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Effect of hydrogen-bonding on the trans to cis photoisomerization of Methyl 4-Hydroxycinnamate

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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 complexes with water and ammonia have been investigated in the gas phase by picosecond pump-probe spectroscopy. The result is analyzed by ab initio calculation.

Experiment: Gas phase OMpCA and its hydrogen bonded complexes were generated under cold condition by using supersonic free jet expansion. The S_1-S_0 electronic spectra of these species were measured by resonant two-photon ionization (R2PI) method with the mass selection. The S_1 state lifetimes of OMpCA and the hydrogen bonded complexes were measured by picosecond pump-probe spectroscopy. (Figure 1)

trans→cis isomerization of OMpCA

Figure 1. Scheme of pump-probe spectroscopy

Result and Discussion: In bare OMpCA, the lifetime at S_1 band origin is obtained to be 8-9 ps. Thus the isomerization occurs in this time scale in the monomer. On the other hand, the lifetimes of OMpCA-H_2O and OMpCA-NH_3 in its S_1 origin increase as long as 1.1 ns and 6.0 ns. In addition, we found in case of OMpCA-H_2O the lifetime of the complexes suddenly decreases with excess energy of 300-600 cm^{-1}. Figure 2 shows the plots of the decay rate constant of OMpCA-H_2O and OMpCA-NH_3 vs excess energy. In the OMpCA-H_2O, the rate constants sharply increase at ~400 cm^{-1} for s-trans and at ~600 cm^{-1} for s-cis conformer respectively. These energies are thought to be the thresholds for the trans→cis isomerization of OMpCA-H_2O. It is clear that the hydrogen bonding at the phenolic OH inhibit the isomerization. Also the H-bonding strength is also important for this inhibition. We discuss this result on the basis of the theoretical calculation.
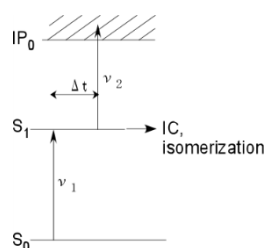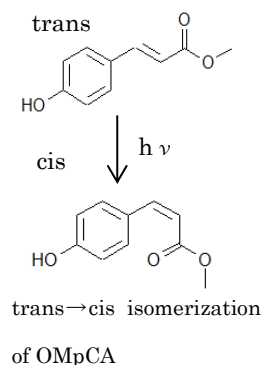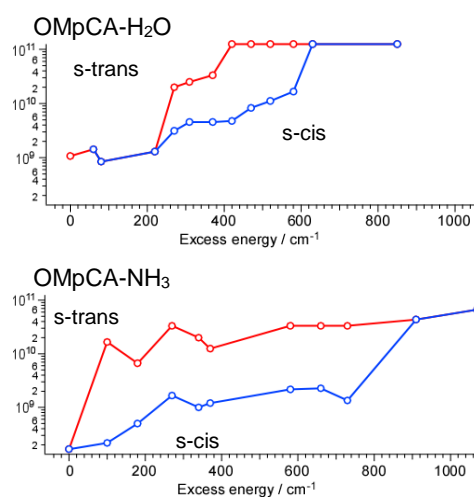

Figure 2. Rate constant of OMpCA-H_2O and OMpCA-NH_3 in S_1 against excess energy