{e} A,$$
$$A^- \xrightarrow{e} W_2,\ A^- \xrightarrow{e} D^+$$

Donor and acceptor molecules are assumed to be in a dielectric with $D=4$ (protein) in the geometrical arrangement given by Deisenhofer *et al.* and in alternative arrangements. For evaluating Eq. (3) the wave functions of the electron before and after transfer from donor (D) to acceptor (A) must be given and ε and S can then be calculated.

1. Wave functions of electrons before and after transfer

In the case of the electron transfer from D^* to W_1 a π electron extending over the special pair D becomes a π electron extending over W_1. The approximate wave function of the electron before and after transfer has first 8 and then 10 antinodes in each of the two molecules of the special pair. It is described by atomic orbitals $\psi_{\mathrm{el},i}$:

$$\psi_{\mathrm{el}} = \sum_i c_i \psi_{\mathrm{el},i} \ . \tag{A1}$$

At small distances r_i of the electron from nucleus i $\psi_{\mathrm{el},i}$ can be represented by a Slater function

$$\psi_{\mathrm{el},i} = N_{S,i} \left[\frac{r_i}{a_0} \right] \exp[-Z_{\mathrm{eff},i} r_i/(2a_0)] \frac{z_i}{r_i} \qquad (\text{for } r_i < r_\pi) \tag{A2}$$

where $Z_{\mathrm{eff},i}=3.25$ for C, 3.90 for N, a_0 is Bohr's radius. For evaluating ε the wave function at large distance is of interest, where the electron is effectively in the field of its counter charge e_0 in a dielectric of permittivity D [potential energy $-e_0^2/(Dr)$]. Since the energy of the electron has a given value $-\varphi$ its wave function at large distance r must fulfill the Schrödinger equation for $V=-e_0^2/(Dr)$ for this energy $-\varphi$. This is the case for the function

$$\psi_{\mathrm{el},i} = N_i \left[\frac{r_i}{a_0} \right]^{n-1} e^{-\alpha r_i} \frac{z_i}{r_i} \quad (\text{for } r_i > r_\pi) \ , \tag{A3}$$

$$\alpha = \sqrt{2m\varphi}/\hbar \ , \tag{A4}$$

$$n = (\alpha a_0 D)^{-1} \tag{A5}$$

(m is the mass of electron) if $r \gg a_0 D$. In the present case of the excited singlet state D^* the values $E=-0.83$ V (Sec. II); $\varphi=0.82$ eV (Sec. IV); $D=4$, $\alpha=0.465$ Å^{-1}, $n=1.02$ are obtained. $N_{S,i}$ and N_i are interrelated since $\psi_{\mathrm{el},i}$ must smoothly go over into (A2) and (A3). For simplicity we apply (A2) for $r \leqq r_\pi$ and (A3) for $r \geqq r_\pi$ where $r_\pi = 1.7$ Å is the van der Waals radius of a π electron. Equalizing (A2) and (A3) at $r = r_\pi$ gives

$$N_i = N_{S,i} (r_\pi/a_0)^{2-n} \exp\{[\alpha - Z_{\mathrm{eff},i}/(2a_0)] r_\pi\} \ . \tag{A6}$$

$N_{S,i}$ is given by normalizing the wave function. Since the electron charge is mainly at $r < r_\pi$ it is reasonable to approximate $N_{S,i}$ by normalizing the Slater function

$$N_{S,i} = \frac{1}{\sqrt{\pi}} \left[\frac{Z_{\mathrm{eff},i}}{2} \right]^{5/2} a_0^{-3/2} \ . \tag{A7}$$

In the case of the wave function of the electron after transfer, ψ_{el} is obtained accordingly. However, it must be taken into account in this case that the electron in W_1^- is bound to a neutral molecule W_1 ($V=0$ at $r > r_\pi$) and to fulfill the Schrödinger equation at large r_i values, n must be taken as zero:

$$\psi_{\mathrm{el},i}=N_i\left[\frac{r_i}{a_0}\right]^{-1}e^{-\alpha r_i}\frac{z_i}{r_i}\quad(\text{for } r_i\geqq r_\pi)\ . \tag{A8}$$

In the transfer considered here, $D^*\xrightarrow{e}W_1$, the initial wave function has 10 antinodes in each of the two molecules in the special pair.[33] At the end the electron is in W_1 and has again a wave function with 10 antinodes.

The wave functions of the different components indicated in Figs. 5 and 6 are obtained in the same manner from free electron model calculations.[33]

In the case of the electron transfer from D' to D^+ the initial wave function cannot be simply considered as a $3d$ orbitals of Fe^{2+}, since 90% of the charge is in the π-electron portion.[47] The wave function (Fig. 6) can be approximated by a sum of atomic contributions [Eq. (A1)].

Two possible electronic structures of D^+ should be considered, since it is not decided from ESR studies[48,49] if the positive charge spreads over both molecules in the oxidized special pair or if it hops between the two molecules in times shorter than 7 ps. In the first case the wave function extends over both molecules, in the second case it is restricted to one molecule and has c_i's larger by a factor of $\sqrt{2}$.

2. Evaluation of Eq. (3)

Considering downhill electron transfer (from electronic wave function $\psi_{\mathrm{el},D}$ to $\psi_{\mathrm{el},A}$) the system is first in the vibronic ground state (vibronic wave functions of donor and acceptor φ_{D0} and φ_{A0}) and at the end in the vibronic state with quantum numbers v and w, respectively (φ'_{Dv} and φ'_{Aw}). (For simplicity it is assumed that only one normal vibration is excited in each molecule.) The transition (from state with wave function $\psi_{\mathrm{el},D}\varphi_{D0}\varphi_{A0}$ to state with wave function $\psi_{\mathrm{el},A}\varphi'_{Dv}\varphi'_{Aw}$) takes place if the two states energetically match. This requires some thermal activation energy Δ_{vw}. The rate of electron transfer then is given by (3)

$$k=\frac{2\pi}{\hbar}S\varepsilon^2 \tag{A9}$$

where

$$\varepsilon=\langle\psi_{\mathrm{el},D}\,|\,V\,|\,\psi_{\mathrm{el},A}\rangle\ , \tag{A10}$$

$$S=\sum_{v,w}e^{-\Delta_{vw}/k_BT}\frac{1}{k_BT}\langle\varphi_{D0}\,|\,\varphi'_{Dv}\rangle^2\langle\varphi_{A0}\,|\,\varphi'_{Aw}\rangle^2\ , \tag{A11}$$

