A simple model is presented for the primary step in the photoinduced electron transfer in the photosynthetic reaction centers of *Rps. viridis* and *Rb. sphaeroides*. The interaction of the chromophore system (consisting of photoexcited donor P, conduction intermediate B, and acceptor H) with the environment is assumed to be negligible until vibronic deexcitation takes place resulting in a stochastically perturbed adiabatic electron transfer. This process constitutes a three-level problem. It is shown that this problem, in the present case, can be approximated by a two-level problem which can simply be solved. The energy level of **B** is found to be 0.06 eV above the level of **P**. The unidirectionality of the electron flow is explained by coincidence of energy levels in the L branch due to evolutionary constraint.

Introduction

In the primary electron-transfer step in the photosynthetic reaction center of purple bacteria the electron donor P, the special pair, a bacteriochlorophyll dimer, is photoexcited to **P** and the electron is transferred within some picoseconds from **P** (via B, the accessory bacteriochlorophyll) to the spectroscopically resolvable intermediate electron acceptor **H**, a bacteriopheophytin (for a recent review see ref 1). Fleming et al.² have found an increase in electron-transfer rate **k** with decreasing temperature which is stronger in *Rps. viridis* than in *Rb. sphaeroides*. The rate of electron transfer from **P** via **B** to **H** along the L-branch is at least 10 times larger than from **P** via **B** to **H** along the M-branch, which structure is nearly symmetric to that of **P**, and this leads to the unidirectionality of the charge separation.

The rate is of the order of a reciprocal picosecond at 10 K. The electron transfer is given by a single rate constant, and a transient bleaching in the **B** absorption region is absent.⁴ These findings are evidence against mechanisms⁵ in which **B** is a distinct, kinetically resolvable intermediary electron acceptor between **P** and **H**.

It is difficult to rationalize the results on the basis of the conventional theory for nonadiabatic electron transfer. A nonadiabatic superexchange-mediated electron transfer from **P** via **B** to **H** has been proposed.³ The unidirectionality was explained as being due to a delicate difference in the electronic interaction terms between the two branches.³ The approach is based on the conventional assumption that the chromophores are strongly coupled to the environment, as described by the Marcus equation⁴ or its quantum mechanical analogues.

In the present approach the interaction with the environment is treated differently, and this leads to a different judgment of the role of specific structural asymmetries in inducing this unidirectionality. In contrast to the model in ref 3, here the difference in energies of **H** and **H** is sufficient to explain the unidirectionality in electron transfer. The results by Fleming et al.² can be rationalized. By its simplicity this approach should be of interest focusing on some important features. Studies on site-specific mutants and on other organisms⁶ should shed light on the
role of the structural asymmetry and help in discriminating between models and in finding more refined models.

Theory

We consider a model which is based on the concept that there is negligible interaction of the chromophore system with the environment until a collision of vibronically excited \( H_L^- \) taking place (caused by random particularities in the transient environmental configuration). In this collision the vibrational energy is dissipated and the electron is trapped at \( H_L \) in a time \( \approx 10 \text{ fs} \) short compared to the time between excitation and trapping \( \approx 1 \text{ ps} \). This process can be considered as a stochastically perturbed adiabatic electron transfer.

The transfer matrix elements \( t_{PB} \) and \( t_{BH} \) for the electron transfers from \( P^* \) to \( B_a \) and from \( B_a \) to \( H_L \), respectively, were obtained by a quantum mechanical approximation. The values (being in the range between \( 5 \times 10^{-2} \) and \( 3 \times 10^{-3} \) eV) were found to depend very sensitively on details in the geometry. These values are based on free electron model wave functions. A refined treatment in which the amplitudes of the electrons in the considered orbitals were taken from INDO calculations and in which the long distance tail of the electronic wave function was calculated by a procedure proposed in ref 8 leads to values in the same range. We assume that \( t_{PB} \) and \( t_{BH} \) are in the above range and that the level of \( \{ B_a \} \) is by a certain amount \( b \) higher than the level of \( \{ P^* \} \), to take into consideration the fact that an intermediate \( B_a \) could not be spectroscopically identified.

