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REVIEW

Primary electron transfer processes in photosynthetic reaction centers from oxygenic organisms

Mahir Mamedov · Govindjee · Victor Nadtochenko · Alexey Semenov

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Abstract This minireview is written in honor of Vladimir A. Shuvalov, a pioneer in the area of primary photochemistry of both oxygenic and anoxygenic photosyntheses (See a News Report: Allakhverdiev et al. 2014). In the present paper, we describe the current state of the formation of the primary and secondary ion–radical pairs within photosystems (PS) II and I in oxygenic organisms. Spectral-kinetic studies of primary events in PS II and PS I, upon excitation by ~20 fs laser pulses, are now available and reviewed here; for PS II, excitation was centered at 710 nm, and for PS I, it was at 720 nm. In PS I, conditions were chosen to maximally increase the relative contribution of the direct excitation of the reaction center (RC) in order to separate the kinetics of the primary steps of charge separation in the RC from that of the excitation energy transfer in the antenna. Our results suggest that the sequence of the primary electron transfer reactions is P680 → Chl_{D1} → Phe_{D1} → Q_A (PS II) and P700 → A_{0A}/A_{0B} → A_{1A}/A_{1B} (PS I). However, alternate routes of charge separation in PS II, under different excitation conditions, are not ruled out.

Keywords Charge separation · Electron transfer · Photosystem II · Photosystem I · Primary processes · Pump-probe laser spectroscopy · Femtosecond time resolution

Abbreviations

PS II	Photosystem II
PS I	Photosystem I
RC	Reaction center
Chl	Chlorophyll
Phe	Pheophytin
Q_A, Q_B	Primary and secondary quinone acceptors of PS II
P680	Special pair chlorophyll molecules P_{D1} and P_{D2} of PS II
P700	Primary electron donor of PS I
A_0	Monomer chlorophyll, an electron acceptor of PS I
A_1	Phylloquinone, secondary acceptor of PS I
F_X, F_A, F_B	Iron–sulfur clusters

Introduction

Virtually all life of higher form is dependent on oxygen, whereas plants, algae, and cyanobacteria produce most of the atmospheric oxygen on our planet (for a discussion on

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evolution, see Bjorn and Govindjee 2015). During oxygenic photosynthesis, light energy is captured and converted into chemical energy by two light-driven pigment–protein complexes called photosystem II (PS II) and photosystem I (PS I) that are embedded in thylakoid membranes (Govindjee and Bjorn 2012). Despite large differences in composition and architecture of the pigment–protein systems, the light-driven primary energy-converting processes are surprisingly similar in these two systems (Semenov et al. 2011; Blankenship 2014).

Natural photosynthesis utilizes two coupled systems, a light-harvesting antenna and a photochemical reaction center (RC) (Govindjee and Bjorn 2012). The photophysical and photochemical reactions in photosynthesis, such as the capture of solar radiation by light-harvesting complexes, excitation energy transfer to the RC, and the initial electron transfer reactions, are among the fastest events in biology, taking place on time scales ranging from tens of femtoseconds (fs) to several hundred nanoseconds (ns) (Shuvalov et al. 1978, 1986; Van Grondelle et al. 1994; Van Grondelle and Novoderezhkin 2006; Shelaev et al. 2010).

Understanding the relationship between the structure and function of photosynthesis is of fundamental importance, by itself, but its application to improve both natural and artificial photosynthetic systems is of importance for the benefit of the human race (Blankenship et al. 2011; Hou et al. 2014). Our understanding of the structure and function of RCs is growing in part due to the use of powerful genetic tools, their integration with optical and magnetic resonance spectroscopies, and the availability of the atomic level structure of the proteins involved. Note that although the crystal structure of photosystems reflects their specific configuration, in the in vivo situation, the system is in continuous movement (fast nuclear and slow conformational motions), which is important for their function. Thus, there is a dynamic picture, which will need to be understood.

In this *minireview*, we describe the current state of the primary electron transfer reactions (formation of the primary and secondary ion–radical pairs) within photosystems I and II.

Photosystem II

Pigment–protein complex of PS II is one of the two primary enzymes of the photosynthetic chain in thylakoid membranes of oxygenic organisms (Wydrzynski and Satoh 2005; see Fig. 1). PS II, the water-plastoquinone oxidoreductase, initially catalyzes light-induced stable charge separation leading to the formation of an ion–radical pair between the primary electron donor P680 and the first quinone acceptor Q_A: $P680^+Q_A^-$. In their pioneering work,

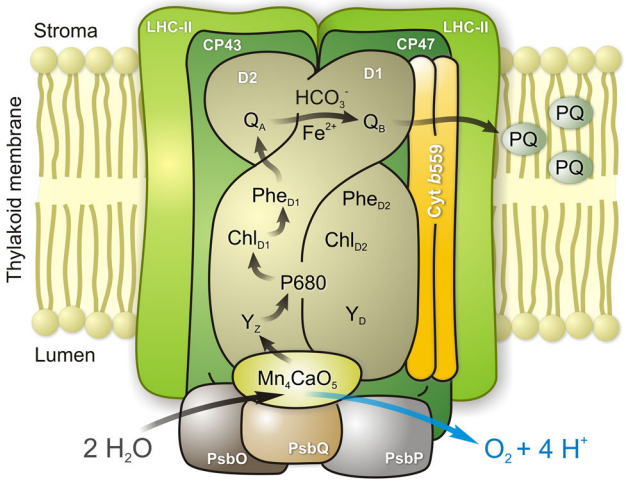

Fig. 1 Schematic representation of photosystem II (PS II) in higher plants and green algae (only core proteins are shown). The pathway of the electron flow through PS II is shown by black arrows, involving mostly the D1 protein, except for Q_A, which is on D2. Other symmetrically related cofactors on D2 (the inactive branch) do not participate in linear electron transfer through PS II. Mn_4CaO_5, inorganic core of the water-oxidizing complex; Y_Z (redox active tyrosine residue on the D1 protein) and Y_D (a tyrosine, on the D2 protein), PQ, mobile plastoquinone molecules; CP43 and CP47, Chl–protein complexes of 43 and 47 kDa; LHC-II, light-harvesting complex II; PsbO (33 kDa), PsbP (23 kDa), and PsbQ (17 kDa), extrinsic proteins of PS II; cyt*b*559, redox active cytochrome *b*559. The diagram also shows a bicarbonate (HCO_3^{2-}) ion, which is known to be bound on a non-heme-iron that sits between Q_A and Q_B. HCO_3^{2-} has been shown to play an essential role in electron and proton transport on the electron acceptor side of PS II. This diagram was adapted from Shevela et al. (2012); courtesy of Dmitriy Shevela

Shuvalov, Klimov, and coworkers (Klevanik et al. 1977; Klimov et al. 1977, 1979, 1986; see also Allakhverdiev et al. 2010) showed that before the formation of $P680^+Q_A^-$, an electron is transferred from P* (P680*) to a pheophytin (Phe) molecule and then to Q_A. The formation of $P680^+Q_A^-$ leads to two chemical events: oxidation of water to molecular oxygen (after four turnover of PS II) and reduction of plastoquinone to plastohydroquinone (after two turnovers of PS II). See Wydrzynski and Satoh 2005, McEvoy and Brudvig 2006, and Renger 2007 for details. These reactions are spatially separated and occur on different sides of the RC in the thylakoid membrane.