V is the perturbation energy of the electron of the donor by the acceptor. This is essentially identical with the usual description,[27,50–52] however, the relation

$$\frac{\delta}{k_BT}e^{-\Delta_{vw}/k_BT}$$

is used for the probability that states v and w match (activation energy Δ_{vw}) where δ is the uncertainty in energy. δ cancels in writing the expression for k. It is assumed that solvent reorganization is unimportant for electron transfer in the present case (the chromophores are sur-

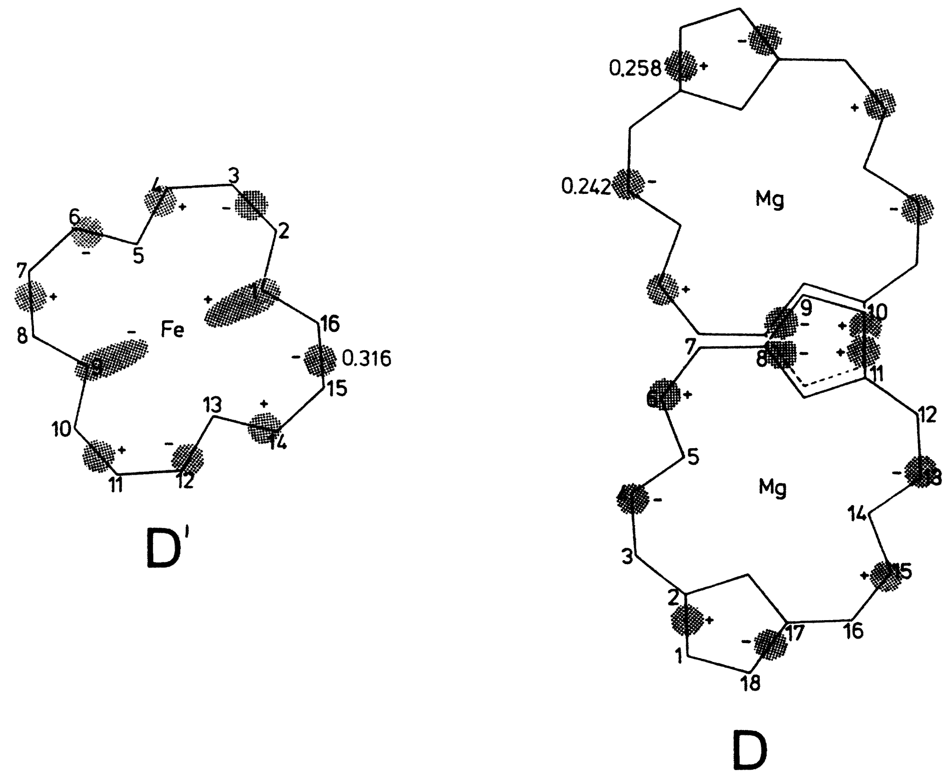


FIG. 5. Upper lobes of wave functions relevant to transition $D'\xrightarrow{e}D^+$ indicated. Special pair D and heme D'.

rounded by an essentially rigid protein portion and the electronic charge, before and after transfer is spread over a large π-electron portion). The electron transfer is considered as being initiated by thermal activation leading to energetic coincidence, environmental reorganization eventually taking place as a consecutive process. A uniform density of energy states is assumed.

The formalism is valid for small perturbation ($\varepsilon < \hbar/2\pi t_c$, where t_c is the time to destroy phase relations in electron transfer, i.e., the time between collisions that can lead to energetic match or destroy match). This is the case in the transitions $D' \xrightarrow{e} D^+$, $D \xrightarrow{e} D'^+$, $W_2^- \xrightarrow{e} A$, $A^- \xrightarrow{e} W_2$, $W_2^- \xrightarrow{e} D^+$, and $A^- \xrightarrow{e} D^+$. If $\varepsilon > \hbar/2\pi t_c$ but still small compared to $k_B T$ (this case is given for transitions $D^* \xrightarrow{e} W_1$, $W_1^- \xrightarrow{e} D^+$, $W_1^- \xrightarrow{e} W_2$, and $W_2^- \xrightarrow{e} W_1$) we use the equation[53,54]

$$k = \frac{1}{t_c} 2\varepsilon S \ . \tag{A12}$$

It is obtained by considering that $\delta = 2\varepsilon$ in the present case and that the rate of the transition $\psi_{\mathrm{el},D}\varphi_{D0}\varphi_{A0} \rightarrow \psi_{\mathrm{el},A}\varphi'_{Dv}\varphi'_{Aw}$, is $1/t_c$ times the probability to reach match by a collision, times the probability that the donor, after removing an electron, is in state v (probability $\langle \varphi_{D0} | \varphi'_{Dv} \rangle^2$), times the probability that the acceptor, after accepting an electron, is in state w (probability $\langle \varphi_{A0} | \varphi'_{Aw} \rangle^2$). We use the value $t_c = 10^{-13}$ s throughout the paper. Jortner[51] gives the value 5×10^{-12} s in ordinary solids based on picosecond spectroscopy, Kenkre and Knox[55] obtained values between 10 fs and 53 ps in the case of excitation transfer.

3. Evaluation of ε

ε is obtained from (A10) by introducing the wave functions given above. The integral can be easily approximated in all cases of neutral acceptors ($D^* \xrightarrow{e} W_1$, $W_1^- \xrightarrow{e} W_2$, $W_2^- \xrightarrow{e} W_1$, $W_2^- \xrightarrow{e} A$, and $A^- \xrightarrow{e} W_2$ where $V=0$ except at $r_i < r_\pi$). In the region $r_i \leqq r_\pi$ V is given by the Slater potential V_i

