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Subpicosecond dynamics in the excited state absorption of all-*trans*-β-Carotene

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Abstract

We have investigated the time evolution of the transient absorption spectrum of all-*trans*-β-carotene in a number of solvents. In all cases we observe a loss of red and a gain of blue S_1 $(2A_g^-) \rightarrow S_N$ excited state absorption on a 0.3–0.4 ps time scale. To explain these observations, a model is proposed in which distorted molecules formed in S_2 $(1B_u^+)$ relax back to the all-*trans* state in S_1 $(2A_g^-)$. © 2002 Published by Elsevier Science B.V.

Abbreviations: Car – carotenoid; ESA – excited state absorption; IC – internal conversion; SE – stimulated emission; Chl – chlorophyll; SADS – species associated difference spectrum; fwhm – full width at half maximum

1. Introduction

Carotenoids (Cars) play a major role in photosynthesis. On one hand they quench chlorophyll (Chl) triplets thereby preventing the formation of singlet excited oxygen, on the other hand they harvest sunlight in a spectral region where Chls do not absorb [1,2]. Energy transfer efficiencies from Cars to (bacterio)chlorophylls can reach up to 100% [1].

In order to understand the transfer mechanisms and pathways, information about the energies and lifetimes of the Car excited states is essential. Cars have several low-lying excited singlet states and these states all have a very short lifetime ($S_2 < 1$ ps, S_1 1–30 ps [3]) due to very fast internal conversion which makes Cars only weakly fluorescent.

Transitions between ground (S_0) and first excited state (S_1) are one-photon forbidden because S_1 has the same inversion symmetry (A_g^-) as S_0. The S_1 $(2A_g^-)$ state of β-carotene is hardly influenced by the environment because of its near-zero associated dipole and it has a lifetime of 10 ± 1 ps in a range of solvents [4]. Energy transfer from the β-carotene S_1 state to Chl *a* is unfavourable because the energy of the lowest excited singlet state (Q_y) of Chl *a* (∼680 nm) is higher in energy than the S_1 state of β-carotene (∼700 nm [5–7]).

The S_0 $(1A_g^-) \rightarrow S_2$ $(1B_u^+)$ transition is one-photon allowed and responsible for the characteristic strong visible absorption of carotenoids (400–550 nm). Due to dispersive interactions the

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solvent can shift the energy of the Car S_2 ($1B_u^+$) state and therefore also change the S_2 lifetime, for an extensive study in the case of β-carotene, see [4]. The $S_2 \rightarrow S_1$ internal conversion time of β-carotene in [4] ranges from 120 to 180 fs. Energy transfer from the β-carotene S_2 state to a Chl competes with this ultrafast internal conversion. Recently, the presence of a 'new' electronic state ($1B_u^-$) was shown in β-carotene [8,9]. Its energy (0–0 at 508 nm) is slightly lower than the S_2 ($1B_u^+$) state [9], and it is believed that this state is an intermediate in the S_2 to S_1 internal conversion process [8]. A transient absorption band in the near infrared was assigned to a $1B_u^- \rightarrow \ell A_g^+$ transition [10].

Dynamics in the S_1 state of Cars are important when considering subpicosecond energy transfer to Chls. For all-*trans*-β-carotene, in addition to the S_2 to S_1 and S_1 to S_0 internal conversion (IC) processes, a fast decay component (0.5 ps) at 620 nm and a slower rise component at 570 nm were recently reported and explained as vibrational relaxation in the S_1 ($2A_g^-$) state [11]. In this work pump–probe data are presented of all-*trans*-β-carotene in different organic solvents after exciting the Car to its S_2 state. Global analysis over a wide spectral range enables us to study the time evolution of entire spectral bands. An evolution in the excited state absorption (ESA) is observed on a somewhat faster time scale (0.3–0.4 ps) than in [11]. To explain the dynamics in S_1, we propose an alternative model that can also explain the broadening and red shift of the S_2 emission that is known to occur on a similar time scale [4].

2. Experimental

2.1. Sample preparation

All-*trans*-β-carotene was purchased from Sigma. The amount of the 15-*cis* form was negligible because almost no absorption band around 337 nm (typical for the 15-*cis* form [12]) was seen before and after the measurements. Ethanol was purchased from Merck, hexane from Baker, benzyl alcohol was synthesized in the chemistry department. All-*trans*-β-carotene was dissolved in these solvents in a 1 mm cuvette to a final optical density (OD) of 0.15–0.40.

