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The light-harvesting function of carotenoids in the cyanobacterial stress-inducible IsiA complex

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ABSTRACT

We present a spectroscopic investigation of the light-harvesting role of carotenoids in aggregates of the IsiA pigment–protein complex of the cyanobacterium *Synechocystis* PCC 6803. The results show that carotenoids in IsiA transfer energy on the sub-100 fs timescale from the S_2 state to chlorophyll to about the same extent as in the related pigment–protein complexes CP43 and CP47. Selective excitation at the red edge of the S_2 absorption of the carotenoids shows that echinenone is more efficient in energy transfer to chlorophyll (37%) when compared to the other carotenoid species in the system (22%).

1. Introduction

Cyanobacteria, also known as blue green algae, are among the oldest life forms. Their ability to perform oxygenic photosynthesis is widely thought to have led several billion years ago to the conversion of a reducing atmosphere into an oxidizing one which marked the beginning of the proliferation of a variety of life forms on Earth. Cyanobacteria are extremely robust organisms found in a variety of climate conditions. They populate the oceans where they are one of the main primary producers, but are also found in freshwater and in the extremely harsh conditions of hypersaline lakes. To the other extreme cyanobacteria can live in the desert and within rocks, thus in very arid conditions. They can survive in exceptionally acidic or basic environments thus showing a tremendous capacity of adaptation. Of particular importance is their capacity to survive and thrive in environments with continuously changing iron concentration and light intensity.

When exposed to iron starvation cyanobacteria start to express the IsiA gene which triggers the synthesis of the IsiA protein or CP43′. This protein binds on average 16 chlorophyll *a* molecules and four carotenoids (β-carotene, zeaxanthin and echinenone in a stoichiometry 2:1:1). IsiA forms circular aggregates (rings) of up to 18 units around the trimeric photosystem I (PSI) core complex in a first ring [1,2] and up to 25 subunits in a second ring [3]. It was estimated that IsiA increases the absorption cross section for PSI up to a factor two [4] thus working as a very efficient accessory light-harvesting antenna. It was shown that energy transfer between the IsiA ring and the PSI core complex takes place on a few ps timescale [5,6]. Physiological studies, however, assigned a photoprotective role to IsiA [7], which was corroborated by ultrafast fluorescence and absorbance-difference spectroscopy [8,9]. Thus IsiA appears to have a dual function; it functions as a light-harvesting antenna by increasing the absorption cross section of PSI, and as energy dissipator. Following our recent paper on the mechanism of energy dissipation in IsiA [9], in this manuscript we further explore the role of carotenoids in the system.

The importance of carotenoids in nature is testified by their ubiquity in living organisms. In photosynthetic organisms, carotenoids are active in light harvesting, photoprotection and structure organization [10,11]. Of vital importance for the survival of the photosynthetic organisms is the role of carotenoids in photoprotection [12]. Carotenoids quench harmful chlorophyll triplet states which are potential singlet oxygen sensitizers and are very effective scavengers of singlet oxygen [11]. This capacity relies on the low-lying carotenoid triplet state whose energy is close enough to effectively quench chlorophyll triplet states and singlet oxygen.

Another pivotal role of carotenoids is in the quenching of chlorophyll singlet excited states under conditions of excess light illumination, a process generally known as nonphotochemical quenching (NPQ) [13–20].

In this paper we report on the light-harvesting role of carotenoids in aggregates of the IsiA protein from the cyanobacterium *Synechocystis* PCC 6803. We show, by making use of femtosecond spectroscopic techniques, that carotenoid to chlorophyll energy transfer takes place on the sub-100 fs timescale and that a major role in the process is played by a red-absorbing carotenoid, most likely echinenone.

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2. Materials and methods

2.1. Sample preparation

IsiA aggregates were isolated and purified as described in [8] from the *psaFJ-null* mutant of the cyanobacterium *Synechocystis* PCC 6803 cells harvested about 30 days after growth in a liquid BG11 medium where iron was omitted. The PsaFJ$^-$ mutant was used for its lower PSI content and higher IsiA PSI-free aggregates presence than the wild type under long identical iron stress conditions [3]. After cells disruption the isolated thylakoid membranes (0.1 mg Chl *a* ml^{-1}) were solubilized with 0.2% (w/v) *n*-dodecyl-β-D-maltoside (β-DM) and centrifuged at 11,000×*g* for 3 min. The supernatant was subjected to a Mono-Q HR 5/5 column (Pharmacia) for ion exchange chromatography (IEC). The running buffer consisted of 20 mM Bis-Tris (pH 6.5), 10 mM $MgCl_2$, 20 mM NaCl, 15 mM $MgSO_4$, 1.5% taurine and 0.03% β-DM. A gradient with $MgSO_4$ up to 500 mM was applied. The IsiA aggregates eluted at an $MgSO_4$ concentration of about 250 mM. The IEC was monitored with an on-line diode array detector (Shimadzu SPD-M10Avp).

