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Dynamics of electron transfer in the oxidation of water by chlorophyll *a* dimer

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The observed temperature dependence of the rate constant for reduction of (Chl $a \cdot 2H_2O)_2^{+}\cdot$ by water is fitted to a theoretical expression for the rate of an intramolecular electronic radiationless transition. The theory assumes a single effective mediating mode and the best-fit value for the frequency of this mode is $\omega_m = 680$ cm^{-1}, which corresponds to high-frequency, intermolecular librations in water. From an explicit calculation of the nonadiabatic-coupling matrix element, an average electron-transfer distance of 11 Å is obtained, consistent with molecular dimensions available for this system.

1. Introduction

Modern time-resolved spectroscopic techniques have permitted precise measurements of the rates of a variety of biochemical reactions [1–3]. Of particular importance are electron-transfer (ET) reactions in photosynthetic systems, which have been the subject of numerous experimental [4–8] and theoretical [9,10] investigations. Many of these reactions exhibit a marked non-Arrhenius temperature dependence indicative of quantum-mechanical tunneling. The present analysis is based on a generalized theory [11,12] for radiationless relaxation via quantum-mechanical tunneling, in which the nuclear motion induces a transition between the electronic states. A central assumption of the theory is that a single normal mode R_m of frequency ω_m mediates the transition. This approach has been successful in describing the relaxation of excited-state rare-earth ions in host crystals [11,12]. It has also been adapted to analyze hydrogen-atom transfer associated with the early events in vision [13].

An important experiment was performed by Fong et al. [14] in which they followed the photooxidation and subsequent dark decay of hydrated chlorophyll *a* (Chl *a*) aggregates (Chl $a \cdot H_2O)_{n \geq 2}$, by ESR techniques. The light-on light-off kinetic response of the ESR signal, attributed [14] to the reduction of (Chl $a \cdot 2H_2O)_n^{+}\cdot$ by water, exhibits two fast exponential components and one considerably slower second-order process. The two first-order processes are readily attributable to the reduction by water of dimeric and oligomeric radical cations [14]. The decay rates exhibit a non-Arrhenius temperature behavior reminiscent of electron transfer processes *in vivo* [4,5]. The temperature dependence of the fastest exponential process was examined in the temperature region from 90 to 300 K in a subsequent experiment [15]. This decay component was attributed [14] to the reduction of the dimer radical cation, (Chl $a \cdot 2H_2O)_2^{+}\cdot$, by water. The path of the one-electron oxidation of water is of great interest because of its role as precursor to oxygen evolution in water photolysis.

In this article, we present a quantum-mechanical two-state model calculation for the rate of electron transfer, W_{10}, which may be relevant to the primary events in photosynthesis. We assume the electron moves in an asymmetric double well, the lowest two states of which are localized near each minimum. Then, we describe the transfer as a transition from localized state ϕ_1 to localized state ϕ_0. This is accomplished by using projection-operator techniques [17,18] to derive a generalized master equation for the populations of the states ϕ_0 and ϕ_1. We solve this equation in the long-time, weak-coupling limit [18,19], and find that the population of state ϕ_1 decays exponentially with a time constant τ given by

$$\tau^{-1} = W_{10} = (\beta \langle N_1 \rangle)^{-1} \int_0^{\infty} \mathrm{d}t \int_0^{\beta} \mathrm{d}\lambda \langle \dot{N}_1(0) \times \dot{N}_1(t + \lambda i\hbar) \rangle \qquad (1)$$

Here $N_1 = |1\rangle\langle 1|$ is the occupation number of the initial electronic state, the brackets denote a canonical ensemble average, and $\beta = (k_B T)^{-1}$ where k_B is Boltzmann's constant.

To obtain a more explicit expression for W_{10}, we follow the prescription of Fong [11,12] for the treatment of electronic radiationless relaxation in condensed media. This requires that we first determine a set of unperturbed (zero-order) energy eigenstates of the system. In our model we shall find these states by invoking the adiabatic approximation, in which the motion of the electron is separated from that of all the nuclei. The significant rate parameters are: $\Delta\epsilon_{10}$, the difference between the minima of the potential-energy surfaces corresponding to the ground ($i = 0$) and first excited ($i = 1$) electronic states; ω_m, the normal mode frequency; g_m, which is proportional to the shift in the equilibrium position of the normal mode; C_{10}, which is proportional to the strength of the coupling between the electronic states.

