Excited-state dynamics of the $1B_u^+$, $3A_g^-$, and $1B_u^-$ states in a carotenoid molecule by 5-fs absorption spectroscopy

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Abstract

The time-resolved absorption spectra of all-*trans*-spirilloxanthin were recorded by the use of extremely stable sub-5-fs pulses covering coherently the main visible range of 520–700 nm. All the theoretically predicted and long-lasting argued states ($1B_u^+$, $3A_g^-$, and $1B_u^-$ states) were clearly identified for the first time. The spectrum of each component and lifetime were determined without ambiguity by the global fitting method. Their lifetimes were in sequence $\sim$10, 25 ± 2, and 140 ± 30 fs.

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In bacterial photosynthetic systems, all-*trans*-carotenoids (CARs), generally having the number of conjugated double bonds $n = 9-13$, are specifically bound to the LH1 and LH2 antenna complexes and play an important function of light harvesting. This function includes the absorption of photons by CARs and subsequent transfer of their singlet energy to bacteriochlorophylls

(BChls). The approximate C_{2h} symmetry of the all-*trans*-conjugated chain gives rise to singlet-excited states that can be classified into kB_u^+, lB_u^-, mA_g^+, and nA_g^- groups.

The Pariser–Parr–Pople calculations by the multi-reference method including singly- and doubly excited configurational interactions (PPP-MR-SDCI) of shorter polyenes showed the presence of the low-lying $1B_u^-$, $3A_g^-$ singlet states in between the well-documented $1B_u^+$ and $2A_g^-$ states [1,2]. The energies of these excited states decrease as linear functions of $1/(2n+1)$, where n is the number of conjugated double bond [3–5].

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In the case of carotenoids having the number of conjugated double bond $n = 11-13$, the state ordering of singlet states is described as follows:

$$1B_u^+ \rightarrow 3A_g^- \rightarrow 1B_u^- \rightarrow 2A_g^- \rightarrow 1A_g^- \text{(ground)}.$$
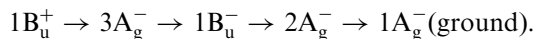
In these carotenoids, the $3A_g^-$ state could not be time resolved by the use of subpicosecond pulses, and the spectral pattern of the $1B_u^-$ and the hot $2A_g^-$ states sometimes mixed. In the present investigation, we utilized sub-5-fs pulses [6–9], in order to identify the $3A_g^-$ and $1B_u^-$ states, and to determine the intrinsic relaxation dynamics of spirilloxanthin ($n = 13$).

All-*trans*-spirilloxanthin ($n = 13$) selected as the first molecule for the serial study of carotenoids was prepared as described previously [3]. In the time-resolved difference transmission measurement, spirilloxanthin (1×10^{-5} M) in tetrahydrofuran (THF) was used as a sample.

The setup for femtosecond time-resolved absorption spectroscopy was described previously [8]. The sub-5-fs 1 kHz pulse train was generated from the noncollinear optical parametric amplifier (NOPA) with a pulse compressor [6,7,9] and its wavelength range is from 500 to 750 nm. Energy of the pump pulse at the sample was about 40 nJ and that of the probe pulse was a quarter of the pump pulse. In order to measure weak pump–probe signals at various wavelengths, we used a multi-channel lock-in amplifier with a 210 Hz chopper. The normalized transmittance changes were measured in the pump–probe delay-time region from -30 to 1000 fs with a 5-fs interval and in the spectral region of 520–700 nm with 117 data points.

Fig. 1 shows selected time-resolved absorption spectra of spirilloxanthin dissolved in THF in the 15–280 fs region. The very initial difference spectrum (15 fs) consists of a pair of stimulated emission peaks around 550–600 nm to be attributed to the $1B_u^+(0) \rightarrow 1A_g^-(0)$ and $1B_u^+(0) \rightarrow 1A_g^-(1)$ transitions, and a pair of transient absorption peaks around 640–685 nm. This difference spectrum can be attributed to the optically allowed $1B_u^+$ state, to which the CAR molecules were to be most efficiently excited upon absorption of photons. The second appearing in the time sequence in the distinct difference spectrum which appears typically at 30 fs, consists of a sequence of
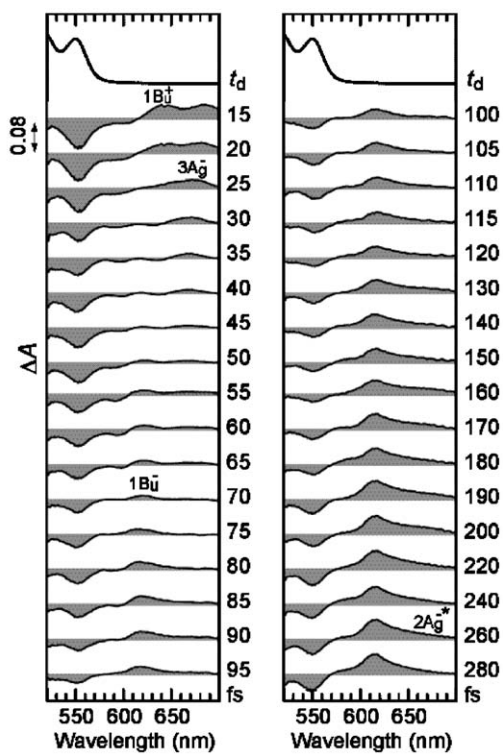

Fig. 1. Selected time-resolved absorption spectra of spirilloxanthin showing typical spectral pattern at delay times of 15, 25, 70 and 260 fs to be ascribed to the $1B_u^+$, $3A_g^-$, $1B_u^-$, and $2A_g^{-*}$ states, respectively.

three negative peaks ascribable to the vibrational progression of the $1B_u^+$ stimulated emission and a positive absorption peak of around 670 nm. This spectral pattern can be ascribed to the $3A_g^-$ state, because the state in spirilloxanthin is energetically next to the $1B_u^+$ state. The third appearing in the sequence is the difference spectrum, which is found typically at 65 fs, consists of a pair of negative signals ascribable to the vibrational progression of the $1B_u^+$ stimulated emission and a broad transient absorption centered around 620–680 nm. This spectral pattern can be assigned to the $1B_u^-$ state based on spectral comparison with the difference spectral pattern reported previously [10]. The fourth in the time sequence of difference spectrum at 220 fs consists of the bleaching of the $1B_u^+(0) \leftarrow 1A_g^-(0)$ stationary absorption and a strong transient absorption peaked at 615 nm. This can be