2.2. Time-resolved measurements

For the 530 nm data, femtosecond pulses were obtained from a titanium:sapphire oscillator-regenerative amplifier (coherent MIRA seed and RegA). The repetition rate was 40 kHz and the initial pulse ~60 fs at 800 nm. The beam was split into two beams one of which was focused on a CaF_2 plate to generate a white light continuum, the probe beam. The other beam was used to pump an optical parametric amplifier (OPA) to obtain the pump beam (~100 fs). The energy per pulse was ~10 nJ and the photon density ~1×10^{14} photons pulse^{-1} cm^{-2}. The 475 nm excitation data were collected with the setup described in [21] with an excitation energy of ~70 nJ per pulse and a photon density of ~6.3×10^{14} photons pulse^{-1} cm^{-2}. The polarization between the pump and probe beams was set at magic angle for both excitation wavelengths. The data were analyzed by making use of global analysis techniques [22]. Since the Evolution Associated Difference Spectra (EADS) represent in general a mixture of molecular states, a target analysis was also applied to the data where a specific kinetic scheme is applied. In this way the Species Associated Difference Spectra (SADS), spectra corresponding to pure molecular species were obtained. The instrument response function was fitted to a Gaussian of ~120 fs (full width at half maximum).

3. Results

Fig. 1 shows the absorption spectrum of the sample. Each monomer of IsiA contains approximately 16 chlorophyll *a* molecules, which give rise to strong absorption in the Q_y and Soret regions around 675 and 435 nm, respectively, and four carotenoids: two β-carotene, one zeaxanthin and one echinenone, absorbing in the 400–540 nm region [8].

3.1. Global analysis of the time-resolved data upon 475 nm excitation

In order to determine whether carotenoids are active in energy transfer to chlorophylls we carried out experiments with non-selective carotenoid excitation at 475 nm. At this wavelength, all the carotenoid species in the sample, i.e. β-carotene, zeaxanthin and echinenone, are excited. The results from a global analysis of the time-resolved data are shown in Fig. 2. Five components are needed for a good fit. The first component (black line) appears at time zero and corresponds to the S_2 excited state of the carotenoids. It shows a broad negative signal corresponding to the carotenoid ground state bleach and stimulated emission around 580 nm but its shape suffers from coherent artifacts and cross-phase modulation effects [23]. It decays to the next spectrum (red[1] line) in 66 fs (the average lifetime of the S_2 state). The S_2 state has now decayed partly to the hot S_1 state, which features ground state bleach below 530 nm and the typical hot $S_1 \rightarrow S_n$ excited state absorption in the 530–650 nm region [24]. In the chlorophyll Q_y region at 680 nm the spectrum presents a negative signal corresponding to the bleach of the Chl ground state meaning that the carotenoid(s) S_2 state is active in energy transfer to chlorophyll(s). The next evolution (red to blue line) takes place in 600 fs; it is characterized by a decrease of the amplitude of the red wing of the hot $S_1 \rightarrow S_n$ transition and corresponds to the vibrational cooling of the carotenoid(s) S_1 state [24]. The carotenoid ground state bleach shows a small decrease which we attribute to an increase of the $S_1 \rightarrow S_n$ excited state absorption in that region superimposed on the bleach signal. In the chlorophyll Q_y region the amplitude of the bleach remains practically unchanged; thus the hot S_1 state is not active in energy transfer to chlorophyll. The next spectrum (blue line) lives for 7.6 ps and corresponds to the decay of the carotenoids S_1 state. Its lifetime is the weighted average of the S_1 lifetimes of the three carotenoid species β-carotene, zeaxanthin and echinenone. This lifetime is similar

