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REVIEW

Electron Transfer in Photosystem I Containing Native and Modified Quinone Acceptors

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Abstract—The pigment–protein complex of photosystem I (PS I) catalyzes light-driven oxidation of plastocyanin or cytochrome c_6 and reduction of ferredoxin or flavodoxin in oxygenic photosynthetic organisms. In this review, we describe the current state of knowledge of the processes of excitation energy transfer and formation of the primary and secondary ion-radical pairs within PS I. The electron transfer reaction involving quinone cofactor in the A_1 site and its role in providing asymmetry of electron transport as well as interaction with oxygen and ascorbate in PS I are discussed.

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Key words: photosystem I, reaction center, electron transfer, asymmetry, primary reactions, quinone acceptors, interaction with oxygen and ascorbate

STRUCTURE OF PHOTOSYSTEM I COMPLEXES

Pigment–protein complex of photosystem I (PS I) is one of the crucial enzymes in the photosynthetic electron transfer chain in thylakoid membranes of oxygenic organisms [1]. PS I complex catalyzes the light-driven reaction of electron transfer from peripheral donor proteins plastocyanin and cytochrome c_6 to ferredoxin and flavodoxin.

The three-dimensional structure of the trimeric form of PS I from the thermophilic cyanobacterium *Synechococcus elongatus* has been obtained by X-ray structural analysis with 2.5 Å resolution [2]. Each monomer has molecular weight ~330 kDa, contains one copy of 12 protein subunits (nine transmembrane and three peripheral) and ~130 cofactors (96 chlorophyll (Chl) *a*, 22 β-carotene, three [4Fe-4S] clusters, two phylloquinone (PhQ), and four lipid molecules). It should be noted that PS I also contains 201 water molecules and a calcium ion. Two transmembrane subunits PsaA and PsaB compose C_2-symmetrical heterodimeric core complex containing most of the electron transfer cofactors.

The electron transfer chain of PS I consists of chlorophyll dimer P700 (Chl1A/Chl1B), A_0 (pairs of Chl molecules designated as Chl2A/Chl3A and Chl2B/Chl3B), A_1 (phylloquinone molecules designated as A_{1A}/A_{1B}), and iron–sulfur clusters F_X, F_A, and F_B (Fig. 1).

It is known that 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 [3, 4]. 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 [4, 5].

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) whose porphyrin planes are parallel to each other (at a distance of 3.6 Å) and perpendicular to the plane of the membrane. The spatial localization of the other two molecules of Chl (Chl2A/Chl2B) roughly corresponds to the localization of two molecules of monomeric bacterio-

Abbreviations: A_{0A} and A_{0B}, primary electron acceptor chlorophylls in ***A*** and ***B*** branches; A_{1A} and A_{1B}, quinone molecules – secondary electron acceptors in ***A*** and ***B*** branches; Chl, chlorophyll; Chl1A/Chl1B, Chl2A/Chl2B, and Chl3A/Chl3B are the first, second, and third molecules of chlorophyll in symmetrical branches of redox cofactors ***A*** and ***B*** in PS I; Cl_2NQ, 2,3-dichloro-1,4-naphthoquinone; P700, dimer of chlorophyll – primary electron donor; PhQ, phylloquinone; PQ, plastoquinone; PS I, photosystem I; RC, reaction center.

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chlorophyll in the RC of purple bacteria, and two additional molecules of Chl (Chl3A and Chl3B) are arranged in a manner similar to the two molecules of bacteriopheophytin in the RC of purple bacteria [6, 7]. 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. 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_{0A} and A_{0B} as a Chl2A/Chl3A (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 at the stromal subunit PsaC.