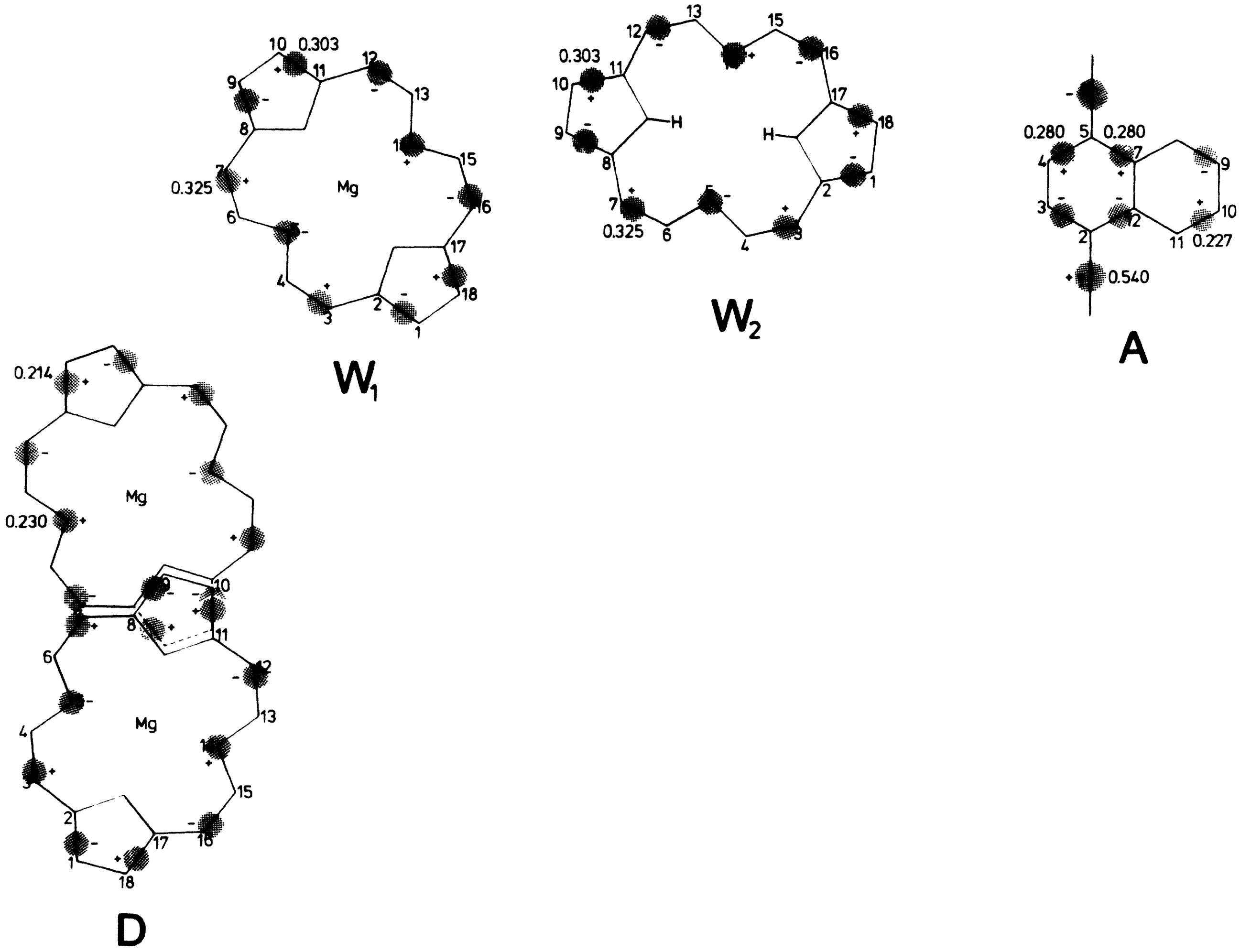


FIG. 6. Wave functions in special pair D, W_1, W_2, and A relevant to transitions $D^* \xrightarrow{e} W_1$, $W_1^- \xrightarrow{e} W_2$, $W_2^- \xrightarrow{e} A$.

$$V_i = -\frac{e_0^2}{r_i}\left[Z_{\mathrm{eff},i} - \frac{a_0}{r_i}\right] + V_0 . \tag{A13}$$

The term $V_0 = 3.8$ eV$(1-1/D) = 2.85$ eV [see Eq. (2)] is added since the potential energy is considered to be zero in the medium, not in the vacuum. According to (A1) and (A10),

$$\varepsilon = \sum_{i,j} c_i c_j \varepsilon_{ij} , \tag{A14}$$

$$\varepsilon_{ij} = \langle \psi_{\mathrm{el},Di} \mid V_j \mid \psi_{\mathrm{el},Aj} \rangle , \tag{A15}$$

where the c_i's and c_j's refer to donor D and acceptor A, respectively. In evaluating ε_{ij} the wave function $\psi_{\mathrm{el},Di}$ given by Eqs. (A3), (A6), and (A7), and $\psi_{\mathrm{el},Aj}$ given by Eqs. (A2) and (A7) for $i \to j$, are divided into components with the orbital axes parallel and perpendicular to the line connecting the atoms (x axis in Fig. 7),

$$\varepsilon_{ij} = \varepsilon_{ij,x} \cos\vartheta_i \cos\vartheta_j + \varepsilon_{ij,yz} \sin\vartheta_i \sin\vartheta_j \cos\alpha_{ij} . \tag{A16}$$

The interaction energy resulting from the first component is easily obtained if we set $r_i = x_i$ and expand the exponential in (A3)

$$e^{-\alpha r_i} = e^{-\alpha x_i} = e^{-\alpha(d_{ij}+x_j)} = e^{-\alpha d_{ij}}(1-\alpha x_j) . \tag{A17}$$

The integrals obtained by introducing these functions and (A13) in (A15) and integrating from $r_j = 0$ to $r_j = r_\pi$ can be solved analytically, and we find

$$\varepsilon_{ij,x} = e^{-\alpha d_{ij}} (d_{ij}/a_0)^{n-1} \mathrm{const} , \tag{A18}$$

$$\mathrm{const} = \frac{e_0^2}{2a_0} N_i N_{S,j} a_0^3 \left[\frac{2}{Z_{\mathrm{eff},j}}\right]^3 (\alpha a_0) \frac{80\pi}{3} , \tag{A19}$$

if the term V_0 in (A13) is neglected and the integral extended to infinity and if the overlap term, which is small in this case, is neglected. We find const$= N_i N_{s,j} \alpha a_0^{-1} I$, where

$$I = \int_{\vartheta=0}^{\vartheta=\pi} \int_{r=0}^{r=\infty} e^{-Z_{\mathrm{eff}} r/2a_0} V x^2 \, d\tau$$
$$= \left[\frac{2}{Z_{\mathrm{eff}}}\right]^3 \frac{e_0^2}{2a_0} a_0^5 \frac{80\pi}{3} \tag{A20}$$

with $x = r\cos\vartheta$, and $d\tau = 2\pi r \sin\vartheta \, d\vartheta \, r \, dr$ (considering the true upper limit r_π and V_0 gives the factor 64.5 instead of 80). α and i relate to donor, j to acceptor. N_i is the normalization constant [Eq. (A6)] for donor, $N_{S,j}$ the normalization constant [Eq. (A7)] for acceptor. In finding the second component r_i and x_i can be taken as constant and we obtain

$$\varepsilon_{ij,yz} = \frac{\varepsilon_{ij,x}}{\alpha d_{ij}} . \tag{A21}$$

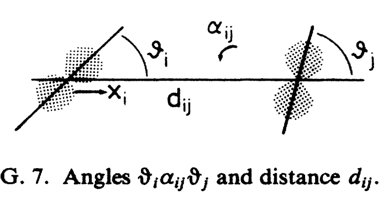


FIG. 7. Angles $\vartheta_i \alpha_{ij} \vartheta_j$ and distance d_{ij}.