In the present treatment the transitions between the zero-order electronic states are induced by the nuclear kinetic energy operator. This is different from the standard approach [9,10] which invokes the electron-exchange operator as the perturbation. The final electronic state, which involves the creating of a positive charge on the donor, results in a significant polarization and consequent reorganization of the solvent (waters of solvation) around the donor. This reorganization is reflected in the shift g_m of the equilibrium position of the solvent. In our treatment 'solvent reorganization' is automatically accounted for by the adiabatic states [12].

The basic assumptions underlying this approach are: (1) the heavy-nuclear motion is harmonic; (2) only a single mode mediates the process and (3) the normal modes in the initial and final states are parallel. In particular, under these restrictions the rate may be represented as [11,12]:

$$\begin{aligned} W_{10} = {} & \left[(2\pi)^{1/2} \hbar^{-2} L_m |C_{10}|^2\right] \sum_{\nu=-2}^{2} \lambda_\nu \\ & \times \left[\frac{\sinh(\beta\hbar\omega_m/2)}{L_m g_m^2 \omega_m^2 (x^2+1)^{1/2}}\right]^{1/2} \\ & \times \exp\left\{ -L_m g_m^2 (2\bar{n}+1) + \frac{\Delta_\nu}{\hbar\omega_m} \right. \\ & \times \left(1/2\hbar\beta\omega_m - \ln\left[x + (x^2+1)^{1/2}\right]\right) \\ & \left. + L_m g_m^2 \frac{(x^2+1)^{1/2}}{\sinh(\beta\hbar\omega_m/2)} \right\} \end{aligned} \qquad (2)$$

where

$$C_{10} = -\left(\hbar^3 \omega_m/2\right)^{1/2} \Delta\epsilon_{10}^{-1} V_{10} \qquad (3)$$

$$x = \Delta_\nu \frac{\sinh(\beta\hbar\omega_m/2)}{L_m g_m^2 \hbar\omega_m}; \ \nu = -2, -1, \ldots, 2 \qquad (4)$$

and

$$\Delta\epsilon_{10} = \epsilon_1(R_0) - \epsilon_0(R_0) \qquad (5)$$

where L_m and ω_m are, respectively, the degeneracy and frequency of the normal mode that mediates the electron transfer; V_{10}, the electronic coupling, is proportional to $\partial V/\partial R_m$ and is defined below (see eq. 11); R_0 is the equilibrium nuclear configuration in the initial state; ϵ_0 and ϵ_1 are, respectively, the Born-Oppenheimer eigenvalues of the initial and final electronic states; $V(r, R)$ is the potential energy, which includes all the electron-electron, nucleus-nucleus and electron-nucleus interactions; and $\bar{n}_m$ denotes the (thermal average) number of phonons mediating the electron transfer. The remaining quantities λ_ν, g_m and Δ_ν are explicitly given in the appendix. A more detailed discussion of the physical basis of this theory as well as a comparison with other approaches to electron-transfer problems can be found in ref. 12.

To evaluate eq. 2 we must determine the rate parameters $\Delta\epsilon_{10}$, C_{10}, ω_m and g_m. We do this by introducing a simple model for electron transfer in section 2.

2. Theoretical interpretation

Electron transfer from a water molecule to (Chl $a \cdot 2H_2O)_2^+ \cdot$ is reflected by the decay of the ESR signal of (Chl $a \cdot 2H_2O)_2^+$. Thus, the rate constant k_1 can be directly identified with the transfer rate, i.e., $k_1 = W_{10}$. We performed a Marquardt [20] nonlinear least-squares fit of the data in ref. 15 to the formula in eq. 2. An initial coarse-grid search in the full four-parameter ($\Delta\epsilon_{10}$, $\hbar\omega_m$, $L_m g_m^2$, $|C_{10}|^2$) space was first carried out to locate roughly the possible minima. Then a more refined search in the three-parameter subspace ($\Delta\epsilon_{10}$, $L_m g_m^2$, $|C_{10}|^2$) with $\hbar\omega_m$ fixed at various values over the range 590–700 cm^{-1} was conducted. The resulting sets of 'best' parameters are given in table 1.

