ON THE MECHANISM OF THE PRIMARY CHARGE TRANSFER IN PHOTOSYNTHESIS

David Chandler, John N. Gehlen and Massimo Marchi *
Department of Chemistry, University of California
Berkeley, CA 94720

ABSTRACT

A computer simulation model of a photosynthetic reaction center due to Marchi, Gehlen, Chandler and Newton (MGCN) provides information about the mechanism for the primary electron transfer in photosynthesis. According to the model, a two step mechanism for the primary electron transfer is not plausible, and the process must occur through a super-exchange pathway. Nevertheless, the kinetics can be nontrivial. In particular, time correlation functions obtained from the MGCN model for some of the dynamical variable pertinent to the primary process exhibit complex relaxation on the same time scale as the primary transfer.

I. INTRODUCTION

This paper discusses some of the results and predictions arrived at through the Marchi-Gehlen-Chandler-Newton (MGCN) model of a photosynthetic reaction center.1 We emphasize those aspects which pertain to the primary charge transfer kinetics.

The MGCN model is based upon a molecular dynamics simulation of Rps. viridis to estimate averages and fluctuations of electrostatic potentials in a proteic complex. Since these quantities are computed from classical dynamics, they must be renormalized or scaled in a way which accounts for electronic polarizability of the system. The scaled averages and fluctuations are combined with information from quantum chemical calculations2 for on-site energies to arrive at the diabatic surfaces controlling the primary charge transfer. These surfaces are described in Sec. II.

Nuclear relaxations found in the MGCN model are described in Sec. III. These are of two types. Energy gap fluctuations occur on a subpicosecond time scale. Inter-ring vibrations have components on a post picosecond time scale. The faster of these motions are manifested in the large tunneling contribution (14 powers of ten!) to the measured recombination rate. The slower motions are on same time scale as the primary transfer kinetics. Hence, they play a role in the nonexponential relaxation observed for that process.

* Present and permanent address: Section de Biophysique des Proteines et des Membranes, Departement de Biologie Cellulaire et Moléculaire, C.E. Saclay, 91191, Gif-Sur-Yvette, France.
Fig. 1: Schematic illustrating the chromophores involved in the primary electron transfer event in a bacteriophotolytic reaction center. The photoexcited special pair (SP*) is called electronic state 1. A charge separated state, SP*-BCL−, with an electronic charge localized on the bacteriophylophyl of the L branch, is called state 2. The observed primary charge transfer state, SP*-BPL−, where the electron is localized on the bacteriophylophyll of the L branch is called state 3. The corresponding unobserved charge separated states on the inactive M branch are called states 2' and 3'. The energy gap between states 1 and 3, $\mathcal{E}$, is the collective nuclear variable that is the primary coordinate controlling the primary electron transfer, $1 \rightarrow 3$. The diabatic free energy functions in this coordinate for the three states 1, 2 and 3 were determined by our calculations to be the functions graphed at the bottom left. Our results for the corresponding free energies of the M branch are shown at the bottom right as a function of the $1 \rightarrow 3'$ energy gap, $\mathcal{E}'$. [These results from Ref. 1.]
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We conclude with a brief Discussion in Sec. IV.

II. DIABATIC SURFACES

The diabatic surfaces for the MGCN model of the photosynthetic reaction center are shown in Fig. 1, along with a schematic description of the system. One sees that the primary charge transfer following photoexcitation, i.e., the electronic transition $1 \rightarrow 3$, is predicted to be a nearly activationless process, in agreement with experiment. The $1 \rightarrow 3'$ process is predicted to be endothermic, which is consistent with experiment in that it implies inactivity of the M branch. One also sees that state 2, corresponding to the electron localized on the accessory bacteriochlorophyll, is predicted to lie at energies far above the intersection of states 1 and 3. This arrangement excludes the possibility of a two step mechanism, a possibility about which much speculation exists in the literature. The issue has not yet been resolved experimentally. Owing to the predicted placement of the state, the primary charge transfer must occur in the model via virtual transition, i.e., by a super-exchange pathway.

According to that mechanism, an electron transfer rate constant would be

$$k_{1 \rightarrow 3} \approx \frac{2 \sqrt{\epsilon}}{h} K^2_{\text{eff}} \left( \langle \delta \epsilon \rangle^2 \right)^{1/2},$$

where $\langle \delta \epsilon \rangle^2$ is the mean square 1-3 energy gap, average in state 1, and $K_{\text{eff}}$ is the effective 1-3 coupling given by

$$K_{\text{eff}} = \left( \frac{H_{12} H_{23}}{\Delta E_{12}} \right)^*.$$

Here, $H_{12}$ and $H_{23}$ are the near-neighbor electronic couplings, and $\Delta E_{12}$ is the 1-2 energy gap. The asterix indicates evaluation at the surface of 1-3 intersection. According to this formula, $H_{12} = H_{23} = 200 \text{ cm}^{-1}$ would yield a rate of roughly one transfer per mole every 1 to 10 ps. This is the time scale for the observed primary electron transfer. A typical value of 200 cm$^{-1}$ for the electronic couplings may seem reasonable, but it is considerably higher than numbers estimated by others.

