

## Ultrafast relaxation kinetics of the dark $S_1$ state in all-*trans*- $\beta$ -carotene explored by one- and two-photon pump–probe spectroscopy

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### ABSTRACT

Femtosecond one- and two-photon pump–probe dispersive spectroscopic measurements have been applied to the investigation of the vibrational relaxation kinetics of the dark  $S_1$  ( $2^1A_g^-$ ) state in  $\beta$ -carotene, combining a higher sensitive detection system with tunable visible and infrared excitation pulses. The two-photon excitation measurements enable the preferential detection of the dark  $S_1$  state. The tunable infrared excitation pulses allowed selective excitation to a different vibrational level of  $S_1$ . The  $S_1$  dynamics at early delay times depend strongly on excitation energy. A dependence of the initial  $S_1$  dynamics on excitation energy is discussed in term of the vibrational relaxation of  $S_1$ .

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### 1. Introduction

All-*trans*-carotenoids play important roles in light-harvesting in both plant and bacterial photosynthesis. In bacterial photosynthesis, carotenoids absorb light energy in the blue–green spectral region and transfer it rapidly and efficiently to nearby bacteriochlorophylls [1]. A detailed understanding of this excitation energy transfer process requires precise knowledge of the electronic excited state structures of carotenoids, because photon energy is frequently stored as electronic excitation of carotenoids before it is transferred to the (bacterio) chlorophylls [1].

The  $S_0$  ground state of all-*trans*-carotenoids has  $A_g^-$  symmetry assuming that their linear polyene backbone has  $C_{2h}$  point group symmetry. The lowest singlet excited state,  $S_1$  (the  $2^1A_g^-$  state), is optically forbidden because it has the same  $A_g^-$  symmetry as the ground state. Therefore, the  $S_2$  ( $1^1B_u^+$ ) state is the lowest one-photon optically allowed state [2]. The ultrafast relaxation kinetics of carotenoids have been widely investigated by pump–probe measurements following one-photon excitation to  $S_2$  [3–10]. Recently, the vibrational relaxation processes of  $S_1$  have attracted much attention because of their unique vibronic character [11–18]. Our previous studies of the femtosecond stimulated anti-Stokes Raman

measurements [11–13] and the dependence of the relaxation kinetics on excitation energy in  $\beta$ -carotene [10] have suggested that the timescale of the vibrational relaxation of the C=C stretching mode in  $S_1$  is comparable with that of the  $S_1 \rightarrow S_0$  internal conversion. In contrast, some other investigators have claimed that hot  $S_1$  is cooled within 1 ps [14–18]. Since the observed  $S_1$  dynamics follow the internal conversion from  $S_2$ , these  $S_1$  dynamics are often complicated by contribution from relaxation process from higher energy singlet states.

Here, a novel approach using direct two-photon excitation to  $S_1$  has been utilized to clarify this situation and to determine the vibronic structures and probe the relaxation kinetics of  $S_1$  [19–31]. Walla et al. have applied two-photon excitation measurements to  $\beta$ -carotene in photosystem I and shown efficient excitation energy transfer from a vibrational hot level of  $S_1$  to  $Q_y$  of chlorophyll *a* [21,23,32]. The efficient energy transfer from a vibrational hot level has been theoretically predicted [33], but the mechanism of this process is not well understood. The pathway of energy flux from  $S_1$  to the  $Q_y$  band of chlorophylls or bacteriochlorophylls is one of the important channels in both plant and bacterial photosynthesis [1]. Therefore, further investigations of the vibrational relaxations in  $S_1$  are important to clarify the mechanism of the excitation energy transfer from vibrational hot states.

Sensitive detection systems using a lock-in amplifier and other techniques have been applied in the previous two-photon pump–probe studies [20–22]. However, previous studies only used single channel detection. Here we use a multichannel detector in order to obtain more complete spectral information on  $S_1$ . Charge coupled

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devices (CCD) have been widely used to in multichannel detectors. However, the data readout time of CCD is not fast enough (exposure and readout time is typically several hundreds milliseconds) and as a result the signal-to-noise ratio of the observed spectra is not always satisfactory because of slow fluctuations of the light source [34]. Therefore, data acquisition times of the order of a few minutes are required in order to obtain a sufficient signal-to-noise ratio at any given delay. The problems can be overcome by using a photo-diode array because it can read out data without delay at the pulse repetitions of 1 kHz [35–38].

In this study, the  $S_1$  relaxation kinetics of  $\beta$ -carotene have been studied by femtosecond pump-dispersive probe spectroscopy following direct two-photon excitation to the  $S_1$  ( $2^1A_g^-$ ) state and by one-photon excitation to the  $S_2$  ( $1^1B_u^+$ ) state, using tunable excitation pulses. The  $S_0$ – $S_1$  transition is two-photon allowed because both  $S_0$  and  $S_1$  have same  $A_g^-$  symmetry [2,39]. The two-photon technique is advantageous because it allows the relaxation kinetics of the low-lying one-photon forbidden  $S_1$  state to be probed without any interference from higher excited states. Several studies have shown the time-resolved  $S_1$  dynamics after two-photon excitation to  $S_1$ . However, the results were not spectrally well resolved [20–22]. In the present experimental setup, a white continuum was used as probe pulses and they were detected by photo-diode arrays where the data readout was synchronized with the rate of excitation pulses (1 kHz). Using this system, the  $S_1$ – $S_n$  transient absorption spectra could be recorded with a high signal-to-noise ratio at ranged delay times. Tunable excitation pulses allowed us to selectively excite different vibrational levels of  $S_1$ .

