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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 S1 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.

Experiment: The supersonic beams of OMpCA and the OMpCA-H2O complex were generated. The S1-S0 electronic spectra of these species were measured by resonant two-photon ionization (R2PI) method with the mass selection by Time-of-Flight tube. The S1 state lifetimes of OMpCA and OMpCA-H2O were measured by picosecond pump-probe spectroscopy. Figure 1 shows the scheme of pump-probe spectroscopy.

Result and Discussion: Figure 2 shows the time profiles of the populations OMpCA and OMpCA-H2O in S1 at various excitation energies. In bare OMpCA, the lifetime at S1 band origin is 8 ps. On the other hand, the lifetime of OMpCA-H2O in its S1 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-H2O 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-H2O. We discuss this result on the basis of the theoretical calculation.