Furthermore, we assume at temperature \( T = 0 \) that the vibronically excited level of \( \{ H_L^- \} \) \( \langle h_0 = 0.17 \text{ eV above ground-state level} \rangle \) coincides with the level of \( \{ P^* \} \), and that the levels, by thermal noise, differ in the average, at temperature \( T \) by \( a = \pm 1/2k_BT \), where \( k_B \) is Boltzmann's constant and \( a \) is the amount by which the level of the vibronically excited system \( \{ P^*B_aH_L \} \) is higher than the level of \( \{ P^*B_aH_L \} \). Because of the strong electronic coupling (in contrast to the conventional case) the time until the phase disturbing collision is taking place is not short compared to the time of oscillation of the electron between \( P \) and \( H_L \).

For simplicity we first neglect \( B_a \) and attribute the transfer matrix element \( t \) to the transfer from \( P^* \) to \( H_L \). According to a well-known relation (see eq A.4 in the Appendix) the probability \( p \) of finding the electron at \( H_L \), in the average, is \( p = 1/2(2e^2/\alpha^2 + (2e)^2) \). The rate is \( (r \text{ vibronic relaxation time}) \)

\[
k_0 = \frac{1}{2\tau} \frac{(2e)^2}{\alpha^2 + (2e)^2}
\]

This relation is obtained by considering the probability of the electron to be trapped in \( H_L \) during the time interval \( \tau \). This probability \( k_0 \) equals the probability of the electron to be in \( H_L \) times the probability \( e^{-\frac{\Delta E}{k_BT}} \) the electron to be trapped when being in \( H_L \); thus \( k_0 = p \tau \). \( k_0 \) gives the transfer rate at a certain \( \Delta \). In general the electronic levels will be slightly scattered around their average value by thermal motion. The standard deviation from the average is \( 1/k_0 \). The thermally averaged electron-transfer rate can be approximately given by

\[
k = \frac{1}{2k_BT} \int_{+\infty}^{+\infty} k_0(a) \, da = \frac{1}{2\tau} \frac{2e^2}{\alpha^2} \arctan \left( \frac{k_BT}{2e} \right)
\]

(1a)

In the considered range \( k_0T \leq 6\alpha \), this equation leads essentially to the same result as eq 1 with a given standard deviation of \( \pm 1/k_0T \).

In considering \( |B_a \rangle \) the three-state problem must be solved (instead of the two-state problem) which is quite complicated. However, in the case that the transfer matrix elements \( t_{PB}, t_{PH}, \) and \( t_{BH} \) are small compared to the energy differences of \( b - E_{B_a} \) and \( b - a = E_{B_a} - E_{H_L} \), approximative perturbation methods can be used. As shown in the Appendix the three-level problem can be reduced to a two-level problem involving an effective-transfer matrix element (Appendix, eq A.3)

\[
\epsilon = \epsilon_{PH} + \epsilon_{PB} e^{-\frac{b}{b-a}}
\]

(2)

where \( \epsilon_{PH} \) is the transfer matrix element for the direct transfer from \( P^* \) to \( H_L \).

The transfer matrix elements \( t_{PB}, t_{PH}, \) and \( t_{BH} \) can be written as products of an electronic and a vibronic factor: \( \epsilon_{PB} = \epsilon_{PH} = \epsilon_{PB} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \), where \( \epsilon_{PB} \) is the vibronic wave functions of donor and acceptor before the electron transfer, \( \epsilon_{PH} \) and \( \epsilon_{BH} \) are the corresponding functions after transfer, and \( \epsilon_v \) and \( \epsilon_w \) are vibrational quantum numbers of donor and acceptor, respectively. This approach is based on the simplifying assumption that single normal vibration is excited. This can be justified; see ref 8. The vibrational energy is dissipated in \( |P^* \rangle \) or \( |H_L^- \rangle \) depending on whether the state where \( |P^* \rangle \) is vibronically excited coincides with the original state or the state where \( |H_L^- \rangle \) is vibronically excited.

In the first case \( \epsilon_{PH} = \epsilon_{PB} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \), \( \epsilon_{PB} = \epsilon_{PB} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \) and \( \epsilon_{BH} = \epsilon_{BH} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \) and in the second case \( \epsilon_{PH} = \epsilon_{PB} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \), \( \epsilon_{PB} = \epsilon_{PB} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \) and \( \epsilon_{BH} = \epsilon_{BH} \epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \). The vibronic terms are evaluated in ref 8. In all cases a value of about 0.6 is obtained.