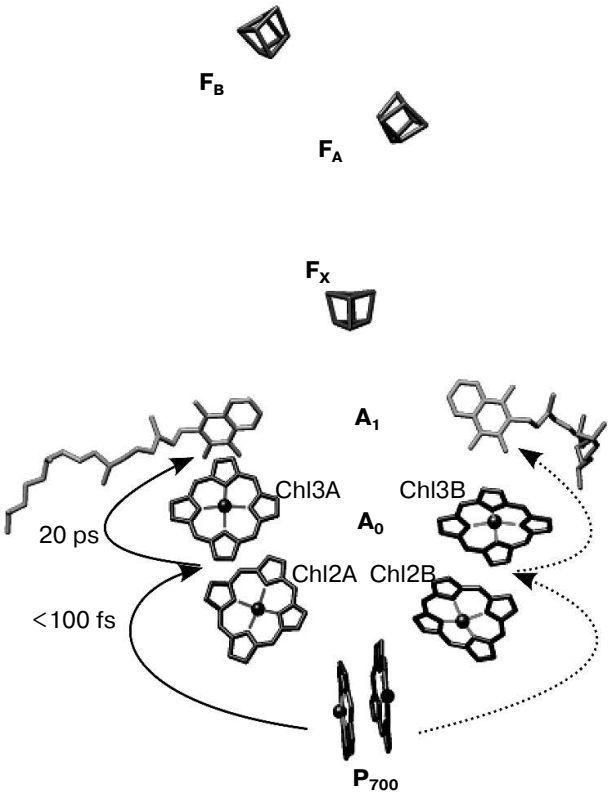

Fig. 1. General view of electron transfer cofactors and electron transfer in PS I.

EXCITATION ENERGY AND ELECTRON TRANSFER IN PS I RC

Most of the previous studies implied that the primary charge separation step from P700* to A_0 occur 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 the 10-50 ps range [8-10]. Recently, we have shown that after preferential excitation of P700 and A_0, formation of the primary radical pair $P700^+A_0^-$ occurs within 100 fs, followed by electron transfer leading to formation of $P700^+A_1^-$ with characteristic time of ~25 ps [5]. Subsequent electron transfer reactions from A_{1A} and A_{1B} to F_X take place with characteristic times of ~200 and ~20 ns, respectively [1, 3, 11, 12]. This is followed by electron transfer from F_X to the terminal iron–sulfur clusters, F_A and F_B, and further to ferredoxin or flavodoxin. Photo-oxidized $P700^+$ is reduced by plastocyanin or cytochrome c_6, returning all the cofactors of PS I back to their initial state [1].

The main difference between PS I and bacterial RC is the impossibility of mechanically separating Chl molecules of the light-harvesting antenna from Chl molecules of the RC without affecting the structural and functional integrity of the enzyme complex. The difficulty is that protein subunits PsaA/PsaB bind not only six Chl molecules, which take part in primary steps of electron transfer, but also 79 antenna Chl molecules. All the 96 Chl molecules in PS I cannot be clearly separated from each other by their spectral features. According to [13], 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. 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 [14-16], but 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 been studied by different approaches, in particular, using sub-picosecond pulse spectroscopy [5, 8-10]. 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 the spectra of the corresponding intermediates, various approaches have been used. For example, Kumazaki et al. [17] extracted the major part of the antenna Chl and, on the resulting complex, recorded two kinetic components with lifetimes of ~0.8 and ~9 ps. These phases 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 sig-

nificantly affect both the structure and function of PS I complex.

There are two basic models describing charge separation in PS I. According to the first model, upon light absorption, primary donor P700 is excited to P700*, that followed by charge separation between P700* and the primary electron acceptor A_0 with formation of ion-radical pair $P700^+A_0^-$. Data obtained by picosecond absorption spectroscopy on the PS I particles from spinach suggested that immediate (less than 1.5 ps) P700 bleaching and 810 nm band formation are due to P700 excitation and P700* state formation [18]. 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 ~14 ps time constant as the formation of the 690 nm band. These spectral changes were interpreted to be due to the formation of the state $P700^+A_0^-$.

In one of the earliest papers, it was demonstrated that selective excitation of PS I by picosecond laser pulses, at 710 nm, results in the formation of $P^+A_0^-$, which is characterized by two bleaching bands at 700 and 689 nm. These bands correspond to the formation of $P700^+$ and to the reduction of primary acceptor A_0, respectively [14].