Table 1

Numerical values of the effective parameters obtained from least-squares fits of eq. 2 to the experimental data in ref. 15

$\hbar\omega_m$ (cm^{-1})	$L_m g_m^2$	$\Delta\epsilon_{10}$ (cm^{-1})	$L_m \lvert C_{10}\rvert^2$ (ergs)^2	χ^2
544	3.781	2483	0.908×10^{-39}	0.471
670	3.850	2434	3.241×10^{-39}	0.057
680	3.859	2434	3.094×10^{-39}	0.022
700	3.744	2441	3.622×10^{-39}	0.027

To interpret the semi-empirical rate parameters of table 1, we introduce a simple model (see fig. 1) in which only the electron being transferred is considered explicitly. It is assumed to move in one dimension along a line between the donor D and the acceptor A. Moreover, we assume that D and A are specific atoms within the supermolecular complex (Chl $a \cdot 2H_2O)_2 \cdot (H_2O)_S$, where $(H_2O)_S$ collectively represents S water molecules of solvation. More precisely, we take the acceptor, A, to be the oxygen atom in the non-structural water at the Mg center of one of the chlorophylls and the donor water molecule D to be located in the solvation water associated with the C-9 keto group of the same chlorophyll. There is some experimental evidence supporting this particular choice [21]. The effective electron-nuclear potential energy is taken to be

$$V(r;\, r_D;\, r_A) = -\bar{V}_D \delta(r - r_D) - \bar{V}_A \delta(r - r_A) \tag{6}$$

where $\bar{V}_D$ and $\bar{V}_A$ are the respective strengths of the attractive delta-function interactions. The strengths are assumed not to depend on the relative positions of D and A.

The true Born-Oppenheimer electronic wavefunctions are those that diagonalize the one-electron Hamiltonian with the interaction, eq. 6. How-

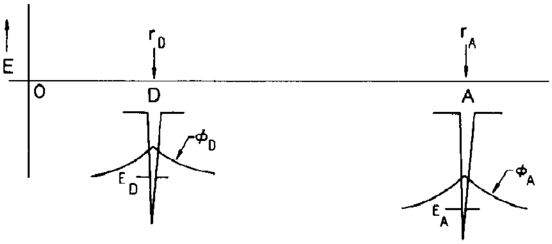

Fig. 1. Schematic diagram of one-dimensional electron transfer from a donor (D) to an acceptor (A). The distance of the delta-function potentials from an arbitrary origin O is denoted by r_D and r_A for the donor and acceptor, respectively. The relative energies of D and A are denoted by ϵ_D and ϵ_A, respectively. The wavefunctions, ϕ_A and ϕ_D, are defined by eq. 7.

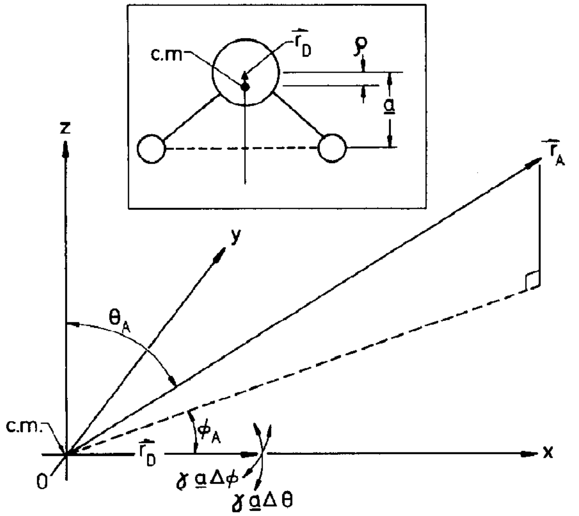

Fig. 2. Schematic diagram of librating water molecule, with center of mass (c.m.) at origin O, interacting with acceptor at $\vec{r}_A$. For simplicity of illustration, the oxygen end of water is placed along the x-axis and the hydrogens are in the x-y plane. The tip of $\vec{r}_D$ is at the center of a in the in-plane libration.

