Primary Process in Light-Harvesting Complex Studied by Pump-Repump-Probe Spectroscopy

K.Sobue[1], K.Abe[1], S.Sakai[2], M.Nango[3], H.Hashimoto[3,4], and M.Yoshizawa[1]
[1]*Department of Physics, Graduate School of Science, Tohoku University, 6-3 Aramaki-aza-aoba, Aoba-ku, Sendai 980-8578, Japan*
[2]*Department of Life and Materials Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan.*
[3]*Department of Physics, Graduate School of Science, Osaka City University, Osaka 558-8585,Japan.*
[4]*OCARINA, Osaka City University, Osaka 558-8585,Japan*
E-mail: m-yoshizawa@m.tohoku.ac.jp

Abstract: Dark excited states of carotenoid in LH1 complex have been investigated by measuring recovery dynamics following the repump. The S* state is different from the S_1 state but is similar to the T state.
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1. Introduction

Carotenoids (Cars) have light-harvesting (LH) and photoprotecting functions in photosynthesis [1,2]. In the LH process of bacterial photosynthesis, light energy is absorbed by Car and transferred to nearby bacteriochlorophyll (BChl) as shown in Fig.1. The S_2 state in Car is the lowest optically allowed singlet excited state capturing the light energy. The S_1, S* and triplet (T) states are optically forbidden, but have important roles in the primary processes. The photoexcited S_2 state relaxes in femtosecond time scale, but excitation energy transfer (EET) to BChl occurs efficiently competing with the ultrafast relaxations. The recently assigned S* state has considerable importance in LH complexes [3,4]. It is a precursor of the T state [5] and has similar Raman signal with the T state [6]. However, essential properties of the S* state have not been well-understood.

In this study, the S_1, S*, and T states in reconstituted LH1 complex have been investigated by pump-repump-probe spectroscopy. Relations and properties of the excited states are discussed by comparing dynamics after selective re-excitation of the excited states.

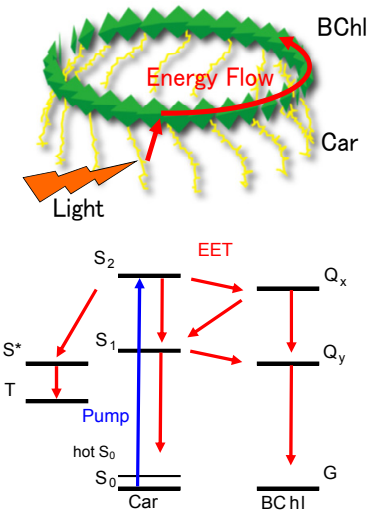

Fig.1. Schematic picture and energy level diagram of LH1 complex.

2. Experimental

The reconstituted LH1(Sph) was prepared from *Rhodospirillum rubrum* G9+ with purified spheroidene [7]. Native LH1 contains spirilloxanthin as a major carotenoid but spheroidene was used in this study, because the S* signal is more pronounced in LH1(Sph) than in LH1 with spirilloxanthin. The solution of LH1(Sph) was dispersed in a poly-vinyl alcohol film on a glass plate. During the laser spectroscopic measurements, the sample was translated to avoid sample degradation and the accumulation of any potential photoproducts.

The femtosecond pump-repump-probe spectroscopy setup was based on an amplified mode-locked Ti:Sapphire laser system. Parts of the amplified pulse were used to drive two independent optical parametric amplifiers generating the first pump and the second repump. Wavelength and delay time of the repump pulse were controlled for selective re-excitation of the excited states generated by the first pump pulse. Additional absorbance change ($\Delta\Delta A$) induced by the repump pulse was observed by white continuum probe. The probe was collected at 1 kHz repetition rate. Noise level of the obtained absorbance change was smaller than 10^{-4} in probe region of 450-1500 nm.

