Excited state conformational dynamics in carotenoids: Dark intermediates and excitation energy transfer

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A B S T R A C T

A consideration of the excited state potential energy surfaces of carotenoids develops a new hypothesis for the nature of the conformational motions that follow optical preparation of the S_2 ($1^1B_u^+$) state. After an initial displacement from the Franck–Condon geometry along bond length alternation coordinates, it is suggested that carotenoids pass over a transition-state barrier leading to twisted conformations. This hypothesis leads to assignments for several dark intermediate states encountered in femtosecond spectroscopic studies. The S_x state is assigned to the structure reached upon the onset of torsional motions near the transition state barrier that divides planar and twisted structures on the S_2 state potential energy surface. The X state, detected recently in two-dimensional electronic spectra, corresponds to a twisted structure well past the barrier and approaching the S_2 state torsional minimum. Lastly, the S^* state is assigned to a low lying S_1 state structure with intramolecular charge transfer character (ICT) and a pyramidal conformation. It follows that the bent and twisted structures of carotenoids that are found in photosynthetic light-harvesting proteins yield excited-state structures that favor the development of an ICT character and optimized energy transfer yields to (bacterio)chlorophyll acceptors.

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Introduction

Carotenoids are essential components in the chromoproteins of photosynthetic organisms owing to their involvement in the mechanisms of photoprotection and light harvesting [1–4]. They serve as efficient antenna chromophores in the mid-visible (500 nm) spectral region where the solar spectrum is most intense. Strong, electric-dipole-allowed transitions from the carotenoid ground state, S_0 ($1^1A_g^-$), to the S_2 ($1^1B_u^+$) excited state (Fig. 1) are followed by downhill energy transfer to the Q_x or Q_y singlet states of chlorophylls (Chls) or bacteriochlorophylls (BChls) over short distances [4,5].

The mechanisms that mediate energy transfer from the S_1 ($2^1A_g^-$) state to the Q_y state are of considerable interest [6–8] because the S_1 state is a *dark* state; transitions between the S_1 and S_0 states are forbidden by symmetry. The selection rules that govern the photophysics of carotenoids apply rigorously only to the planar all-*trans* structures belonging to the C_{2h} point group;

transitions between states of the same symmetry or pseudoparity are electric-dipole forbidden [9,10]. The carotenoid binding sites observed in light-harvesting and reaction-center proteins, however, contain bent and twisted structures, often in close proximity to Chls. An example of this type of interaction is shown in Fig. 2 from the structure of the LH2 (B800–B850) light-harvesting protein from purple bacteria [11]. Energy transfer from the S_1 state is evidently optimized in light-harvesting proteins by placing the carotenoid nearly in van der Waals contact with an adjacent Chl so that the Coulomb coupling between them is as large as possible [7,8,12,13]. Owing to the properties of the conjugated polyene backbone, it is likely that the bent and twisted carotenoid structures further enhance the energy-transfer yield by increasing the transition dipole strength of formally dark electronic states and by promoting the development of an intramolecular charge-transfer (ICT) [3] character.

In this contribution, a hypothesis is presented that accounts for several aspects of carotenoid photophysics in terms of excited state conformational motions with respect to one or more of the conjugated C–C and C=C bonds. These motions naturally account for the

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[3] *Abbreviations:* ICT, intramolecular charge transfer; (B)Chl, (bacterio)chlorophyll; ESA, excited-state absorption; CARS, coherent anti-Stokes Raman scattering; SE, stimulated emission; 2DES, two-dimensional electronic spectroscopy; PB, photobleaching.
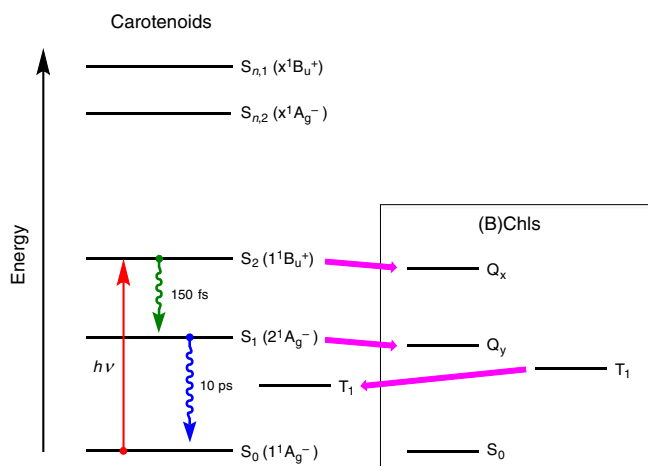
Fig. 1. Energy levels and pathways for nonradiative decay in carotenoids and for excitation energy transfer from carotenoids to (B)Chls in photosynthetic light-harvesting proteins. Nonradiative decay transitions from the S_2 and S_1 states are indicated with wavy arrows. The lifetimes of the states indicated are approximately those of β-carotene. The actual values will depend on the extent of π-electron conjugation of the carotenoid and on the nature of attached functional groups. Energy transfer pathways, forward from the carotenoid S_2 and S_1 states and reverse from the (B)Chl T_1 state, are indicated with filled arrows.