The X-ray crystal structure of dimeric PS II core complexes from *Thermosynechococcus elongatus*, a thermophilic cyanobacterium, is now available at 1.9 Å resolution (Umena et al. 2011). Each PS II monomer is composed of 19 protein subunits, 25 integral lipids, 35 chlorophyll (Chl) *a* molecules, 2 pheophytin (Phe) molecules, 11 carotenoid molecules, 2 plastoquinones (PQ), Mn_4CaO_5 cluster, chloride ions, and >1,350 water molecules. The PS II core complex contains the RC (D1/D2/cyt*b*559), the inner antenna (CP43 and CP47), and three peripheral (PsbO,

PsbP, PsbQ) proteins; this is the minimal unit capable of oxidizing water and reducing plastoquinone molecules.

The RC D1/D2 proteins are located approximately symmetrically with respect to the transmembrane region, which is very similar to the arrangement of the L/M subunits in bacterial RC (BRC) (Michel et al. 1986; Komiya et al. 1988). Four Chls (special pair chlorophyll molecules P_{D1} and P_{D2}, and two accessory chlorophylls, Chl_{D1} and Chl_{D2}), two pheophytins (Phe_{D1} and $Pheo_{D2}$), and two plastoquinones (Q_A and Q_B) are arranged in two nearly symmetrical branches (Ferreira et al. 2004; Loll et al. 2005; Umena et al. 2011). In addition, there is a bicarbonate ion bound to the non-heme iron between Q_A and Q_B (see e.g., Shevela et al. 2012); this bicarbonate acts as a bridge for electron and proton transfer from Q_A to Q_B (see e.g., a theory by Fletcher 2014). The arrangement of the electron transfer cofactors in the PS II complex is depicted in Fig. 1.

The dynamics of excitation energy transfer and charge separation in PS II has been extensively investigated by various techniques including time-resolved pump-probe absorption spectrometry (Wasielewski et al. 1989; Govindjee and Wasielewski 1989; Durrant et al. 1992; Hastings et al. 1992; Muller et al. 1996; Groot et al. 1997; Greenfield et al. 1996, 1999; Holzwarth et al. 2006a, b; Romero et al. 2010), time-resolved fluorescence (Gatzen et al. 1996; Konermann et al. 1997, Andrizhiyevskaya et al. 2004), spectral hole burning (Groot et al. 1996; Zazubovich et al. 2003), Stark spectroscopy (Frese et al. 2003; Romero et al. 2012), two-pulse photon echo (Wink et al. 1987; Louwe and Aartsma 1995; Prokhorenko and Holzwarth 2000), and Fourier transform infrared (FTIR) spectroscopy (Berthomieu et al. 1990; Noguchi et al. 1998).

While these methods have provided information on the rates and processes involved, there is still no consensus on the times of the dynamic processes and the role of different pigments in excitation energy and charge transfer events (see e.g., Greenfield et al. 1996; Greenfield and Wasielewski 1996; Novoderezhkin et al. 2007; Berera et al. 2009; Romero et al. 2014; Fuller et al. 2014). Remaining questions include information on the existence of a sub-picosecond energy equilibrium process, on the rates for primary charge separation, and for excitation energy transfer steps, as well as on the identity of the pigments involved as charge transfer intermediates.

The details of the mechanism of how RCs function, both from structural and functional points of view, are now understood in much greater depth for RCs from the anoxygenic purple photosynthetic bacteria than from PS II. In the purple bacterial RC, only one branch is active although the inactive branch can be forced into operation with modification of amino acid chains on both branches (Allen and Williams 1998; Haffa et al. 2004; Marchanka et al. 2010).

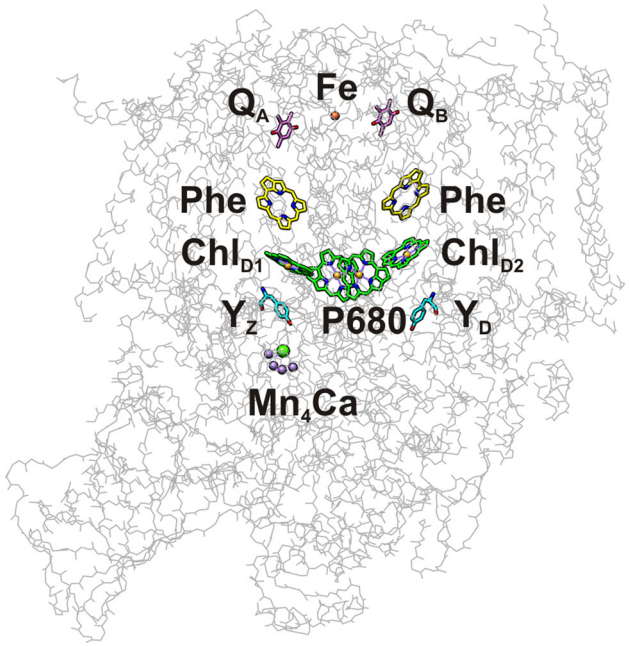

Fig. 2 3D structure of the PS II core complex (the view is parallel to the membrane plane). The redox cofactors are displayed inside the protein backbone. P680, the reaction center chlorophyll dimer; Chl_{D1}, Chl_{D2}, chlorophyll molecules on D1 and D2 proteins; Phe, pheophytin, one on D1 and another on D2; Q_A (on D2), a one-electron acceptor plastoquinone; Q_B (on D1), a two-electron acceptor plastoquinone (adapted from Semenov et al. 2011)

As in the bacterial RC, electron transfer in PS II is known to proceed only along one branch, the D1 branch (despite having identical cofactors along the D2 branch of the RC; note, however, that Q_A is on D2), with the formation of $P680^+Phe^-_{D1}$ and then $P680^+Q^-_A$ (Fig. 2) (see also Shkuropatov et al. 1997, 1999). The preference for one branch over the other must be due to the protein environment around the cofactors, which may alter their redox potentials, thus making electron transfer to those cofactors favorable. (For a general discussion, see Björn et al. 2009.) One of the reasons for asymmetric electron transfer between prosthetic groups located on different polypeptides is due to different molecular dynamics on the two sides. Our understanding of the primary processes in photosynthesis will not be complete without explanation of the strong asymmetry in electron transport, as mentioned above.

