Electronic Energy Transfer in Photosynthetic Bacterial Reaction Centers

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Abstract. We present simulations of energy transfer in reaction centers of the purple bacteria Rhodopseudomonas viridis and Rhodobacter sphaeroides. Calculations using a weak coupling model based on Förster's theory give transfer rates that are at least an order of magnitude slower than the results from recent femtosecond transient absorption studies. The discrepancy between experimental and theoretical results is discussed in terms of the various assumptions upon which the model is based.

1. INTRODUCTION

Most studies of energy transfer in photosynthetic systems start with the assumption that the electronic excitation, or exciton, migrates among chromophores in an incoherent (i.e., random walk) fashion until it is either trapped or decays radiatively. The question of exciton coherence has been discussed in the context of photosynthesis, however, no application of these ideas to specific photosynthetic systems has been made. The relevant electronic states are assumed to be localized on individual pigments and to interact through dipole–dipole coupling. Such a picture along with the assumption of fast vibrational dephasing allows one to describe energy transport as a classical kinetic process. The rate constants for site-to-site transfer are generally calculated from the Förster's standard very weak coupling approach.

The success of the weak coupling theory in describing energy transfer rates in a variety of systems is well known; however, recent experiments have cast some doubt as to its validity in certain photosynthetic systems. Among these are circular dichroism (CD) studies that show exciton interactions as large as 100–200 cm⁻¹ in the antenna complex of Prosthecochloris aestuarii⁵ and the observation of ultrafast energy transfer in the chlorophyll (Chl) a/b protein⁶ and in isolated reaction centers of Rhodopseudomonas viridis and Rhodobacter sphaeroides.⁷ The lack of structural information on all but a handful of photosynthetic systems makes it difficult to obtain a detailed picture of the energy transfer process. Fluorescence decay measurements address only the overall trapping kinetics rather than the actual mechanism of transfer between two sites.

The recent determination of the structures of reaction centers from the purple bacteria Rps. viridis⁸ and Rb. sphaeroides⁹ has provided theorists with a precise physical model for developing a microscopic understanding of energy and electron transfer in these systems.

While much attention has been devoted to the study of electron transfer in Rps. viridis and Rb. sphaeroides, only recently have attempts been made to measure the rate of energy transfer.⁵⁶ Though these studies do not probe the interactions between charge-separated states, an understanding of the nature of the optically allowed states is essential in order to know what is prepared and measured in kinetic spectroscopic experiments. Using femtosecond transient absorption spectroscopy, Breton et al.⁵ found that excitation transfer from any of the accessory pigments to the primary electron donor state occurred in less than 100 fs. More recent studies⁵ found this to be true over the temperature range 10 – 300 K. These results suggest that the separation of time scales between vibrational relaxation and transfer, inherent in the description of energy transport as an incoherent hopping process, may not be valid. Indeed, one would not expect energy and phase relaxation times to be much faster than 100 fs. Recent experiments by Shank and coworkers⁹ determined dephasing times in the dye molecules cresyl violet and Nile blue to be 75 fs and 85 fs, respectively. Assuming that the absorption bands in the 10 K absorp-

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tion spectrum of *Rps. viridis* (see Fig. 2) contain no in-
homogeneous contribution to the lineshape, the width of
the bands (~190 cm$^{-1}$) put a lower limit of ~30 fs on the
dephasing time. While a weak coupling approach un-
doubtedly appears to be unwarranted, it is nevertheless
important to demonstrate this fact and to estimate the
magnitude of the error through simulations. This pro-
vides a starting point for building a more precise model
of the transfer process.

Calculation of dipole coupling matrix elements using
the point dipole approximation gives interaction ener-
gies as large as 120 cm$^{-1}$ between adjacent pigment
molecules in bacterial reaction center complexes. These
are consistent with those obtained from CD spectra of
light harvesting complexes from higher plants, as men-
tioned earlier. Coupling elements of this magnitude in-
dicate an appreciable mixing of the individual pigment
states, thus making the monomer electronic states a
seemingly poor basis for carrying out calculations of
energy transfer rates using first-order perturbation
theory.