Another approach to reveal the nature of the primary reactions in PS I complexes is based on subtracting the transient spectrum of the oxidized (closed) RC from the spectrum of the reduced (open) RC [19]. 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. Hastings et al. [15] 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 $P700^+A_0^-$. In that paper, a non-selective excitation at 590 nm was used, and therefore the phase with lifetime of 4 ps reflected 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 the rate constant in kinetics of the primary radical pair formation. Moreover, to obtain a good signal/noise ratio, Hastings et al. [15] 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. [16] 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, same authors obtained a characteristic time of ~1.3 ps for the formation of $P700^+A_0^-$ and of ~13 ps for the subsequent reaction $A_0 \rightarrow A_1$ [20]. Similar results were obtained earlier by White et al. [21] for PS I complexes isolated from spinach.

Melkozernov et al. [22] investigated fast spectral changes in PS I from the cyanobacterium *Synechocystis* sp. PCC 6803 using 150-fs laser flashes with maxima at 660, 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. In so doing, $P700^*A_0 \rightarrow P700^+A_0^-$ should be the rate-limiting reaction, and the quasi-equilibrium in the antenna should be established in about 3 ps. Other authors consider that the excitation energy transfer in the antenna is the slower step with characteristic times about 20-25 ps [16, 23].

Muller et al. [24] 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 they assumed that the primary charge separation should occur in 6-9 ps. They also suggested 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. [24] and Holzwarth et al. [25, 26] revealed kinetic components with characteristic times of 6, 20, and 40 ps. Holzwarth and coworkers [25, 26] 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 $P700^+A_1^-$. However, according to electrostatic calculations, the functioning of monomeric Chls 2A/2B as primary donors and monomeric Chls 3A/3B as primary acceptors seems unlikely, since in this case the electron transfer would be thermodynamically unfavorable [27].

PRIMARY STEPS OF CHARGE SEPARATION WITH PREFERENTIAL EXCITATION OF REACTION CENTER CHLOROPHYLLS BY 20-FEMTOSECOND PULSES

In the majority of studies on the fast kinetics of spectral changes in PS I, flashes with duration >100 fs were used, as well as powerful flashes resulting in two quanta arriving into the same RC and annihilation of the exciton-induced excitation and distortion of the spectral change kinetics.

In previous works [5, 28, 29], we have used a complex approach including short (~20 fs) laser flashes with relatively low energy (20 nJ) with maximum at 720 nm. Under these conditions, time-dependent changes of differential spectra of PS I from *Synechocystis* sp. PCC 6803 were measured. Since the femtosecond pulse with 20 fs duration has a bandwidth of 40 nm, antenna pigments (chlorophylls and carotenoids), which absorb in a short wavelength region of the Q_y-band, are not excited. Under these conditions, about half of the RC chlorophyll molecules (i.e. molecules of P700 and A_0) were excited direct-

ly, whereas the other half received excitation energy from the nearest molecules of the antenna chlorophyll. Each PS I complex absorbed about 0.10-0.15 quanta due to relatively low pumping pulse energy, which was less than 20 nJ. These conditions allowed us to reduce the contribution of bi- and multiexcitonic excitation of PS I into spectral-kinetic dependencies, so it became negligible.

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. According to spectral-kinetic measurements, this process was observed as a separate kinetic component, which clearly differs from charge transfer component(s). 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.

Figure 2a shows these difference spectra of PS I obtained upon excitation of sample (720 nm) by a 22-fs pulse at different time delays. During the time delay shorter than 100 fs (Fig. 2, a and b) spectra undergo significant evolution: primary peak of the bleaching at 690 nm at time delay $t = 0$ transformed to bleaching band with two peaks at 690 and 705 nm until $t = 100$ fs. The bleaching peak at 690 and 705 nm can be attributed to A_0 (690 nm) and P700 (705 nm), which indicates formation of the primary ion-radical pair $P700^+A_0^-A_1$ with characteristic time less than 100 fs.

