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**Ab initio modeling of primary processes in photosynthesis :
protein induced activation of bacteriochlorophylls for efficient
light harvesting and charge separation**

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Chapter 6

General Discussion and Future Prospects: Asymmetry and Electron Transfer

The results presented in this work uncover a specific state of frustration for the Mg-coordinated histidines in the LH2 system, which is pushed closer to the corresponding BChl *a* molecule due to protein-induced steric and electrostatic stress. This results in a much larger charge transfer, which depends also on the relative orientation of the two molecules, and in an abnormal electronic configuration of the axial histidine. Differences in the relative orientation of the BChl *a*-His components between P_L-His L173 and P_M-His M202 are also responsible for an enhancement in the electron charge asymmetry in the special pair of the BRC. However, it is found that the charge asymmetry is an intrinsic property of the two bacteriochlorophylls *a* and originates from protein-induced structural distortions of the porphyrin rings and is strongly enhanced by out of plane orientation of the P_L 3¹ acetyl group. The specific orientation of the acetyl is controlled to a large extent by the hydrogen bond with His L168, although this interaction appears to be in competition with

other electrostatic and orbital energy terms. By changing the acetyl orientation the electronic, optical, and thus biophysical properties of the special pair can be tuned. It is also established that one of the four axial histidines present in the bacterial reaction center has a different electronic structure than the other three due to a hydrogen-bonded water at the N_π nitrogen. This interaction brings the coordinated histidine and the bacteriochlorophyll *a* closer.

Although the focus of this thesis was not in the electron transfer process, the presented results have interesting implications for an emerging electron transfer mechanism. It has been recently discovered that protein dynamics drives the first steps in photosynthetic charge separation [113,114]. However, taking into account that the primary electron transfer happens on a very short time scale of ~ 3 ps, there is not much time for the protein to undergo serious rearrangements. Certainly, 3 ps is enough to move one or even several protons around, leading to the concept of a proton-coupled electron transfer (PCET), where the transfer of a proton assists the electron transfer. Activation of small molecules, redox-driven proton pumps and radical initiation all involve the coupling of protons to electrons, which is the basic mechanism for bioenergetic conversion. [132] Generally, two types of PCET are distinguished: co-linear, in which both the proton and electron are transferred along the same direction and orthogonal PCET, where the proton and electron are transferred to disparate acceptors.

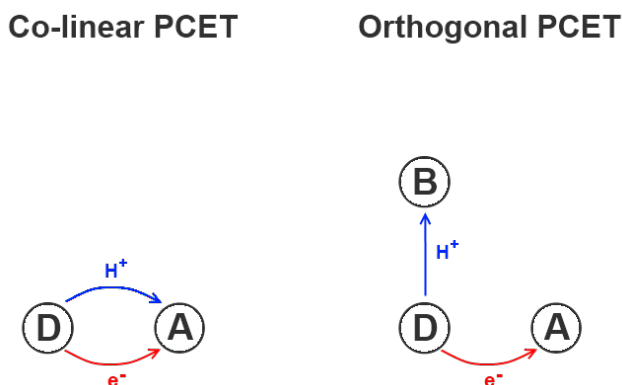


Figure 6.1: Two types of proton-coupled electron transfer.

It has been reported that the water molecule between His M202 and B_A is important for optimization of the primary electron transfer rate and that steric exclusion of that water in a mutant generates *ca.* an 8-fold decrease in the decay rate of the P^* state. [133] Moreover, a hydrogen bond between the water molecule and the 13^1 carbonyl of B_A is observed in the oxidized special pair $P^{+\bullet}$ but deemed weak or nonexistent in the special pair neutral ground state. It is also suggested that a possible through-bond connection between the special pair and B_A facilitated by His M202 and the water molecule may exist. [133] Therefore, it can be temporarily assumed that the special histidine with the hydrogen bond to a water molecule found in chapter 4 is in fact His M202. If the proton transfer, or just a shift in the hydrogen bond equilibrium, had to occur first between His M202 and the associated water molecule, that histidine would gain partially anionic character and it would be stabilized by the presence of the magnesium ion. This would in turn change the relative geometry of His and BChl *a*, including shortening of the Mg– N_τ distance, and induce a larger charge transfer to the special pair (see Fig. 6.2). Interestingly,

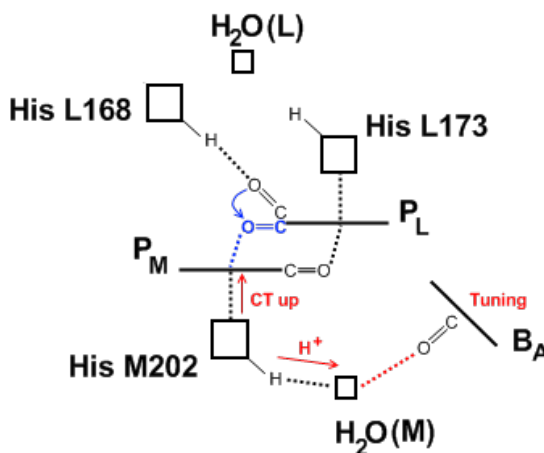


Figure 6.2: A schematic representation of the proposed proton-coupled electron transfer process in the bacterial reaction center. The red color indicates changes occurring after special pair excitation and before the electron transfer, while the blue color depicts changes taking place after the electron transfer and before the special pair reduction.

P_M is found to have more electron density than P_L both in the ground and

excited state. [63] The additional negative charge would facilitate the electron transfer from P^* . On the electron acceptor, B_A , the 13^1 carbonyl is conjugated to the π electron system of its porphyrin ring. Therefore formation of a hydrogen bond with the water molecule (or H_3O^+) provides an opportunity to fine-tune the redox potential, making the accessory bacteriochlorophyll *a* easier to reduce and lowering the free energy of the $P^+B_A^-$ state. All together this would facilitate the electron transfer from P^* to B_A .

In order to stabilize the positive charge on the special pair and to prevent charge recombination, the 3^1 acetyl of P_L could be rotated if enough driving force is available to break the hydrogen bond with His L168. Such a rotation will alter the electronic structure of the bacteriochlorophyll *a* dimer. Molecular dynamics simulations suggest that the acetyl rotates on oxidation, while coupled-cluster calculations on gas-phase energetics of that process indicate that *ca.* 7 kcal/mol driving force is provided by the preference of the charged BChl *a* Mg to be coordinated to the carbonyl rather than to the methyl group. [122, 134, 135] This energy is enough to break the hydrogen bond between P_L and His L168. In that respect the acetyl group would act as a valve to protect the system from too fast charge recombination. In all known reaction centers an electron moves at least one step down to acceptor chain before the oxidized primary donor is reduced.

The possibility of the above-mentioned through-bond connection between the primary electron donor and acceptor, the speculated proton transfer, and the 3^1 acetyl rotation to block recombination of the cation radical are intriguing suggestions and therefore their significance and realism should be further explored. Particularly a thorough investigation of the acetyl rotation profile and constraints, as well as the associated impact on the electronic structure of P before and after the primary electron transfer should be pursued. Finally, the proton transfer possibility and path should be addressed by employing more extensive models within the QM/MM approach.