

Excited States and Electron-transfer Mechanism in the Photosynthetic Reaction Center of *Rhodobacter sphaeroides*: SAC-CI Theoretical Study

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The SAC-CI calculations clarify the natures of the excited states and the electron-transfer (ET) processes in the photosynthetic reaction center (PSRC) of *Rhodobacter (Rb.) sphaeroides*. The absorption spectrum was assigned with the averaged error of 0.11 eV. The electronic factors calculated from the SAC-CI wave functions clarified the mechanism of the unidirectionality of the ET in *Rb. sphaeroides*. It is controlled by the ET step from bacteriochlorophyll (B) to bacteriopheophytin (H), not from the special pair (P) to B as in the *Rhodospseudomonas (Rps.) viridis* reported previously: the electronic factor of the A-branch ET is 20 times larger than that of the B-branch. An analysis clarified that the unidirectionality originates from the inter-chromophore distances, and further that the hyperconjugations of the methyl groups with the π electrons of the chromophores have primary contributions to the electronic factor.

Light-induced transmembrane ET in the PSRC is a key step of the energy production in the green plants and bacteria.¹ The structure and function of these PSRCs resemble each other. In *Rb. sphaeroides*, the PSRC protein contains seven chromophores: bacteriochlorophyll-*a* dimer (Special Pair, **P**), two bacteriochlorophyll-*a* monomers (**B_A** and **B_B**), two bacteriopheophytin-*a* monomers (**H_A** and **H_B**), and two ubiquinones (**Q_A** and **Q_B**). Figure 1 shows the chromophore alignment in the PSRC, which has pseudo- C_2 axis. An excited electron at **P** is sequentially transferred only along the A-branch as indicated in Figure 1.² This ET is also well-known to be highly efficient. In our previous study on the ET in a bacterial PSRC of *Rhodospseudomonas (Rps.) viridis*, the unidirectionality of the ET was explained by the electronic factor calculated with the SAC-CI wave functions: The electronic factor for the ET from **P** to **B_A** was 15 times larger than that from **P** to **B_B**.^{3,4} Decomposition analysis clarified that the origin of the asymmetric electronic factor is in the interchromophore distance

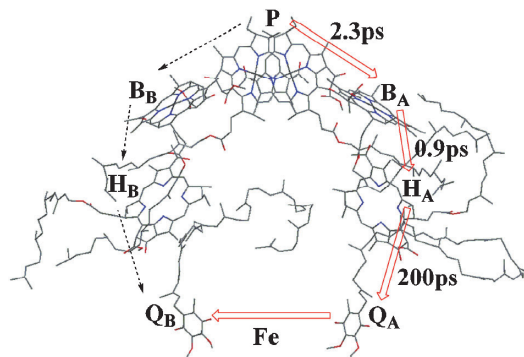


Figure 1. Chromophores in the PSRC of *Rb. sphaeroides*.

between **P** and **B**.^{3,4} That of the A-branch is 0.5 Å shorter than that of the B-branch. However, in *Rb. sphaeroides*, the **P** to **B** distance is similar in the two branches,⁵ suggesting another origin. In this study, the excited states and electron transfer in the PSRC of the *Rb. sphaeroides* were examined by SAC-CI⁶ method, and the results were compared with those for *Rps. viridis*.

The structure of the PSRC was taken from a X-ray structure (1OGV⁵). For the computational model of the chromophores, the substituents lying between the chromophores were kept in the model. The coordinates of the chromophores were optimized with B3LYP/6-31G* level. The effect from the rest of the protein was treated by a point charge model using AMBER force field.⁷ The SAC-CI calculations was performed for each chromophores with D95 basis sets⁸ for the H, C, O, and N atoms, and (533/5)[52121/41] sets⁹ for the Mg atoms. All valence orbitals were correlated in the SAC-CI calculations. For **P**, the orbitals with the energy of $-33 \sim 33$ eV were taken into the active space. The perturbation selection was performed for the double excitation operators with the threshold of 1×10^{-5} and 1×10^{-6} a.u. for the ground and excited states, respectively. See Supporting Material for the detail of the calculations.

In Table 1, the excited states of the PSRC calculated by the SAC-CI method are summarized. The results are compared with the experimental data. Total 15 states were calculated in the energy region of 1.3–2.8 eV, and the 6 peaks in the experiments were consistently assigned and their nature were clarified. The rms error in the SAC-CI excitation energy was 0.11 eV, indicating that the present assignments are reliable. This assignment provides a starting point for future photochemical studies of the PSRC. The first peak, which is important as the initial state of the ET, is assigned to the first excited state of **P**. From HOMO to LUMO excitation dominates 50% of the weight in the wave function.

Using these SAC-CI wave functions, we calculated the electronic factor $|H_{IF}|^2$ in the ET rate constant.

$$k^{\text{ET}} = \frac{2\pi}{\hbar} |H_{IF}|^2 (FC) \quad (1)$$

FC is Frank–Condon factor which describes the contribution from the nuclear dynamics. We note that the ET rate constant is proportional to the electronic factor. The details of the calculation method are found in the previous paper.⁴ The results are summarized in Figure 2. The energy levels of the states were taken from a previous experimental study.¹¹ For the ET from **P** to **B**, the calculated electronic factors for the A- and B-branches are very close to each other: 3.93×10^3 and $3.63 \times 10^3 \text{ cm}^{-2}$, respectively. However, for the ET from **B** to **H**, the electronic factor for the A-branch ET is 20 times larger than that for the B-branch: 10.5×10^3 and $0.52 \times 10^3 \text{ cm}^{-2}$, respectively. For the *Rps. viri-*

