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Excited state dynamics of Methyl 4-hydroxycinnamate studied by picosecond pump-probe spectroscopy

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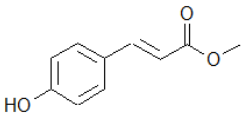
Introduction: Methyl 4-hydroxycinnamate (OMpCA) is known as a model compound of photoinduced trans → cis isomerization of Photoactive Yellow Protein (PYP). However, the dynamics of the isomerization hasn't been fully understood yet. In order to elucidate the dynamics, the lifetime of the S_1 state of OMpCA and its hydrogen bonded complex with water has been investigated in a supersonic beam by picosecond pump-probe spectroscopy. The result is analyzed by ab initio calculation.



OMpCA

Experiment: The supersonic beams of OMpCA and the OMpCA-H_2O complex were generated. The S_1-S_0 electronic spectra of these species were measured by resonant two-photon ionization (R2PI) method with the mass selection by Time-of-Flight tube. The S_1 state lifetimes of OMpCA and OMpCA-H_2O were measured by picosecond pump-probe spectroscopy. Figure 1 shows the scheme of pump-probe spectroscopy.

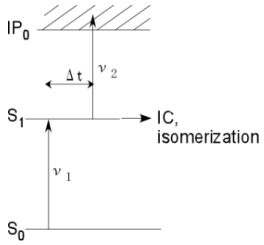


Figure 1. Scheme of pump-probe spectroscopy

Result and Discussion: Figure 2 shows the time profiles of the populations OMpCA and OMpCA-H_2O in S_1 at various excitation energies. In bare OMpCA, the lifetime at S_1 band origin is 8 ps. On the other hand, the lifetime of OMpCA-H_2O in its S_1 origin becomes as long as 930 ps. In addition, the lifetime of the complex sharply decreases with excess energies; it becomes 10 ps at the energy of 630 cm^{-1} above the band origin. Figure 3 shows the plots of the decay rate constant of OMpCA-H_2O vs excess energy. The rate constants sharply increase at 400 cm^{-1} for s-trans and at 600 cm^{-1} for s-cis conformer. These energies are thought to be the thresholds for the trans→cis isomerization of OMpCA-H_2O. We discuss this result on the basis of the theoretical calculation.

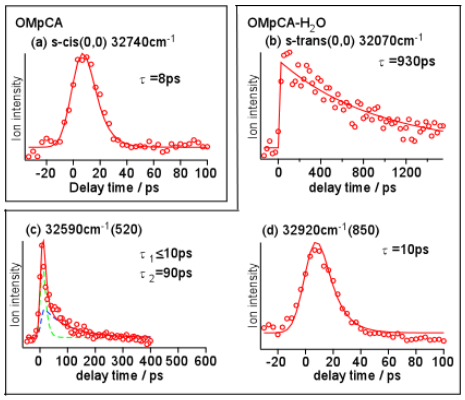


Figure 2. Pump-probe time profiles of (a) OMpCA and (b)-(d) OMpCA-H_2O complex

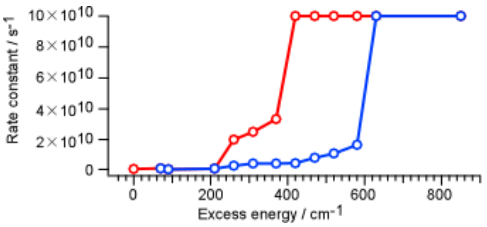


Figure 3. Decay rate constant of OMpCA-H_2O in S_1 against excess energy