

# PICOSECOND DYNAMICS OF PRIMARY ELECTRON-TRANSFER PROCESSES IN BACTERIAL PHOTOSYNTHESIS

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**ABSTRACT** The primary electron transfer processes in *Rhodopseudomonas sphaeroides* R-26 were studied as a function of temperature by means of picosecond spectroscopy. The first chemical step of the bacterial photosynthesis involves an electron transfer from the excited state of a bacteriochlorophyll a dimer,  $(BChl)_2$ , to a bacteriopheophytin (BPh) to form the radical ion pair  $(BChl)_2^+ BPh^-$ . The upper limit for the formation time of this ion-pair was found to be 10 ps, at temperatures in the range 300–4.2° K. Similarly, the second chemical step, involving electron transfer from  $BPh^-$  to an ubiquinone-iron complex (QFe), was found to have a lifetime of  $\sim 150$  ps, also independent of temperature in the same range. We interpret the absence of temperature dependence as indicating that process 2 proceeds via a tunneling mechanism. Utilizing our results in conjunction with electron tunneling theories, we calculate the distance between  $BPh^-$  and Q(Fe) to be 9–13 Å. Our results also imply a closer proximity between  $(BChl)_2$  and BPh.

## INTRODUCTION

Studies on the reaction centers of photosynthetic bacteria have been very helpful in understanding fundamental aspects of the photosynthetic process, primarily because photosynthetic bacteria have a simpler photosynthetic system than green plants, composed of a single antenna-reaction center apparatus. Picosecond absorption studies on these bacterial reaction centers have yielded new information regarding the primary chemical steps of the photosynthetic process. In this report we present studies of the picosecond dynamics of the first two photo-induced electron transfer processes in the reaction centers of *Rhodopseudomonas sphaeroides* R-26. These processes are studied over a wide temperature range, 300–4.2° K, and the temperature data are used to discuss the mechanism of the electron transfer.

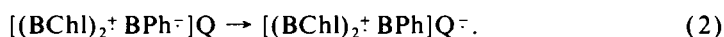
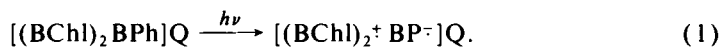
The bacterial reaction center contains a bacteriochlorophyll a dimer  $(BChl)_2$ , which absorbs at 865 nm and 605 nm, two bacteriochlorophylls a that absorb at 800 nm and 595 nm, two bacteriopheophytins (BPh) absorbing at 760 nm and 535 nm, and ubiquinone-10 (Q) associated in some way with iron. Until recently the  $(BChl)_2$  and Q were considered to be actively involved in the primary electron transfer process,  $(BChl)_2$  being the "primary electron donor" and Q the "primary electron acceptor." However, Netzel et al. (1) showed that 530-nm picosecond excitation of BPh bleached within  $\leq 10$  ps the 865 nm  $(BChl)_2$  absorption. Subsequent studies by Kaufmann

et al. (2) and Rockley et al. (3) over a wider spectral range revealed that 530-nm light absorption results in the bleaching of the BPh (540-nm) and (BChl)<sub>2</sub> (600-nm) bands. The simultaneous disappearance of the absorptions of both species implies a strong coupling between the two chemical systems (BChl)<sub>2</sub> and BPh. The studies presented in refs. 2 and 3 also found that the lifetime of the recovery of bleaching at 540 nm is about 150 ps. It was observed (4), though, that when the QFe system was chemically reduced, the decay lifetime becomes as long as 10 ns. The understanding of the nature of the (BChl)<sub>2</sub> ↔ BPh interaction after light absorption was the result of further experiments by Dutton et al. (5), which showed that the characteristic 1,250-nm absorption band of the (BChl)<sub>2</sub><sup>+</sup> cation radical was formed within ~ 10 ps. In addition, another intermediate was found to be formed, again within ~ 10 ps, absorbing in the visible (2, 5). Fajer et al. (6) have presented evidence that this intermediate is the bacteriopheophytin radical anion, BPh<sup>-</sup>. The above results (2, 5, 6) identify then as the primary step of photosynthesis in *R. sphaeroides* an electron transfer process from the (BChl)<sub>2</sub> dimer to BPh to form the [(BChl)<sub>2</sub><sup>+</sup> BPh<sup>-</sup>] radical ion pair.