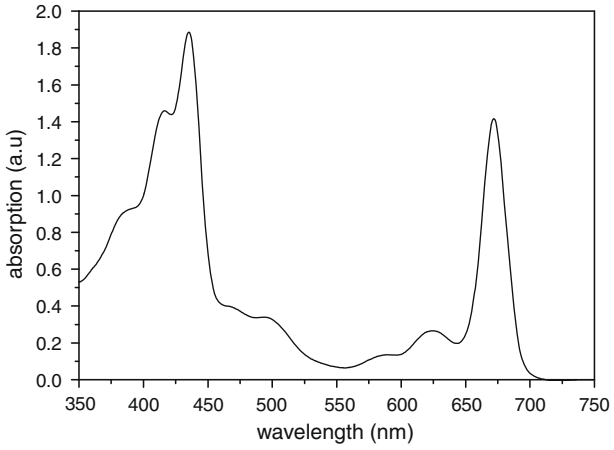

Fig. 1. Absorption spectrum at room temperature of IsiA aggregates.

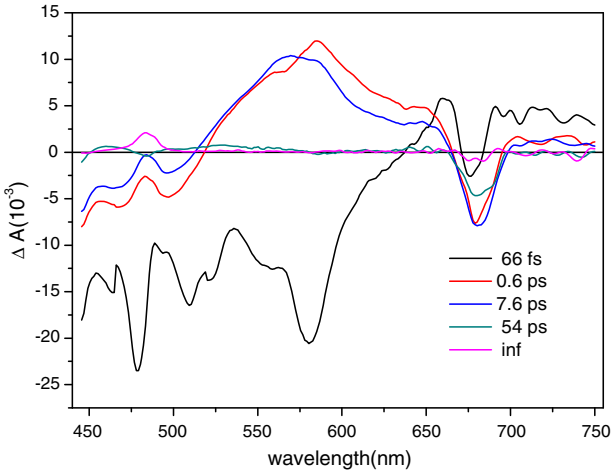

Fig. 2. Evolution Associated Difference Spectra that follow from a global analysis of the data upon 475 nm excitation.

[1] For interpretation of color in Figs. 2–6, the reader is referred to the web version of this article.

to the values obtained for β-carotene in CP43 and CP47 [25–27]. Concomitantly with the decay of the S_1 state in 7.6 ps a small decay of the Chl Q_y state occurs due to singlet–singlet annihilation processes within the Chl excited states. The absence of a clear increase in the 675 nm trace shows that the carotenoid S_1 states are not active in energy transfer to chlorophyll(s). The blue spectrum is replaced by the next one (green line) which corresponds to the excited chlorophyll state and lives for only 54 ps, indicating that the Chl excited state is strongly quenched, in agreement with time-resolved fluorescence and absorption data presented earlier [8,9]. Thus an energy dissipation mechanism is active in the system. Based on the results from transient-absorption spectroscopy upon selective chlorophyll excitation [9] we proposed that a carotenoid S_1 state accepts energy from the excited chlorophyll(s) providing a quenching channel since its excited state lifetime is much shorter than that of the excited state of chlorophyll. The last spectrum (magenta line) displays a very small residual bleach in the Chl Q_y region and an overall small signal and does not decay on the timescale of the experiment; we assign it to a small concentration of long-living (triplet) species.

3.2. Target analysis of the time-resolved data upon 475 nm excitation

In order to quantify the carotenoid to chlorophyll energy transfer efficiency upon 475 nm excitation, we carried out a target analysis with the kinetic scheme depicted in Fig. 3A. The model consists of four compartments: the initially excited carotenoids S_2 state partly relaxes to the hot S_1 state with a fraction Φ_1 of 74% and partly transfers energy to chlorophyll with a fraction Φ_2 of 26%. The fraction Φ_2 was fixed in order to obtain a ratio of 0.45 between the minima of the carotenoid S_1 and Chl* SADS (*vide infra*). The hot S_1 state undergoes vibrational relaxation to the S_1 state with a rate constant $k_1 = 1.4\ ps^{-1}$ and does not transfer energy to chlorophyll. The carotenoid hot S_1 and S_1 states decay to the ground state with rate constants $k_2 = 0.32\ ps^{-1}$ and $k_3 = 0.13\ ps^{-1}$, while the chlorophyll excited state decays to the ground state with a rate constant $k_4 = 0.017\ ps^{-1}$.