In bacterial RCs, Shuvalov et al. (1978), using ps differential spectroscopy, had initially suggested that monomeric bacteriochlorophyll (B_A) is an intermediate carrier between P870 and BPhe. The optical signature of this intermediate state was finally observed as an additional transient absorption band at ~1,020 nm that was assigned

to the formation of B_A^- (Lauterwasser et al. 1991; Arlt et al. 1993); the reduction of B_A and BPhe had lifetimes of ~2.3 and ~0.9 ps, respectively. Later, Holzwarth and Muller (1996) suggested that these processes are reversible and forward electron transfer times for both the steps are ~2.5 ps.

Another important question associated with electron transfer within photosynthetic RC is to know the precise nature of the primary electron donors and acceptors. A generally accepted notion is that in bacterial RC, electron transfer is driven by the first singlet excited state of a special pair of bacteriochlorophyll (P870). However, data derived from RC complexes isolated from *Rb. sphaeroides* mutant strain (YM210) (van Brederode et al. 1997) and wild type (van Brederode et al. 1999) showed that excitation of the monomeric bacteriochlorophyll in the active *A*-branch of the RC (B_A) drives ultrafast transmembrane electron transfer, without the involvement of P*, demonstrating, in the opinion of the authors, a new and efficient mechanism for solar energy transduction in photosynthesis. However, this view seems unlikely since B_A^* should transfer excitation energy to P870 within 100 fs (Vulto et al. 1997). The idea that accessory BChl* acts as a primary electron donor, for bacterial RC, and Chl*, for PS II RC, leads to a number of problems (see Shelaev et al. 2011 for discussion) and requires convincing proof, which is currently unavailable.

Classical mechanistic models have assumed that in PS II reaction center, P_{D1} and Phe_{D1} are the primary electron donor and the acceptor, respectively. However, data derived from isolated RC (D1–D2–cyt*b*559) and PS II core complexes have led to the conclusion that the primary electron donor is Chl_{D1} and the primary electron acceptor is Phe_{D1} under physiological conditions, as well as at cryogenic temperatures, while P_{D1} is a secondary donor (Prokhorenko and Holzwarth 2000; Groot et al. 2005; Holzwarth et al. 2006a, b; Novoderezhkin et al. 2007; Di Donato et al. 2008; Raszewski et al. 2008; Renger and Schlodder 2010). Using visible/mid-infrared pump-probe experiments, Groot et al. (2005) and Di Donato et al. (2008) have shown that the initial formation of the radical pair $Chl_{D1}^+Pheo_{D1}^-$ occurs in a significant fraction of PS II RCs on a sub-picosecond timescale, whereas $P680^+$, which has the appropriate (close to +1.2 V) oxidizing power for water oxidation (+0.8 V), is formed after ~6 ps, followed by radical pair relaxation.

Transient absorption experiments at 77 K with various excitation conditions of the isolated PS II reaction center preparations demonstrated that at least two different excited states, $(Chl_{D1}Phe_{D1})^*$ and $(P_{D1}P_{D2}Chl_{D1})^*$, give rise to two different pathways for ultrafast charge separation (Romero et al. 2010). This was supported by the modeling by Novoderezhkin et al. (2011) and Romero et al. (2014). Therefore, one can conclude that Phe_{D1} is an electron acceptor, P_{D1} is an electron donor, and Chl_{D1} can act both as an electron donor and as an acceptor (Romero et al. 2012; Kruger et al. 2014). We may assume that this functional flexibility may be the key for the successful performance of the PS II RC.

One of the newest and most powerful technique for deciphering the spectral dynamics of electronic transitions, the 2-dimensional electronic spectral analysis, of isolated PS II RC (D1–D2–cyt*b*559), supports the involvement of the two electron transfer pathways, as mentioned above (Fuller et al. 2014; Romero et al. 2014).

At 278 K, both the isolated PS II RCs and the PS II core complexes, when excited by 20-fs pulses centered at 700–710 nm, show that the initial electron transfer reaction takes place within ~1 ps, with the formation of $P680^+Chl_{DI}^-$ charge-separated state (Shelaev et al. 2008, 2011). Subsequent electron transfer from Chl_{D1}^- occurs within ~14 ps, leading to the formation of the secondary radical pair $P680^+Pheo_{D1}^-$.

The formation of $P680^+Chl_{D1}^-$ (where, Chl_{D1} is Chl-670; Shelaev et al. 2011) needs to be independently checked by further experiments, since this information is critical for understanding the precise mechanism of the primary charge separation. Difference absorption measurements, in the fs/ps range, at different delay times, with PS II core complexes, excited by 20-fs 710 nm light, show a rise time of ~ 11 ps for the initial formation of anion radical band of pheophytin molecule (Phe^-) at 460 nm (Nadtochenko et al. 2014); this agrees with an earlier measurement of Phe, at 545 nm (Shelaev et al. 2008, 2011). The latter was attributed to charge separation between P680* and Phe_{D1}, i.e., to the formation of the ion–radical pair $P680^+Phe_{D1}^-$. Further, the reduction of Q_A by electron transfer from Phe_{D1}^- was accompanied by relaxation of the 460-nm band, which occurs within ~250 ps. A slow component (11–14 ps) of the Phe reduction excludes, in our opinion, the possible role of the Phe molecule as the primary electron acceptor at least under the excitation condition used, while Chl_{D1} accepts an electron from P680* within ~1 ps.