development in the S_2 state of an ICT character within a few hundred femtoseconds of optical excitation. This picture emerges from a discussion of the excited-state potential-energy surfaces and light-driven conformational motions of shorter polyenes, *trans*-stilbene, and of protonated Schiff bases and cyanines. The key step in the photophysics of all these systems is an intramolecular conversion of the initial momentum in the excited state along C–C bond-compression and C≡C bond-stretching motions of the conjugated polyene into motions of the torsional coordinates, which develops the character of a biradical. This sequence of events and the dynamics that follow account for the detection via ultrafast spectroscopy of three intermediate states, S_x [14], X [15], and S^* [16], and suggest a possible explanation for the distinct photophysics observed in some experiments when the wavelength of the excitation pulses is tuned. Further, the distorted structures
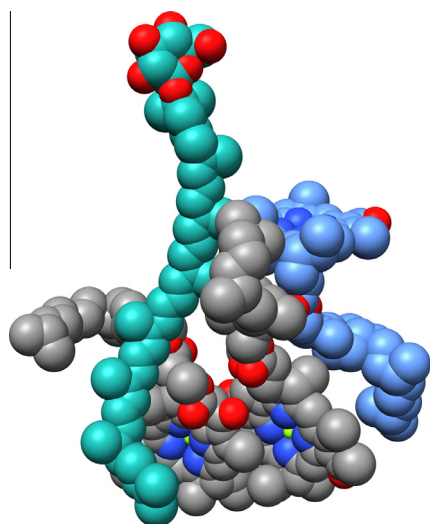

Fig. 2. Interaction of rhodopin glucoside (green) with the B800 BChl monomer (blue) and the B850 BChl *a* dimer (grey) in the LH2 protein from *Rhodopseudomonas acidophila* (PDB entry 1NKZ) [11]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observed in light-harvesting proteins can be viewed in this picture as preparing conformations in the ground state that favor a prompt assumption of excited state ICT character. A brief discussion of the possible use of femtosecond nonlinear spectroscopy with heterodyne detection to address aspects of this hypothesis will also be presented.

Potential energy surfaces and vibrational dynamics

The central argument of this contribution, that carotenoids undergo ultrafast motions along torsional coordinates upon photoexcitation, is founded upon a consideration of common features of the potential energy surfaces of the singlet excited states of conjugated molecules. As noted above, however, the motions that are initially launched by the optical transition are directed from the Franck–Condon structure along the normal modes of vibration that compress the C–C bonds and lengthen the C≡C bonds, effectively resulting in bond order reversal in the conjugated region [17–20]. This displacement initiates radiationless transitions well prior to the timescales associated with quenching of the excited state via photoisomerization.

As one important example, simulations by Levine and Martínez [21] show how the initial motions away from the Franck–Condon geometry after optical preparation of the 1^1B_u state of *trans*-2-butadiene result in a strong mixing with the dark 2^1A_g state. The result is an induction of transitions to and from the 1^1B_u and 2^1A_g states and an inversion of the initial energy ordering of the two states. Fig. 3 describes this behavior qualitatively in terms of a crossing of diabatic potential energy curves. In <10 fs, torsional displacements about either double bond begin and relaxation along a steep gradient in the 2^1A_g state occurs. A 90° twisted minimum-energy structure near to a conical intersection with the ground state (1^1A_g) potential surface is assumed in <50 fs [22,23]. Nonradiative relaxation through the conical intersection to the ground state then yields the original configuration or a photoisomerized configuration. This sequence of events is consistent with the information obtained by Trulson and Mathies [24] from resonance Raman intensity profiles, which indicate that the 1^1B_u state undergoes a very rapid conversion to the 2^1A_g state by moving primarily along C≡C stretching coordinates prior to the onset of out-of-plane or twisting motions.

For ethylene, butadiene, and the cyanines 1122-C and 1144-C, the path from the Franck–Condon structure to a conical intersection with the ground state at the 90° twisted geometry is considered barrierless [25–31]. But for *trans*-stilbene, an extensive body of experimental and theoretical studies indicates that a transition-state barrier between planar and twisted conformations occurs at low torsional angles, close to the Franck–Condon geometry [32]. The descent to the twisted minimum and through the conical intersection to the S_0 state involves propagation through a potential energy region that has a doubly excited ($\pi^*\pi^*$) character [33–35]. In general, as the length of a conjugated polyene increases, the energy of the transition state increases because the delocalized π^* character in a given C–C bond decreases. Similarly, because the π^* character increases in the higher singlet states as the energy level increases, the barrier height and the modulation depth to the twisted minimum would be expected to decrease.

The analysis by Olivucci, Robb, Schlegel, and coworkers [27,36–40] of the potential energy surfaces of models for retinal protonated Schiff bases (PSBs) and the structurally related cyanines emphasizes the crucial role of the barrier between planar and twisted conformations on the excited state dynamics. The gradients of the potential energy surface near the Franck–Condon geometry are effectively controlled by the conjugation length [27]. Bond length alternation and torsional forces act