At zero time delay, the bleaching peak is at 690 nm, which corresponds to maximum overlapping of absorption bands of Chl molecules in the Q_y band and the spectrum of the excitation pulse (Fig. 2a). At time delay more than 10 fs, bleaching at 690 nm decreased and an additional absorption band at 705 nm appeared. This process occurred between first 10 and 60 fs (Fig. 2b) and, probably, corresponded to the energy transfer. The kinetic curve of the bleaching peaks at 705 and 690 nm ratio ($\Delta A_{705}/\Delta A_{690}$) can be modeled within the framework of the quantum beat formalism [30, 31]. The quantum beat theory for two interacting states A_0^* and P700* has been described in detail [5]. According to this model, excitation oscillates between A_0 and P700 chromophores (Fig. 2b). These oscillations will be damped if an additional process would not lead to coherence relaxation. In RC of PS I, such a process of coherence dissipation evidently corresponds to electron transfer from P700 to A_0 (Fig. 2b). The formation of the primary ion-radical pair $P700^+A_0^-$ explains the deviation from theoretical curve of the quantum beat model at time delays more than 80 fs and almost constant ratio $\Delta A_{705}/\Delta A_{690}$ in the time range between 80 fs and ~10 ps.

Significant changes in differential spectra emerge in the time scale from picoseconds to hundreds of picoseconds (Fig. 3). These changes are caused by two processes: energy transfer to primary electron donor P700 followed by rapid charge separation with sequential formation of both primary $P700^+A_0^-A_1$ and secondary ion-radical pairs $P700^+A_0A_1^-$. Specific spectral features of the differential spectrum of $P700^+A_0A_1^-$ are shown in Fig. 3. The features include: bleaching band at 705 nm, which is related to $P700^+$ formation; bleaching band at about 685 nm and a specific peak at 692 nm, which are caused by Kerr shift of the A_0 absorption band; bleaching band between 658 and 578 nm, which is probably related to Kerr shift of antenna carotenoid absorption band and, finally, absorption