Results and Discussion

If \( \epsilon_{PB} \) is neglected and \( b \gg a \) we obtain from eq 2 that \( \epsilon = 2\epsilon_{PH} \epsilon_{BH} \epsilon_{PH} \), and with \( \epsilon_{PH} = \epsilon_{PH} = \epsilon_{BH} = 10^{-2} \text{ eV} \) and \( b \gg a \) this gives \( \epsilon = 2 \times 10^{-3} \text{ eV} \); this estimated \( \epsilon \) value is in accord with the value of \( \epsilon = 3.2 \times 10^{-3} \text{ eV} \) obtained from experimental data (see below). The estimated values of \( \epsilon_{PB} \) and \( \epsilon_{BH} \) are within the range given above and the value of \( b \) is in accord with the finding (see Note Added in Proof) that the probability \( P_{BH} \) of finding the electron in \( B_a \) during the transfer process is about 16%. In our model

\[
P_{BH} = \frac{1}{2} \left( \frac{2\epsilon_{PB}}{b} + \left( \frac{2\epsilon_{BH}}{b-a} \right)^2 \right)
\]

(3)

(see Appendix, eq A.5) and with \( \epsilon_{PB} = \epsilon_{BH} = (b/2)^{1/2} \) and \( a = 0 \) we find \( P_{BH} = 2/e/b \). With \( \epsilon = 3.2 \times 10^{-3} \text{ eV} \) and \( P_{BH} = 0.16 \) this gives \( b = 0.04 \text{ eV} \). If we set \( \epsilon_{BH} = 3\epsilon_{PB} \) (as suggested from
INDO calculation) instead of \( \epsilon_{\text{BH}} = \epsilon_{\text{GLU}} \) the slightly different value \( b = 0.06 \text{ eV} \) is obtained.

With the above value \( \epsilon = 3.2 \times 10^{-3} \text{ eV} \), and with \( r = 3.4 \times 10^{-13} \text{ s} \) curve 1 in Figure 1 is obtained from eq 1a, in agreement with experimental points given by Fleming et al. for *Rps. viridis*.\(^2\)

If we set \( \epsilon = 3.6 \times 10^{-3} \text{ eV} \) and \( r = 5.9 \times 10^{-13} \text{ s} \) curve 2 is obtained, in agreement with the data observed for *Rb. sphaeroides*.\(^2\)

The slight differences in \( \epsilon \) and \( r \) are reasonable, considering the sensitivity of \( \epsilon \) on small changes in geometry and the dependence of relaxation processes on structural details.

We have assumed that the state where \( \text{P}^* \) (or \( \text{H}_2^* \)) is vibrationally excited coincides with the original state. The possibility that both states coincide with the original state can also be given. Then \( k \) is the sum of two about equal terms and thus the sensitivity of relaxation processes on structural details.

Assuming \( r \) is unaffected by the substitution, the ratio of rates

\[
\frac{k_{L}(\text{GLN or LEU})}{k_{L}(\text{GLU})} = \frac{k_{L}(\Delta T + \Delta)}{k_{L}(\Delta)} = \frac{k_{T} + \Delta}{k_{T} - \Delta} \quad \text{(5)}
\]

and for the given values \( T = 300 \text{ K}, \epsilon = 3.2 \times 10^{-3} \text{ eV}, \text{ and } \Delta = 0.03 \text{ eV} \) this gives \( q = 0.5, \) corresponding to a 50\% reduction in rate. This is in good agreement with the 40\% reduction observed in ref 10. With the simplifying assumptions considered here the rate should decrease with decreasing temperature in the case of the mutants and reach a 7 times smaller value at \( T = 0, \) in contrast to the wild type where the rate increases with lowering temperature (Figure 1).

The exchange of GLU104 for GLN or LEU is accompanied by a hypsochromic shift of the absorption band of \( \text{H}_2 \) by 6 nm corresponding to an increase in excitation energy of 0.026 eV for GLN and by a slightly larger shift for LEU (band of \( \text{H}_2 \) and \( \text{H}_2 \) unresolved).\(^10\)

A hypsochromic shift is expected since the electron density in the keto carboxyl group in ring V is increased in exciting \( \text{H}_2 \) from (0.13)\(^2\) e to (0.18)\(^2\) e (O atom) and from (0.03)\(^2\) e to (0.10)\(^2\) e (C atom). By summing up the Coulomb terms we find the expected increase in excitation energy 0.02 eV. The good agreement with the measured value is a test supporting the model.