By means of difference spectra obtained by chemical and photochemical trapping techniques, evidence was presented for the formation of the same radical anion identified as BPh<sup>-</sup> in systems other than the bacterium *R. sphaeroides* R-26. For example, Shuvalov and Klimov (7) provided such evidence in the case of *Chromatium minutissimum*, Tiede et al. (8) and van Grondelle et al. (9) in the case of *Chromatium vinosum* and Shuvalov et al. (10) on *Rhodospseudomonas viridis*. The above studies support the generality of the proposed primary step in the *R. sphaeroides* photosynthesis.

The second step of photosynthesis is envisioned to involve an electron transfer from the [(BChl)<sub>2</sub><sup>+</sup> BPh<sup>-</sup>] to Q with a lifetime of about 150 ps. Strong support in favor of an electron transfer from the complex to Q came from the studies of Kaufmann et al. (11), where the time-resolved optical changes at 640 nm and 540 nm were monitored in intact, ubiquinone-depleted and reconstituted reaction centers. In contrast to intact samples where the 640-nm (BPh<sup>-</sup>) band decayed with a 150-ps lifetime, the ubiquinone-depleted samples also exhibited fast formation at 640 nm but no decay was observed for more than 600 ps. A similar behavior was found for the 540-nm band (BPh ground state absorption), where after an initial < 10-ps bleaching, there was a repopulation (rise in absorbance) within 150 ps for the intact and reconstituted species, while the Q-depleted sample showed no repopulation for at least 1 ns.

The above discussion, based on previous results, shows that the first two chemical processes of bacterial photosynthesis can be written as:



In the present paper we report the dependence of the dynamics of the above two processes on temperature. The electron transfer rates are measured directly in the temperature range 300–4° K by following the time dependence of transient absorptions induced by 530-nm or 625-nm picosecond pulses.



## METHODS

In the experiments described here, a passively mode-locked Nd<sup>3+</sup> glass laser was used. The optical arrangement of the double-beam picosecond absorption experiment is shown schematically in Fig. 1 (12). The laser fundamental pulse at 1,060 nm generates in a KD\*P crystal a ~6 ps 5 mJ second harmonic pulse at 530 nm, which is used for excitation. The 625-nm excitation pulse was generated as a Stokes band through stimulated Raman scattering of the 530 nm light by cyclohexane. The interrogation beam consisted of either a picosecond continuum formed by focusing part of the 530 nm beam in a cell containing octanol or by the stimulated Raman scattering of the 1,060-nm light by CCl<sub>4</sub>. The interrogating (*I*) and reference (*I*<sub>0</sub>) beams (Fig. 1), after exciting the spectrometer, were focused on a vidicon detector, consisting of a silicon target for the visible, while a lead sulfide target was used for detection in the infrared region. The data were processed and analyzed by a combination of an optical multichannel analyzer (Princeton Applied Research Corp., Princeton, N.J.) and a Nova computer (Data General Corp., Southboro, Mass.).

The low temperature measurements were performed in a variable temperature cryo-tip helium Dewar flask (Air Products & Chemicals, Inc., Allentown, Penn.). The temperature was measured by a gold/Chromel thermocouple and was kept constant to  $\pm 0.5^\circ\text{K}$ . The sample medium was a 1:2 mixture of water and ethylene glycol placed in a 2-mm optical path length cell. The data points shown in Figs. 2-4 are the average of 12 pairs of excitation/no excitation experiments at room temperature and 6 pairs for the lower temperatures. The optical density change reproducibility is  $\pm 0.02$ .

*Rhodospseudomonas sphaeroides* R-26 were grown anaerobically in the light on succinate as a carbon source. Photosynthetic reaction centers were provided to us by Professor Colin Wraight of the University of Illinois at Urbana.