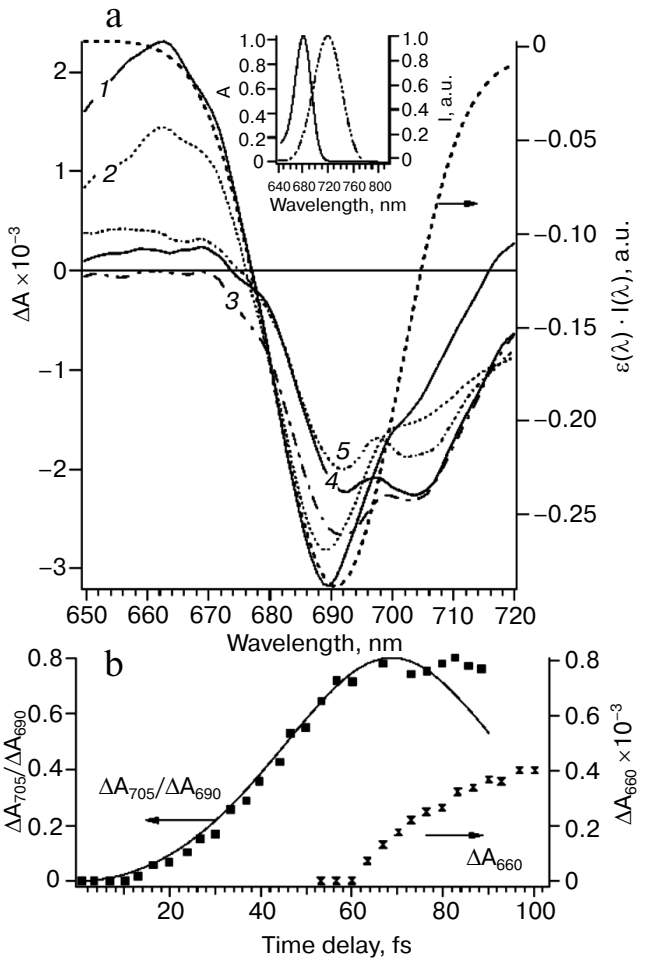

Fig. 2. a) Differential absorption spectra evolution within 0-100-fs time region at time delays (fs): *1*) 0; *2*) 20; *3*) 50; *4*) 60; *5*) 100. Excitation energy 20 nJ, wavelength 720 nm, pulse duration 22 fs. The dotted line represents the inverted overlap between absorption spectrum of PS I ε(λ) and the spectrum of the excitation pulse I(λ) (right axis). Inset: absorption spectrum of PS I RCs at the Q_y band (left axis) and normalized laser pulse spectrum (right axis). b) Kinetics of the ratio of differential absorption $\Delta A_{705}/\Delta A_{690}$ (left axis, experimental points are shown by filled squares, solid line is a theoretical curve simulated by the quantum-mechanical mixing of two excited energy levels) and kinetics of differential absorption of ΔA_{660} after 60 fs (right axis, hourglass symbol).

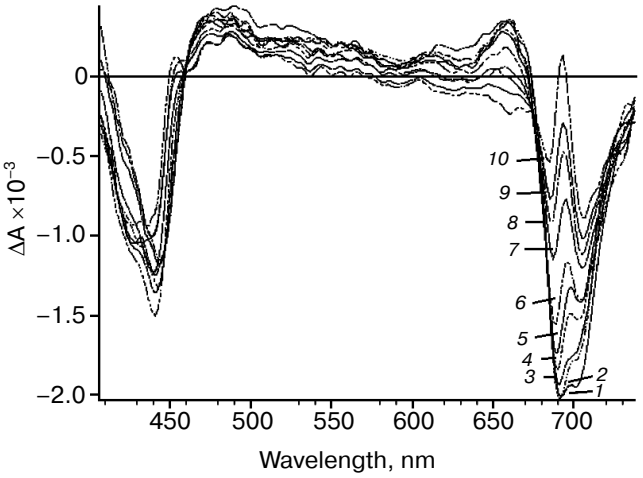

Fig. 3. PS I differential absorption spectra after excitation by 22-fs pulse at 720 nm. Time delay: *1*) 85 fs; *2*) 150 fs; *3*) 500 fs; *4*) 2 ps; *5*) 4 ps; *6*) 8 ps; *7*) 20 ps; *8*) 30 ps; *9*) 50 ps; *10*) 90 ps.

dip at 458 nm. Besides, the bleaching in the Soret band (about 440 nm) and wide absorption band between 449 and 578 nm can be attributed to $P700^+$ absorption. In the short-wavelength region of the spectrum (<413 nm), the edge of the secondary acceptor phylloquinone absorption band appears.

These results can be summarized by the following scheme.

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

In our recent work on cyanobacterial PS I complexes, time-resolved differential spectra were obtained upon excitation of PS I complexes by femtosecond pulses with maxima at different wavelengths (670, 700, and 720 nm). It was found that the ratio of number of excited antenna Chls to the number of excited Chls in RC depended on spectral characteristics of the exciting pulse [28]. Upon excitation by light pulses with maxima at 670 and 700 nm, the bleaching, caused by excitation of antenna chlorophylls, hinders registration of the processes in the RC. These data allowed us to explain possible causes of mismatching of the results of primary steps of electron transfer kinetic investigation in different laboratories. In the case of significant contribution of antenna excitation, it is difficult to reveal the kinetics of the primary stages of electron transfer between redox-cofactors P700, A_0, and A_1 because of energy transfer to the primary electron donor.

Chl2A/Chl2B and Chl3A/Chl3B molecules, which form the primary acceptor A_0, are characterized by unusual axial ligands: water molecules in case of Chl2A/Chl2B and methionine residues in case of Chl3A/Chl3B. The methionine residues (M688PsaA and M668PsaB) are present in all known species of plants and cyanobacteria. These methionine residues have been mutated to leucine, histidine, and asparagine [29, 32, 33].