The Species Associated Difference Spectra are shown in Fig. 3B. The black line corresponds to the spectrum of the excited carotenoid S_2 state with ground state bleach below 520 nm and stimulated emission in the 520–620 nm region; its shape is similar to the carotenoid S_2 spectrum in artificial light-harvesting dyads [24]. The red spectrum features the typical hot $S_1 \rightarrow S_n$ excited state absorption in the 530–650 nm region and carotenoid ground state bleach below 530 nm [11]. The blue spectrum corresponds to the carotenoid S_1 state with excited state absorption blue shifted with respect to the hot S_1 state and ground state bleach below 525 nm. The green spectrum corresponds to the chlorophyll excited state and features Chl Q_y bleach around 675 nm and a region of excited state absorption below 620 nm. The excited state absorption region appears to be rather ill-resolved due to the low chlorophyll excited state absorption signal. It must be noted that at 475 nm the excitation is non-selective with respect to the different carotenoid species so that the S_2, hot S_1 and S_1 spectra obtained from the target analysis should be regarded as a mixture of β-carotene, zeaxanthin and echinenone S_2, hot S_1 and S_1 states. Fig. 3C shows selective kinetic traces at 446, 590 and 680 nm, respectively. The first trace shows the recovery of the Car bleach, while the trace

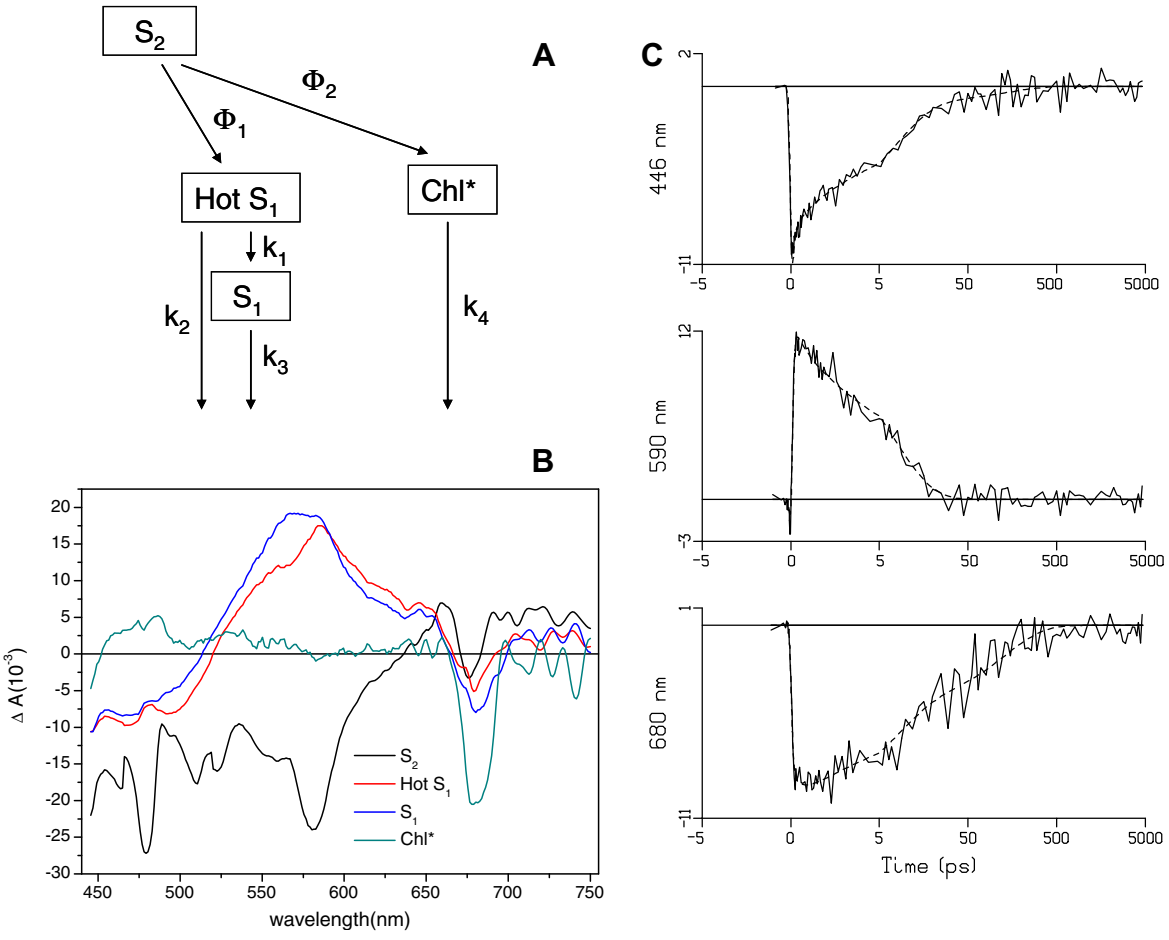

Fig. 3. (A) Target kinetic model. (B) Species Associated Difference Spectra upon 475 nm excitation. (C) Selected kinetic traces (Δ*A* in mOD).