Subtraction of the $P680^+$ spectrum measured at 455 ps delay, from the spectra at 23 or 44 ps delay, revealed the spectrum of Phe_{D1}^-, which is very similar to that measured earlier by a steady-state method (Klevanik et al. 1977; Klimov et al. 1977). The spectrum of Phe_{D1}^- formation includes a bleaching (or red shift) of the 670 nm band (675 nm at low temperature) and indicates the nearby location of Chl-670 and Phe_{D1} (Nadtochenko et al. 2014). According to another measurement in the femtosecond–picosecond time range, Chl-670 was identified as Chl_{D1} (Shelaev et al. 2011). The decay kinetics of the stimulated

emission at 685 nm indicates the existence of at least two emitting centers with a lifetime of ~1 and ~14 ps. These components are due to the formation of $P680^+Chl_{D1}^-$and $P680^+Phe_{D1}^-$, respectively.

The transient absorbance spectra at 0.3, 1.1, 35, and 455 ps, time delays are shown in Fig. 3. The spectrum at 1.1 ps delay mostly represents the spectrum of the primary charge-separated state $P680^+Chl_{D1}^-$, while the spectra at 35 and 455 ps delays refer to that of the subsequent $P680^+Phe_{D1}^-$ and $P680^+Q_A^-$ states, respectively. The inset in Fig. 3 shows the difference $\Delta\Delta A$ absorbance spectrum, obtained by subtraction of the ΔA spectrum at 0.15 ps from that at 3 ps delay. This $\Delta\Delta A$ spectrum clearly reveals that the bleaching at 670 nm is due to the reduction of Chl_{D1} to Chl_{D1}^-.

Thus, considering all of the above, it is evident that two different sets of cofactors (exciton states) (van Stokkum et al. 2004) give rise to two different charge separation pathways (Romero et al. 2010; Novoderezhkin et al. 2011; Romero et al. 2014). When there are two alternative charge separation pathways, disorder in the system can destroy one of them and create a condition for the other to exist. Consequently, the measured kinetics (averaged over disorder) will contain a superposition of components corresponding to different pathways. As a result, various experimental methods sensitive to different aspects of the electron transfer can produce a large spread in the estimated 'time constants' of primary charge separation. Under specific conditions, e.g., at 278 K, and using pump-probe laser spectroscopy, with 20-fs time resolution, and excitation at 710 nm of PS II complexes, charge separation was shown to involve the formation of two subsequent ion–radical pairs, $P680^+Chl_{D1}^-$ (~1 ps) and $P680^+Phe_{D1}^-$ (~14 ps), in active D1-branch (Shelaev et al. 2008, 2011; Nadtochenko et al. 2014). Thus, the results can be described by the following scheme.

$$(P680Chl_{D1})^* \xrightarrow[\sim 0.9\ ps]{} P680^+Chl_{D1}^- \xrightarrow[\sim 14\ ps]{} P680^+Phe_{D1}^- \xrightarrow[\sim 250\ ps]{} P680^+Q_A^-$$

The very first experiments by Wasielewski et al. (1989), using 500 fs 610 nm laser light, were interpreted to mean that the formation of $P680^+Phe^-$ and disappearance of P680* took place in ~3 ps, at 4 °C in PS II RCs.

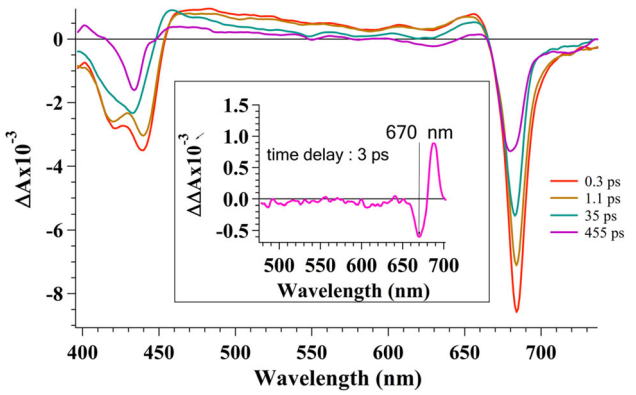

Fig. 3 Difference (light-minus-dark) absorbance changes (ΔA) at different delays (indicated in the figure) in PS II core complexes from spinach, at 278 K, excited by 20-fs pulses of 710 nm light. The *inset* shows the difference ($\Delta\Delta A$) absorbance spectrum obtained by subtraction of the ΔA spectrum at 0.15 ps from that at 3 ps delay (adapted from Shelaev et al. 2011)

Photosystem I

Pigment–protein complex of photosystem I (PS I) is one of the key enzymes of the photosynthetic electron transfer chain in thylakoid membranes (Golbeck 2006). The simpler prokaryotic (cyanobacterial) version contains the same cofactors and performs the same major function as its eukaryotic (algae and higher plants) counterpart. PS I catalyzes the light-driven one-electron transfer from peripheral protein donor, plastocyanin, and/or cytochrome c_6, to ferredoxin and/or flavodoxin.

The electron density map of trimeric PS I complexes from the cyanobacterium *T. elongatus* with a resolution of 2.5 Å (Jordan et al. 2001) led to an accurate model for the architecture of pigments, cofactors, and proteins in that system. PS I of cyanobacteria contains 12 protein subunits, 96 chlorophyll (Chl) molecules, 22 carotenoids, three [4Fe–4S] clusters, two phylloquinones, and four lipid molecules. Two transmembrane subunits PsaA and PsaB form a C_2 symmetric heterodimeric core complex containing most of the cofactors. The pairs of Chl and phylloquinone molecules are arranged in two symmetric branches, *A* and *B,* and are bound with PsaA and PsaB subunits, respectively.

The electron transfer chain of PS I consists of P700 (Chl1A/Chl1B, alternatively called eC-A1/eC-B1), A_0 (pairs of Chl molecules designated as Chl2A/Chl3A, and Chl2B/Chl3B, also called eC-B2/eC-A3 and eC-A2/eC-B3), A_1 (phylloquinone molecules designated as A_{1A}/A_{1B}), and iron–sulfur clusters F_X, F_A, and F_B (Fig. 4). It is now known that the electron transfer in PS I occurs through both branches of the redox cofactors from P700 to F_X, but the degree of asymmetry of this transfer and the factors that cause it are not clear (Guergova-Kuras et al. 2001a, b; Srinivasan and Golbeck 2009). In addition, to date the kinetics of the primary charge separation and the nature of the primary electron donor and acceptor in PS I remain controversial (Holzwarth et al. 2006a, b; Srinivasan and Golbeck 2009; Di Donato et al. 2010; Shelaev et al. 2010).