In this paper, we present results from Master equation
simulations of energy transport in *Rps. viridis* and *Rb.
sphaeroides* based on Förster's weak coupling theory. As
we shall see, the use of monomer spectral data and X-ray
data to calculate the site-to-site transfer rates leads to
energy transfer times which are at least an order of mag-
nitude slower than those obtained by femtosecond
photobleaching experiments. The quantity of interest in
these simulations is the time-dependent population of the
low energy exciton band of the bacteriochlorophyll di-
mer. It is apparent from viewing the absorption spectrum
shown in Fig. 2 that direct transfer of energy from any of
the accessory pigments to the lower exciton state cannot
occur through the Förster mechanism; the spectral over-
lap is negligible. Energy transfer via this mechanism
must involve the upper exciton state, which carries only
10-20% of the total oscillator strength of the dimer. In
the next two sections, we discuss the six-state model
used in our simulations and relevant aspects of the weak
coupling theory. Results and Discussion are presented in
Section 4.

2. REACTION CENTER MODEL

The reaction centers of *Rps. viridis* and *Rb. sphaeroides*
have remarkably similar structures as far as the location
of the pigments is concerned. The six pigments compris-
ing the core of the reaction center are arranged in ap-
proximate C$_2$ symmetry on two polypeptide units known
as the L and M branches. Each branch consists of two
bacteriochlorophyll (BChl) molecules and a bacterio-
photophtyn (BPh) molecule. Two of the BChl molecules,
one on each branch, form a strongly interacting dimer,
which, when excited in the lower exciton (P$_0$) band,
becomes the primary electron donor. The structure of the
chromophores in the reaction center of *Rb. sphaeroides*
is shown in Fig. 1.

The electronic states involved in the energy transfer
experiments are the Q$_y$ (S$_0$ $\rightarrow$ S$_1$) transitions on the
individual chromophores. The low temperature optical ab-
sorption spectrum of *Rps. viridis* in this region of the
spectrum is shown in Fig. 2. Assignments based on linear

![Fig. 1. Structure of the chromophores in the reaction center of *Rb. sphaeroides*. Distances are in angstroms.](image)

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Our model for energy transport in reaction centers consists of four Qₐ states, two BPhs and two BCHls, interacting with one another and the two exciton states of the special pair through a dipole-dipole mechanism. The transition dipole strengths for BCHl a and BPh a are taken as 41 D² and 39 D², respectively. For BCHl b and BPh b we use 30 D² and 19 D² (see Ref. 15). Knapp et al. used transition dipole moments of 45 D² and 30 D² in order to accurately reproduce the CD spectrum of *Rps. viridis*. We also present results using these values. The transition dipole moment of 10 D² for the upper exciton band, P, was determined by using the angle between the Qₐ transition moments of the monomers and a monomer transition dipole of 45 D². The absorption and fluorescence lineshapes are assumed to be Gaussian with the widths obtained from literature values. The spectral parameters used in our calculations are summarized in Table 2. The transition dipole directions are defined by the pyrrole nitrogen atoms on rings I and III of the porphyrin macrocycles. The distance between pigments is taken as the distance between the midpoints of the vectors connecting the same two nitrogen atoms. The rate constant for transfer between any two pigments is calculated using the spectral overlap integral defined by Förster. Since the position of the individual emission bands in vivo has not been measured (energy transfer is too fast), we take the position of the relaxed Qₐ states to be that calculated from the in vivo absorption spectra and the value of the Stokes shift of the monomer in ether solution. The large exciton interaction in the special pair gives rise to a lower exciton band which is substantially red-shifted from the remainder of the bands. The spectral overlap between this band and the individual emission components is negligible; thus in our model internal conversion from the P band provides the only process which feeds excitation to the lower exciton state. The internal conversion rate has not been measured, so in our model it is an adjustable parameter; however, for

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1. BChl = bacteriochlorophyll; BPh = bacteriopheophytin; L = L-branch polypeptide; M = M-branch polypeptide.
2. Ref. 17; diethyl ether. 3. Ref. 14; acetone. 4. Ref. 15. 5. Ref. 16.
6. Estimated from μ = 45 D² (1 – cos α); α = 37°.