## 2. Experimental

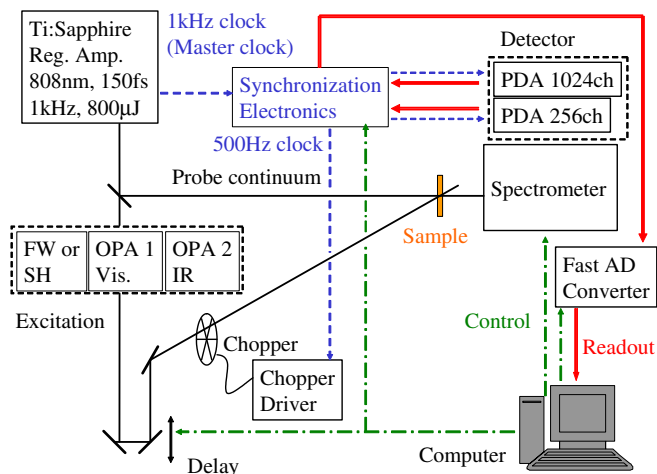
The experimental setup used for the femtosecond one- and two-photon pump-probe measurements with the sensitive detection system is illustrated in Fig. 1. A mode-locked Ti:Sapphire oscillator (Avesta) and a kHz regenerative amplifier (Spectra Physics, Spitfire) was used as the femtosecond light source. Output pulses were divided into excitation and probe pulses. Outputs of two types of optical parametric amplifiers were used as the excitation pulses. One was pumped by second harmonic pulses (3.06 eV) and the output photon energy could be tuned between 1.77 eV and 2.58 eV. The other one was pumped by the fundamental pulses (1.53 eV) and the output photon energy could then be tuned between 0.95 eV and 1.13 eV. The excitation pulses were modulated

at 500 Hz by an optical chopper (MC1000A, Tholabs) locked to the laser repetition of 1 kHz. Excitation intensity was set to 50 nJ/pulse for one-photon excitation measurements and 1  $\mu$ J/pulse for two-photon excitation measurements. A white continuum generated in a 5.0 mm sapphire plate was used as the probe pulses. The probe pulses were detected by photo-diode arrays (1024 pixels NMOS linear image sensor S3903-1024Q or 256 pixels InGaAs linear image sensor C8061-01, Hamamatsu) following passage through a spectrometer (MS3504I, Monochromator-Spectrograph Imaging, SOLAR TII Ltd.). The data from the photo-diode array were read out at the pulse repetition rate and digitized by a fast analog to digital conversion card (1.25 Ms/s and 16 bit resolution, NI-6251, National Instruments). The timing between the modulation frequency of the excitation pulses and the data readout was synchronized by a home-built system. By using the photo-diode array as the detection system, the signal-to-noise ratio could be increased more than a factor of 10 (noise level is less than  $10^{-4}$  OD) compared with our previous study using a CCD detector [34].

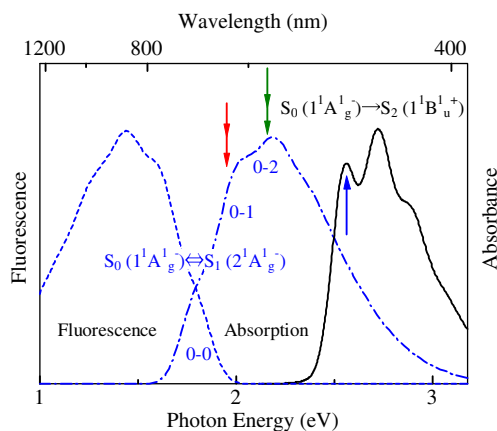
The instrumental response function of the system, determined by cross-correlation between the excitation and probe pulses, was better than 150 fs. The cross-correlation function was used to determine the precise zero time delay at each probe energy. After chirp compensation, experimental error of the determined zero time delay was less than 20 fs.

All-*trans*- $\beta$ -carotene was purchased from Wako Pure Chemical Industries Ltd. and purified by crystallization from benzene, twice. The purified sample was dissolved in cyclohexane and circulated in a flow cell with quartz windows, that has an effective optical path-length was 0.5 mm. The optical density of the sample was 1.0 at the absorption maximum of the steady-state absorption (2.73 eV). All measurements were performed at room temperature.

The steady-state absorption spectrum of  $\beta$ -carotene in cyclohexane is shown in Fig. 2. The absorption and fluorescence spectra of  $S_1$ , calculated from the parameters determined by the steady-state  $S_1$  fluorescence measurement in solution [40], are also shown in Fig. 2. The vibrational structures in the steady-state spectra are mainly due to the C=C and C–C stretching modes [40]. For the one-photon pump-probe measurement, the excitation energy was set to 2.54 eV corresponding to the 0–0 transition of  $S_2$ . Excitation energies of 0.98 eV and 1.05 eV were selected for the two-photon excitation measurements. These energies correspond to 0–1 and 0–2 two-photon transitions of the C=C stretching modes in  $S_1$ , respectively. A pump-probe measurement following 0–0



**Fig. 1.** A schematic picture of multichannel kHz detection system. FW: fundamental wave, SH: second harmonics, OPA: optical parametric amplifier, PDA: photo-diode array, AD: analog to digital.



**Fig. 2.** Steady-state spectra of  $\beta$ -carotene in cyclohexane. The  $S_1$  absorption (broken line) and fluorescence (dashed-and-dotted line) spectra were reconstructed using the parameters determined from measurement of the  $S_1$  fluorescence [40]. The single arrow and the double arrows indicate energies of one-photon excitation (OPE) to  $S_2$  and two-photon excitations (TPEs) to  $S_1$ , respectively.

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