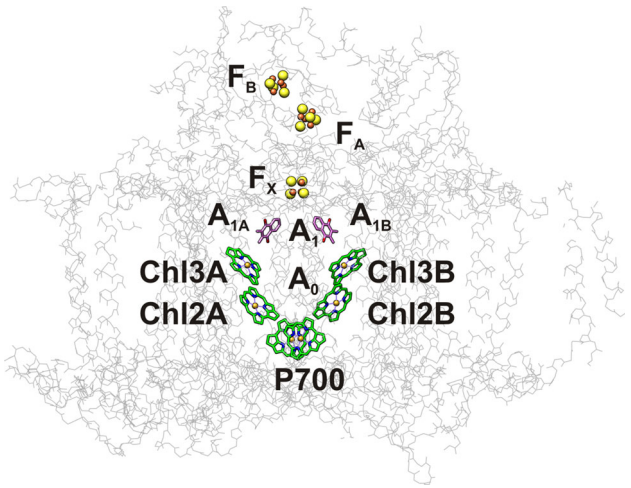

Fig. 4 3D structure of photosystem I complex (the view is parallel to the membrane plane). The redox cofactors are displayed inside the protein backbone. P700, the primary electron donor; Chl2A, Chl2B as well as Chl3A and Chl3B, chlorophyll *a* molecules (see text for details); A_{1A} and A_{1B}, phylloquinone molecules; F_X, F_A, F_B, iron–sulfur clusters; type: 4Fe–4S (adapted from Semenov et al. 2011)

As mentioned above, out of 96 Chl molecules, six are electron transfer cofactors located near the contact surfaces of the PsaA and PsaB subunits. The chlorophyll dimer P700 consists of two Chl *a* molecules (Chl1A/Chl1B), the porphyrin planes of which are parallel to each other (at a distance of 3.6 Å) and perpendicular to the plane of the membrane (Fig. 5). The spatial localization of the other two molecules of Chl *a* (Chl2A/Chl2B) roughly corresponds to the localization of two molecules of monomeric bacteriochlorophyll in the RC of purple bacteria, and two additional molecules of Chl *a* (Chl3A and Chl3B) are arranged, in a manner, similar to the two molecules of bacteriopheophytin in the RC of purple bacteria (Deisenhofer et al. 1985; Komiya et al. 1988). The planes of the porphyrin rings of Chl2A (Chl2B) and Chl3A (Chl3B) molecules are parallel (with distance of 3.9 Å), but they are slightly more shifted relative to each other than Chl1A and Chl1B (Fig. 5). The mutual arrangement and relatively close distance between central Mg^{2+} atoms of Chl2A and Chl3A, and Chl2B and Chl3B (8.7 and 8.2 Å, respectively) imply the possibility of significant interaction between these pairs of Chl molecules. This fact allows us to consider A_0 as a Chl2A/Chl3A (and/or Chl2B/Chl3B) dimer.

As indicated above, PS I also includes two molecules of phylloquinone (A_{1A} and A_{1B}). Branch *A* includes Chl molecules labeled Chl1A, Chl2A, Chl3A, and phylloquinone A_{1A}, while branch *B* includes Chl1B, Chl2B, Chl3B, and phylloquinone A_{1B}. The two cofactor branches of the electron transfer chain merge onto the inter-polypeptide iron–sulfur cluster F_X. Terminal electron acceptors–[4Fe-4S] clusters F_A and F_B are located on the stromal subunit PsaC.

Most of the previous studies put the primary charge separation step from P700* to A_0 in PS I RC in the 0.8–4 ps time range, and the subsequent electron transfer from primary electron acceptor A_0 to the secondary electron acceptor A_1 was suggested to occur in 10–50 ps range (see Brettel and Leibl 2001; Savikhin 2006; Savikhin and Jankowiak 2014 for a review). However, Shelaev et al. (2010) have shown that after preferential excitation of P700 and A_0, formation of primary radical pair $P700^+A_0^-$ occurs, within 100 fs, and the formation of $P700^+A_1^-$ has a characteristic time of ~25 ps. Subsequent electron transfer reactions from A_{1A} and A_{1B} to F_X take place with characteristic times of ~200 and ~20 ns, respectively (Brettel 1988; Setif and Bottin 1989; Guergova-Kuras et al. a, b;

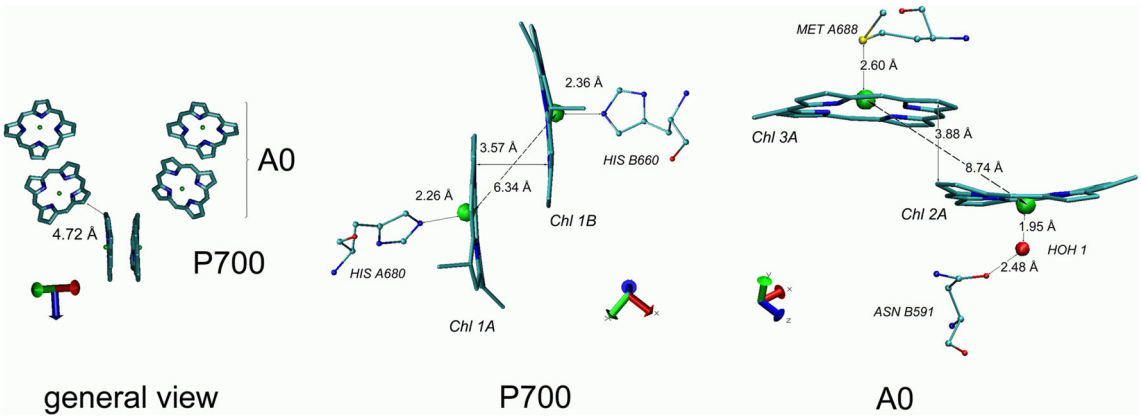

Fig. 5 *Left* a general view of P700 and A_0 in PS I. *Middle* details of P700, *Right* details of A_0. The diagrams show relative arrangement in the dimers of chlorophyll molecules for both the primary electron donor P700 (Chl1A and Chl1B) and the primary electron acceptor A_{0A} (Chl2A/Chl3A) in PS I in branch A of the redox cofactors, as well as the key amino acids in the vicinity. The axial ligands to the central Mg atom of chlorophyll molecules and the distance, in angstroms, between the plane of the porphyrin rings and Mg atoms are also shown. For further information, see Fig. 4 and its legend

Srinivasan and Golbeck 2009). This is followed by electron transfer from F_X to the terminal iron–sulfur clusters, F_A and F_B, and further to the soluble protein ferredoxin or flavodoxin. Photooxidized $P700^+$ is reduced by plastocyanin or cytochrome c_6, returning all the cofactors of PS I back to their original state, where the primary electron donor P700 is reduced and all subsequent acceptors are oxidized (Golbeck 2006).