## RESULTS

The ~6-ps, second-harmonic, 530-nm pulses of the mode-locked Nd<sup>3+</sup>:glass laser are predominately absorbed in the reaction center by bacteriopheophytin *a* (BPh). The electronic excitation is subsequently transferred from BPh\* to the (BChl)<sub>2</sub>. This energy transfer process is most probably not rate-limiting, the primary photochemistry being initiated by (BChl)<sub>2</sub>\*. As discussed in the Introduction, the dimer radical cation (BChl)<sub>2</sub><sup>+</sup> is characterized by an infrared absorption with a maximum at ~1,250 nm. The BPh<sup>-</sup> radical anion is characterized by visible absorptions in the range 600–700 nm. Therefore, to study the dynamics of the electron transfer process 1 after 530-nm excitation, we utilized the picosecond continuum to monitor transient absorptions at 1,250 and 640 nm. Fig. 2 shows the behavior at 1,250 nm. It is evident from this figure that the maximum of the transient absorbance at 1,250 nm is reached within ~10 ps, in agreement with the results of Dutton et al. (5). After the initial ultrafast rise, the absorption at 1,250 nm remains constant for at least 260 ps (Fig. 2). Use of longer echelons does not provide any evidence of decay up to 1 ns. We believe that the temperature dependence of the kinetic behavior at 1,250 nm is quite unusual and particularly important for the electron transfer mechanism. We observe that there is no change in the dynamics over the wide temperature range of room to liquid helium, 4.2°K. The behavior of the 640-nm band was found to be analogous. Fig. 3 shows that the maximum transient absorbance at 640 nm (BPh<sup>-</sup>) is achieved within 10 ps and

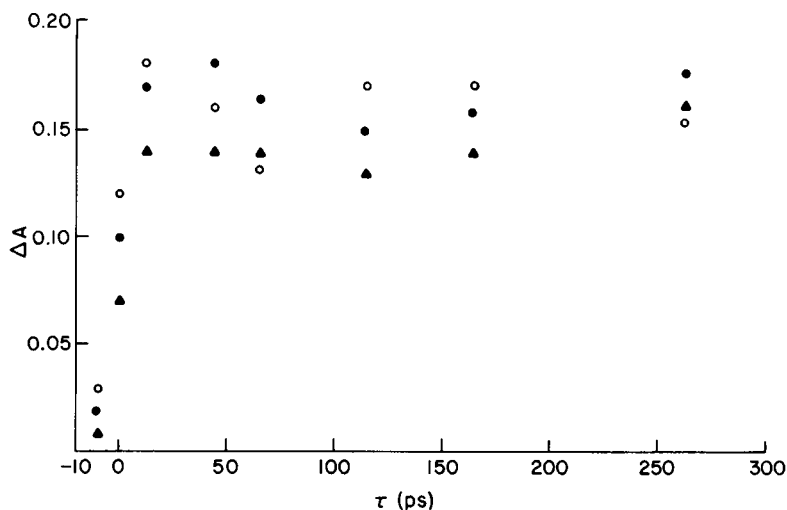


FIGURE 2 Picosecond kinetics of the laser-induced (530 nm) absorption changes of *R. sphaeroides* R-26 reaction centers at 1,250 nm. The sample temperature is: ●, 295°K; △, 77°K; and ○, 4°K.

subsequently decays with a lifetime of about 150 ps. The decay time remains the same, within the experimental uncertainty, from 300°K to 4.2°K, while no rise time in the absorbance at 640 nm can be observed over the same temperature range. The decay of the absorbance at 640 nm is determined by the electron transfer reaction from  $\text{BPh}^-$  to the ubiquinone-10 iron complex. On the basis of the results presented in Figs. 2 and 3, we can conclude that over the temperature range 300–4.2°K,  $(\text{BChl})_2^+$  and  $\text{BPh}^-$  are