2.2. Transient absorption

Data were recorded with a femtosecond spectrophotometer, described in detail elsewhere [13]. Shortly, the output of a Ti:Sapphire oscillator was amplified by means of chirped pulse amplification (Alpha-1000 US, B.M. Industries), generating 1 kHz, 800 nm, 60 fs pulses. This light was used for generating single-filament white light in a 2 mm sapphire plate used as the probe and for driving a home-built, non-collinear optical parametric amplifier (OPA), tunable in the visible [14]. After prism compression a 15 nm (fwhm) bandwidth was obtained around the excitation wavelength (~475 nm, 30–50 nJ/pulse). The magic angle spectra were obtained by rotating the polarization of the pump with a Berek polarization compensator (New Focus, 5540). Time-gated spectra were recorded with a home-built camera consisting of a double diode array read out at the laser frequency (1 kHz). Typically 2000 difference absorbance spectra were averaged per delay.

2.3. Data analysis

The spectra were fitted with a global analysis fitting program [15]. A sequential model with increasing lifetimes was assumed where each species evolves into the next one. Note that these species associated difference spectra (SADS) are not necessarily associated with 'pure states'. Dispersion within the probe continuum was fitted with a third order polynomial, and the obtained parameters agreed very well with those found for similar experiments. The instrument response is mainly determined by the uncompressed white light and in the fitting procedure a Gaussian was assumed with a fitted fwhm of ~100 fs, similar to the value obtained from the analysis of the birefringence in water.

3. Results

Difference absorbance spectra at room temperature were measured after exciting in the S_2 state

of all-*trans*-β-carotene dissolved in ethanol, hexane and benzyl alcohol. Because of the dispersion present in our data, we show measured traces at a few particular probing wavelengths (corrected for the dispersion, solid lines in Fig. 1), and the SADS and associated lifetimes that result from a global analysis (Fig. 2). The dashed lines in Fig. 1 correspond to the global fit in Fig. 2.

Upon exciting β-carotene to its S_2 state a very fast stimulated emission (SE) from S_2 was observed, see the negative signals at early times in Fig. 1 and the first SADS (solid lines) in Fig. 2. The emission from S_2 shows vibronic peaks in hexane and ethanol at ~525 nm (Fig. 2a and b),

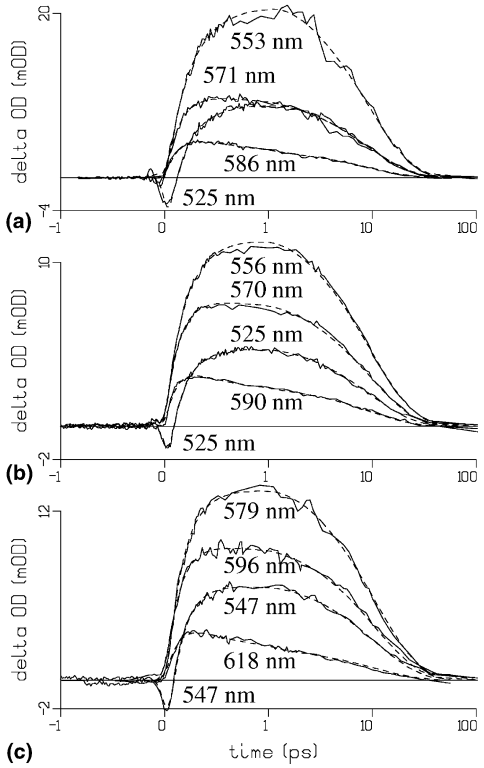

Fig. 1. Absorption changes of all-*trans*-β-carotene in hexane (a), ethanol (b) and benzyl alcohol (c), at RT after 475 nm excitation (fwhm 15 nm). The fwhm of the instrument response function is 100 fs. Pump and probe were set to magic angle. Shown are four typical probing wavelengths. The dashed lines correspond to the global fits shown in Fig. 2. The traces have been corrected for the fitted dispersion in the white light. Note that the time axis is linear between −1 and 1 ps, and logarithmic at later delay times.