Table 1. Excited states of the PSRC of *Rb. sphaeroides*

State (Chro. ^a)	SAC-CI		E _{ex} . ^c	Osc. ^d	Exptl. ^e E _{ex} . ^c
	Main configurations ^b (C > 0.3)				
2 ¹ A(P)	0.69(H→L) + 0.42(H-1→L+1) + 0.39(H-1→L)		1.32	0.64	1.42
2 ¹ A(B _B)	-0.90(H→L)		1.39	0.44	1.55
2 ¹ A(B _A)	-0.87(H→L)		1.48	0.35	1.55
3 ¹ A(P)	0.65(H-1→L) - 0.37(H→L) + 0.33(H→L+1)		1.77	0.07	
2 ¹ A(H _B)	-0.83(H→L)		1.79	0.27	1.63
2 ¹ A(H _A)	0.85(H→L)		1.86	0.28	1.63
4 ¹ A(P)	0.78(H→L+1) + 0.48(H-1→L)		1.88	0.02	1.79
3 ¹ A(B _A)	0.88(H-1→L)		1.95	0.18	2.07
3 ¹ A(B _B)	0.86(H-1→L)		2.01	0.16	2.07
5 ¹ A(P)	0.79(H-1→L+1) - 0.47(H-1→L)		2.06	0.01	
6 ¹ A(P)	-0.79(H-2→L) - 0.43(H-3→L+1)		2.22	0.13	
7 ¹ A(P)	-0.65(H-2→L+1) - 0.61(H-3→L)		2.35	0.27	
3 ¹ A(H _A)	0.86(H-1→L)+0.37(H→L+1)		2.37	0.15	2.30
3 ¹ A(H _B)	0.86(H-1→L)+0.39(H→L+1)		2.38	0.14	2.30
8 ¹ A(P)	0.61(H-2→L+1) - 0.55(H-3→L) + 0.35(H-2→L)		2.84	0.00	
Δ _{rms} ^f			0.11		

^aChromophore. ^bH and L denote HOMO and LUMO, respectively. ^cExcitation energy in eV. ^dOscillator strength in a.u. ^eRef. 10. ^fRoot mean square error in the excitation.

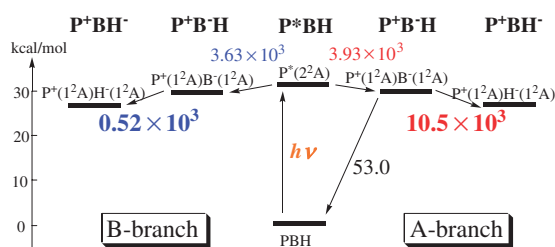


Figure 2. Electronic factor $|H_{IF}|^2$ (in cm^{-2} unit) of the ET in the PSRC of *Rb. sphaeroides*.

dis studied previously,^{3,4} the electronic factor for the A-branch was larger than the B-branch for both ET's from **P** to **B** and from **B** to **H**. The present result indicates that the origin of the A-branch selectivity in *Rb. sphaeroides* is ascribed to the electronic factor of the ET from **B** to **H**. A narrow path in the B-branch from **B** to **H** makes the A-branch ET favorable.

We also calculated the electronic factor for the charge recombination from $\text{P}^+\text{B}_\text{A}^-$ to the ground state. The result (53.0 cm^{-2}) is 200 times smaller than that of the ET, which indicates that the electronic factor also controls the efficiency of the ET in the PSRC.

To clarify the origin of the asymmetry in the electronic factor, we performed a decomposition analysis. Since off-diagonal elements of the Fock matrix dominantly contributes to the electronic factor,^{3,4} the decomposition into atom-atom contributions provides useful information about the detailed route of the ET. For the ET from **B_A** to **H_A**, the largest contribution comes from the pair H106 (**H_A**) and C13 (**B_A**) as shown in Figure 3. The distance between the two atoms is 2.95 \AA , while that of the corresponding pair is 3.96 \AA in the B-branch. Since the electronic interaction decays exponentially to the interchromophore distance, the difference of 1 \AA becomes critical. On the other hand, the distance between **P** and **B** in the A-branch is very close to that of B-branch, which results in the similar magnitude of the electronic factor. The asymmetry in the structure is the origin of the unidirectional ET, similarly to the case of *Rps. viridis*.^{3,4}

It is very interesting to note that the methyl groups play a crucial role in the ET. Figure 3 shows the donor and acceptor orbitals in the ET from **B_A** to **H_A**. The analysis showed the importance of the amplitude on H106 (**H_A**) in the acceptor orbital. This is due to

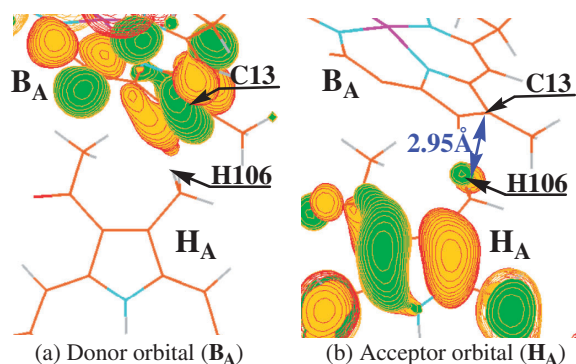


Figure 3. (a) Donor and (b) acceptor orbitals in the electron transfer from **B_A** to **H_A**.

the hyperconjugation between the methyl group and the π -system of **H_A**. Such crucial contribution of the hyperconjugation seems to be common in all ET's in the PSRC, and should be recognized as a general principle.

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