

# B-side Electron Transfer in Bacterial Photosynthetic Reaction Centers Revealed by a Few-Cycle Pulse Laser

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**Abstract.** B-side electron transfer in wide-type reaction centers from *Rhodobacter sphaeroides* 2.4.1 was investigated by broadband real-time vibrational spectroscopy.  $H_B^-$  was found to be generated in less than 50 fs after the excitation of 6.3 fs laser pulse, and its decay lifetime was determined to be  $\sim 280$ fs and 1.4ps, which is extremely fast compared with the one occurring in A-side. Considering the ultrafast of the generation time of  $H_B^-$ ,  $B_B$  rather than P was found to be the initial electron donor to the H. Hence, the initial charge-separated state is determined to be  $B_B^+H_B^-$  state.

## 1 Introduction

The symmetric structure of the reaction center (RC) provides two possible electron-transfer pathways. However, the functional asymmetry has been discovered and only the A-branch is active in charge transfer to form  $P^+H_A^-$  as the initial charge-separated state when the primary electron donor (P) is excited. The function of the B-branch cofactor is not yet clearly understood and only limited research result has been reported [1-2]. According to these previous studies, the B-branch function is very complicated and its electron transfer pathway is discovered to be dependent on the excitation wavelength, i.e. dependent on whether P or B (a monomer bacteriochlorophyll) or H (a bacteriopheophytin) is excited or to which excited state ( $Q_y$ ,  $Q_x$ , or Soret band) they are excited.

In the present study, we utilize the ultrashort laser pulse at visible range to investigate the kinetic of B-side electron transfer and properties of the initially generated charge pair state.  $B_B$  was found to act as the initial electron donor rather than P. Electron transfer takes place from  $B_B$  to  $H_B$  in less than 50 fs, and decay components of the charge-separated  $B_B^+H_B^-$  state are determined to be  $\sim 280$ fs and 1.4ps, which is extremely fast compared with the one occurring in A-side.

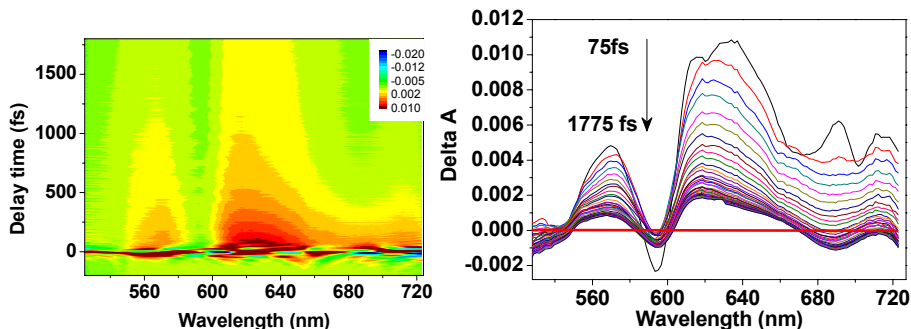
## 2 Experimental method and material

Both pump and probe pulses (7.2 fs, 525nm to 723nm) were generated from a noncollinear optical parametric amplifier laser system [3]. All the experiment was performed at a constant temperature

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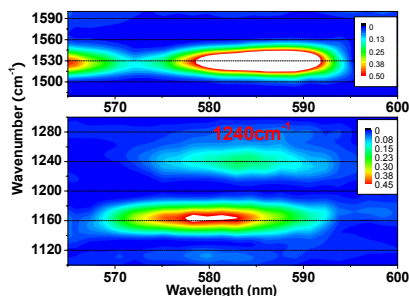
(293K). RCs from *Rhodobacter sphaeroides* 2.4.1 were prepared as described previously [4]. The anaerobically grown wide-type (WT) RCs contain spheroidene. RCs were suspended in a buffer solution of 20mM Tris-HCl (PH 8.0) with 0.1% N, N-Dimethyldodecylamine-N-oxide.

### 3 Results and discussions



**Fig. 1.** (a) Two-dimensional (probe photon energy versus probe delay time) pseudo-color display of the time dependence of the absorbance changes  $\Delta A$ . (b) The time-resolved difference absorption spectrum probed at delays from 75 to 1775 fs.

Fig. 1a shows the two-dimensionally plotted difference absorption spectra. In Fig. 1b, we plot the probe photon energy dependence of time-resolved spectra from 75 to 1775 fs with an integration width of 50 fs. A negative signal at 595 nm is due to the ground-state bleaching of P and/or B. There is a strong photon induced absorption (PIA) bands located around 630 nm. According to previous studies, this PIA signal is attributed to formation of the  $H_B^-$  anion [1-2]. Then what is the electron donor for this charge separation? As shown in Fig. 1b,  $H_B^-$  is formed just after the excitation of few-cycle visible laser (shorter than 50 fs), which is much faster than the one generated under excitation at 390nm with laser pulse duration of hundred femtosecond [1]. Thus, the  $P^+$  seems unlikely to be the initial electron donor, because the formation of  $P^+$  from  $P^*$  usually occurs on the 1~2 ps time scale, which is too slow to explain the ultrafast electron transfer to  $H_B$ . Because we excited the  $Q_x$  state of both B and P, considering the proximity of  $B_B$  to  $H_B$ , the  $B_B$  is much more likely to be the initial electron donor. Thus the corresponding charge-separated state initially formed can be assigned to be  $B_B^+H_B^-$ , which is similar with the one excited under 390 nm [1-2]. Femtosecond decay component of 280fs and picosecond one of 10ps (maximum delay time is 50ps) have been determined for the  $B_B^+H_B^-$  state.



**Fig. 2.** Two-dimensional contour map of FT amplitude spectra of the pump-probe signal.

The advantage of real-time vibrational spectroscopy is that both the electronic and vibrational dynamics can be observed at the same time under exactly same experimental condition. To gain a

better understanding of the vibronic coupling mechanisms, the vibrational mode frequencies have been realized by the fast Fourier transform (FFT) analysis of  $\Delta A$ , as shown in Fig. 2. The vibrational mode with frequency of  $1239\text{ cm}^{-1}$  can uniquely refer to the *cis* nature of the 15,15' carbon-carbon double bond as characteristic for spheroidene in the RC [5], which provides a fingerprint by which the carotenoid molecule can be identified. Therefore, it is reasonable to assign the vibrational mode at  $1240\text{ cm}^{-1}$  observed in the range of 570-590nm in Fig. 2 due to the carotenoid. Thus, the one located at  $1530\text{ cm}^{-1}$  and  $1162\text{ cm}^{-1}$  can be attributed to C=C and C-C stretching in the carotenoid, respectively. However spheroidene seems can not be excited directly, the observed signal may be explained by the energy transfer from  $B_B$  to carotenoid  $S_1$  state during  $\sim 50$ fs, which has been proved to be an effective path in purple-bacterial photosynthetic core antenna [6].

## 4 Conclusion

Electron at the B-side is found to transfer from  $B_B$  to  $H_B$  in less than 50 fs after the excitation using femtosecond real-time vibrational spectroscopy. Decay components of the initial charge-separated  $B_B^+H_B^-$  state are determined to be 280fs and 1.4ps, which is extremely fast in contrast to the processes in A-side. Such short formation and decay time of the electron transfer may arise from the requirement of preventing the photodamage in RCs. Since the A-branch cofactor absorbs the infrared light to undergo electron transfer to convert the light to chemical potential energy, meanwhile, the B-branch will absorb the light at residual range, i.e., the visible and/or UV light, to avoid the photon damage of these light to the A-branch cofactors and guarantee the successful electron transfer.

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