Ultrafast Optical Responses of Three-Level Systems in $\beta$-Carotene: Resonance to a High-Lying $n^1A_g^-$ Excited State

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Received August 18, 2005

Abstract—Ultrafast optical phenomena in all-trans-$\beta$-carotene have been investigated by femtosecond absorption and fluorescence spectroscopy. Following a resonant pump pulse, both fluorescence and absorbance changes have a decay time of 150 fs. The signals are assigned to the lowest optically allowed singlet excited state, $1^1B_u^+$. Transmittance changes induced by nonresonant pump pulses depend on the pump photon energy. They are interpreted in terms of the ac Stark effect in three-level systems and two-photon absorption of the pump and probe pulses generating a high-lying $n^1A_g^-$ state.

DOI: 10.1134/S1054660X06020204

1. INTRODUCTION

All-trans-carotenoids play important roles in the light-harvesting function of bacterial photosynthesis [1, 2]. Light energy is initially absorbed by carotenoids and transferred to bacteriochlorophylls with very high efficiency. Carotenoids serve a photoprotective function to suppress the production of harmful singlet oxygen. The linear polyene structure of carotenoids has also attracted much interest in relation to conjugated polyene backbone. The lowest optically allowed excited state is the $1^1B_u^+$ state, but there are other optically forbidden states below the $1^1B_u^+$ state [3, 4]. The excited states and their kinetics have been intensively investigated in carotenoids. It has been well established that the photoexcited $1^1B_u^+$ state relaxes until the $2^1A_g^-$ state, which is the lowest dark singlet excited state within a few hundred femtoseconds. However, the $1^1B_u^+$ state has been proposed as an intermediate state of the relaxation [5–8]. The ultrafast dynamics of the initial relaxation is not well understood.

Recently, the relaxation kinetics in $\beta$-carotene has been investigated using sub-20-fs pulses. Cerullo et al. have observed two transient transmittance changes before the formation of the $2^1A_g^-$ state. The 10-fs signal observed around 1.6 eV has been assigned to the $1^1B_u^+$ state, and the 150-fs signal at 1.25 eV has been assigned to the $S_\gamma$ state (implicitly, the $1^1B_u^-$ state) [9, 10]. In spirilloxanthin that has a longer conjugation length than $\beta$-carotene, the $3^1A_g^-$ state has been proposed as another additional intermediate state [11]. However, the lifetimes of the $1^1B_u^+$ state obtained in these studies are much shorter than the lifetime determined by time-resolved fluorescence spectroscopy [12–14]. Novel pump–repump–probe and pump–dump–probe measurements have been applied to study the intermediate states of the relaxation kinetics. Larsen et al. have reported that the relaxation kinetics in $\beta$-carotene depends on the excitation energy and proposed a new singlet excited state labeled $S^\beta$ [15]. Another excited state labeled $S^\beta$ has been proposed in carotenoids in solution and light-harvesting complexes [16, 17]. These studies show that it is not straightforward to compare results measured under different conditions, e.g., different excitation photon energies, temporal resolutions, and solvents.

Nonlinear optical properties in three-level systems have been a subject of much interest in recent years because of the variety of nonlinear effects and large resonance enhancement. The dynamic (ac) Stark effect has been investigated in various types of three-level systems: the A-type system with nearly degenerated lower levels, the V-type system with nearly degenerated upper levels, and the $\Sigma$-type system with three well-separated levels [18–22]. Resonant two-photon absorption in the $\Sigma$-type three-level system is useful to study the properties of the excited states [23–26]. The nonlinear optical phenomena are observed as transmittance changes in time-resolved absorption spectroscopy. Therefore, their effects should be taken into account in the study of the ultrafast dynamics of the excited states.

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NONLINEAR OPTICS AND SPECTROSCOPY
In this study, the initial relaxation kinetics in all-trans-β-carotene has been investigated by femtosecond fluorescence and absorption spectroscopy using a same resonant pump pulse. Nonlinear optical responses induced by tunable nonresonant pump pulses have been measured by femtosecond absorption spectroscopy and discussed considering resonances in three-level systems.