The main difference between PS I and bacterial RC is the impossibility of mechanically separating Chl molecules of the light-collecting antenna from Chl molecules of the RC without losing the native character of the PS I pigment–protein complex. This is due to the association of 79 molecules of Chl with the same heterodimer of protein subunits PsaA/PsaB, which binds six Chl molecules of the initial region of the RC electron transfer chain. All the 96 Chl molecules, in PS I, cannot be clearly separated, from each other, by their spectral features. According to Karapetyan et al. (2006), the major part of the antenna Chl pool has absorption maximum at 670–680 nm, whereas only some Chl molecules (possibly dimers or trimers) are characterized by an absorption band at 690–710 nm. Although it is generally accepted that a special pair of Chl molecules (P700) has absorption maximum at 700–705 nm and the maximum absorption of the chlorophyll acceptor A_0 is at 685–690 nm (Shuvalov et al. 1986; Hastings et al. 1994; Savikhin et al. 2001), their spectra partially overlap with the spectra of several molecules of the antenna chlorophyll in the same spectral region.

Excitation energy transfer in the antenna and the electron transfer in RC of PS I have now been studied by different approaches, in particular, using sub-picosecond pulse spectroscopy (for review, see Savikhin 2006, Savikhin and Jankowiak 2014). However, primary reactions of electron transfer cannot be distinctly separated from reactions of the excitation energy transfer in the antenna because these reactions occur within the same time range. To separate the electron transfer and the excitation energy transfer and to clearly detect kinetics of the primary stages of electron transfer and spectra of the corresponding intermediates, various approaches have been used in several laboratories. For example, Kumazaki et al. (2001) extracted the major part of the antenna Chl and, on the resulting complex, recorded two kinetic components with characteristic lifetimes of 0.8 and 9 ps, which were assigned to the primary separation of charges. Note that a decrease in the total Chl content to 12–14 molecules is very likely to significantly change both the structure and function of PS I complex.

There are two main models describing charge separation in PS I. According to the first model—upon absorption of light, primary electron donor P700 is excited to P700*, and then the primary charge separation occurs between P700* and the primary acceptor A_0, resulting in the formation of the ion–radical pair $P^+A_0^-$ in less than $\sim$10 ps. We note that pioneering work in this field was done first by Fenton et al. (1979) and then by Wasielewski et al. (1987). The data derived from spinach PS I particles using picosecond transient absorption spectroscopy led to the suggestion that the immediate ($<\sim$1.5 ps) bleach of P700 and formation of the 810 nm band are due to the excitation of P700 to P700* (Wasielewski et al. 1987). In the near-infrared region of the spectrum, the 810 nm band induced by excitation of samples diminished to about 60 % of its original intensity with the same 13.7 ps time constant as the formation of the 690 nm band. These spectral changes were interpreted to be due to the formation of the charge-separated state $P700^+A_0^-$, where A_0 is the primary electron acceptor chlorophyll molecule. Then the electron on A_0^-, from $P^+A_0^-$ state, is transferred onto phylloquinone A_1 during 50 ps, and then in $\sim$200 ns, it is transferred onto the iron–sulfur cluster F_X (for a review, see Brettel and Leibl 2001).

One of the earliest papers with spectral and time (ps) resolution by Shuvalov et al. (1986) demonstrated that selective excitation of PS I by picosecond laser pulses, at 710 nm, results in the formation of $P700^+A_0^-$, which is characterized by two bleaching bands: at 700 nm corresponding to $P700^+$ due to the oxidation of P700 dimer and at 689 nm attributed to the formation of A_0^-.

Another approach to answer questions on the precise steps of the primary events is based on subtracting the transient spectrum of the oxidized (closed) RC from the spectrum of the reduced (open) RC, as was used by Nuijs et al. (1986). This approach allowed the authors to remove spectral changes caused by excitation energy transfer in the antenna and to reveal spectral features reflecting electron transfer in the RC. The kinetics of energy transfer in the antenna was suggested to be independent of the redox state of P700 (Savikhin 2006). Hastings et al. (1994) had used this approach for PS I particles from cyanobacteria and observed two kinetic phases with lifetimes of 4 and 21 ps. These components were assigned to the generation and disappearance of the ion–radical pair $P700^+A_0^-$.

Hastings et al. (1994) had used a non-selective excitation at 590 nm, and therefore the phase with lifetime of 4 ps included not only the oxidation of P700, but also the energy transfer in the antenna. Thus, the time constant of 4 ps could represent the upper limit of rate constant in kinetics of the primary radical pair production. Moreover, to obtain a good signal/noise ratio, Hastings et al. (1994) used laser flashes with rather high energy that induced excitation annihilation and shortened the total time of reaching the state of one-exciton excitation in the antenna. Savikhin et al. (2000) used a similar approach and obtained 10 ps as the time of formation of $P700^+A_0^-$. They excited

PS I with 100-fs flashes with 660-nm maximum. Later, using a simple model of electron transfer and approximating the kinetics by two free parameters, Savikhin et al. (2001) obtained a characteristic time of 1.3 ps for the formation of $P700^+A_0^-$ and of 13 ps for the subsequent reaction $A_0 \rightarrow A_1$. Similar results were obtained earlier by White et al. (1996) for PS I complexes isolated from spinach.

Melkozernov et al. (2000) investigated fast spectral changes in PS I from the cyanobacterium *Synechocystis* sp. PCC 6803, using 150-fs laser flashes with maxima at 560, 693, and 710 nm. They suggested that the change in the absorption at 700 nm was caused by primary separation of charges and occurred in about 20 ps. They believed that the $P700^*A_0 \rightarrow P700^+A_0^-$ should be the rate-limiting reaction, whereas the quasi-equilibrium in the antenna should be established in about 3 ps. But other authors consider that the excitation energy transfer in the antenna is the slower step (20–25 ps) (Savikhin et al. 2000; Gobets and van Grondelle 2001; Muller et al. 2003).