at 590 nm is taken as representative of the decay of the Car S_1 state. The 680 nm trace shows the rise and decay of the Chl excited states. Note that the Chl* SADS has a minimum of −21 mOD, and the maximum concentration is 0.26, due to the 26% energy transfer efficiency from S_2. The product of both numbers, −5.5 mOD corresponds to the minimum of the green EADS in Fig. 2.

3.3. Global analysis of the time-resolved data upon 530 nm excitation

The carotenoid echinenone has attracted considerable attention for its possible roles in light sensing and energy dissipation [9,28,29]. In order to elucidate its role in light harvesting in IsiA aggregates we carried out a measurement upon excitation at 530 nm. At this wavelength echinenone is expected to have a larger extinction coefficient than β-carotene and zeaxanthin (*vide infra*).

Fig. 4 shows the EADS obtained from a global analysis upon selective 530 nm excitation. Five components are needed for a good fit of the data. The first EADS (black line) appearing at time zero is associated with the carotenoid S_2 state, with ground state bleach below 540 nm and a contribution of Raman scattering mixed with a band-shift-like signal in the 630–700 nm region. It decays in 91 fs to the second EADS (red line). This spectrum displays carotenoid ground state bleach below 525 nm and a pronounced excited state absorption typical of the hot $S_1 \rightarrow S_n$ transition in the 525–650 nm region. This spectrum is considerably red shifted compared to the corresponding spectrum obtained with 475 nm excitation; in particular, the excited state absorption region appears to be broader than the typical $S_1 \rightarrow S_n$ transition to the longer wavelength side of the spectrum (cf. Fig. 6). This suggests that due to the carbonyl group, echinenone experiences enhanced conformational disorder compared to β-carotene and zeaxanthin or that its S_1 state in IsiA aggregates has a partial charge transfer character. In the Chl Q_y absorption region the spectrum presents a strong negative signal corresponding to the bleach of the Chl ground state; both energy transfer from the carotenoid(s) S_2 state to the chlorophyll(s) and direct chlorophyll excitation contribute to this signal (based on the absorption spectrum of chlorophyll and echinenone, we estimate ∼30% direct chlorophyll excitation at 530 nm excitation). This EADS decays to the next one (blue line) in 1 ps. The evolution reflects the vibrational cooling of the hot S_1 state. In the Chl bleach region there is an apparent increase of the bleach; we do not think this is due to energy transfer from the carotenoid hot S_1 state but rather to a decrease of carotenoid excited state absorption around 675 nm (see also the target analysis results). Energy transfer form the hot S_1 state to Chl is thus negligible. The next evolution (blue to green line) shows the decay of the carotenoid S_1 state in 5.1 ps. In the 675 nm region we see hardly any evolution. This can be due to a partial decay of the Chl bleach which offsets the decay of the Car S_1 excited state absorption. The absence of an increase in the 681 nm trace on the 5 ps timescale shows that the carotenoid S_1 state is not active in energy transfer to chlorophyll(s). The green EADS decays to the long-living component (magenta line) in 71 ps. About 60% of Chl bleach disappears on this timescale meaning that the Chl excited state is strongly quenched compared to free chlorophyll [9]. The component reflected by the last spectrum lives for 400 ps. We note that the estimate of the last lifetime is quite uncertain since the time evolution of the system was measured up to 100 ps.

