NONRADIATIVE DECAY DYNAMICS OF METHYL-4-HYDROXYCINNAMATE AND ITS MONOHYDRATED COMPLEX REVEALED BY PICOSECOND PUMP-PROBE SPECTROSCOPY

T. EBATA, D. SHIMADA, R. KUSAKA, and Y. INOKUCHI, *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*; M. EHARA, *Institute for Molecular Science, 38 Myodaiji, Okazaki 444-8585, Japan*.

The lifetimes of methyl 4-hydroxycinnamate (OMpCA) and its mono-hydrated complex (OMpCA-H_2O) in the S_1 state have been measured by picosecond pump-probe spectroscopy in a supersonic beam. For OMpCA, the lifetime of the S_1 - S_0 origin is 8 - 9 ps. On the other hand, the lifetime of OMpCA-H_2O complex at the origin is 930 ps, which is 100 times longer than that. Furthermore, in the complex the S_1 lifetime shows rapid decrease at an energy of 200 cm^{-1} above the origin and becomes as short as 9 ps at 500 cm^{-1}. Theoretical calculations with symmetry-adapted cluster-configuration interaction (SAC-CI) method suggest that in OMpCA, the trans - cis isomerization occurs smoothly without a barrier on the S_1 surface, while in OMpCA-H_2O complex, there exists a barrier along the isomerization coordinate. The calculated barrier height of OMpCA-H_2O is in good agreement with that estimated from the lifetime measurements.