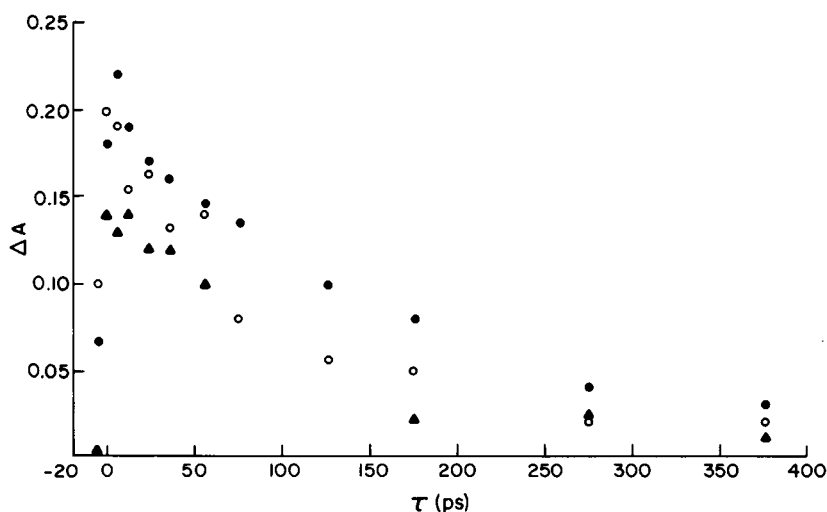


FIGURE 3 Picosecond kinetics of the laser-induced (530 nm) absorption changes of *R. sphaeroides* R-26 reaction centers at 640 nm. The sample temperature is: ●, 295°K; △, 58°K; and ○, 4°K.

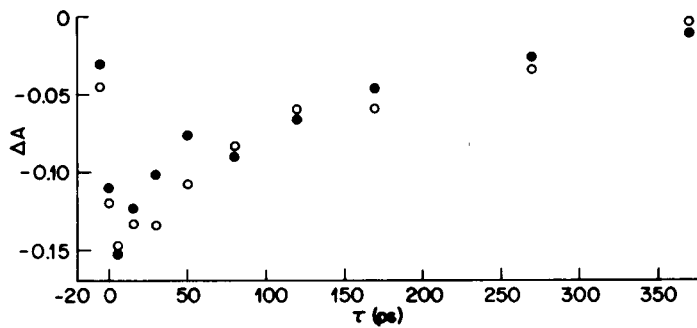


FIGURE 4 Picosecond kinetics of the laser-induced (625-nm) absorption changes of *R. sphaeroides* R-26 reaction centers at 540 nm. The sample temperature is: ●, 295°K, ○, 4°K.

formed in a time  $\leq 10$  ps and that the decay of  $\text{BPh}^-$ , presumably by electron transfer to Q, is temperature-independent. As an additional check of the above conclusions, studies were performed to monitor the dynamics of the BPh component of the reaction center as a function of temperature. This was accomplished by exciting with a 625-nm picosecond pulse generated by the 530-nm pulse. The photo-induced absorbance changes were monitored at 540 nm (BPh). These results are shown in Fig. 4. The 540 nm absorption was found to be bleached within  $\sim 10$  ps as a result of the formation of  $\text{BPh}^-$ . This bleaching subsequently recovers with a measured lifetime of 150 ps equal to the decay time of the 640-nm absorption. This should be true if ground-state BPh is to be regenerated by the electron transfer from  $\text{BPh}^-$  to Q (Eq. 2). Confirming our conclusions on the temperature dependence of the rates of reactions 1 and 2 is the lack of any dependence of the dynamics at 540 nm on temperature.

## DISCUSSION

Summarizing our experimental results, we note that the rate of the electron transfer reaction from  $\text{BPh}^-$  to Q (Eq. 2) is temperature-independent from 300 to 4.2°K within experimental error. In addition, over the same temperature range, the formation of the radical ion pair  $[(\text{BChl})_2^+ \text{BPh}^-]$  (Eq. 1) is completed within 10 ps.