ε can then be evaluated in the five cases $D^* \xrightarrow{e} W_1$, $W_1^- \xrightarrow{e} W_2$, $W_2^- \xrightarrow{e} W_1$, $W_2^- \xrightarrow{e} A$, $A^- \xrightarrow{e} W_2$ by summation over i and j [Eq. (A14)]. In evaluating (A14) we have considered each antinode as a pseudoatom of carbon ($Z_{\mathrm{eff},i} = 3.25$). This simplification has little influence on the result. The c_i's and c_j's are given by the free electron model, see Figs. 5 and 6. The numerical values of the c_i's are indicated at some lobes; all other c_i's are given by these values by symmetry.

In all cases with charged acceptor ($D' \xrightarrow{e} D^+$, $D \xrightarrow{e} D'^+$, $W_1^- \xrightarrow{e} D^+$, $W_2^- \xrightarrow{e} D^+$, $A^- \xrightarrow{e} D^+$) an additional contribution besides (A18) and (A21) results from the Coulomb energy of the electron in the field of the counter charge. It can be estimated easily and it turns out to be small in the present cases and is neglected.

The ε values thus obtained are given in Table I. In judging the results it should be realized that only a few terms in the sum in (A14) are important (the contribution of the antinodes of donor and acceptor that are nearest to each other).

4. Evaluation of S

a. $D' \xrightarrow{e} D^+$

Vibronic excitation of acceptor D^+. For calculating S the integrals $\langle \varphi_{D0} | \varphi'_{Dv} \rangle$ and $\langle \varphi_{A0} | \varphi'_{Aw} \rangle$ must be evaluated. This is illustrated in the case of the electron accepted by the special pair, assuming that the positive charge extends over both molecules. With the increasing charge density due to the extra electron (wave function indicated in Fig. 5) the bonds 1-2, 8-9, 10-11, 17-18 compress and the bonds 1-18, 9-10, 2-3, 7-8, 11-12, 16-17 (where the extra electron has a node and is therefore antibonding) extend. Essentially, the C-C valence vibrations of bonds 1-2, 8-9, 10-11, 17-18 (1400 cm^{-1}, $\omega_A = 2.64 \times 10^{14}$ s^{-1}) are excited, i.e., a number of normal vibrations of roughly the same frequency. We assume for simplicity that the situation can be described as excitation of a single vibration. This is correct if all the excited normal vibrations have the same frequency.[56]

$\langle \varphi_{A0} | \varphi'_{Aw} \rangle^2$ is given by the expression

$$\langle \varphi_{A0} | \varphi'_{Aw} \rangle^2 = e^{-\beta_A} \frac{\beta_A^w}{w!} ,$$

with (A22)

$$\beta_A = \frac{\omega_A}{2\hbar} \sum M_i \rho_i^2 ,$$

where M_i is the mass of the nucleus of atom i, and ρ_i is the distance between equilibrium position of atom i before and after electron transfer. In the present case, as shown in the following, β_A is small (the change in bond lengths is small): the system that has accepted the electron is most frequently found in the vibrationless state ($w = 0$).

TABLE I. Electron transfer reactions. Midpoint potentials, free-energy change, barrier height, and related parameters, Franck-Condon factor, perturbation energy and rate constant.

	E_D(V)	E_A(V)	ΔG^0 (eV)	φ (eV)	α (Å^{-1})	n	S (eV^{-1})	ε (eV)	k (s^{-1})
$D'\xrightarrow{e}D^+$	0.33	0.46	−0.13	1.98	0.722	0.65	2.4	1×10^{-5} 1×10^{-6} 1×10^{-7}	2×10^6 ($d_1=18$ Å) 2×10^4 ($d_1=21$ Å) 2×10^2 ($d_1=24$ Å) 2.6×10^6 (expt.)
$D\xrightarrow{e}D'^+$	0.46	0.33	+0.13	2.11	0.745	0.63	1.6×10^{-2}	1×10^{-6}	2×10^2 ($d_1=21$ Å)
$D^*\xrightarrow{e}W_1$	−0.83	−0.83	0	0.82	0.465	1.02	16.6	5×10^{-2} 2×10^{-2} 5×10^{-3}	10^{13} ($d_2=7$ Å) 6×10^{12} ($d_2=10$ Å) 2×10^{12} ($d_2=13$ Å) $\simeq10^{13}$ (expt.)
$W_1^-\xrightarrow{e}W_2$	−0.83	−0.63	−0.2	0.82	0.465	0	5.2	4×10^{-2} 3×10^{-3} 3×10^{-4}	4×10^{12} ($d_3=7$ Å) 3×10^{11} ($d_3=10$ Å) 5×10^9 ($d_3=13$ Å) 2×10^{11} (expt.)
$W_1^-\xrightarrow{e}D^+$ (excited singlet)	−0.83	−0.83	0	0.82	0.465	0	16.6	5×10^{-3}	2×10^{12} ($d_2=10$ Å)
$W_1^-\xrightarrow{e}D^+$ (triplet)	−0.83	−0.43	0.4	0.82	0.465	0	0.86	5×10^{-3}	1×10^{11} ($d_2=10$ Å)
$W_1^-\xrightarrow{e}D^+$ (ground state)	−0.83	+0.46	−1.29	0.82	0.465	0	1.3×10^{-4}	1×10^{-2}	3×10^7 ($d_2=10$ Å)
$W_2^-\xrightarrow{e}W_1$	−0.63	−0.83	+0.2	1.02	0.518	0	2.4×10^{-3}	3×10^{-3}	2×10^8 ($d_3=10$ Å)
$W_2^-\xrightarrow{e}D^+$ (excited singlet)	−0.63	−0.83	+0.2	1.02	0.518	0	7.6×10^{-3}	2×10^{-5}	3×10^4 ($d_4=17$ Å)
$W_2^-\xrightarrow{e}D^+$ (triplet)	−0.63	−0.43	−0.2	1.02	0.518	0	5.1	9×10^{-5} 2×10^{-5} 3×10^{-6}	4×10^8 ($d_4=14$ Å) 2×10^7 ($d_4=17$ Å) 5×10^5 ($d_4=20$ Å) 4.6×10^7 (expt.)
$W_2^-\xrightarrow{e}D^+$ (ground state)	−0.63	+0.46	−1.09	1.02	0.518	0	1.1×10^{-3}	7×10^{-5}	5×10^4 ($d_4=17$ Å)

TABLE I. (*Continued*).