Muller et al. (2003) have proposed an alternative model for primary charge separation in PS I. They investigated PS I complex from *Chlamydomonas reinhardtii* and, based on modeling the kinetics and analysis of the differential absorption spectra, assumed that the primary charge separation should occur in 6–9 ps. They also assumed that the primary radical pair is not $P700^+A_0^-$, but $P700^+Chl2^-$ or $Chl2^+Chl3^-$, where Chl2 and Chl3 are, respectively, the distal and proximal molecules of a Chl monomer in the RC relative to P700. Data of Muller et al. (2003), Holzwarth et al. (2006b), and Muller et al. (2010) revealed three kinetic components, with characteristic times of 6, 20, and 40 ps. Holzwarth and coworkers have proposed a scheme for the primary charge separation, in PS I, according to which the fastest component corresponds to the formation of the primary radical pair $Chl2^+Chl3^-$ and the two slower components to the radical pairs $P700^+Chl3^-$ and $P700^+A_1^-$. This model was supported by sub-picosecond infrared spectroscopy studies (Di Donato et al. 2010). However, according to electrostatic calculations, the functioning of monomeric Chls 2A/2B as primary donor(s) and monomeric Chls 3A/3B as primary acceptor(s) seems unlikely, since in this case the electron transfer would be thermodynamically unfavorable (Ptushenko et al. 2008).

In the majority of studies on the fast kinetics of spectral changes in PS I, flashes with duration >100 fs were used; further, these flashes were of high intensity, resulting in two quanta arriving into the same RC, and thus there was exciton–exciton annihilation and distortion of the spectral change kinetics. Shelaev et al. (2010) have used a complex approach including short ($\sim$ 20 fs) flashes with relatively low power (20 nJ) centered at 720 nm with a bandwidth of 40 nm (fwhm, full width at half maximum). Thus, a predominant excitation of the primary electron donor—the chlorophyll dimer P700—was made possible (Shelaev et al. 2010). Under these conditions, about half of the chlorophyll RC molecules (i.e., molecules of P700 and A_0) were excited directly, whereas the other half received excitation energy from antenna (An*) to RC pigments that were not excited directly by the femtosecond pulses. These conditions were chosen to maximally increase the relative contribution of the direct excitation of the RC in order to separate the kinetics of primary stages of the charge separation in the RC from the kinetics of the excitation energy transfer in the antenna. Excitation in antenna is transferred to P700 in a non-radiative way; this non-radiative energy transfer was observed as a separate kinetic component from that of charge transfer event(s) in RC by spectral-kinetic measurements. Based on these findings, it was possible to reveal the difference spectra of the intermediates $(P700A_0)^*$, $P700^+A_0^-$, and $P700^+A_1^-$, and to describe the kinetics of transitions between these intermediates (Shelaev et al. 2010; Semenov et al. 2012; Sun et al. 2014). Figure 6 shows these difference spectra, $\Delta A(\lambda,t)$, of PS I obtained upon excitation by a 720 nm 25 fs pulse, at different time delays. Spectra at early delay times (Fig. 6a, b) represent mostly spectra of the primary radical pair $P700^+A_0^-$, whereas the spectrum in Fig. 6c contains a mixture of $P700^+A_0^-$ and $P700^+A_1^-$ states. The spectrum in Fig. 6d (delay time 100 ps) belongs to the ion–radical pair $P700^+A_1^-$.

The obtained results can be summarized by the following scheme:

$$(P700A_0)^* \rightarrow (P700^+A_0^-) \rightarrow (P700^+A_1^-)$$
$$<100\ \text{fs} \qquad \sim 25\ \text{ps}$$

Semenov et al. (2012) have reported time-resolved spectra in the 400–740 nm range, obtained upon excitation of PS I by femtosecond pulses, with maxima at 3 different wavelengths (670, 700, and 720 nm); this work was designed to test the hypothesis that contradictions in the literature on the kinetics and differential spectra of PS I, studied by the femtosecond pump–probe method, were mainly caused by differences in the duration and spectra of the exciting pulses. Different experimental conditions gave different results and different interpretation of data on the initial states of PS I excitation; these were caused by different degrees of superposition of the excitation of the antenna, P700 and A_0. With a significant contribution of the excitation of the antenna, it is difficult to separate the kinetics of the initial steps of the electron transfer between the redox cofactors P700, A_0, and A_1 from the background of energy transfer from

