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快 报

# 在吡啶溶液中细菌叶绿素 a 分子 $S_3$ - $S_1$ 转换过程的实时观测\*

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**摘 要:** 采用飞秒荧光亏蚀技术研究细菌叶绿素 a 在吡啶溶液中的内转换过程. 我们用 400 和 800 nm 飞秒光作为泵浦与探测光. 该研究给出了细菌叶绿素 a 分子的  $S_3$ - $S_1$  转换过程的实时观测, 同时观测到随后的两个弛豫过程. 细菌叶绿素 a 在吡啶溶液中的内转换时间为 226fs.

**关键词:** 细菌叶绿素 a; 飞秒荧光亏蚀; 内转换

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## Direct Measurement of Conversion Time of

## Bacterio-chlorophyll a from the $S_3$ to $S_1$ State in Pyridine Solution\*

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**Key words** Bacteriochlorophyll a, Femtosecond time-resolved stimulated emission pumping fluorescence depletion, Internal conversion

Bacteriochlorophylls ( Bchls ) play very important roles in the bacterial photosynthetic system. They are responsible for the charge separation in the reaction center and energy transfer in the light-harvesting complexes. Bchl a is the most widely distributed pigment found in photosynthetic bacteria which presents in purple, green sulfur bacteria. Bchl a molecules exist in both the reaction centers and the light-harvesting complexes. Bchl a including the excited states properties of Bchl a, have been studied by both experimental and

theoretical methods<sup>[1-4]</sup>. But the knowledge of its higher single excited state is of little. The objective of our study is to investigate the internal conversion time of Bchl a in pyridine solvents at the room temperature. As far as we have known, this is the first measurement of the internal conversion of Bchl a from  $S_3$  to  $S_1$ .

To determine the time of internal conversion, the femtosecond time-resolved stimulated emission pumping fluorescence depletion ( FS TR SEP FD ), developed by Kong and coworkers was used<sup>[5]</sup>. As the detailed

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description of the method has been given in Ref.[ 6 ], only a brief description was given here. Two femtosecond pulses have been used in the FS TR SEP FD. One of the pulse excited the sample molecular to produce fluorescence. With a delay time , another laser pulse carried out the stimulated emission pumping ( SEP ) from the excited state to ground state. The fluorescence depletion recordered reflects the vibration relaxation of the excited state.

The absorption spectra of Bchl a in pyridine<sup>[7]</sup> were shown in Fig. 1. The electronic excitations from the ground state to the four configurations resulted in four bands. These bands<sup>[7]</sup> were called  $Q_x$  ,  $Q_y$  ,  $B_x$  and  $B_y$  of which the Q bands were found at 500 ~ 700 nm , corresponding to the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  while the B bands appeared at 350 ~ 450 nm which were assigned to the  $S_0$ - $S_3$  and  $S_0$ - $S_4$ . In this report , excitation at 400 nm showed time-resolved fluorescence depletion spectra of Bchl a.

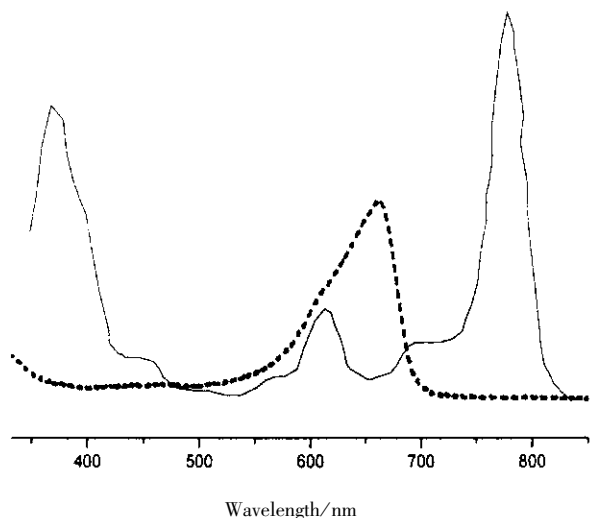


Fig. 1 Absorption spectra of Bchl a in pyridine ( solid ) and OX750 in acetone ( desh )

The fluorescence from Bchl a was measured as a function of the delay time between the probe and pump pulse at a range from - 1 to 8 ps. The FS TR SEP FD signals of Bchl a have been measured in pyridine solutions. The experimental results can be fitted by the deconvolution of Eq.( 1 ). Here  $R(t - \tau)$  was the correlation function.