	E_D(V)	E_A(V)	ΔG^0 (eV)	φ (eV)	α (Å^{-1})	n	S (eV^{-1})	ε (eV)	k (s^{-1})
$W_2^- \xrightarrow{e} A$	−0.63	−0.165	−0.465	1.02	0.518	0	10	1×10^{-3} 1×10^{-4} 1×10^{-5}	1×10^{11} ($d_5=11$ Å) 1×10^{9} ($d_5=14$ Å) 1×10^{7} ($d_5=17$ Å) 3×10^{9} (expt.)
$A^- \xrightarrow{e} W_2$	−0.165	−0.63	+0.465	1.485	0.625	0	8.8×10^{-8}	5×10^{-5}	2 ($d_5=14$ Å)
$A^- \xrightarrow{e} D^+$ (triplet)	−0.165	−0.43	+0.265	1.485	0.625	0	3.7×10^{-5}	2×10^{-9}	10^{-6} ($d_6=28$ Å)
$A^- \xrightarrow{e} D^+$ (ground state)	−0.165	+0.46	−0.625	1.485	0.625	0	4.8	2×10^{-7} 5×10^{-8} 5×10^{-9}	3×10^{3} ($d_6=23$ Å) 1×10^{2} ($d_6=25$ Å) 1 ($d_6=28$ Å) 1×10^{2} (expt.)

To approximate the decrease in length of bonds 1-2, 8-9, 10-11, 17-18, in which the additional π electron has an antinode the relation

$$\frac{\Delta l}{\text{Å}} = -0.37\frac{\sigma}{\text{Å}^{-1}} \tag{A23}$$

is used. Δl is the change in bond length, σ the density of this electron in the center of the bond (measured in number of electrons per unit length).[56] σ is given by the free electron model. For bond 1-2 we find from Ref. 33 taking into account that the electron is spread over two molecules,

$$\sigma = \frac{1}{2l}\left[0.3203\sin\frac{2\pi l}{4.419l}\right]^2 = \frac{1}{l}0.050$$

(where $l=1.4$ Å is the bond length) and therefore $\Delta l = -1.3\times10^{-2}$ Å. (The simple perimeter model would give $\sigma=(1/2)(2/18l)[\sin(4\pi/9)]^2=(1/l)(0.9/18)=(1/l)0.05$.)

The resulting shift in equilibrium position of the nuclei 1, 2, 8, 9, 10, 11, 17, and 18 and of the corresponding nuclei in the second molecule of special pair D is approximately $\frac{1}{2}\times1.3\times10^{-2}$ Å. Similarly, the change in length of bonds 3-4, 6-7, 12-13, and 15-16 is

$$\sigma = \frac{1}{2l}\left[0.3006\sin\frac{2\pi(\frac{3}{2})l}{4.419l}\right]^2 = \frac{1}{l}0.032$$

and therefore $\Delta l = -8.2\times10^{-3}$ Å.

Therefore, if the electron extends over both molecules,

$$\sum M_i \rho_i^2 = 16(2\times10^{-23}\ \text{g})[(\tfrac{1}{2}\times1.3\times10^{-2}\ \text{Å})^2 + (\tfrac{1}{2}\times8.2\times10^{-3}\ \text{Å})^2] .$$

According to (A22) $\beta_A=0.24$ and therefore $\langle\psi_{A0}\,|\,\psi'_{Aw}\rangle^2$ is 0.84 for $w=0$, 0.19 for $w=1$, and 0.02 for $w=2$. For the present purpose this simple approximation is sufficient. A low-frequency lattice vibration was considered but does not contribute appreciably.

In a more rigorous description a normal vibration analysis would be required and it should be taken into account that several normal vibrations k can be excited. $\langle\varphi_{A0}\,|\,\varphi'_{Aw}\rangle^2 = e^{-\beta_A}(\beta_A^w/w!)$ has to be replaced by a product

$$\prod_k e^{-\beta_{Ak}}\frac{\beta_{Ak}^{w_k}}{w_k!} \tag{A24}$$

where

$$\beta_{Ak} = \frac{\omega_{Ak}}{2\hbar}\frac{\left[\sum M_i A_{ki}\rho_i \cos\alpha_{ki}\right]^2}{\sum M_i A_{ki}^2} , \tag{A25}$$

A_{ki} is the amplitude of atom i if normal vibration k is excited, α_{ki} the angle between the direction of ρ_i and A_{ki}. In Ref. 56 such an analysis was made in considering the electronic excitation of some π-electron systems and the simplified model considering only one normal vibration was found to be well justified.

Vibronic excitation of donor D′. In removing the electron from D' the four Fe-N bonds extend since the wave function in Fig. 4 has antinodes in bonds Fe-1 and Fe-9, the complementary wave function of the twofold degenerate set has antinodes in bonds Fe-5 and Fe-13. Bonds 1-2, 1-16, 9-8, and 9-10 and bonds 5-4, 5-6, 13-12, and 13-14 compress since there are nodes of the wave function in Fig. 5 or of the complementary wave function in these bonds. The breathinglike mode then is essentially excited. From resonance Raman spectroscopy[47] this mode is at $\omega_D=(1372\ \mathrm{cm}^{-1})2\pi c$ and atoms 1,5,9,13 on the one hand, and atoms 2,4,6,8,10,12,14,16 on the other hand, are displaced by about 0.01 Å. Then $\sum M\rho_i^2$ is approximately $12(2\times10^{-23}\ \mathrm{g})(0.01\ \text{Å})^2$ and therefore [according to Eq. (A22)] $\beta_D=0.3$, $\langle\varphi_{D0}|\varphi'_{Dv}\rangle^2=0.74$ for $v=0$, 0.22 for $v=1$, 0.03 for $v=2$.