ever, if D and A are sufficiently far apart, then the wavefunctions are well approximated by the single states of the *isolated* delta-function wells [22]:

$$\phi_X(r;\, r_D,\, r_A) = (\alpha_X)^{1/2}\exp(-\alpha_X|r-r_X|),\quad X = \mathrm{D},\mathrm{A} \tag{7}$$

where the associated energies are

$$\epsilon_X = -\alpha_X^2\hbar^2/2m_e, \qquad X = \mathrm{D},\mathrm{A} \tag{8}$$

and

$$\alpha_X = m_e\bar{V}_X\hbar^{-2}, \qquad X = \mathrm{D},\mathrm{A} \tag{9}$$

and m_e is the electron's mass. Moreover, the donor site ($X = \mathrm{D}$) is associated with the first excited-state ($i = 1$) and the acceptor ($X = \mathrm{A}$) with the ground-state ($i = 0$).

Using eq. 3 we can rewrite the coupling constant as

$$|C_{10}|^2 \equiv |C_{DA}|^2 = \hbar^3\omega_m|V_{DA}|^2/(2M_m\Delta\epsilon_{DA}^2) \tag{10}$$

where

$$V_{DA} \equiv \int \phi_D(\partial V/\partial R_m)\phi_A\,\mathrm{d}r \tag{11}$$

and M_m is the mass of the normal mode. However, the mediating mode R_m is in general a function of all the atomic displacements, u_i, i.e.

$$R_m = \sum_i C'_{mi}u_i \tag{12}$$

where the C'_{mi} are constants (i.e., elements of the transformation matrix that diagonalizes the dynamical matrix in the harmonic approximation). Moreover, the inverse of eq. 12 is

$$u_i = \sum_j C_{ij}R_j \tag{13}$$

where R_j are the normal modes. Therefore, since V is a function only of the displacements of D and A, we have

$$\partial V/\partial R_m = C_{Dm}\,\partial V/\partial r_D + C_{Am}\,\partial V/\partial r_A \tag{14}$$

where

$$C_{Xm} \equiv \partial r_X/\partial R_m, \qquad X = \mathrm{D},\mathrm{A} \tag{15}$$

Combining eqs 7,8, 11 and 14 and integrating by parts, we obtain

$$V_{DA} = -\hbar^2 m_e^{-1}(\alpha_A\alpha_D)^{3/2}\mathrm{sgn}(r_D - r_A) \times\left[C_{Dm}e^{-\alpha_A|r|} - C_{Am}e^{-\alpha_D|r|}\right] \tag{16}$$

where $|r| = r_D - r_A$ and sgn(x) is 1 if $x > 0$ and -1 if $x < 0$.

An additional simplification is now introduced to permit an explicit evaluation of the transformation coefficients $C_{X\mathrm{m}}$. The best fit to the kinetic data shows that the promoting mode for electron transfer lies at 680 cm^{-1} (see table 1). Fourier transform infrared spectra indicate the presence of a broad, diffuse absorbance beginning at approx. 700 cm^{-1} which is ascribed to intermolecular librations in water clusters [23,24]. Therefore, we assume the mediating mode is a strictly localized intermolecular libration of a water molecule of solvation with a frequency of approx. 680 cm^{-1}. The maximum-frequency libration is chosen since it is the most efficient in mediating the relaxation [12]. The electron of the donor is assumed to be localized initially on the oxygen atom of the water. Fig. 2 shows a schematic diagram in which the center of mass of the water is at the origin. The orientation of the coordinate system is chosen so that the normal coordinates are the displacements along the indicated arcs. Only the librations with associated motion of the O atom can mediate electron transfer. These are $\underline{a}\Delta\Phi$ and $\underline{a}\Delta\theta$, where $\Delta\Phi$ and $\Delta\theta$ are angular displacements lying in the $x-y$ and $x-z$ planes, respectively, and $\underline{a}$ is the distance between the O atom and the midpoint of a line connecting the H atoms (see fig. 2).

