

Systematic study on *trans* → *cis* photoisomerization of cinnamate derivatives

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[Introduction] We have been investigating the nonradiative decay (NRD) and the *trans* (E) → *cis* (Z) photoisomerization of cinnamic acids (Fig.1). In our previous work, we reported that the photoisomerization route is different between *para*-hydroxy methylcinnamate (*p*-HMC) and those of *m*- and *o*-HMC^[1]. In this study, we report a study of methylcinnamate (MC, Fig.1) and its methanol complex.

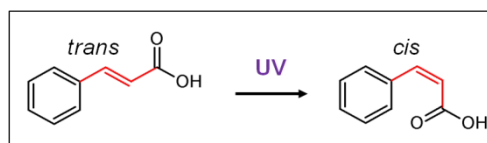


Fig. 1 *trans* → *cis* photoisomerization of methylcinnamate

[Experimental] We applied several spectroscopic measurements; laser induced fluorescence (LIF) and resonant-2-photon ionization (R2PI) for the UV spectroscopy and lifetime measurement of the excited state under jet-cooled gas phase condition. Low temperature matrix isolated FTIR spectroscopy was performed for identifying the photoproduct after UV irradiation. In addition, optimized structures and vertical excitation energy were obtained by DFT chemical calculation at PBE0/cc-pVDZ level.

[Results and Discussion] The low temperature matrix isolated FTIR spectroscopy revealed that MC exhibits the photoisomerization after UV irradiation similar to other derivatives. Fig. 2 shows the R2PI spectrum of jet-cooled MC, where band A, B and C were detected. The measurement of ionization potential suggests the band C is attributed to $S_2(^1\pi\pi^*)$ and the bands A and B to $S_1(^1n\pi^*)$. We found that the lifetimes of the vibronic bands of S_1 rapidly decrease with the excess energy, indicating that the S_1 decays to T_n state *via* intersystem crossing. The lifetime of band origin of $S_2(^1\pi\pi^*)$, that is band C, is obtained to be equal to or less than 10 ps. In addition, the transient T_1 state generated after NRD of S_2 is detected. So, the photoisomerization from $S_2(^1\pi\pi^*)$ is thought to occur by the “ $^1\pi\pi^*(trans) \rightarrow ^1n\pi^* \rightarrow T_1 \rightarrow S_0(cis)$ ” route (Fig. 3). In case of MC-MeOH complex, the $S_2(^1\pi\pi^*)$ lifetime is lengthened to be 180 ps. This indicates that the H-bonding to the C=O group of MC lifts the $^1n\pi^*$ energy so that the internal conversion from the S_2 is prohibited.

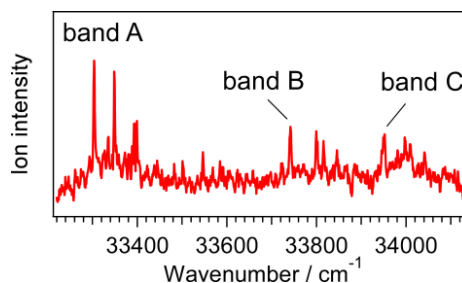


Fig. 2 R2PI spectrum of jet-cooled MC

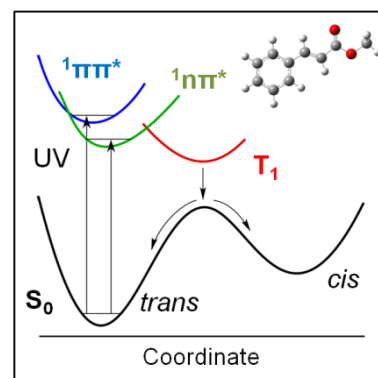


Fig. 3 The photoisomerization route of MC

[Reference] [1] S. Kinoshita *et al.*, *Phys. Chem. Chem. Phys.*, 2018, **20**, 17583-17598