Doubt on Experimental Evidence for a Superexchange-Mediated Primary Electron Transfer in Photosynthetic Reaction Centers

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The key question with regard to the pathway of the primary electron transfer (ET) in photosynthetic reaction centers is addressing the role of the monomer bacteriochlorophyll (B) which connects the primary donor $^1P^*$ and the bacteriopheophytin (H) as revealed in the X-ray structural analysis of *R. viridis* [1] and *Rb. sphaeroides* [2]. B is expected to participate through the state (P^+B^-). There are in principle two ways of such an involvement of B:

(1) P^+B^- is a real kinetic intermediate in a two-step ET as supported by recent femtosecond time resolved spectroscopy at 300 K [3]

$$^1P^*BH \rightarrow P^+B^-H \rightarrow P^*BH^- .$$

(2) P^+B^- enhances a unistep electron transfer between $^1P^*$ and H through a superexchange mechanism [4, 5]

$$^1P^*BH \rightarrow P^+BH^- .$$

So far, the only *direct* experimental evidence for mechanism (2) has been considered to be the anisotropy of the electric field induced changes of the fluorescence quantum yield [6].

The conclusions in [6] refer to the following experimental observations: The measured quantity is the fluorescence intensity of $^1P^*$ which increases in the presence of an externally applied electric field. This increase is due to a net decrease in the rate of the forward electron transfer reaction which competes with the prompt fluorescence. The decrease results from the change in the free energy difference between the state $^1P^*$ and the dipolar product state, (P^+B^-) or (P^+H^-), in the presence of an electric field. Because of the dependence of the free energy difference on the orientation of the dipole moment of either (P^+B^-) or (P^+H^-) in the electric field, the intensity of the fluorescence becomes likewise orientation dependent. By photoselection the fluorescence of reaction centers with these dipole moments preferentially oriented parallel or perpendicular to the electric field can be detected. If the angle ξ between the transition moment $\boldsymbol{p}(^1P^* \rightarrow P)$ and the dipole moment $\boldsymbol{\mu}(P^+B^-)$ is smaller than the magic angle (54°), the electric field modulation is larger for a polarization parallel to the electric field as compared to a polarization perpendicular to it. In case the angle $\xi > 54°$ the electric field modulation is expected to be smaller for a polarization parallel to the electric field.

Lockhart et al. [6] studied reaction centers of *Rb. sphaeroides* and measured an electric field induced anisotropy of the fluorescence indicating ξ larger than the magic angle. We have repeated these measurements (being more selective due to polarized excitation at 860 nm) and essentially confirm these results.

The conclusions from the measurement have been derived [6] from an estimate of the angles, $\xi(P^+B^-) \cong 49°$ and $\xi(P^+H^-) \cong 58°$, based on the X-ray crystal structure coordinates of *R. viridis* [1]. Comparison of the measured angle with the calculated one suggested the direct involvement of P^+H^- in the primary electron transfer according to mechanism (2).

Lockhart et al. [6] obtained the direction of the two dipole moments $\boldsymbol{\mu}(P^+B^-)$ and $\boldsymbol{\mu}(P^+H^-)$ by drawing a vector between the geometric center of P and the center of either the B of H macrocycle using the X-ray structure coordinates for *R. viridis* [1]. We have repeated the calculation of the angle ξ with the same results.

However, if we account for an asymmetric charge distribution on the dimer cation state P^+ the conclusions in [6] cannot be maintained. Such a charge asymmetry shows up in magnetic resonance experiments and is calculated in molecular orbital studies on the radical ion P^+ in reaction centers of *R. viridis* [7]. The derived ratio of charge densities is in favour of the dimer-halve bound to the L-protein subunit. Basing our calculations on the total charge distribution due to all atomic orbitals, we obtain $\xi(P^+B^-) \cong 59°$ and $\xi(P^+H^-) \cong 63°$. These calculations show that the

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conclusions drawn in [6] are ambiguous. Thus, the electric field induced polarization of the fluorescence as observed for reaction centers of *Rb. sphaeroides* [6] which points to an angle ξ larger than the magic angle can be well reconciled with both, a two-step (1) and a unistep superexchange (2) primary electron transfer mechanism. However, deviations from the calculated angle ξ cannot be excluded since the initial charge distribtuion of P^+ may differ from the steady state distribution which determines the magnetic resonance phenomenology [7].

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