Recall that, in deriving eq. 16, we have assumed that A and D move along the same straight line, i.e., the motion has been treated as though the system were in one physical dimension (see fig. 1). We take r_D to be the projection of $\vec{r}_D$ onto the vector $(\vec{r}_A - \vec{r}_D)$ between D and A. Furthermore, from the definition of center of mass we have

$$|\vec{r}_D| = \rho = \gamma \underline{a} \tag{17}$$

where

$$\gamma = 2m_H/(m_O + 2m_H) \tag{18}$$

and ρ is the distance between the center of mass of the water and the oxygen atom (fig. 2). Since $\gamma = 1/9$ and $\underline{a} \approx 0.6$ Å, $r_D \ll r_A$ and we can replace the difference vector simply by $\vec{r}_A$. From fig. 2, we have

$$\vec{r}_A = r_A\left[\sin\theta_A \cos\Phi_A \hat{\imath} + \sin\theta_A \sin\Phi_A \hat{\jmath} + \cos\theta_A \hat{k}\right] \tag{19}$$

and

$$\vec{r}_D = \rho[\hat{\imath} + \Delta\Phi\hat{\jmath} + \Delta\theta\hat{k}] \tag{20}$$

then, the projection of $\vec{r}_D$ onto $\vec{r}_A$ is

$$r_D \approx \rho[\sin\theta_A \cos\Phi_A + \sin\theta_A \sin\Phi_A \Delta\Phi + \cos\theta_A \Delta\theta] \tag{21}$$

From eqs 15 and 21 we calculate the rate of change of r_D with the librational normal mode $R_m = \underline{a}\Delta\Phi$:

$$C_{D\mathrm{m}} = \gamma \sin\theta_A \sin\Phi_A \tag{22}$$

and the librational mode $R_m = \underline{a}\Delta\theta$:

$$C_{D\mathrm{m}} = \gamma \cos\theta_A \tag{23}$$

The other coefficient $C_{A\mathrm{m}}$ is zero, as the acceptor is not involved in the mediating mode. Combining eqs. 16 and 22, we have

$$|V_{DA}|^2 = \hbar^4 m_e^{-2} (\alpha_A\alpha_D)^3 \gamma^2 \sin^2\theta_A \sin^2\Phi_A \times \exp(-2\alpha_A|r|) \tag{24}$$

Furthermore, we assume that the waters are randomly oriented. Then, averaging over all the solid angle (θ_A, Φ_A), we obtain the average transfer matrix element:

$$|V_{DA}|^2 = \hbar^4 (\alpha_A\alpha_D)^3 \gamma^2 e^{-2\alpha_A|r|}/3m_e^2 \tag{25}$$

The above model is now used to estimate the electron-transfer distance. Combining eqs 10 and 25, we have

$$|C_{DA}|^2 = \mathrm{const} \times e^{-2\alpha_A|r|} \tag{26}$$

where

$$\mathrm{const} \equiv \hbar^7 \omega_m (\alpha_A\alpha_D)^3 \gamma^2 / 6M_m \Delta\epsilon_{DA}^2 m_e^2 \tag{27}$$

We estimate ϵ_D, which is essentially the ionization potential of an H_2O molecule in a water cluster, using the Born-Haber cycle. The value [25] of -4.11 eV for the hydration enthalpy of Na^+ is assumed for that of H_2O^+, and $\epsilon_D = 7.3$ eV is obtained. From the best-fit value of $\Delta\epsilon_{DA} = 2434$ cm^{-1} (table 1), we have $\epsilon_A = 7.6$ eV, which corresponds to $\alpha_D = 1.22 \times 10^8$ cm^{-1} and $\alpha_A = 1.26 \times 10^8$ cm^{-1}. Finally, taking M_m to be the reduced mass associated with water libration, i.e., $M_m =$

$2m_Hm_O/(2m_H + m_O) = 2.95 \times 10^{-24}$ g, we arrive at the electron transfer distance $|r| = 11.0$ Å. The average electron-transfer distance of 11 Å obtained above is consistent with the picture of electron transfer from a donor water molecule associated with the free C-9 keto carbonyl of (Chl $a \cdot 2H_2O$) to the radical macrocycle through a non-structural water complexed to the Mg atom of the Chl *a* molecule containing this carbonyl group.