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Table 1. Assignment of Absorption Bands in Bacterial Reaction Centers

<table>
<thead>
<tr>
<th>Species</th>
<th>λ (nm)</th>
<th>Assignment¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Rps. viridis</em></td>
<td>790</td>
<td>BPhₐ</td>
</tr>
<tr>
<td></td>
<td>805</td>
<td>BPhₐ</td>
</tr>
<tr>
<td></td>
<td>834</td>
<td>BCHlₐ/BChlₐ</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>965</td>
<td>P</td>
</tr>
<tr>
<td><em>R. sphaeroides</em></td>
<td>758</td>
<td>BPhₐ/BPhₐ</td>
</tr>
<tr>
<td></td>
<td>803</td>
<td>BCHlₐ/BChlₐ</td>
</tr>
<tr>
<td></td>
<td>815</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>870</td>
<td>P</td>
</tr>
</tbody>
</table>

Table 2. Spectral Properties of Monomeric Pigments and Dimer States

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>μ² (Debye²)</th>
<th>Δω (FWHM cm⁻¹)</th>
<th>Stokes shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCHl a</td>
<td>41.0⁶</td>
<td>535</td>
<td>190</td>
</tr>
<tr>
<td>BPh a</td>
<td>39.0⁴</td>
<td>555</td>
<td>260</td>
</tr>
<tr>
<td>BCHl b</td>
<td>30.0⁴ (45.0⁶)</td>
<td>535</td>
<td>190</td>
</tr>
<tr>
<td>BPh b</td>
<td>19.0⁴ (30.0⁶)</td>
<td>555</td>
<td>260</td>
</tr>
<tr>
<td>P</td>
<td>10.0⁴</td>
<td>300</td>
<td>–</td>
</tr>
</tbody>
</table>

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reasons discussed earlier, the lower limit for this process is \(-30\) fs. As we shall see, however, the actual value for the rate constant matters little since energy transfer from the accessory pigments to the P state is the rate-limiting step in populating the primary donor state.

3. THEORY

We assume that exciton migration among the six states in our model occurs through an incoherent mechanism and solve for the occupation probabilities of the individual sites. This involves finding the solution to the following set of coupled differential equations known as the Pauli Master equation\(^1\)

\[
\frac{dP_i(t)}{dt} = \sum_{j=1}^{6} F_{ij} P_j(t) \left( P_i + \frac{1}{\tau_i} \right) P_i(t). \tag{1}
\]

\(F_{ij}\) is the rate constant for transfer from site \(j\) to site \(i\), \(P_i(t)\) is the time-dependent probability of finding the exciton on the \(i\)th site. \(\tau_i\) represents the time constant for any decay process, other than energy transfer, from the \(i\)th state. When \(i\) corresponds to the lower exciton state, \(1/\tau_i\) is the rate constant for primary charge separation. We disregard radiative decay of the exciton since it is slow on the time scale of our simulation results (\(-5\) ps).

It is convenient to transform Eq. (1) to matrix-vector notation. We thus have

\[
\dot{P}(t) = W \cdot P(t), \tag{2}
\]

where \(P(t)\) is a vector of site occupation probabilities and \(W\) is a matrix of site-to-site transfer rates with the individual elements given by

\[
W_{ij} = (1 - \delta_{ij})F_{ij} - \delta_{ij} \sum_{k=1}^{6} F_{ik} + \frac{1}{\tau_i}. \tag{3}
\]

Eq. (2) is solved subject to the initial condition \(P(0)\)

\(\text{(i.e., the initial position of the exciton)}\) through numerical diagonalization of the rate matrix. The solution is

\[
P(t) = \mathbf{G}(t) \cdot P(0), \tag{4}
\]

where \(\mathbf{G}(t) = \exp(Wt)\) is the Green's function of the system. The matrix elements, \(G_{ij}(t)\), give the probability that the exciton occupies the \(i\)th site given that it occupied the \(j\)th site initially. The elements of Green's function matrix are given by

\[
G_{ij}(t) = \sum_{k=1}^{6} T_{ik} \exp(\lambda_k t) T_{kj}. \tag{5}
\]

where \(T\) is the matrix of eigenvectors and \(\lambda_k\) the eigenvalues. The structure of \(W\) guarantees that all the eigenvalues are negative. The rate matrix elements are calculated from the overlap of the fluorescence spectrum of the donor and absorption spectrum of the acceptor as in Ref. 19:

\[
F_{ij} = \frac{4\pi^2(10^{-21})}{h^2c^2n^2R_0^6} K^2 \int_0^\infty \mu_i^2(\omega)\mu_j^2(\omega) d\omega, \tag{6}
\]

where the orientation factor, \(K^2\), is given by

\[
K^2 = (u_i \cdot u_j - 3(u_i \cdot r_j)(u_j \cdot r_j))^2. \tag{7}
\]

