

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

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The lifetimes of methyl 4-hydroxycinnamate (OMpCA) and its mono-hydrated complex (OMpCA-H<sub>2</sub>O) in the S<sub>1</sub> state have been measured by picosecond pump-probe spectroscopy in a supersonic beam. For OMpCA, the lifetime of the S<sub>1</sub> - S<sub>0</sub> origin is 8 - 9 ps. On the other hand, the lifetime of OMpCA-H<sub>2</sub>O complex at the origin is 930 ps, which is 100 times longer than that. Furthermore, in the complex the S<sub>1</sub> lifetime shows rapid decrease at an energy of 200 cm<sup>-1</sup> above the origin and becomes as short as 9 ps at 500 cm<sup>-1</sup>. 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<sub>1</sub> surface, while in OMpCA-H<sub>2</sub>O complex, there exists a barrier along the isomerization coordinate. The calculated barrier height of OMpCA-H<sub>2</sub>O is in good agreement with that estimated from the lifetime measurements.