Energetic match of D' and D^+. The level of acceptor D^+ is below the level of D' by $-\Delta G^0=0.13$ eV [difference between midpoint potentials of D'/D'^+ and D/D^+ (Table I) multiplied by e] and therefore the following states of D' and D^+ almost coincide [activation energy $\Delta_{vw}=(v\omega_D+w\omega_A)\hbar+\Delta G^0$ small] (Fig. 8) (as usually assumed, the energy loss is identified with the loss of free energy, which is not strictly correct):

$$v=0,\quad w=1,\quad \Delta_{01}=0.044\ \mathrm{eV}\ ,$$

$$v=1,\quad w=0,\quad \Delta_{10}=0.040\ \mathrm{eV}\ .$$

In all other cases the activation energy is much larger and the corresponding contribution to S can be neglected. Therefore

$$S=\frac{1}{k_BT}e^{-\beta_D-\beta_A}(e^{-\Delta_{01}/k_BT}\beta_A+e^{-\Delta_{10}/k_BT}\beta_D)$$

with $\beta_D=0.3$, $\beta_A=0.24$. Thus $S=2.4\ \mathrm{eV}^{-1}$.

We have neglected the environmental reorganization after the electron transfer by which the levels of D'^+ and D are lowered. The loss of free energy before the relaxation of the environment then is somewhat smaller than when bringing the system into the relaxed state, i.e., smaller than $-\Delta G^0=0.13$ eV. If this loss is zero (second case considered at the end of Sec. IV: energy levels of vibrationless states before and after electron transfer coincide; electron transfer is followed by environmental reorganization, and then the electron is trapped at acceptor D^+) we find:

$$S=\frac{1}{k_BT}e^{-\beta_D-\beta_A}=22\ \mathrm{eV}^{-1}\ .$$

In case the positive charge in D^+ is not spread, but is localized in one molecule of the special pair the change in bond lengths is twice the change in the case considered above, then ρ_i^2 in (A22) is four times larger, but the sum extends over half the number of terms, and therefore $\beta_A=2\times0.24=0.48$ and we find $S=2.7\ \mathrm{eV}^{-1}$ in the first case considered in Sec. IV, $S=18\ \mathrm{eV}^{-1}$ in the second case.

b. $D\xrightarrow{e}D'^+$

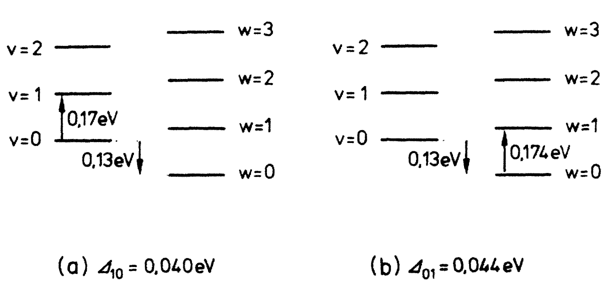
The reverse reaction $D\xrightarrow{e}D'^+$ is uphill by $\Delta G^0=0.13$ eV. The system has to be activated thermally by this amount to reach the same probability of energetic match as in the foward reaction, and therefore S is obtained by multiplying the S value of the forward reaction, e.g., 2.4 eV^{-1} with $e^{-\Delta G^0/k_BT}$:

$$S=2.4\ \mathrm{eV}^{-1}e^{-0.13\ \mathrm{eV}/k_BT}=1.6\times10^{-2}\ \mathrm{eV}^{-1}\ .$$

All the other electron transfer rates are evaluated accordingly.

The values of ε, S, and k given in Table I are based on the assumption that the positive charge extends over both molecules in D^+. If it extends only over one molecule of the special pair S changes slightly and ε is smaller by a factor $1/\sqrt{2}$ since the sum in (A1) has half the number of terms, each term being larger by a factor of $\sqrt{2}$ (normalization condition). Therefore, the k value can be smaller by a factor of 2 in some cases and this difference is not relevant.

Of particular interest is the electron transfer from W_2^- to A, where the rate is increasing when lowering temperature[57] (Fig. 9). The loss of free energy is $-\Delta G^0=0.465$ eV. We assume that the energy level of A^- is by 2×0.17 eV $=0.34$ eV below the level of W_2^- and that the residual loss of free energy $0.465-0.34$ eV $=0.125$ eV is the loss



(a) Δ_{10} = 0,040eV (b) Δ_{01} = 0,044eV

FIG. 8. Electron transfer $D'\xrightarrow{e}D^+$. Energy released in electron transfer is expended for vibronic excitation of donor (a) or acceptor (b).

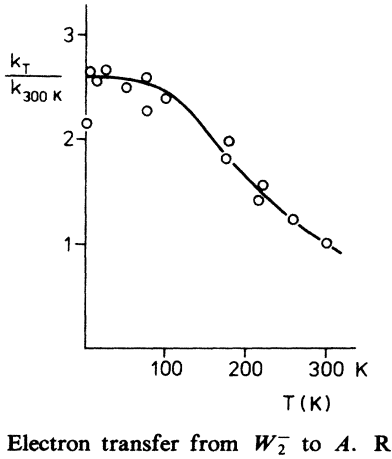


FIG. 9. Electron transfer from W_2^- to A. Rate $k_T/k_{300\ \mathrm{K}}$ against T for $\delta=0.01$ eV. Theoretical curve and points according to Ref. 57.

by environmental reorganization subsequent to electron transfer. In this case (activationless electron transfer)

$$S=\frac{1}{k_BT}e^{-\beta_D-\beta_A}\left[\frac{\beta_A^2}{0!2!}+\frac{\beta_D\beta_A}{1!1!}+\frac{\beta_D^2}{0!2!}\right]$$

$$=\frac{1}{k_BT}e^{-\beta_D-\beta_A}(\beta_D+\beta_A)^2\frac{1}{2!}=10\ \text{eV}^{-1}$$

is larger than in all other cases where an activation energy is required for energetic match. S (and thus rate k) then is proportional to $1/T$. This is actually observed at sufficiently high temperature (Fig. 9), while at low temperature k tends to be temperature independent. This is explained by the fact that the vibronic levels are not sharp (a sum of normal vibrations with very similar frequencies is excited). Assuming a uniform distribution within width δ, the probability of energetic match is proportional to ε/k_BT at $k_BT \gg \delta$ and proportional to $(\varepsilon/k_BT)(k_BT/\delta)$ at $k_BT<\delta$. The theoretical curve (Fig. 9) for $\delta=0.01$ eV agrees well with the observation (points), in contrast to the conventional $1/\sqrt{T}$ dependence. A corresponding approximation is made in the case of the electron transfer from A^- to D^+, where also the rate is increasing when lowering temperature [M. R. Gunner, D. E. Robertson, and P. L. Dutton (private communication)].