3. Results and Discussion

Figure 2 shows absorbance change (ΔA) spectra of LH1(Sph) following the first S_2 pump (500 nm, 100 fs). The signal at a delay time of 2 ps has two peaks at 525 nm and 550 nm. They are assigned to the S* and S_1 states, respectively. A small dip at 590 nm is bleaching of the Q_x state of BChl induced by EET from Car to BChl. The S_1 state relaxes with a time constant of 5.8 ps. The S* state decays with a time constant of 20 ps. The 525 nm peak observed at 50 ps remains much longer than 100 ps. It is assigned to the T state. The EET efficiency from Car to BChl in LH1(Sph) determined by comparing the intensities of the Q_y signal induced by the S_2 pump and the Q_x pump is 65 %.

The 560 nm repump pulse at a delay time of 2ps was used to re-excite the S_1 state. The ΔΔA spectrum at 0.2 ps after the repump has a negative peak at 550 nm as shown in Fig.3. It is assigned to bleaching of the S_1 transient absorption. The S_1 bleaching recovers with a time constant of 0.73 ps. The signal assigned to the S* state does not affected by the S_1 repump.

The ΔΔA spectrum following the S* repump (525 nm, 2 ps) has a negative peak at 525 nm and broad tail at long wavelength side. The 525 nm signal is assigned to bleaching of the S* state. It recovers with a time constant of 0.14 ps. On the other hand, the broad tail has a recovery time of about 20 ps. The broad tail is assigned to bleaching of the hot S_0 state, because the hot S_0 state has broad absorption below the S_0-S_2 absorption. The 525 nm repump excites both the S* and hot S_0 states. The independent ΔΔA signals between the S_1 repump and the S* repump show that the highly re-excited states from the S_1 and S* sates are independent.

The 525 nm repump at a delay of 50 ps after the S_2 pump re-excites the T state. The ΔΔA signal is similar to that of the S* repump except lack of the broad tail. It is consistent with the assignment of the broad tail to the hot S_0 state. The bleaching at 525 nm recovers with a time constant of 0.17 ps. The 525 nm bleaching and its recovery time suggest that the re-excited state from the T state is equal to that from the S* state. However, the S* state has been distinguished from the T state by the transient changes of the photoinduced absorption and Raman signal [6]. The transient state so-called the S* state should be assigned to the vibrational excited triplet (hot T) state.

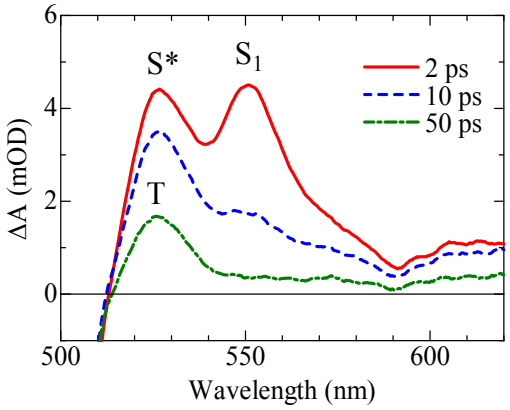

Fig.2. Absorbance change in LH1(Sph) following the S_2 pump.

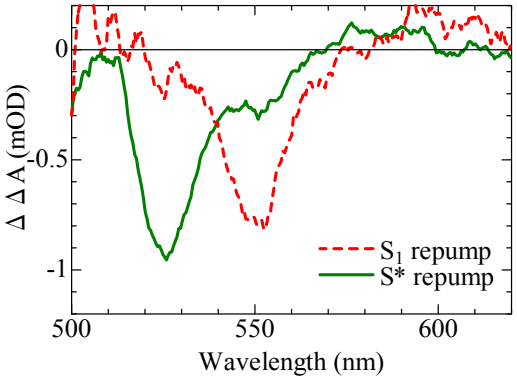

Fig.3. Absorbance changes at 0.2 ps following the S_1 repump (560 nm, 2 ps) and the S* repump (525 nm, 2 ps).

4. Conclusion

The transient absorbance change previously assigned to the S* state of carotenoid in LH1 has two components. The broad repump signal with slow recovery is assigned to the hot S_0 state. The sharp repump signal at 525 nm with fast recovery is assigned to the hot T state because of the similarity to the repump signal of the T state.

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