$$\Delta I = \int_{-\infty}^{+\infty} R(t - \tau - \tau_{ic}) dt - S_e \times \int_{-\infty}^{+\infty} \exp\left(-\frac{t}{\tau_e}\right) R(t - \tau - \tau_{ic}) dt - S_p \times \int_{-\infty}^{+\infty} \exp\left(-\frac{t}{\tau_p}\right) R(t - \tau - \tau_{ic}) dt \quad (1)$$

Fig. 2 showed the fluorescence depletion spectra in different solutions. The internal conversion time  $\tau_{ic}$  can be determined directly from Fig. 2. The other parameters were shown in previous paper<sup>[6]</sup>. The internal conversion time of Bchl a in pyridine was  $(226 \pm 67)$  fs. A 400 nm femtosecond laser pulse to the electronically excited state  $S_3$  excited the Bchl a molecule. Due to the fact that the detection wavelength corresponds to the  $S_1$ - $S_0$  state , the internal conversion process was attributed to the Bchl a molecule from the  $S_3$  state to the  $S_1$  state.

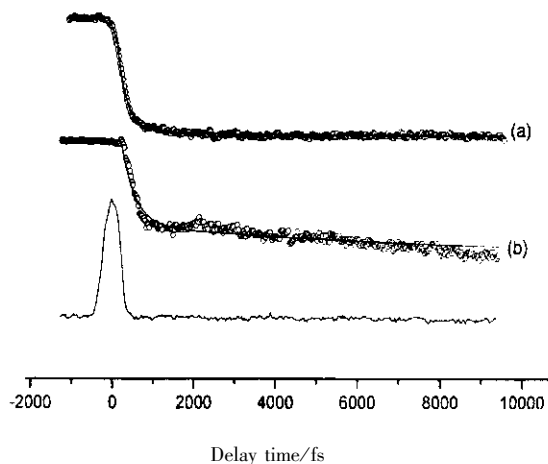


Fig. 2 The time-resolved fluorescence depletion spectra of Bchl a in ( a ) pyridine ( b ) LD700 in acetone at room temperature

The circles represent experiment data , where as the solid lines represent simulated results.

We cannot observe the internal conversion process of the dye molecule OX750 in solutions at 400 nm excitation probed at 800 nm that has been shown in the previous paper<sup>[6]</sup>. The reason can be ascribed that the 400 nm laser pulse can excite the OX750 to its first excited state and we detected the fluorescence from it , so no internal conversion process can be observed. The internal conversion process was shown in Fig. 3.

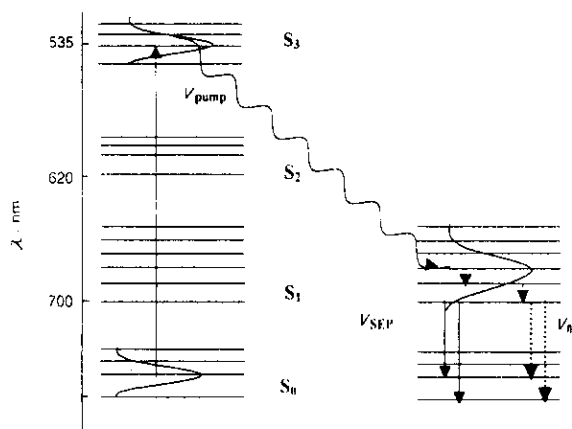


Fig. 3 Schematic representation of the ultrafast process in photoexcited Bchl a molecules in solution

Bchl a molecules in the ground state,  $S_0$  have a vibrational-rotational levels. Optical absorption,  $V_{\text{pump}}$  promotes this distribution to a band of vibrational states in the excited electronic state,  $S_3$ , from which deactivate to the  $S_1$  state via internal conversion. Then the initial vibrational excess energy relaxes to the other levels through an IVR process. These vibrational hot molecules are cooled by the solvent to the lowest level of the  $S_1$ . After a several delay times, the second pulse,  $V_{\text{SEP}}$  performs stimulated emission pumping (SEP) from the electronic excited state to the ground state. The rest of the excited molecules emit the fluorescence,  $V_f$  in several nanosecond.

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