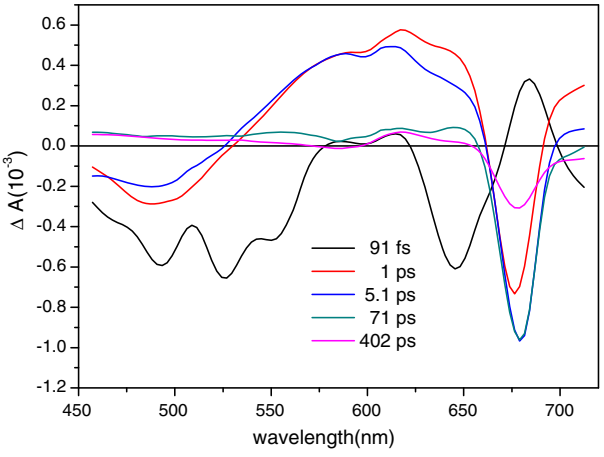

Fig. 4. Evolution Associated Difference Spectra (EADS) estimated from a global analysis of the data upon 530 nm excitation.

3.4. Target analysis of the time-resolved data upon 530 nm excitation

In order to identify the Car to Chl energy transfer pathways and to quantify the relative efficiencies a target analysis model has been applied to the data. The model, shown in Fig. 5A, consists of five compartments: the carotenoid S_2 state excited at time zero partly relaxes to the hot S_1 state (rate constant $k_1 = 6.9\ ps^{-1}$) and transfers energy to the Chl with a rate constant $k_2 = 4.1\ ps^{-1}$ implying an efficiency of (37±3)%. The hot S_1 state relaxes to the ground state ($k_3 = 0.2\ ps^{-1}$) and to the S_1 state ($k_4 = 0.8\ ps^{-1}$) but does not contribute to energy transfer to the Chl(s). The S_1 state relaxes to the ground state with the same rate constant as the hot S_1 state ($k_3 = 0.2\ ps^{-1}$). The Chl_1^* compartment undergoes spectral relaxation to Chl_2^* ($k_5 = 0.0048\ ps^{-1}$). Two chlorophyll compartments are necessary since there is a small but clear evolution in the chlorophyll spectral shape after carotenoid relaxation (cf. the 4th and 5th EADS in Fig. 4). The two chlorophyll pools are quenched by energy transfer to the low-lying carotenoid S_1 excited state ($k_6 = 0.0093\ ps^{-1}$, $k_7 = 0.0025\ ps^{-1}$). The model also takes into account an estimated 30% of direct chlorophyll excitation. The resulting SADS are displayed in Fig. 5B. The black SADS belongs to the carotenoid S_2 state with ground state bleach below 530 nm and a band-shift-like signal in the 620–700 nm region. The red line corresponds to the hot S_1 state of the carotenoid with a pronounced excited state absorption in the 530–680 nm region and ground state bleach below 530 nm. The blue line represents the vibrationally relaxed carotenoid S_1 state with absorption features similar to the previous SADS but slightly blue shifted. The two chlorophyll pools Chl_1^* and Chl_2^* (green and magenta spectra) display the bleach of the Q_y state around 680 nm and a region of excited state absorption below 650 nm. The quenching of the Chl excited state via S_1 was introduced in the light of the results obtained upon 675 nm excitation which strongly suggest that a low-lying carotenoid excited state is involved in the quenching process [9]. Note that Chl ESA around ∼560 nm in the target analysis is flatter than the 71 ps EADS obtained from the global analysis (Fig. 4). This indicates that the 71 ps EADS contains a small contribution from a carotenoid S_1 state [16] and that the quenching compartment is necessary in the target kinetic model.

Fig. 5C shows selective kinetic traces at 493, 593 and 681 nm, respectively. The first trace shows the recovery of the Car bleach, while the trace at 593 nm is taken as representative of the decay of the Car S_1 state. The 681 nm trace shows the rise and decay of the Chl excited states. Note that the Chl_1^* SADS has a minimum of −1.85 mOD, and the maximum concentration is 0.56, due to the 30% direct excitation and 37% energy transfer efficiency from S_2. The product of both numbers, −1.0 mOD corresponds to the minimum of the green EADS in Fig. 4. From this target analysis, the ratio between the minima of the carotenoid S_1 and Chl_1^* SADS is estimated to be 0.45 (which was used above with 475 nm excitation).