Ultrafast optical measurements showed that branch ***A*** mutants (M688LPsaA, M688NPsaA and M688HPsaA) demonstrate $A_0 \rightarrow A_1$ electron transfer deceleration, whereas branch ***B*** mutants' (M668LPsaB, M668NPsaB and M668HPsaB) kinetics do not reveal any difference from the kinetics observed in the case of wild-type PS I [29, 33]. These data indicate asymmetrical contribution of the ***A*** and ***B*** cofactor branches to the secondary ion-radical pair $P700^+A_1^-$ formation. Time-resolved EPR-spectra of PS I from M688NPsaA and M668NPsaB mutants at a frequency of 95 GHz (in W-band) at 100 K showed that charge recombination kinetics of wild-type PS I and ***B***-branch mutant were similar and significantly differed from the kinetics in the case of PS I from ***A***-branch mutant [34]. Electron spin echo envelope modulation (ESEEM) analysis revealed that distances between the centers of ion-radical pairs $P700^+A_1^-$ for wild-type PS I and ***B***-branch mutant correspond to electron transfer only through branch ***A*** [34]. Ultrafast optical measurements at room temperature showed that electron transfer in PS I from *Synechocystis* sp. PCC 6803 is asymmetrical with the contribution of branch ***A*** being up to 80% [29].

REACTIONS OF LIGHT-DEPENDENT QUINONE OXIDATION IN THE A_1-SITE

PS I RC contains two molecules of phylloquinone (PhQ) that are characterized by extremely low midpoint redox potential (from −700 to −820 mV) [27, 35, 36] in comparison with ubiquinones and plastoquinones in the Q_A site of PS II and purple bacteria RCs (from −100 to 0 mV) [37, 38]. One of the promising approaches for investigation of electron transfer involving quinone cofactors in PS I is substitution of the PhQ molecule in the A_1 site by quinones with different redox potentials (such as benzoquinone, naphthoquinone and antraquinone derivatives). This can be accomplished by using cyanobacterial mutants, such as *menB* deletion strain, which carry a mutation in the PhQ biosynthetic pathway [39]. At the same time, biosynthesis of other quinones in this mutant is not affected. The empty A_1 site in this case is occupied by plastoquinone-9 (PQ), which can be easily replaced by other quinones [40].

Since the PQ redox potential in A_1 is ~95 mV more positive than the potential of native PhQ, the forward electron transfer from A_1 to F_X in the PS I from the MenB mutant becomes ~1000 times slower, while the charge recombination – ~25 times faster in comparison with wild-type PS I [41].

One of the most important advantages of *menB* PS I as a model system for investigation of the electron trans-

fer mechanism involving quinone is that it requires neither the use of organic solvents nor the removal of the PsaC subunit to replace the PQ in the A_1-site. This minimizes possible changes in electrostatic properties and conformation of the protein. Thus, the *menB* mutant provides new ways for the study of kinetic and thermodynamic aspects of the electron transfer.

An interesting approach to investigation of electron transfer involving quinone is the prevention of electron transfer from the quinone to the iron–sulfur clusters. This can be achieved by substitution of PQ by the naphthoquinone derivative 2,3-dichloro-1,4-naphthoquinone (Cl_2NQ), which has much more positive midpoint potential. The redox potential of Cl_2NQ in dimethylformamide is about –50 mV, which is 400 mV more positive than the corresponding value for PhQ. In this case, the forward electron transfer to F_X is thermodynamically unfavorable, and the electron recombines from the quinone cofactor in the A_1-site to $P700^+$ (Fig. 4).

Charge recombination kinetics of PS I with Cl_2NQ in the A_1 site obtained by time-resolved spectrometry and EPR spectroscopy demonstrate significant decrease of characteristic time of the main kinetic component in comparison with intact complexes from *menB* containing PQ [42]. In the case of Cl_2NQ, at room temperature charge recombination is ~30 times faster than in PS I from *menB* and is ~900 times faster in comparison with PS I from the wild type (Fig. 4). Furthermore, analysis of the low-temperature EPR spectra of the iron–sulfur centers F_A/F_B showed that in contrast to native complexes isolated from the wild-type cyanobacteria and *menB* mutant, in PS I containing Cl_2NQ the photoreduction of iron–sulfur clusters does not occur. These data indicate that in the latter case electron transfer from quinone cofactor to the iron–sulfur clusters is completely prevented. Moreover, it was shown that at low temperature, only the quinone molecule in the ***A***-branch participates in electron transfer.

