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Dark excited states of carotenoid in light harvesting complex probing with femtosecond stimulated Raman spectroscopy

O. Yoshimatsu[1], K. Abe[1,2], S. Sakai[3], T. Horibe[2,4], R. Fujii[2,5], M. Nango[2,5], H. Hashimoto[2,4,5], and M. Yoshizawa[1,2]

[1]Dep. of Physics, Graduate School of Science, Tohoku University, Japan
[2]JST, CREST, Japan
[3]Dep. of Life and Materials Engineering, Nagoya Institute of Technology, Japan.
[4]Dep. of Physics, Graduate School of Science, Osaka City University, Japan.
[5]OCARINA, Osaka City University, Japan.

Abstract. Vibrational dynamics of dark excited states in carotenoids have been investigated using tunable Raman pump pulses. The S_1 state has same vibrational dynamics in light-harvesting complex (LH1) and solution. The S* state in LH1 has similar vibrational modes with the triplet state of carotenoid. However, the so-called S* state in solution does not have the modes and is concluded to be different from the S* state in LH1.

1 Introduction

In light harvesting (LH) complexes of photosynthetic purple bacteria, light energy is absorbed by carotenoid (Car) and transferred to nearby bacteriochlorophyll (BChl) as shown in Fig.1. After photoexcitation to the optically allowed S_2 state of carotenoid, internal conversion to the optically forbidden S_1 state takes place within a few hundred femtoseconds. The following internal conversion to the S_0 ground state occurs on a picoseconds timescale. Ultrafast spectroscopic studies have shown that the excitation energy transfer to BChl takes place from S_2 and/or S_1 competing with these internal conversion processes [1,2]. Besides these singlet states, it has been reported that an additional optically forbidden state, which is termed S*, have considerable importance in the light-harvesting function [3,4]. It is the precursor on the reaction pathway toward triplet formation and plays a critical role in efficient excitation energy deactivation in the LH1 complex [5]. However, the entire picture of ultrafast energy flow in the LH complex has not been obtained yet.

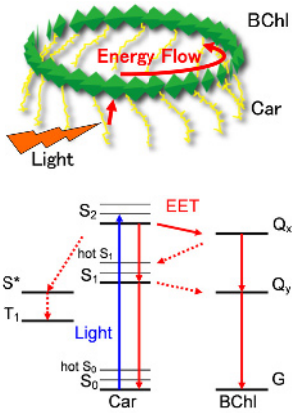

Fig. 1. Schematic picture and energy level diagram of LH1.

In this study, vibrational dynamics of spirilloxanthin in LH1 complex and cyclohexane solution have been investigated by femtosecond stimulated Raman spectroscopy (FSRS) [6]. The dark excited states (S_1 and S*) are selectively observed using tunable Raman pump pulses resonant to the transient absorption.

2 Experimental

The native LH1 complex from *Rhodospirillum rubrum* S1 contains spirilloxanthin as a major carotenoid. In this study, the reconstituted LH1 with purified spirilloxanthin was prepared as described elsewhere [7] to investigate the effect due to other kinds of carotenoids that may be involved. The solution of LH1(Spx) was dispersed in a poly-vinyl alcohol film on a glass plate. The solution of the native LH1 was measured using a 1 mm optical path length cell. During the laser spectroscopic measurements, the sample was translated to avoid sample degradation and the accumulation of any potential photoproducts.

The femtosecond absorption and stimulated Raman spectroscopy setup was based on an amplified mode-locked Ti:Sapphire laser system. Two independent optical parametric amplifiers were used to generate the first pump and Raman pump pulses. The first pump pulse was resonant to S_2 of spirilloxanthin (500 and 540 nm, 100 fs) and the tunable narrowband Raman pump pulse (560-620 nm, 20 cm^{-1}) was resonant to S_1 or S* of spirilloxanthin. A probe pulse after the sample was collected at 1 kHz repetition rate. Noise level of the obtained absorbance change (ΔA) was smaller than 10^{-4} in the probe region of 450-1500 nm.

3 Results and discussion

The results obtained in the native LH1 and the reconstituted LH1(Spx) show that the effects due to the reconstitution and other kinds of carotenoids are negligibly small. Therefore, it is concluded that the reconstituted spirilloxanthin in LH1(Spx) is identical to that in the native LH1. The reconstitution of purified carotenoids is a powerful technique to study the energy transfer and relaxation dynamics in the LH1 complex.

Absorbacne changes of spirilloxanthin after the Car S_2 pump are similar in LH1 and solution as shown in Fig.2. Initially, the transient absorption due to S_2 appears in near-infrared region. S_2 relaxes to S_1 with a time constant of 80 fs. The transient absorption due to S_1 appears at 620 nm in LH1 and at 600 nm in solution. Difference of the absorption peak is due to influence of the surrounding proteins in LH1. The lifetime of S_1 is 1.3 ps in LH1 and 1.4 ps in solution. The transient absorption at 5.0 ps has a peak at shorter wavelength than the S_1 absorption. It has been termed S* both in LH1 and solution because of similaities of the spectra and decay time (about 5 ps), but in this study we used S^*_{LH1} and S^*_{sol}, respectively. S^*_{LH1} is followed by the long-lived signal assigned to the triplet excited state (T_1), while spirilloxanthin in solution does not have the long-lived signal.