\(u_i\) and \(u_j\) are unit vectors in the direction of the transition dipole moments and \(r_j\) is the unit vector along the line connecting the centers of the two chromophores. \(R_0\) is the actual center-to-center distance, and \(n\) is the refractive index of the protein environment, taken to be 1.33.\(^{26}\) The overlap integral in Eq. (6) is written in terms of the transition dipole moments, rather than the more usual form involving the molar extinction coefficient and fluorescence lifetime. If we assume Gaussian lineshapes, the spectral overlap can be evaluated analytically. We thus have

\[
\mu_i^2(\omega) = \mu_i^2(\omega_0) \exp[-(\omega - \omega_0)^2/2\sigma_i^2], \tag{8}
\]

where \(\omega_0\) denotes the peak frequency and \(\sigma\) the width of the band. \(\mu_i^2(\omega_0)\) is chosen so that

\[
\int_0^\infty \mu_i^2(\omega) \exp[-(\omega - \omega_0)^2/2\sigma_i^2] d\omega = \mu_i^2(\exp^t). \tag{9}
\]

The final result for the rate constant can be written in terms of the width and the energy gap, \(\Delta\), between the peak positions of the monomer absorption and emission spectra:

\[
F_{ij} = \frac{4\pi^2(10^{-21})}{h^2c^2n^2R_0^6} K^2 \frac{\mu_i^2\mu_j^2}{2\pi\sigma_0\sigma_j} \left( \frac{1}{2\sigma_i^2} + \frac{1}{2\sigma_j^2} \right)^{1/2}
\times \exp \left[ -\frac{-\Delta^2}{4\sigma_i^2\sigma_j^2} \left( \frac{1}{2\sigma_i^2} + \frac{1}{2\sigma_j^2} \right)^{-1} \right]. \tag{10}
\]

4. RESULTS AND DISCUSSION

Using the above methods, we calculated the time-dependent site occupation probabilities for initial conditions corresponding to an excitation localized on the M and/or L side accessory pigments. All calculations were carried out at \(T = 298\) K.

Fig. 3 shows the probability of the excitation being in the lower exciton band in \(Rps.\ viridis\) after exciting the various accessory pigments. In Fig. 3C the excitation is
Fig. 3. Population of various electronic states in *Rps. viridis* after excitation into absorption bands corresponding to different accessory pigments. A, Excitation initially localized on BPh; B, Excitation initially localized on BPhM; C, Excitation initially shared between BChl* L* and BChl* M*, $\mu^2_{\text{BChl L}} = 30.0$ D$^2$, $\mu^2_{\text{BPh L}} = 19.0$ D$^2$, $\mu^2_{\text{P_0}} = 10.0$ D$^2$, $T = 298$ K.

Initially distributed over both BChls, since experimentally it is impossible to excite one branch preferentially due to the near perfect overlap of their Q transitions. The calculations show that there is a rise time of the order of 2–3 ps associated with the P state. This is clearly in contrast with the results of Breton et al., who found no rise time in the photobleaching of this state with a time resolution less than 100 fs. We also performed simulations using the values 45 D$^2$ and 30 D$^2$ for the transition dipole moments of BChl b and BPh b, respectively. These values naturally lead to a faster rate of energy transfer; however, the calculated results still substantially underestimate the true transfer time (Fig. 4).

Similar results are seen in *Rb. sphaeroides*. Fig. 5 shows the populations of the two bridging BChl Q states and the P state after exciting into the BChl band at 803 nm. In both species, the difference in the rates of transfer to the P state from the two BChls reflects small differences in the distances and orientation factors. In all these results, the internal conversion (P$\rightarrow$P) rate constant was chosen to be (100 fs)$^{-1}$. Using a value of (10 fs)$^{-1}$ gives only a slight increase in the rate. The electron transfer rate of (2.8 ps)$^{-1}$ was taken from Ref. 5. The fact that in this model the rate-determining step is the population of the P state is not surprising, given that this state carries only a fraction of the oscillator strength of the special pair. It is interesting, however, to note that the upper excitation band is positioned so that its Franck–Con...