Note Added in Proof. In a recent paper by Holzapel et al.,\(^11\) the primary electron transfer in reaction centers of *Rb. sphaeroides* was investigated with femtosecond time resolution, and the results were described by assuming that the electron in \( \text{P}^* \) is transferred to \( \text{B}_{12} \) with time constant 3.5 ps and from there to \( \text{H}_{12} \) with time constant 0.9 ps. The slow population and fast depopulation of \( \text{B}_{12} \) was assumed to account for the small transient absorption changes corresponding to a transient population of \( \text{P}^*\text{B}^*\text{H} \) of 16\%. In the present view the short-living transient is a state where \( \text{P}, \text{B}_{12}, \text{ and } \text{H}_{12} \) share the electron and the small absorption change is due to the fact that \( \text{B}_{12} \) shares 16\% only. According to the Appendix, eq A.4, this state is populated in about 0.5 ps after exciting \( \text{P} \), and according to Figure 1 it decays into the vibrionic ground state of \( \text{H}_2 \) with a time constant of 3 ps. In the given range (delay time \( t \) up to 20 ps) this scheme describes the experimental results given in Figs. 1 and 2 in the paper by Holzapel et al. The absorption rises within the flash duration of 100 fs. The subsequent absorption change can be described in the first picoSecond by \( q(1-\exp(-t/T)) \) with \( t = 0.5 \text{ ps}, \alpha = 3 \times 10^{-4} \text{ eV} \) (case of Fig. 1 in ref 13), \( \alpha = -20 \times 10^{-4} \text{ eV} \) (case of Fig. 2a), and \( \alpha = 40 \times 10^{-4} \text{ eV} \) (case of Fig. 2b). The change after the first picoSecond can be described accordingly with \( t = 3 \text{ ps}, \alpha = -35 \times 10^{-4} \text{ eV} \) (case of Fig. 1), \( \alpha = 50 \times 10^{-4} \text{ eV} \) (case of Fig. 2a), and \( \alpha = -8 \times 10^{-4} \text{ eV} \) (case of Fig. 2b).

Acknowledgment. We are grateful to Dr. M. Plato for his INDO data and to the referee for drawing our attention to ref 10. Financial support by the Deutsche Forschungsgemeinschaft for E.V.K. is gratefully acknowledged.

Appendix

A system including three electronic levels is considered. There are the donor state \( \text{P}^* \) of the excited special pair, the state of the accessory bacteriochlorophyll \( \text{B}^* \), and the acceptor state \( \text{H}^* \). The intermediate molecule is assumed to drastically improve the electron transfer from the donor to the acceptor, being

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(9) This evolutionary concept was given in ref 8 and was later supported by X-ray and protein sequence analysis showing the presence of postulated pair of proteins and genetic relation.


Observation of ESR Spin Flip Satellite Lines of Trapped Hydrogen Atoms in Solid H₂ at 4.2 K

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(Received: March 20, 1989; In Final Form: August 30, 1989)

ESR spectra of H atoms, produced in γ-irradiated solid H₂, were studied at 4.2 K. Two main lines of the ESR spectra of H atoms that are separated by about 500 G accompanied two weak satellite lines. Both satellite lines and main lines decrease with the same decay rate. In the D₂-H₂ mixtures, the satellite-line intensity depends upon the number of matrix protons. The spacing of the satellites from the main line is equal to that of the NMR proton resonance frequency. It was concluded that the satellite lines were not ascribable to paired atoms but to spin flip lines due to an interaction of H atoms with matrix protons. The analysis of the spin flip lines and the main lines suggests that H atoms in solid H₂ are trapped in the substitutional site.

Introduction

The role of quantum mechanical tunneling in reactions H₂ (D₂, HD) + H (D) has been one of the important problems in the theory of chemical kinetics. When hydrogen atoms are produced by γ-iradiolysis of solid hydrogen at an ultra low temperature, the hydrogen atoms react with hydrogen molecules by tunneling. Miyazaki et al.¹⁻⁵ have obtained the following results on the


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