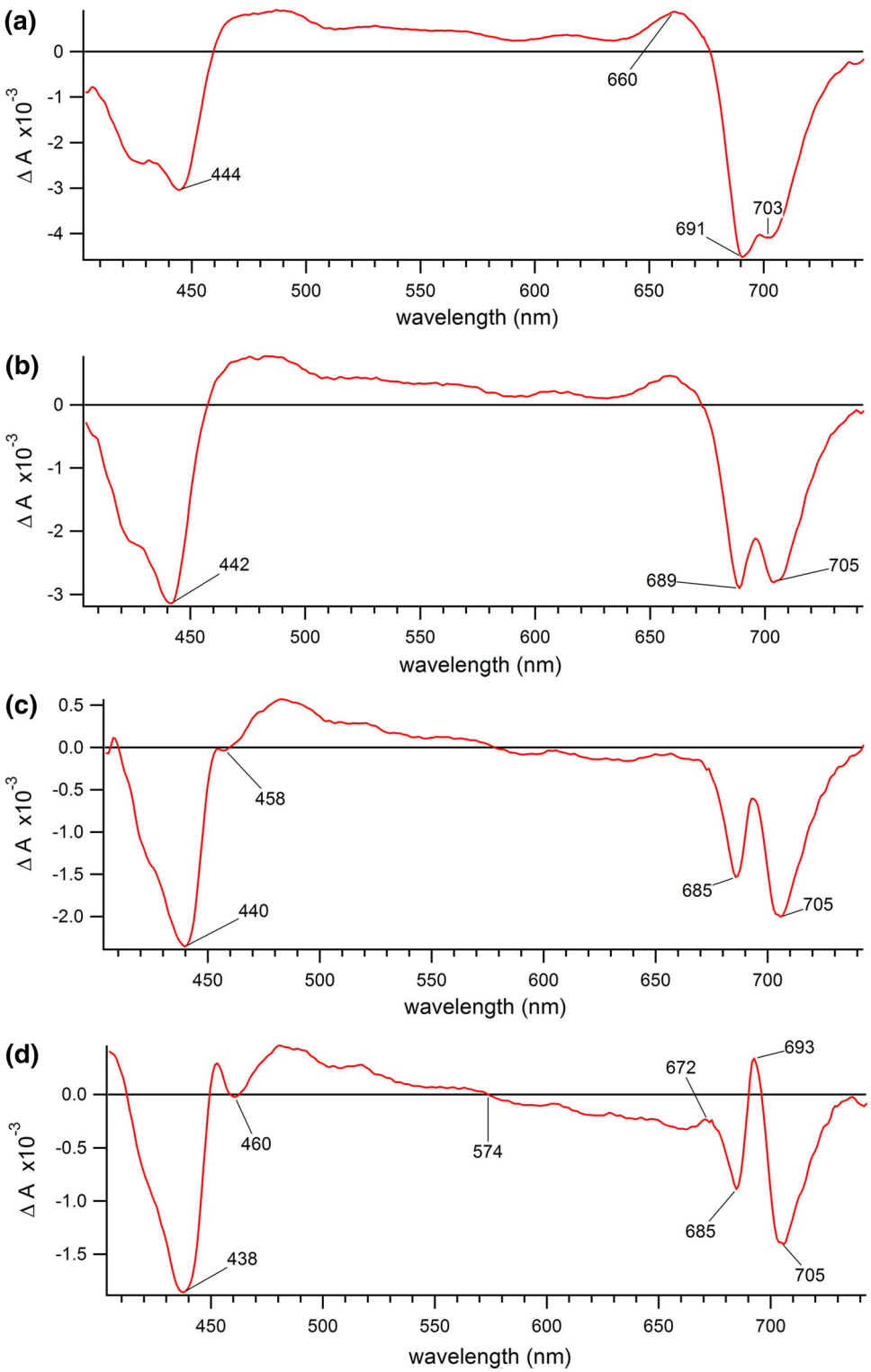

Fig. 6 Difference absorption spectra after excitation of PS I complexes, obtained from *Synechocystis* sp. PCC 6803, with laser pulses centered at 720 nm. Pulse duration—25 fs, energy—20 nJ, bandwidth—40 nm. Time delay—150 fs (**a**), 2 ps (**b**), 30 ps (**c**), and 100 ps (**d**) (adapted from Semenov et al. 2012)

the antenna to the primary electron donor. The ratio between the number of excited chlorophyll molecules of the antenna and of the RC was shown to depend on spectral characteristics of the pump pulses. In all cases, an ultrafast (<100 fs) formation of the primary radical pair $P700^{+}A_0^{-}$ was recorded. However, on excitation by pulses with maxima at 670 or 700 nm, detection of the charge separation was masked by the much more intense bleaching at the chlorophyll Q_y band due to excitation of the bulk antenna chlorophylls.

Chl2A/Chl2B and Chl3A/Chl3B molecules, which make up the primary acceptor A_0, are characterized by unusual axial ligands: water in the case of Chl2A/Chl2B and methionine residues in the case of Chl3A/Chl3B. The methionine residues (Met688PsaA and Met668PsaB) are conserved in all known species of plants and cyanobacteria. These methionine residues have been replaced in some cyanobacteria mutants by leucine, histidine, and asparagine residues (Cohen et al. 2004; Dashdorj et al. 2005; Sun et al. 2014).

Ultrafast optical and time-resolved EPR measurements have demonstrated asymmetric contribution of cofactor branches *A* and *B* in the formation of secondary ion–radical pair $P700^+A_1^-$ (Dashdorj et al. 2005; Savistky et al. 2010; Sun et al. 2014). Analysis of the electron spin echo envelope modulation (ESEEM) at low temperatures showed that the distances between the centers of ion–radical pairs $P700^+A_1^-$ in PS I from the wild type and from the *B*-branch mutant correspond to electron transfer only through the *A*-branch (Savitsky et al. 2010). Ultrafast optical measurements at room temperature showed that electron transfer in PS I from *Synechocystis* sp. PCC 6803 is asymmetric, with 66–80 % contributed by the A-branch and 20–34 % contributed by the B-branch (Sun et al. 2014).

In our opinion, the general pattern of primary electron transfer reactions is similar in both PS II and PS I. In both cases, the primary electron donor is represented by strongly interacting Chl molecules forming the dimer, while the secondary electron acceptors are represented by quinones. However, the primary reaction between P700 and A_0 in PS I (<0.1 ps) is $\sim$10 times faster, than that between P680 and Chl_{D1} in PS II ($\sim$0.9 ps). It seems that significant interaction between Chl2 and Chl3 molecules, which make up the primary acceptor A_0, may be responsible for the faster kinetics of the primary ion–radical pair formation in PS I.

According to the data obtained by Shelaev et al. (2008, 2011) and Nadtochenko et al. 2014), the next step of electron transfer in PS II is the reduction of Phe_{D1} by Chl_{D1} (lifetime $\sim$14 ps). This step is absent in PS I. Subsequent transfer of an electron to plastoquinone Q_A in PS II is characterized by a lifetime of $\sim$250 ps, while the reduction of phylloquinone A_1 in PS I is $\sim$10 times faster ($\sim$25 ps). The major factors responsible for the electron transfer rates include free energy (ΔG), reorganization energy (λ), and distance between the cofactors. The ΔG values between Phe_{D1} and Q_A in PS II and between A_0 and A_1 in PS I are roughly similar; thus, there are no reasons considering different λ values for these regions of two systems. However, the edge-to-edge distance between Phe_{D1} and Q_A in PS II is $\sim$8.4 Å (Umena et al. 2011), while the distance between A_0 and A_1 in PS I is $\sim$6.5 Å (Jordan et al. 2001). According to Moser–Dutton ruler (Moser et al. 1992), this difference may account for the $\sim$ 10 times faster kinetics of quinone reduction in PS I.

Summarizing these considerations, the sequence of the primary electron transfer reactions in PS II and PS I can be presented as follows:

$$\begin{aligned} P680^* &\rightarrow (\sim 1\ \text{ps}) \rightarrow Ch1_{D1} \rightarrow (\sim 14\ \text{ps}) \rightarrow Phe_{D1} \\ &\rightarrow (\sim 250\ \text{ps}) \rightarrow Q_A - \text{for PS II and} \\ P700^* &\rightarrow (<100\ \text{fs}) \rightarrow A_{0A}/A_{0B} \rightarrow (\sim 25\ \text{ps}) \\ &\rightarrow A_{1A}/A_{1B} - \text{for PS I.} \end{aligned}$$

However, alternative mechanism of charge separation in PS II under different excitation conditions cannot be ruled out.

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