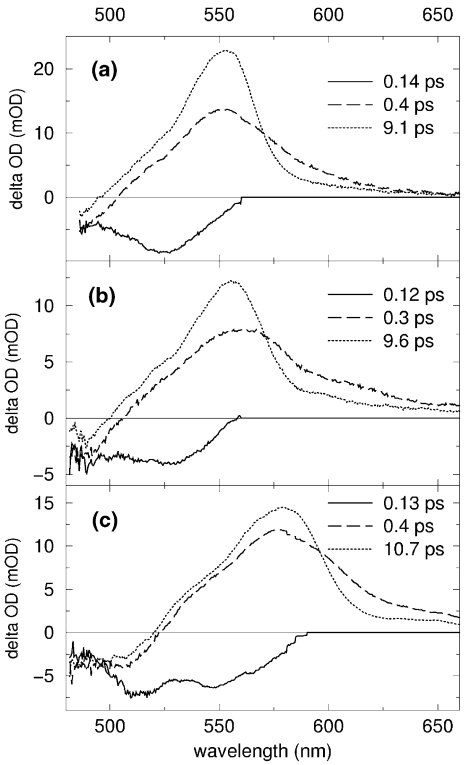

Fig. 2. Species associated difference spectra (SADS) and associated lifetimes that result from a global fit. (a) In hexane, (b) in ethanol, and (c) in benzyl alcohol. The instantaneous solid spectrum is replaced by the dashed spectrum (120–140 fs), which in turn relaxes to the dotted spectrum in 0.3–0.4 ps. The dotted spectrum decays to zero in 9–11 ps. See also Table 1. The first SADS was set to zero above 560 nm (hexane, ethanol), and 590 nm (benzyl alcohol).

and in benzyl alcohol at ~513 and ~547 nm (Fig. 2c), well separated from the S_2 bleach. Estimates of the S_2 lifetimes are complicated by uncertainties in the width of the instrument response function (~100 fs fwhm). The fitted S_2 lifetimes are 140 ± 30 fs (hexane), 120 ± 30 fs (ethanol) and 130 ± 30 fs (benzyl alcohol), close to literature values of 120–180 fs [4].

On these time scales, the first SADS is replaced by the second SADS (dashed line) which displays an excited state absorption peaking in the region 550–575 nm. Following formation of this absorbing state in β-carotene, a further spectral evolution occurs and with a time constant of 0.3–0.4 ps, the second SADS in Fig. 2 is replaced by the third

Table 1
Solvent dependence of the photophysical properties of all-*trans*-β-carotene

Solvent	ν_{abs} (cm^{-1})	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)	$\nu_{3,abs}$ (cm^{-1})
Hexane	22220 ± 50	140 ± 30	0.4 ± 0.1	9.1 ± 0.5	18090 ± 100
Ethanol	22120 ± 50	120 ± 30	0.3 ± 0.1	9.6 ± 0.5	17990 ± 100
Benzyl alcohol	21280 ± 50	130 ± 30	0.4 ± 0.1	10.7 ± 0.5	17260 ± 100

Photophysical parameters: ν_{abs}, steady-state absorption maximum; τ_1, τ_2, τ_3, lifetimes resulting from the global fit; $\nu_{3,abs}$, S_1 $(2A_g^-) \rightarrow S_N$ absorption maximum.

SADS (dotted line). Red ESA is lost and blue ESA is gained during this process. The traces at the three red most probing wavelengths in each panel of Fig. 1 clearly show these different kinetics. The spectral changes are too big to actually reflect a red shift of the emission from S_2 (like observed with fluorescence up-conversion [4]) considering the initial amplitude of the S_2 SE in combination with its short lifetime. In all traces and spectra the evolution of the ESA on a time scale of 0.3–0.4 ps demonstrates a significant population of an 'intermediate state'.

After this relaxation, the ESA can be safely assigned to the S_1 $(2A_g^-) \rightarrow S_N$ absorption. The S_1 lifetime (9–11 ps) is in agreement with literature values [4,16]. A clue to the identification of the S_N state as the $2B_u^+$ state comes from the fact that the S_1 $(2A_g^-) \rightarrow S_N$ absorption shows the same dispersive shift as the S_0 $(1A_g^-) \rightarrow S_2$ $(1B_u^+)$ transition depending on the polarizibility of the environment. All the relevant properties concerning the relaxation of all-*trans*-β-carotene are listed in Table 1.

4. Relaxation process

We observe a loss of red and a gain of blue ESA on a time scale of 0.3–0.4 ps in all-*trans*-β-carotene. Note the difference of our data with a true blue shift, which would indicate a pure solvent relaxation (associated with a shift of the S_1 potential well). Similar kinetics have been reported earlier for all-*trans*-β-carotene [11], and for other carotenoids like all-*trans*-neurosporene [17] and spheroidene [18]. How to explain these observations?

In [11], the observed spectral evolution in all-*trans*-β-carotene is explained in terms of vibrational relaxation in S_1. However, we note that intramolecular vibrational relaxation in S_2 is very fast (<50 fs) [4,19], and consequently we may assume that also in S_1 true vibrational relaxation occurs on a sub-100 fs time scale. On the other hand, coherent nuclear wavepackets have been observed in photosynthetic and other pigments (see for example [20–22]), and consequently some nuclear degrees of freedom may remain hot over a picosecond.

Alternatively we consider the proposed relaxation from $1B_u^-$ to $2A_g^-$ (S_1). Although a $1B_u^- \rightarrow \ell A_g^+$ absorption cannot be completely excluded as the origin of the early red ESA, the time scales we measure (0.3–0.4 ps) are somewhat longer than the proposed decay time (0.2 ps) of the $1B_u^-$ state [10].