Due to uncertainties in the electronic couplings, it is important to consider predictions of the MGCN model that are independent of these couplings. Two additional predictions considered in Ref. 1 which are of this type are the temperature dependence of the primary rate and the relative size of the singlet recombination rate to the unexcited SP (a process which occurs naturally if subsequent electron transfer steps are blocked). Both of these quantities must be computed from a quantum mechanical treatment of the spectral density fluctuations. At low temperatures this treatment is necessary due to the importance of zero point motions. A classical calculation predicts that an
activationless rate increases with lowering temperature according to \( k \propto \langle \delta E \rangle^2 \langle 1/\sqrt{T} \rangle \). A quantum calculation\(^1\) shows, however, that the rate increases by only a factor of 2 or 3 in going from room temperature to cryogenic temperatures. For the recombination or back reaction, a quantal analysis is necessary because the ground state surface intersects state 3 in the extreme inverted region, and in that region, nuclear tunneling can be important. A classical calculation would predict a back reaction 10\(^{-20}\) times slower than the forward reaction. A quantum calculation\(^1\) shows that nuclear tunneling enhances the back rate by fourteen orders of magnitude yielding a relative rate of 10\(^{-4}\).

The quantum mechanical calculations have been done approximately, assuming the energy gap fluctuations obey linear response. We have shown that this is a reasonable approximation in this proteic system.\(^1\) In that case, the spectral density for the energy gap fluctuations can be obtained from the Fourier transform of the energy gap auto correlation function. In a truly linear system, this spectral density is independent of temperature, and a classical molecular dynamics evaluation of the spectral density is appropriate. Figure 2 shows a spectral density so obtained. Next, one may apply the standard quantum mechanical formula which relates the electron transfer rate constant to
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the spectral density.\textsuperscript{3} This formula is correct to the extent that the energy gap response is indeed linear, and that a rate constant is well defined. This latter condition is perhaps problematical, as we discuss later. Applications of the formula to compute both the temperature dependence of the primary rate and the relative back rate agree reasonably well with experiment.\textsuperscript{1}

Incidentally, in view of Fig. 2, it is clear that no single mode dominates the energy gap fluctuations. These fluctuations are truly collective variables with a significant fraction of the entire proteic complex contributing.

One may wonder if these results are very sensitive to the type of molecular detail included in the computer simulated model of \textit{Rps. viridis}. A reasonably complete sensitivity analysis has not yet been done. However, the rough positioning of the diabatic surface can be understood from dielectric continuum arguments.\textsuperscript{2} This result may suggest that the behavior exhibited in Figs. 1 and 2 are relatively generic, and reasonably insensitive to features such as the amino acid charge states (which are generally unknown for these proteic complexes). Nevertheless, it should be mentioned that others have carried out molecular modeling of reaction centers and arrived at results very different than those shown here.\textsuperscript{4,5} There are many possible reasons as to why they have arrived at results different from ours — including short runs,\textsuperscript{4} neglect of polarization effects,\textsuperscript{4} truncation of Coulomb potentials,\textsuperscript{4,5} and assumed transferability of redox potentials.\textsuperscript{5}

III. RELAXATION

Figure 3 shows the autocorrelation function for the 1-3 energy gap fluctuations in the MGCN model at room temperature. The primary relaxation is on a subpicosecond time scale. The consequences of this behavior on the electron transfer kinetics can be understood from a surface hopping model.

In particular, suppose there is a probability, \( p \), that a 1-3 transition will occur whenever the 1-3 energy gap, \( \varepsilon \), is zero. Then, the survival probability of state 1 after a time \( t \) is given by

\[
S(t) = \left\langle (1 - p)^{N(t)} \right\rangle ,
\]

where \( N(t) \) is the number of times the \( \varepsilon = 0 \) surface is crossed in a trajectory of time length \( t \). The indicated average is an equilibrium average over trajectories initiated in the state 1. At long times, \( N(t) \) is extensive in \( t \). For all times, \( \langle N(t) \rangle / t \) is independent of time. The survival probability can be rewritten as

\[
S(t) = \exp \left\{ \langle N(t) \rangle \ln(1 - p) + \frac{1}{2} \langle (\delta N(t))^2 \rangle \ln^2(1 - p) + \ldots \right\}
\]

\[
= \exp[-kt + D(t)] ,
\]
Fig. 3: The 1-3 energy gap time correlation function, \( C(t) = (\delta \varepsilon(t) \delta \varepsilon(0))_1 \), of the photosynthetic reaction center at room temperature. The mean square fluctuation is \( \langle (\delta \varepsilon)^2 \rangle_1 = (7.23 \text{ kcal/mole}) k_B T \). These results are from Ref. 1.