Comparison with other formalisms. It is of interest to compare the present approach with approaches by Hopfield, Jortner, and Marcus. In the present approach, in the case of the electron transfer from cytochrom c to the special pair, $S=2.4\ \text{eV}^{-1}$, and $\varepsilon=1.0\times10^{-5}$ eV for $d=18$ Å ($d=d_1$ in Fig. 2) and thus $k=(2\pi/\hbar)S\varepsilon^2=2\times10^6\ \text{s}^{-1}$ in agreement with experiment. For various d values ε can be approximated by $\varepsilon=(3.9\ \text{eV})\exp(-\alpha d)$ with $\alpha=0.72$ Å^{-1} and thus

$$k=(4\times10^{17}\ \text{s}^{-1})e^{-(1.44\ \text{Å}^{-1})d}\,. \tag{A26}$$

Hopfield's and Jortner's approaches are based on considerably smaller S values. Hopfield[58] calculated S from the semiclassical expression $S=(2\pi\sigma^2)^{-1/2}\exp[-(E_D-E_A-\Delta)^2/2\sigma^2]$ assuming the values $\Delta=1$ eV, $E_D-E_A=0.05$ eV and $\sigma^2=0.06\ \text{eV}^2$ (for 300 K) and obtained the value $S=10^{-3}\ \text{eV}^{-1}$. The basic reason for the small S value of this electron transfer reaction which is characterized by a small free-energy loss and a large solvent reorganization energy ($\Delta=1$ eV), is the high thermal activation to overcome the solvent reorganization energy. Jortner[52] used a quantum-mechanical model, similar to the one used here, but assumed a value $\beta_D+\beta_A=46$ which is much larger than the value $\beta_D+\beta_A=0.54$ obtained here and thus the factor $e^{-(\beta_D+\beta_A)}$ in the expression for S then is much smaller. Therefore, in Hopfield's and Jortner's approach the distance between donor and acceptor calculated from the known value of the rate constant is much smaller than the actual distance. Jortner considered the possibility of superexchange type coupling to explain the discrepancy. In the present view this discrepancy is due to the particular choice of parameters.

In Jortner's case the assumed phonon coupling strength $\beta_D+\beta_A=46$ corresponds to the value $\sum_{\text{donor,acceptor}}\rho_i^2=(0.4\ \text{Å})^2$. This follows from Eq. (A22) with $\omega_D=\omega_A=2.64\times10^{14}\ \text{s}^{-1}$, $M_i=2\times10^{-23}$ g. In the present view the value expected for the above sum is much smaller. If the electron would be confined to one bond in the donor before electron transfer and to one bond in the acceptor after transfer the change in bond length would be about 0.1 Å (half of the difference between single and double bond length), and therefore

$$\sum_{\substack{\text{donor,}\\ \text{acceptor}}}\rho_i^{2'}=4\left[\frac{0.1\ \text{Å}}{2}\right]^2=(0.1\ \text{Å})^2\,.$$

In reality the electron cloud is spread over several bonds (say over m bonds in the donor before transfer and over n bonds in the acceptor after transfer). Then

$$\sum_{\substack{\text{donor,}\\ \text{acceptor}}}\rho_i^2=2m\left[\frac{0.1}{2m}\right]^2+2n\left[\frac{0.1}{2n}\right]^2$$

$$=\frac{(0.1\ \text{Å})^2}{2}\left[\frac{1}{m}+\frac{1}{n}\right]\,.$$

For a rough estimate $m=n=4$ and therefore

$$\sum\rho_i^2=\frac{(0.1\ \text{Å})^2}{4}=(0.05\ \text{Å})^2\,.$$

This is much smaller than the above value $(0.4\ \text{Å})^2$. However, in the present view ($\beta_D+\beta_A=0.54$) Eq. (A22) gives

$$\sum_{\substack{\text{donor,}\\ \text{acceptor}}}\rho_i^2=(0.05\ \text{Å})^2\,,$$

in agreement with this estimate.

Marcus and Sutin[27] assumed that the rate is given by the expression

$$k=(10^{13}\ \text{s}^{-1})e^{-\beta d'}e^{-\Delta G_r^*/RT} \tag{A27}$$

with $\beta=1.2$ Å^{-1} and $\Delta G^*=7.1\ \text{kJ}\,\text{mol}^{-1}$. d' is the separation of the closest C atoms of the two reactants (15 Å according to the x-ray analysis of Deisenhofer *et al.*, i.e., 6 Å smaller than the center to center distance d) minus an amount of 3 Å to allow for the extension of the π-electron orbital beyond the carbon nucleus. Thus $d'=d-9$ Å. The value of β and the preexponential factor $10^{13}\ \text{s}^{-1}$ were obtained by adjustment to experimental rate constants in nonbiological systems such as monolayer assemblies. If we substitute d for d' we obtain for $T=300$ K,

$$k=(10^{13}\ \text{s}^{-1})e^{-\beta d}e^{\beta(9\ \text{Å})}0.059$$

$$=(2.9\times10^{16}\ \text{s}^{-1})e^{-(1.2\ \text{Å}^{-1})d}\,. \tag{A28}$$

In the relevant case $d=21$ Å both Eqs. (A26) and (A28) give a similar value $k\cong10^5\ \text{s}^{-1}$. In judging the result it should be taken into account that the constants in the Marcus-Sutin approach are extracted from experimental rate constants while this is not the case here.

The present approach is in accord with experimental results on the electron transfer in monolayer assemblies, in glassy matrices,[59] and in arrangements where donor and acceptor are separated by a rigid steroid spacer.[60] Miller *et al.* showed in a great number of cases that the rates of electron transfer from diphenyl ($-$) to different acceptors (typical cases are pyrene and naphthoquinone) can be described as a function of the free-energy loss, using the value $\lambda_v = 0.4$ eV for the intramolecular reorganization energy which is related to the phonon coupling strength by $\beta_D + \beta_A = \lambda_v / \hbar\omega = 0.4 \text{ eV}/0.17 \text{ eV} = 2.4$. From the change in π-electron distribution accompanying the electron transfer from diphenyl ($-$) to pyrene or naphthoquinone we find the value $\beta_D + \beta_A = 2.5$ in good agreement with the above value 2.4. In Miller's case the solvent reorganization energy is quite important in contrast to the present case, where a rigid environment of the chromophores is assumed to be necessary for an efficient energy-storing device.