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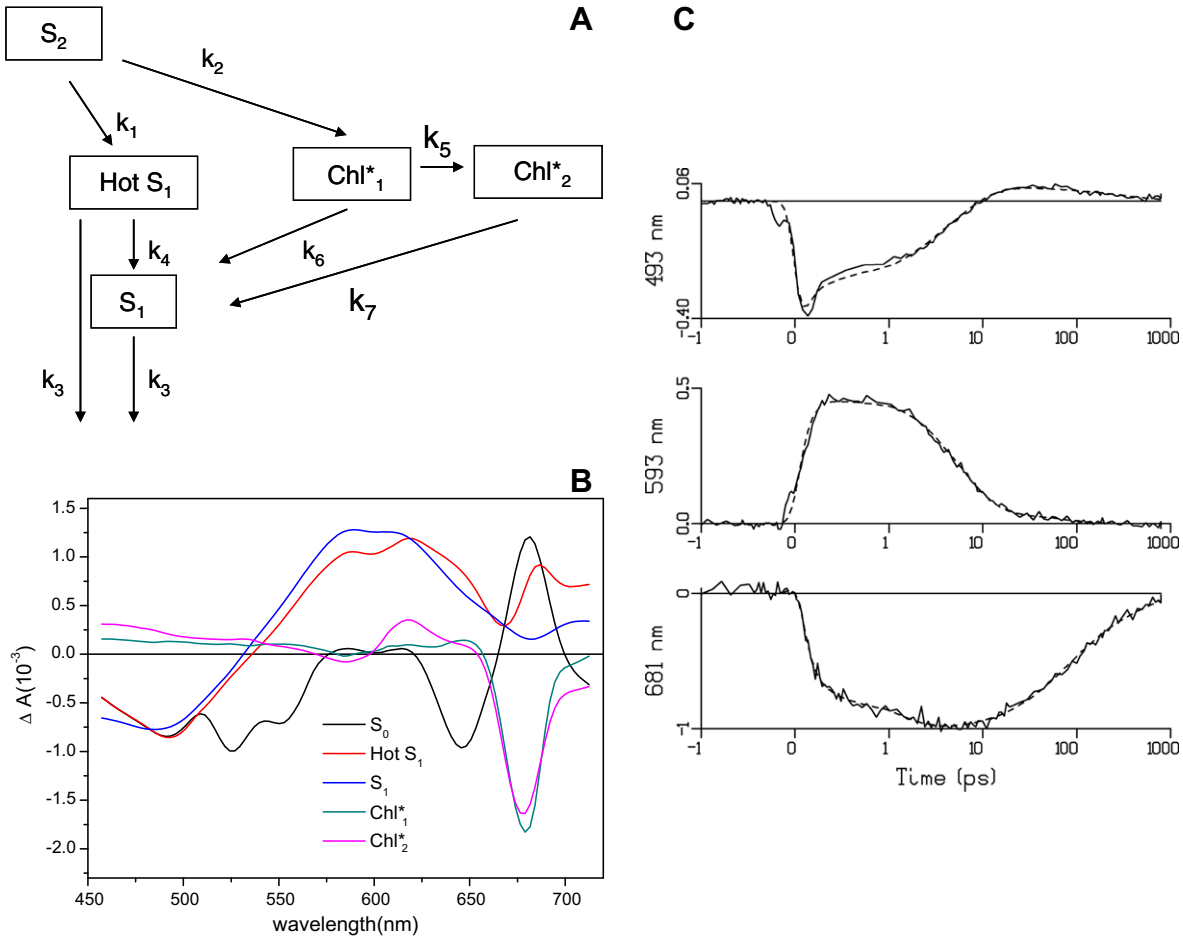

Fig. 5. (A) Target kinetic model. S_2 and Chl_1 absorb, respectively, 70% and 30% of the excitation. (B) Species Associated Difference Spectra upon 530 nm excitation. (C) Selected kinetic traces (ΔA in mOD).

4. Discussion

Our results show that carotenoids function as light-harvesting pigments in IsiA aggregates. The results from the target analysis of the time-resolved data upon selective excitation of the S_2 state of a red carotenoid at 530 nm show that energy transfer takes place from the carotenoid S_2 state only with an efficiency of (37±3)%. In order to determine whether more blue-absorbing carotenoids are involved in energy transfer to chlorophyll we carried out experiments with excitation at 475 nm. At this wavelength we estimate that all the carotenoid species present in the sample, i.e. echinenone, zeaxanthin and β-carotene have a similar extinction coefficient [11,28]. The results from a target analysis of the data upon 475 nm excitation show that energy transfer takes place from the carotenoid(s) S_2 state only with an energy transfer efficiency of about 26%. By assuming that at 475 nm the extinction coefficient of the three carotenoid species is comparable, we obtain that the red carotenoid is far more efficient in energy transfer as compared to the blue-absorbing carotenoids (37% and 22%, respectively). For both excitation wavelengths energy transfer takes place from the carotenoid(s) S_2 state only, with at most a negligible contribution form the hot S_1 state upon 530 nm excitation, in agreement with the fact that the conjugated chain of all three carotenoids in the system have an effective conjugation length between 10 and 11, so that their S_1 excited states are expected to be lower in energy than the Q_y state of chlorophyll *a*. [11,24].