where

\[
k = p \langle N(t) \rangle / t .
\]

(5)

The quantity \( D(t) \) is of the order of \( p^2 \). With the linear response approximation, it can be expressed in terms of the spectral density of energy gap fluctuations.\(^4\) For the purposes of the present discussion, however, it suffices to note that for large \( t \)

\[
D(t) \sim p^2 \langle [\delta N(t)]^2 \rangle ,
\]

(6)

which is linear in \( t \) because \( N(t) \) is extensive in that regime. "Large \( t \)" means times long enough for energy gap fluctuations to relax.

In view of these formulas and Fig. 3, it would appear that the population of the initial photoexcited state 1 will relax exponentially on time scales of
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\[ \frac{\langle \delta r(0) \cdot \delta r(t) \rangle}{\langle (\delta r)^2 \rangle} \]

Fig. 4: The autocorrelation function for \( r(t) \), the vector between the centers of the special pair bacteriochlorophyll, SPL, and the accessory bacteriochlorophyll, BCL, in a photosynthetic reaction center at room temperature. The mean square fluctuation is \( \langle (\delta r)^2 \rangle_1 = 0.128 \text{Å}^2 \).

roughly a picosecond or longer. Further, if \( p \) times the energy gap relaxation time is small compared to \( k^{-1} \), then the rate constant is simply \( k \) of Eq.(5). It coincides with the classical golden rule rate constant. Whether the energy gap correlations are indeed negligible beyond a picosecond requires further analysis of the MGCN model.

While the energy gap fluctuations seem relatively fast, other nuclear motions exhibit correlations on post picosecond time scales. Some of these motions are pertinent to the primary electron transfer kinetics. Specifically, the separation of adjacent chromophores. Figure 4 shows that these distances vibrate as underdamped oscillations with a period of around 2ps. Low frequency motions of this time scale seem to be detected in experimental probes of the primary transfer kinetics.\(^7\) Interring distances can enter into the kinetics through the electronic couplings, Eq.(2). These matrix elements depend sensitively upon the distances between adjacent redox centers.
As such, an appropriate kinetic model for time scales of 1 ps or longer is

\[ S(t) = \left\langle \exp \left[ - \int_0^t dt' k(t') \right] \right\rangle \]  \hspace{1cm} (7)

where \( k(t) \) is the rate "constant" given by Eq. (1) with \( K_{\text{eff}} \) varying in time as neighboring chromophores move in time. Quantitative applications of Eq. (7) requires models for the dependence of the electronic couplings on chromophore configurations. Qualitatively, we may anticipate predictions of nonexponential kinetics through the cumulant estimate

\[ S(t) \approx \exp \left[ - \langle k \rangle t + \int_0^t dt' \langle t - t' \rangle \delta k(0) \delta k(t') \right] \]  \hspace{1cm} (8)

There have been suggestions that observed non exponential kinetics may be due to an inhomogeneous distribution of thermodynamic driving forces.\(^5\) The literal interpretation of this suggestion contrasts with the dynamical model, either Eqs. (4) or (7). The near linear response relaxation of the MGCN model\(^1\) is contrary to the inhomogeneity hypothesis.

We hope to soon present results based upon Eqs. (4) and (7) and the molecular dynamics of the MGCN model.\(^6\)

IV. DISCUSSION

The rapid primary electron transfer of the photosynthetic reaction centers involves an interplay between nuclear and electronic time scales. The coherence between these motions will increase as one lowers temperature from the room temperature case considered in Sec. III. Indeed, the dephasing time of energy gap fluctuations can, at low enough temperatures, exceed 1 ps. This issue as well as the quantal nature of fluctuations will be important to analyze in a quantitative treatment of low temperature kinetics.

It seems that many of the experimental observations concerning the electron transfer in the photosynthetic reaction center can be treated theoretically without addressing the precise nature of the electronic couplings between chromophores. It illustrates the power of Marcus' general view of electron transfer processes. Nevertheless, a full treatment requires knowledge of this coupling — including the quantitative analysis of the primary transfer kinetics, as discussed at the end of Sec. III. We hope that accurate calculations of these couplings will soon be carried out.

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