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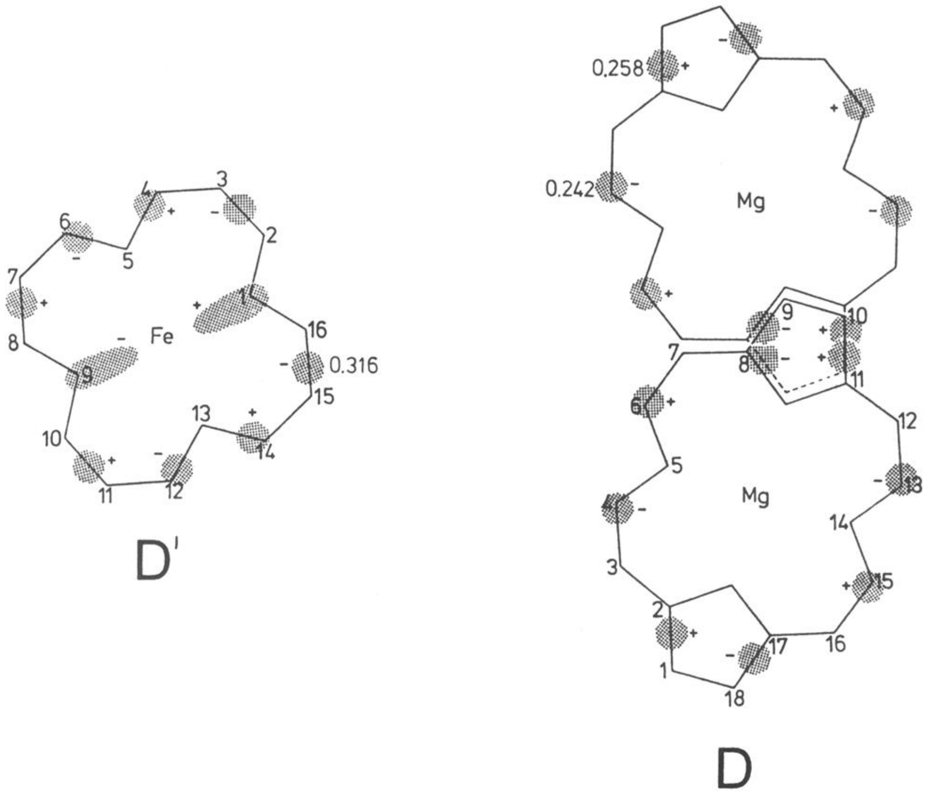

FIG. 5. Upper lobes of wave functions relevant to transition $D' \xrightarrow{e} D^{+}$ indicated. Special pair D and heme D'.

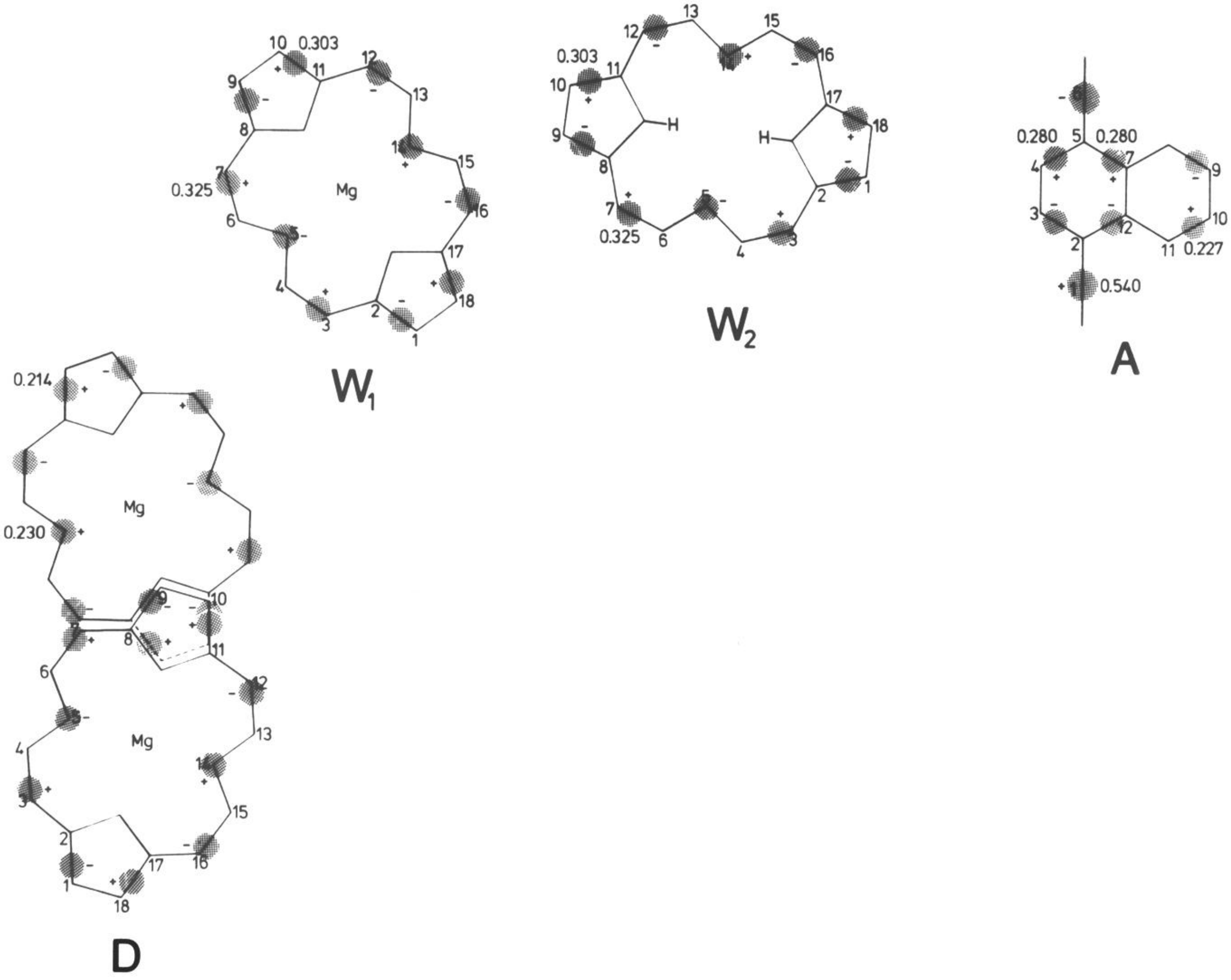

FIG. 6. Wave functions in special pair D, W_1, W_2, and A relevant to transitions $D^* \xrightarrow{e} W_1$, $W_1^- \xrightarrow{e} W_2$, $W_2^- \xrightarrow{e} A$.

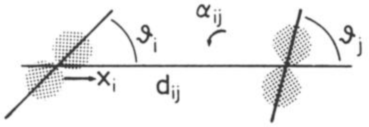

FIG. 7. Angles $\vartheta_i \alpha_{ij} \vartheta_j$ and distance d_{ij}.