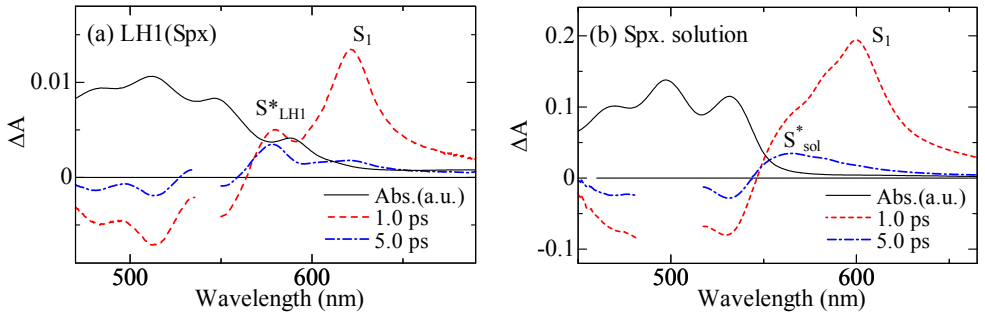

Fig. 2. Absorbance change of (a) LH1 and (b) spirilloxanthin solution after the Car S_2 pump. Stationary absorption spectra are shown together (thin solid black curves).

FSRS signals on the Stokes side in LH1 are shown in Fig.3. Two intense signals without the Car S_2 pump (Noex.) are assigned to ν_1 (C=C stretch.) and ν_2 (C-C stretch.) modes of S_0. At 1.0 ps after the Car S_2 pump, broad new signals are observed around 1770 and 1240 cm^{-1} by the S_1 resonant Raman pump (Fig.3(a)). Since their decay times are equal to the S_1 lifetime, they are assigned to the

ν_1 and ν_2 modes of S_1, respectively. The high-frequency shift in S_1 is explained in terms of the vibronic coupling through the vibrational mode with A_g symmetry. On the other hand, the signal obtained by the S^*_{LH1} resonant Raman pump (Fig.3(b)) does not have the S_1 signal but has a peak at 1264 cm^{-1}. The peak decreases slightly with a time constant of 5 ps and shifts to 1272 cm^{-1}. The 1264 cm^{-1} mode and the long-lived 1272 cm^{-1} mode are assigned to S^*_{LH1} and T_1, respectively. S^*_{LH1} has similar vibrational modes to T_1.

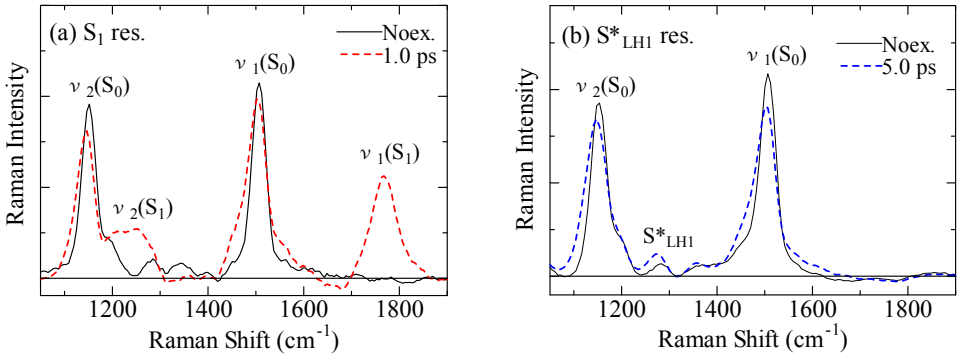

Fig. 3. FSRS signals of LH1 obtained by (a) the 620 nm Raman pump (S_1 resonance) and (b) the 580 nm Raman pump (S^*_{LH1} resonance) after the Car S_2 pump. Noex: without the Car S_2 pump.

FSRS signals of spirilloxanthin in solution was measured using the 600 nm (S_1 resonance) and 560 nm (S^*_{sol} resonance) Raman pump pulses. The observed S_1 Raman signal is almost identical to that in LH1. On the other hand, the signal induced by the S^*_{sol} resonant Raman pump does not have the 1264 cm^{-1} and long-lived 1272 cm^{-1} modes. The Raman signal of S^*_{sol} obtained by global fitting are almost equal to those of the S_0 ground state except small low energy shift. It is concluded that S^*_{sol} is different from S^*_{LH1}. It may be the hot S_0 state.

4 Conclusion

Resonant FSRS has revelaed the vibrational dynaimcs in Car. The S_1 state has almost same dynamics in LH1 and solutuon. The S^*_{LH1} state has similar vibrational modes with the T_1 state. On the other hand, the S^*_{sol} state is different from the S^*_{LH1} state and is suggested to be the vibrationaly excited ground state (hot S_0).

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