The energy transfer pathway(s) and efficiency in particular for the 475 nm excitation data are overall very similar to those obtained for the related complexes CP43 and CP47 of photosystem II [27,30]. When the results are compared to the major light-harvesting complexes LHCII and CP29, carotenoids appear to be much less efficient in light harvesting in IsiA compared to the latter two systems [21,31].

If we compare the two kinetic models in Figs. 3A and 5A for the 475 and 530 nm excitations, respectively, we see that in the 530 nm excitation experiment the target kinetic model required one more chlorophyll compartment compared to the 475 nm excitation experiment. The Chl spectra in fact undergo a (small) spectral evolution on a timescale of 70 ps following energy transfer from the carotenoids excited at 530 nm (cf. green to magenta evolution in Fig. 4). The same feature could be present at 475 nm excitation but the lower signal-to-noise ratio prevented us from seeing it. On the other hand, excitation at 530 nm is much more selective compared to excitation at 475 nm. Thus when the system is excited at 530 nm we expect to have energy transfer to specific chlorophylls whose excited state energy would then equilibrate with the chlorophyll pool. The target kinetic model in Fig. 5A also shows quenching of chlorophyll fluorescence via the carotenoid S_1 excited state. Since at 475 nm excitation the quenching carotenoid would have a small contribution to the carotenoid spectrum (approximately 25% of the total carotenoid signal), we did not include the quenching via the carotenoid excited state in Fig. 3A.

We have recently proposed that the red carotenoid echinenone is likely to be the quenching pigment in IsiA [9]. The same carotenoid has been proposed to be the quencher in the OCP-mediated energy dissipation mechanism [29]. Fig. 6 shows the spectrum of the

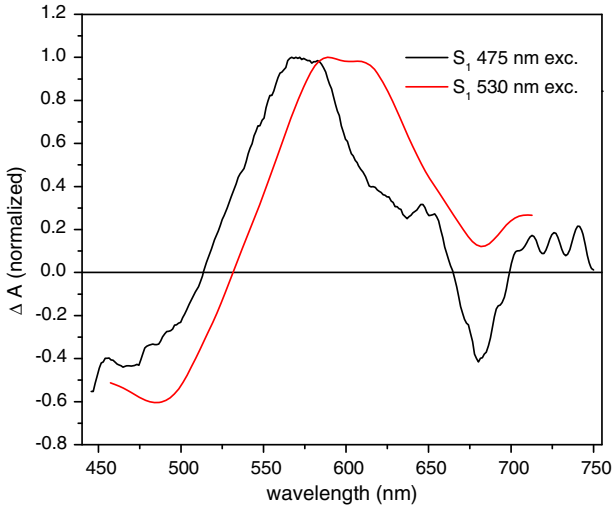

Fig. 6. Relaxed S_1 state obtained from the target analysis upon 475 (black line) and 530 nm (red line) excitations.

relaxed carotenoid S_1 state for the two excitation wavelengths, 475 and 530 nm, respectively. While the former displays the typical shape of the $S_1 \rightarrow S_n$ transition, the latter shows a broad feature to the red of the $S_1 \rightarrow S_n$ absorption which is an indication of either enhanced conformational disorder of echinenone when compared to β-carotene and zeaxanthin or of an intramolecular charge transfer state mixed with the S_1 state [16,28]. The S_1 state obtained upon 475 nm excitation shows a bleach in the Chl Q_y region due to singlet–singlet annihilation processes taking place on a timescale comparable with the lifetime of the S_1 state.

It is interesting to compare the spectrum obtained upon 530 nm excitation with those obtained by Polívka et al. for echinenone in OCP [28]. The remarkable similarity of the spectral shape above 570 nm confirms that at 530 nm the carotenoid echinenone is predominantly excited.

Acknowledgments

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