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Study of nonradiative decay process and *trans* → *cis* isomerization of *para*-, *meta*-, *ortho*-hydroxy methylcinnamate

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[Introduction] It is well known that cinnamic acid and its derivatives exhibit *trans*(E) → *cis*(Z) isomerization upon the photo-excitation to the S₁(ππ*) state. However, its mechanism is not fully understood yet. In our previous works, we reported that *para*-methoxy methylcinnamate



Fig.1 HMC structural isomers

excited to the S₁ state relaxes to the T₁ transient state *via* fast multistep decay process. In addition, it was suggested that the T₁ state is responsible in the isomerization. In this study, the nonradiative decay (NRD) process involving the isomerization of hydroxy methylcinnamate (HMC) structural isomers (Fig.1) has been investigated by UV spectroscopy and lifetime measurement in a jet-cooled gas phase and low temperature matrix isolated FTIR spectroscopy. The low temperature matrix isolated FTIR spectroscopy revealed that all of the HMC structural isomers exhibit the isomerization after UV irradiation. However the S₁ lifetime at *v* = 0 level is quite different between *p*-HMC (9 ps), *m*-HMC (10 ns) and *o*-HMC (6 ns). Based on our experimental results and theoretical calculation, we will discuss the difference of the isomerization routes of HMC structural isomers.

[Experimental] We used several spectroscopic measurements; UV laser spectroscopy and lifetime measurement for the jet-cooled gas phase molecules, and cold matrix FTIR spectroscopy for identifying the products. In addition, theoretical calculation is carried out to search possible NRD and isomerization routes by GRRM theory with TD-DFT calculation.

[Results and Discussion] *p*-HMC : The S₁ lifetime at *v* = 0 level is 9 ps. By using nanosecond UV-DUV spectroscopy, we found the transient state and its energy and lifetime is determined as 19020 cm⁻¹ and 27 ns respectively. The transient state was assigned to T₁ state. We concluded that the major isomerization route of *p*-HMC is S₁(*trans*, ππ*) → ¹nπ* → T₁ → S₀(*cis*)” (Fig. 2).

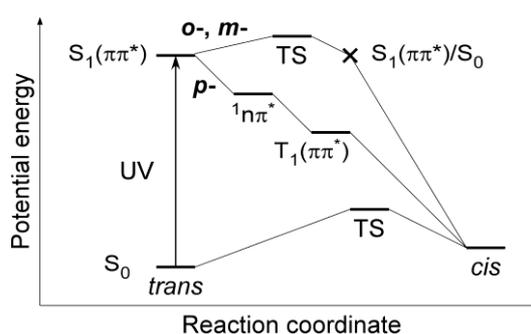


Fig.2 Isomerization routes of HMC

m-, *o*-HMC : It is found that the NRD channel of *m*-, *o*-HMC is become open at excess energy = 1000 cm⁻¹, 600 cm⁻¹ respectively. Different from *p*-HMC, the T₁ state is not observed in both molecules. We conclude that the dominant isomerization route of *m*-, *o*-HMC are “S₁(*trans*, ππ*) → twisting along the C=C double bond on the S₁ state → S₀(*cis*)” (Fig. 2).

[Reference] K. Yamazaki *et al.*, *J. Phys. Chem. Lett.* **7**, 4001 (2016)