X-band EPR-spectroscopy data obtained under steady-state illumination revealed that upon substitution of PQ by Cl_2NQ, almost twofold decrease of the $P700^+$ signal was observed [43].

In the presence of a high concentration of ascorbate (5 mM) under steady-state illumination, even in the case of PS I with Cl_2NQ in the A_1-site, electron transfer from A_1 acceptor through iron–sulfur clusters to ascorbate becomes possible (Fig. 4). This is proved by the observed increase of the $P700^+$ EPR signal amplitude in the presence of ascorbate [43]. This can be explained considering ascorbate as a cyclic electron flow mediator: in the reduced state, it can donate electrons to the photooxidized $P700^+$, and in the oxidized state, it can accept electrons from the terminal iron–sulfur clusters $(F_A/F_B)^-$.

On the other hand, it is possible that the exogenous electron acceptors directly interact with the quinone cofactor in the A_1-site. Measurements of oxygen uptake

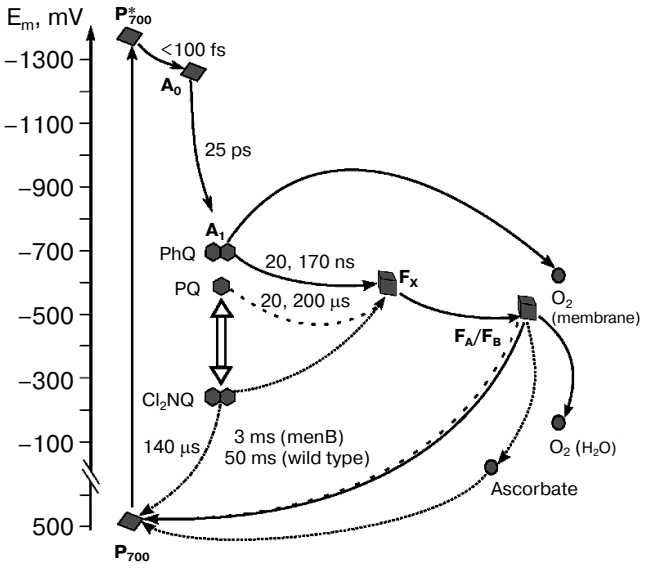

Fig. 4. Forward and backward reactions in PS I from wild type (PhQ, solid line) and *menB* mutant, which contains PQ (dashed line) or Cl_2NQ (dash-dot line) in the A_1-site. The diagram also shows the sites of oxygen reduction in PS I and the pathway of electron transfer in the presence of high concentrations of ascorbate (dotted line) under steady state illumination.

under steady-state illumination suggested the involvement of the quinone cofactor in oxygen reduction in isolated PS I complexes [44]. It was shown that under low and medium light intensities, oxygen uptake rates in PS I from the wild type and *menB* strain were similar and increased with increasing light intensity. At the same time, under high light intensity, oxygen uptake rate by PS I continues to increase in the case of the wild type and reaches a steady state in case of *menB*. The only significant difference between the samples was the difference in midpoint redox potentials of the quinones in the A_1 site, which is more auspicious for interaction with oxygen in the case of PS I from the wild type (PhQ). The authors suggested that under high light intensity, two different ways of electron transfer to oxygen coexist: reaction of oxygen with iron–sulfur clusters and its reduction by quinone cofactor in the A_1 site (Fig. 4). It was proposed that the first process occurs under moderate illumination, whereas the second occurs at high light intensities.

Thus, the role of the quinone cofactor in electron transfer in PS I may not be restricted only to participation in the forward transfer from the primary acceptor A_0 to the iron–sulfur clusters. There are reasons to believe that phylloquinone molecules A_{1A} and A_{1B} in symmetrical branches of cofactors ***A*** and ***B*** are significant for electron transfer asymmetry and may participate in the interaction with oxygen, preventing overreduction of the cofactors of the PS I electron transfer chain under high light intensity.

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