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don overlap with the thermally equilibrated BChl states is essentially perfect. An analogous case exists with the charge-separated states and the lower exciton band.

Before proceeding, several comments are in order regarding our implementation of the weak coupling theory. Firstly, for any two pigments whose band positions differ in frequency, the ratio of the forward and reverse rates must obey the detailed balance condition

$$W_f = W_r \exp((E_f - E_r)/kT).$$

In our calculations, the down-hill energy transfer rate is evaluated using Eq. (9), and the slower uphill rate is set to the value obtained by the above relation. The Boltzmann factor is obtained from the peak frequencies of the two relevant absorption bands. Secondly, the use of experimental lineshapes to calculate the spectral overlap integral is complicated by the effects of inhomogeneous broadening; however, this would seem to lead to a value for the overlap integral that would overestimate the rate. Finally, the use of the Stokes shift from data taken in a polar solvent such as ether to calculate the positions of the emission bands in the reaction center complex might lead to a small error in the calculated spectral overlap due to the difference in solvent and protein reorganization energies. However, the spectral overlap between the emission bands of the bridging BChls and the absorption band of the P, state using the values in Table 2 is essentially perfect; any change in band positions would not lead to a substantially larger value for the overlap integral.

Our simulations provide a clear example of the inadequacy of the weak coupling theory to describe energy transfer in a photosynthetic system whose structure is known. Causgrove et al. have recently carried out fluorescence depolarization studies on the green bacterium Prosthecocchloris aestuarii. They concluded that energy migration occurs between exciton states located on different protein subunits. While an approach similar to the one carried out here would seem appropriate for inter-protein transfer, the dynamics of energy transfer between pigments on the same subunit requires a more sophisticated theoretical approach. In addition, our own studies on the Chl a/b protein have shown that transfer of excitation from Chl b to Chl a occurs in less than 100 fs. The Chl b molecules in this complex are thought to be arranged in very close proximity to one another giving rise to strong exciton splittings.

The large discrepancy between the experimental work of Breton et al. and the simulation results shown here indicate that a more detailed model of energy transfer is needed. One possible extension involves the actual mechanism of the electronic coupling. In the reaction centers, the center-to-center distance from adjacent pigments on the same branch is approximately 11 Å; the edges of neighboring pigment molecules are, however, very nearly in van der Waals contact. This suggests that one might need to include exchange terms and higher order multipole terms in the calculation of the coupling matrix elements. Particularly interesting is the problem of the effect of finite relaxation times on the dynamics and the question as to whether time-resolved measurements would distinguish between different models. The interplay between electronic coupling, electron–phonon

Fig. 4. Population of various electronic states in Rps. viridis after excitation into the BPh, band. $\mu^2 (\text{BChl} b) = 45.0 \text{ D}^2$, $\mu^2 (\text{BPh} b) = 30.0 \text{ D}^2$, $T = 298 \text{ K.}$

Fig. 5. Population of various electronic states of Rb. sphaeroides after excitation into the BChl absorption band. $\mu^2 (\text{BChl} a) = 41.0 \text{ D}^2$, $\mu^2 (\text{BPh} b) = 39.0 \text{ D}^2$, $\mu^2 (P,) = 10.0 \text{ D}$, $T = 298 \text{ K.}$
coupling, and phonon relaxation rates is a complicated theoretical problem. Our current effort in this area uses Redfield relaxation theory. In this approach, an excitonic–vibronic Hamiltonian including dissipative coupling to a thermal bath is used to derive the equation of motion for the density matrix. Application of Redfield theory to electron transfer in bacterial reaction centers has been discussed by Friesen and Wertheimer. This method allows a detailed investigation of the dynamics of transport taking into account arbitrarily strong electronic interactions as well as finite vibrational relaxation and dephasing times for both intramolecular and protein modes. This will be discussed in a future publication.

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