Although we cannot rule out the possibility that either vibrational relaxation in S_1 and/or the transient population of the $1B_u^-$ state is the cause of the observed spectral evolution, we suggest a third explanation, namely a structural re-organization of the Car molecule. With this suggestion we build on the earlier observation that in Cars of photosynthetic bacteria new pathways of S_2 deactivation have been observed whose relative contributions strongly depend on the (dynamic) configuration of the Car [18,23]. We refer to the natural tendency of Cars to photo-isomerize, and therefore have an extremely small but non-zero chance to twist from the *all-trans* to the *cis* configuration in the excited state. We further refer to the earlier work by Foggi et al. [24], who suggested that a structural change in all-*trans*-β-carotene takes place following excitation that decayed in about 250 fs as detected by the optical Kerr effect. Therefore we propose that for the A_g^- states the all-*trans* form is most stable, whereas in the B_u^+ states twisting of the originally all-*trans* configu-

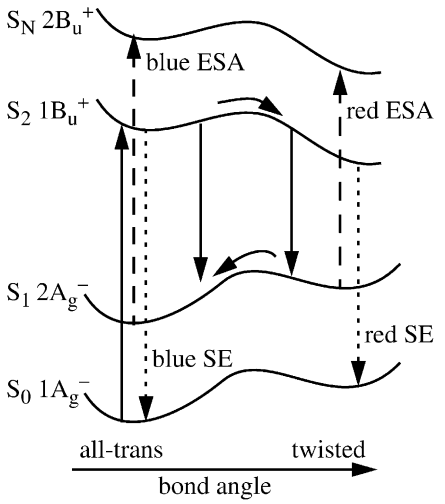

Fig. 3. Proposed energy surfaces for the β-carotene singlet excited states with respect to a bond angle around which twisting of the molecule may occur. In this scheme it is assumed that for the A_g^- states the all-*trans* form is most stable, whereas in the B_u^+ states twisting of the originally all-*trans* configuration is initiated. Upon exciting to S_2, formation (in S_2) and decay (in S_1 after IC) of twisted configurations with time will change the transitions between the excited states like the $S_2 \rightarrow S_0$ emission (dotted arrows) and the $S_1 \rightarrow S_N$ absorption (dashed arrows).

ration is initiated, see Fig. 3. In this model the twisting involves only small bond rotations on the time scale of the $S_2 \rightarrow S_1$ IC. These small twists of the Car molecule in S_2 decrease the probability for decay to the all-*trans* S_1 and increase the transition to the twisted configuration. Therefore, upon IC from S_2 to S_1, a mixture of all-*trans* and slightly twisted Car molecules will be formed in the S_1 state. Because the molecule is then in an A_g^- state (like S_0) the configuration with the lowest S_1 energy is probably the all-*trans* form and the twisted molecule will start to relax to this configuration on a subpicosecond time scale.

The loss of red and a gain of blue ESA that we observe in our measurements can now be explained in terms of relaxation within the S_1 manifold. Note that this depends on the detailed shape of the energy surface of the S_N state. We argued that the S_N state is a B_u^+ state which in our model necessarily gives rise to a loss of red and a gain of blue $S_1 \rightarrow S_N$ absorption. We conclude that a slight twist (of a significant population) is consistent with our data. A further indication for this picture is provided by measurements of the $S_2 \rightarrow S_0$ emission in all-*trans*-β-carotene [4]. Our model (Fig. 3) predicts a red shift of this emission. With fluorescence up-conversion techniques a broadening of the S_2 emission and a simultaneous loss of emission on the blue side of the spectrum were indeed observed on a time scale of 0.3 ps. Note that this time scale in combination with a shorter S_2 lifetime in our model does not imply that a small fraction twists. In our experiments we do not observe an evolution in the S_2 SE because the fluorescence signals at a few-hundred femtosecond delay are obscured by a huge ESA. It could be detected with fluorescence up-conversion [4], because this technique is only sensitive for fluorescence. We conclude that both phenomena, S_2 'relaxation' and S_1 'relaxation', can be described by the formation and decay of twisted states of the β-carotene molecule.

These twisted or 'hot' S_1 states might participate in the energy transfer from S_1 to a Chl Q_y state. Several studies indicate that this might well be the case. An evolution in the ESA of spheroidene is associated with Car to bacteriochlorophyll excitation energy transfer (EET) in the LH2 complex of *Rb. sphaeroides 2.4.1* [18]. It is suggested that a major part of the Car $S_1 \rightarrow$ Chl EET in LHCII is due to efficient transfer from hot vibronic states of the Cars [25].

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