3. Discussion

The electron-transfer process treated in this work has a lifetime on the order of 10^{-1} s, and five orders of magnitude larger than that, 10^{-6} s, for the reduction of P680$^+$ by electrons from water splitting [1] [26]. If the present model is also applicable to the in vivo reduction of P680$^+$, then we need to rationalize the great difference in these lifetimes. It has been well documented [12] that W_{10} depends sharply on the parameters $\hbar\omega_m$, Lg_m^2 and $\Delta\epsilon_{10}$. Here we note, in addition, that W_{10} can also be greatly enhanced by shortening $|r|$, the electron-transfer distance, by virtue of the exponential dependence in eq. 26 of $|C_{DA}|^2$ on $|r|$. On halving $|r|$, from 11 to 5.5 Å, W_{10} is increased by seven orders of magnitude, which would fall in the range of rates compatible with that observed for P680$^+$ reduction. The value of $|r| \approx 5$–6 Å for the electron-transfer distance seems reasonable, although a direct measurement of this value is unavailable.

The polarization and subsequent reorganization of the waters of solvation are reflected in the shift g_m^2 (see table 1) of the equilibrium orientation of the liberating water. Thus, the role of libration would be analogous to polarization reorganization around the donor as in the sense of other electron-transfer theories. Moreover, in the limit of very low temperatures ($T \to 0$), where the donor and acceptor nuclei can be considered as 'frozen', the rate yields a constant nonzero value [13] in agreement with other theories [9,10].

Finally, an important assumption of our model is to approximate the Born-Oppenheimer electronic states by the states of the isolated donor and acceptor. We argue that this should be a good approximation as long as D and A are well separated, as they turn out to be in this particular case. In general, however, if D and A are close together, it is necessary to use the true electronic states that take proper account of the electron-exchange interaction.

Appendix

In deriving eq. 2 we assume that the heavy nuclei oscillate harmonically about fixed equilibrium positions. In addition, the rate expression, eq. 2, takes into account only a single mode (m), with which are associated the parameters given in eqs A1–A5.

$$p_m \equiv \Delta\epsilon_{10}/\hbar\omega_m \tag{A1}$$

and

$$\begin{aligned}
\lambda_{-2} &\equiv g_m^2 \bar{n}_m^2 \\
\lambda_{-1} &\equiv -2g_m^2(2\bar{n}_m + 1)\bar{n}_m + \bar{n}_m \\
\lambda_0 &\equiv g_m^2[6\bar{n}_m(\bar{n}_m + 1) + 1] \\
\lambda_1 &\equiv -2g_m^2(2\bar{n}_m + 1)(\bar{n}_m + 1) + \bar{n}_m + 1 \\
\lambda_2 &\equiv g_m^2(\bar{n}_m + 1)^2
\end{aligned} \tag{A2}$$

Furthermore, the parameter g_m is a dimensionless displacement that is proportional to R_m.

$$g_m \equiv (\omega_m/2\hbar)^{1/2} R_m \tag{A3}$$

$$\bar{n}_m = (\exp(\beta\hbar\omega_m) - 1)^{-1} \tag{A4}$$

and, finally

$$\Delta_\nu \equiv \Delta\epsilon_{10} - \nu\hbar\omega_m \tag{A5}$$

where $\bar{n}_m$ is the Bose–Einstein distribution number of the effective mediating mode.

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[1] P680 denotes the electron-donor pigment in green plant photosynthesis that absorbs light with a red maximum in the vicinity of 680 nm.

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