If thermodynamic equilibrium can be achieved within the 10-ps time scale so that temperature is a well-defined quantity, the above results suggest that process 1 is also temperature-independent. In the case where the actual energy transfer process  $\text{BPh}^*$  to  $(\text{BChl})_2$  is rate-determining at all temperatures, this would imply an extremely fast formation rate and temperature independence is then expected, because no equilibrium can be established. An alternative explanation, according to which electron transfer process 1 has a temperature dependence and the reaction is much faster than 10 ps at 4.2°K, is unlikely. Our results are quite unusual because chemical reactions, electron transfer reactions included, are expected to show an activated behavior, which in the majority of cases described well by the phenomenological Arrhenius equation,  $k =$

$A \exp(-E_a/kT)$ . It is important therefore to try to understand the meaning of our temperature-independent data by considering the mechanism of the electron transfer process at a fundamental level. It is also important to see if, from the dependence of the dynamics on temperature, we can obtain any information about the coupling and distance of the relevant chemical species in the bacterial reaction center.

We can consider the following general possibilities for the mechanism of the electron transfer process: (a) transfer of the electron over the crossing of the potential surfaces of reactants and products; (b) transfer through bridging systems; (c) semiconductive transfer; and (d) electron tunneling. Processes a, and b, involve thermal activation and are therefore not applicable in our case. Semiconduction, c, first proposed as a possible mechanism for biological electron transfer by Szent-Gyorgi, (13) is also an activated process, as it involves bridging of a valence-to-conduction-band gap of the order of 1–2 eV for biological materials. Our data eliminated therefore processes a, b, and c and point strongly to a quantum mechanical electron tunneling process, where the electron does not hop over the energy barrier but tunnels through it. For a tunneling process at low enough temperatures, where only the zero point level of the molecular vibrations is significantly occupied, the tunneling rate is expected to be temperature-independent. At higher temperatures, even a tunneling process may be expected to show a temperature dependence. In fact in many chemical systems where electron (or proton) tunneling has been proposed as operating (14–18), the transfer rate shows a high-temperature activated behavior and a low-temperature constant limiting rate. For example, such a behavior has been observed in a photosynthetic system by DeVault and Chance (19). Their study involved the light-induced electron transfer reaction from a cytochrome to the  $(\text{BChl})_2^+$  in *C. vinosum*. They found that in the temperature range 300–100°K the electron transfer shows an activated behavior with an apparent activation energy  $\Delta E^* \simeq 0.14$  eV. At temperatures below 100°K the transfer rate is temperature independent.

The tunneling process in *C. vinosum* (19) was visualized as involving the transfer of the electron through the potential barrier to a continuum of free electron states. This approach has been modified by Blumenfeld and Chernavskii (20) and Hopfield, (21) who pointed out the importance of the coupling of the electronic and nuclear motions (vibronic coupling). Now the electron transfer process proceeds nonradiatively and the coupling to the vibrations provides the necessary energy dissipation channel.

A theoretical description of electron tunneling with vibronic coupling in biological systems has been advanced by Hopfield (21). In this model, mathematically isomorphous to the Forster-Dexter theories of energy transfer (22, 23) and to the theory of outer sphere electron transfer (24, 25), the electron transfer rate is proportional to the overlap  $\int D_D(E) D_A(E) dE$  of an electron removal  $D_D(E)$  and an electron insertion  $D_A(E)$  functions.  $D_D(E)$  and  $D_A(E)$  obtain their width from the coupling to the molecular vibrations and therefore their overlap is temperature dependent. This coupling results in an activated-type behavior for the tunneling process itself, with an apparent activation energy determined by the quality  $(E_D - E_A - \Delta)^2$ , where  $E_D - E_A$  is the difference of the electron energy between donor and acceptor and  $\Delta$  is a vibronic