2. EXPERIMENTAL

The time-resolved absorption and fluorescence spectroscopy setup shown in Fig. 1 was based on a mode-locked Ti : sapphire laser system [6, 8]. The output pulse was separated to pump, probe, and gate pulses. The pump and probe pulses were used in the time-resolved absorption spectroscopy. Tunable pump pulses were generated by optical parametric amplifiers pumped by the second harmonic or fundamental pulses of the Ti : sapphire laser. The fundamental pump pulse was separated from the gate using a resettable mirror. The durations of the pump pulses are 120–150 fs depending on the photon energy. White continuum generated in a 5.0 mm sapphire plate was separated to probe and reference pulses and detected by a spectrometer with CCD (JOBIN WON, SR460) through optical fibers. The relative polarization of the pump and probe pulses was set to parallel, because orientational relaxation of the carotenoid molecule is negligible within a few picoseconds [27].

The optical Kerr gate method using a 1.0-mm quartz glass was utilized in the fluorescence spectroscopy. The gate was the fundamental pulse (1.56 eV). The Kerr medium was placed between crossed film polarizers (FP). The first FP was set parallel to the pump polarization. The gated fluorescence signal was detected by a spectrometer with a CCD. The time-resolved fluorescence spectroscopy was measured using the same pump pulses with the absorption spectroscopy only blocking the probe pulse.

The temporal responses of the setup were determined by cross-correlations between the excitation pulse and the probe or gate pulse. The full width at half maximum of the cross-correlation was about 200 fs. Time constants of the kinetics were determined by the best fit using exponential functions with convolution of the system response, which was assumed to have a Gaussian shape. The chirp of the probe pulse caused dispersion of the zero delay in the absorption spectroscopy. It was compensated in the data analysis using the cross-correlation signal between the pump and probe at each wavelength. Dispersions of a sample cell and the film polarizer were also taken into account in the analysis.

All-trans-β-carotene was purchased from Wako Pure Chemical Industries, Ltd., and recrystallized twice from benzene. The sample in cyclohexane was circulated using a 1-mm flow cell at room temperature.

3. INITIAL RELAXATION KINETICS FOLLOWING RESONANT PUMP

Figure 2 shows time-resolved spectra and temporal responses of fluorescence and absorbance changes of β-carotene in cyclohexane. The pump with a photon energy of 2.5 eV is resonant to the stationary absorption and excites the $1^1B_u^+$ state. The fluorescence at a delay time of 0.1 ps appears around 2.2 eV. It is assigned to the $1^1B_u^+$ state, because the $1^1B_u^-$ and $2^1A_g^-$ states are optically forbidden and their energies suggest a much larger Stokes shift [3, 4]. The temporal response of the fluorescence (open circles in Fig. 1b) shows simultaneous increase and fast decay. The kinetics can be fitted to an exponential decay function convoluted with the system response. The lifetime of the $1^1B_u^+$ state is obtained as $150 \pm 40$ fs.

The photoinduced absorbance change at 0.1 ps is classified into four components according to the previously reported results [5–8]. The first is the bleaching above 2.45 eV. This is due to depletion of the ground state. The second is the negative signal at 2.3–2.4 eV. It is assigned to stimulated emission from the $1^1B_u^+$ state. The third is a positive peak at 2.2 eV. It is assigned to the $2^1A_g^-$ state. The 2.2-eV peak appears with a time constant of 150 fs and decays with a lifetime of 8.5 ps. The last is a near-infrared transient absorption at 1.25 eV. The near-infrared signal has the same temporal response as the fluorescence, as shown in Fig. 1b. Therefore, it is assigned to the $1^1B_u^+$ state instead of the $S_1$ state proposed by the sub-20-fs study [9].