

Ultrafast relaxation kinetics in all-*trans*-carotenoids

Daisuke Kosumi

Department of Physics

Carotenoids have linear polyene structure and show ultrafast optical response and large third order optical nonlinearity. They play important roles in bacterial photosynthesis, such as light harvesting, photoprotection, and stabilization of pigment-protein complex. Light energy absorbed by carotenoids is transferred to bacteriochlorophylls with very high efficiency. The excitation energy transfer to bacteriochlorophylls have been reported to occur from the S_2 ($1^1B_u^+$) and S_1 ($2^1A_g^-$) excited states of carotenoids. The S_1 state is the lowest singlet excited state, but it is optically forbidden. The S_2 state is the lowest optically allowed excited state. Recent theoretical and experimental investigations have revealed existence of intermediate states lying between the S_2 and S_1 states depending on a number of conjugated double bonds n of the polyene backbone. Therefore, the relaxation kinetics of carotenoids is very important in the excitation energy transfer process of the photosynthesis. However, the initial relaxation kinetics of carotenoids has not been well understood yet. A role of the intermediate state has not been clarified. The S_2 lifetime in β -carotene determined by femtosecond fluorescence spectroscopy is 150 fs, but the lifetimes of the S_2 and intermediate states reported by femtosecond absorption spectroscopy are 10 fs and 150 fs, respectively. To resolve this discrepancy, the direct comparison of the femtosecond fluorescence and absorption measurements under the same excitation condition is needed.

In this study, the ultrafast relaxation kinetics of the S_2 and S_1 states and resonant nonlinear optical effects in homologs of all-*trans*- β -carotene with different conjugation lengths ($n = 7 \sim 15$) and all-*trans*-lycopene ($n=11$) have been investigated using tunable excitation pulses. The contradiction of the S_2 lifetime is resolved. The conjugation length dependence of the relaxation kinetics is investigated and the intermediate state related to the S_2 relaxation is discussed.

The initial relaxation kinetics of β -carotene was observed by the femtosecond time-resolved fluorescence spectroscopy as well as the absorption spectroscopy. The observed fluorescence is assigned to the S_2 state, because the signal intensity indicates the optically allowed state with large radiative relaxation rate. The S_2 lifetime is determined to be 150 fs. The ultrafast optical responses following the nonresonant photoexcitation have been experimentally investigated in β -carotene and theoretically analyzed in terms of a Σ -type three level system of the S_0 (the $1^1A_g^-$ ground state), S_2 , and higher lying S_n ($n^1A_g^-$) states. The observed signals are assigned to nondegenerate two photon absorption from the S_0 state to the S_n state and dynamical Stark effect in the three level system. No intermediate state between the S_2 and S_1 states is needed for the explanation of the signals in β -carotene.

Nonradiative relaxation rate of large molecules has been often explained by the energy

gap law that the relaxation rate between two electronic states decreases exponentially with increase of the energy gap between the two states. Therefore, the relaxation kinetics of the carotenoids with different conjugation length is discussed in terms of the relative energy gap. Figure 1 and 2 show the relaxation rates of the S_1 and S_2 states obtained by the femtosecond time-resolved absorption and fluorescence spectroscopies, respectively. The energy gaps are estimated using the effective conjugation lengths determined by the stationary absorption. The S_1 relaxation rates are well explained by the energy gap law (A broken line in Fig.1). However, the S_2 relaxation rates have a maximum for $m9'$ -carotene ($n=9$) and show the reverse trend for the energy gap law in the longer carotenes ($n \geq 11$). It is explained by the intermediate state lying between the S_2 and S_1 states in the longer carotenoids. The reverse trend of the S_2 relaxation rates in the longer carotenoids was explained by the intersection of potential surface of the S_2 and intermediate states. However, the kinetics of the intermediate state has not been directly observed by the femtosecond time-resolved spectroscopies in this study. The lifetime of the intermediate state estimated by the S_2 decay and S_1 rise time constants is expected to be shorter than 100 fs.

In conclusion, the S_2 lifetimes of the carotenoids have been correctly determined by the femtosecond fluorescence spectroscopy. The ultrafast optical responses in β -carotene are explained by the photoexcited S_2 state and the nonlinear optical effects in the S_0 , S_2 , and S_n three level system. The conjugation length dependence of the S_2 lifetime suggests that the intermediate state between the S_2 and S_1 states should have a role to facilitate the S_2 relaxation faster in the longer carotenoids ($n \geq 11$).

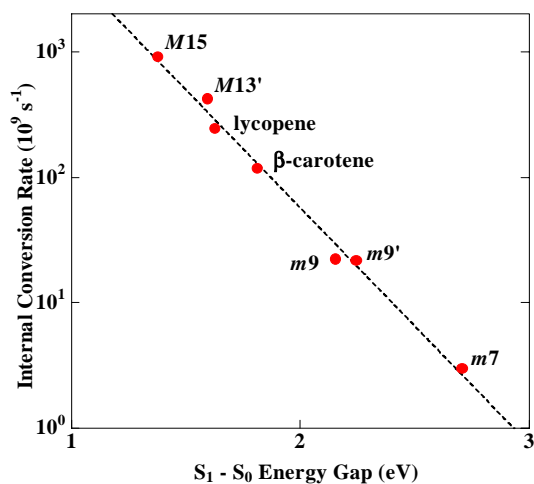


Fig. 1: The conjugation length dependence of relaxation rates of the S_1 state as a function of the S_1 - S_0 energy gap.

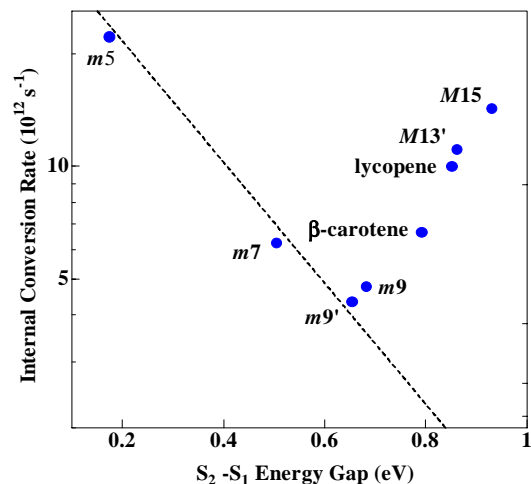


Fig. 2: The conjugation length dependence of relaxation rates of the S_2 state as a function of the S_2 - S_1 energy gap.