coupling parameter. Therefore, the closer the energy difference  $E_D - E_A$  is to the value of  $\Delta$ , the smaller is the apparent activation energy, resulting in a weaker temperature dependence. If all other factors are equal, this will also result in a faster rate.  $E_D - E_A$  can be estimated by using standard redox potentials. Calculations based on this proposal give  $E_D - E_A \simeq 0.4$  eV for process 2 (26). The observed absence of temperature dependence implies that an appropriate value of the vibronic coupling parameter  $\Delta$  for process 2 is 0.4 eV. It is interesting that on the basis of arguments on the efficiency of the photo-induced charge separation process, Hopfield (27) has estimated the  $\Delta$  of process 1 to be  $\sim 0.4$  eV. In the case of the cytochrome to bacteriochlorophyll electron transfer in *C. vinosum* (19), on the other hand, where a slow temperature-dependent rate is observed, the difference  $E_D - E_A - \Delta$  has been estimated to be  $-0.95$  eV (21) or  $-1.25$  eV (27), depending on the choice of the value of oxidation potential of the cytochrome.

Our results on the electron transfer rates can be utilized in conjunction with models for the tunneling process to obtain structural information with respect to the separation of the donor and acceptor species. A general model for electron transfer has been proposed by Jortner (28). This model considers electron transfer in terms of the theory of nonradiative multiphonon decay in condensed phases (29). If the coupling of the electron to the molecular vibrations is much stronger than the coupling to the phonons of the medium, as expected for a biological system, as in our case, the low temperature transfer probability  $W$  is given by (25):

$$W = (2\pi/\hbar^2 \langle \omega_s \rangle) |V_{DA}(R)|^2 F, \quad (3)$$

where  $F$  is a Franck-Condon factor given by

$$F = \exp(-S) S^p / p!. \quad (4)$$

$S$  is an effective coupling constant to the molecular vibrations characterized by a mean frequency  $\langle \omega \rangle$ ,  $p = (E_D - E_A)/\hbar \langle \omega \rangle$  and  $\langle \omega_s \rangle$  is the mean frequency of the medium phonons.  $S$  can be approximated through the high temperature expression for the apparent activation energy  $\Delta E^*$ , found to be close to zero in our experiments:

$$\Delta E^* = (E_D - E_A - S\hbar \langle \omega \rangle)^2 / 4S\hbar \langle \omega \rangle. \quad (5)$$

It should be pointed out that the Jortner (28) and Hopfield (21) models, mentioned earlier, describe the same physics, and in the high temperature limit are isomorphic with the identification  $S\hbar \langle \omega \rangle_{\text{Jortner}} = \Delta_{\text{Hopfield}}$ .

To obtain the coupling between donor and acceptor in process 2, we utilize our experimental value for the rate along with reasonable ranges of values for  $\hbar \langle \omega \rangle$  and  $\hbar \langle \omega_s \rangle$ ,  $\hbar \langle \omega_s \rangle = 10\text{--}100$   $\text{cm}^{-1}$  and  $\hbar \langle \omega \rangle = 400\text{--}1,600$   $\text{cm}^{-1}$ . We thus estimate, using Eqs. 3–5, that the interaction matrix element  $V_{DA}$  between donor and acceptor is in the range  $0.5\text{--}2$   $\text{cm}^{-1}$ . Due to differences in suppositions about param-



eters in the two theories, our data analyzed through Hopfield's theory would give a higher  $V_{DA}$  of  $\sim 4 \text{ cm}^{-1}$ . This coupling can be compared to the coupling between bacteriochlorophyll and cytochrome in *C. vinosum*, estimated by Hopfield (21) to be  $\sim 3 \text{ cm}^{-1}$  and by Jortner (28) to be in the range  $0.1\text{--}0.4 \text{ cm}^{-1}$ . We can also compare these values for  $V_{DA}$  with the coupling of  $1 \text{ cm}^{-1}$  estimated in the case of outer sphere electron transfer in the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6\text{--Fe}^{3+}(\text{H}_2\text{O})_6$  system (30). To calculate the electron transfer distance, we need  $V_{DA}$  as a function of distance, including many electron exchange effects  $V_{DA} = 10 \text{ cm}^{-1}$  for  $R = 10 \text{ \AA}$  and  $d\ln V_{DA}/dR \simeq 1.3 \text{ \AA}^{-1}$  (28). Using these values, we calculate the distance between BPh and Q to be about  $11\text{--}13 \text{ \AA}$ . In Hopfield's theory a  $V_{DA}$  of  $\approx 4 \text{ cm}^{-1}$  would correspond to  $\approx 9 \text{ \AA}$  for this separation. Because the exact geometry is not known, the point between the molecules to which this distance refers cannot be assigned with certainty. Assuming a model similar to Hopfield's (21, 27), this distance would correspond to the separation between the edge atoms.

