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Study of the substituent effects on *trans* → *cis* photoisomerization of cinnamic acid derivatives

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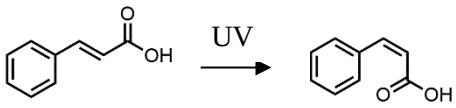
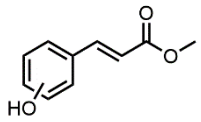
Cinnamic acid and its derivatives exist as the stable *trans* forms in the S_0 state. After the UV excitation to the S_1 state, they isomerize to the *cis* form through several electronic states. In previous study, we reported the nonradiative decay (NRD) process of hydroxy methylcinnamate (HMC). The major isomerization route of *p*-HMC is S_1 (*trans* ππ*) → ^{1}nπ* → T_1 → S_0 (*cis*), while that of *o*-HMC and *m*-HMC is S_1 (*trans*, ππ*) → twisting along the C=C bond by 90 degrees on the S_1 state → S_0 (*cis*) state[1].



trans form *cis* form

Fig. 1 Photoinduced isomerization of cinnamic acid



o, *m*, *p*-HMC

Fig. 2 structural isomers of HMC

In this study, we investigated the effect of the complexity of ester sites. We measured electronic spectra by using resonant two photon ionization (R2PI) method and laser induced fluorescence (LIF) method, and measured lifetimes of excited states by using pump-probe spectroscopy under the jet-cooled condition (~ 10 K). As target molecules, we chose *p*-methoxy methylcinnamate (*p*-MMC), *p*-methoxy ethylcinnamate (*p*-MEC), and 2-ethylhexyl-4-methoxy cinnamate (2EH4MC, used in the main ingredient of sunscreen rejents), whose ester sites are methyl, ethyl, and 2-ethylhexyl groups respectively. We'll discuss how the complexity of the ester change the electronic spectrum as well the S_1 lifetime. Also, we investigated the effect of substituent position for MEC, that is structural isomers. They showed difference in the UV absorption and S_1 lifetimes (Fig. 3). For, example, the S_1 lifetime at $v = 0$ of *p*-MEC is $\tau = 70$ ps, while that of *o*-, and *m*-MEC is $\tau = 10$ ns and 30 ns respectively. In addition, they show different excess energy dependences (Fig. 4). For *o*, *m*-MEC, the NRD channel becomes open at ~ 1400 cm^{-1} and ~ 1100 cm^{-1} respectively. Thus, MEC structural isomers proceed the different NRD route similar to HMC.

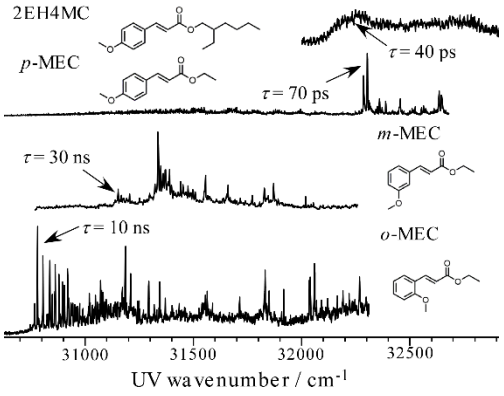


Fig. 3 $S_1 \leftarrow S_0$ electronic spectra and S_1 lifetimes (R2PI)

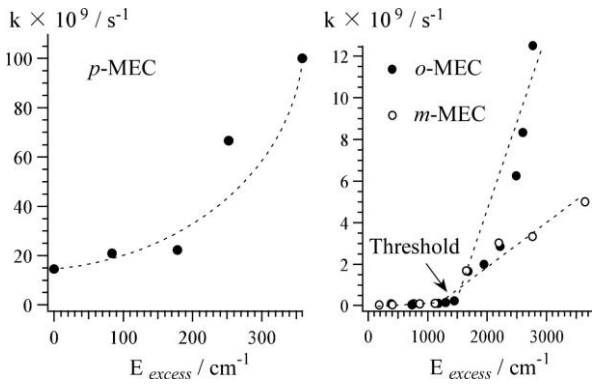


Fig. 4 decay rate constants vs excess energy of MEC

[Reference] [1] K. Yamazaki et al., J. Phys. Chem. Lett. 7, 4001 (2016)