It is worth mentioning that triplet-triplet energy transfer between aromatics, which also proceeds by an exchange type mechanism, is characterized by a similar range of interaction distances (31).

In process 1 the data show that the formation time of the ion pair  $(\text{BChl})_2^+ \text{BPh}^-$  is  $< 10 \text{ ps}$ . As we mentioned earlier, that this upper limit of the formation time is temperature-independent between  $300$  and  $4.2^\circ\text{K}$  suggests but does not prove that the electron transfer process 1 proceeds also through electron tunneling. One should also consider the possibility of a barrierless transfer for process 1. That no activated behavior is seen for electron transfer process 2 implies that the respective potential barrier activation energy is significantly high, so that the rate of over-the-barrier transfer cannot compete effectively with the rate of tunneling through the barrier. For example, for the rate of transfer over the barrier to be able to compete at room temperature with the tunneling rate, assuming Arrhenius pre-exponential factors of  $10^{15}\text{--}10^{13} \text{ s}^{-1}$ , the potential barrier should be of the order of  $4\text{--}5 \text{ kcal mol}^{-1}$ . Electron transfer in process 1, unlike the reaction in process 2, involves an excited state, that of  $(\text{BChl})_2$ . It is easier to achieve electron removal from an excited state than from the ground state, as the ionization potential is reduced by the respective excitation energy, which for a vibrationally relaxed  $(\text{BChl})_2$  is  $\sim 1.34 \text{ eV}$ . In this respect an extremely fast rate for process 1 is not surprising. This implies again a strong coupling and close proximity between  $(\text{BChl})_2$  and BPh in the reaction center as in a time of  $\leq 10 \text{ ps}$  minimal translational or rotational diffusion motion can take place. The proximity between the two molecules is also supported by the extremely fast energy transfer from the initially excited BPh to  $(\text{BChl})_2$ . The relative orientation between the bacteriochlorophyll dimer and the bacteriopheophytin is not known, although polarized absorption studies by Vermeglio and Clayton (32) indicate that the plane of the BChl dimer is nearly perpendicular to the plane of the membrane, and similarly the BPh ring is also tilted with respect to the membrane. The above result suggests that the planes of  $(\text{BChl})_2$  and BPh may be not far from parallel.

## CONCLUSIONS

Summarizing our results, we note that the photo-induced formation of the radical ion pair  $[(\text{BChl})_2^+ \text{BPh}^-]$  (process 1) takes place in a time  $\leq 10$  ps. This upper limit for the formation time remains the same over the temperature range 300–4.2°K. Similarly, the lifetime of the electron transfer from  $\text{BPh}^-$  to Q (process 2) is 150 ps, also independent of temperature in the range 300–4.2°K. The lack of temperature dependence observed is consistent with the models for electron tunneling with vibronic coupling which can lead to temperature-independent rates for appropriately exoergic (downhill) transfers. The size of inferred coupling parameter is consistent with predictions about this system (27). From our data we therefore conclude that process 2 and possibly process 1 proceed through electron tunneling. The potential barriers of the electron transfer appear to be quite high (probably higher than 4–5 kcal mol<sup>-1</sup>), so that activated electron transfer does not compete effectively with tunneling. Theoretical analysis of our experimental findings allows us to estimate the BPh-Q distance as being about 9–13 Å. A shorter distance between  $(\text{BChl})_2$  and BPh is also expected from our results.

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