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# Elucidation of *trans* → *cis* photoisomerization route of cinnamate by using supersonic jet/laser spectroscopy and an automated reaction route mapping method

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【 **Introduction** 】 We have been investigating the mechanism of the *trans* → *cis* photoisomerization of cinnamates (Fig. 1). In our previous study, we reported that the photoisomerization route of *para*-hydroxy methylcinnamate (*p*-HMC) is different from those of *m*-, *o*-HMC. [1] In this study, we investigated the photoisomerization route of the simplest cinnamate, methylcinnamate (MC) and compared it with other substituted cinnamates.

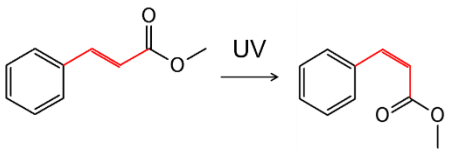


Fig. 1 *trans* → *cis* photoisomerization of methylcinnamate

【**Experimental and Computational method**】 Laser induced fluorescence (LIF) and 2 color resonant 2 photon ionization (2C-R2PI) methods were applied for measurements of electronic spectrum and lifetime under the jet-cooled gas phase condition. In addition, photoisomerization route was searched by global reaction route mapping method combined with time dependent density functional theory (GRRM/TD-DFT) calculation at ωB97XD/6-311G(d,p) level.

【**Results and Discussion**】 From the LIF and 2C-R2PI spectroscopic measurements, we identified both the $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$ states. The 0,0 band of $S_1$ is 660 $cm^{-1}$ lower than that of $S_2$. The $S_1$ state decays to $T_1$. The $S_2(\pi\pi^*)$ lifetime is equal to or shorter than 10 ps, followed by the production of the transient $T_1$ state. These results suggest that $S_2$ of MC decays to $S_1$ by internal conversion (IC) and then decays to triplet state by intersystem crossing (ISC).

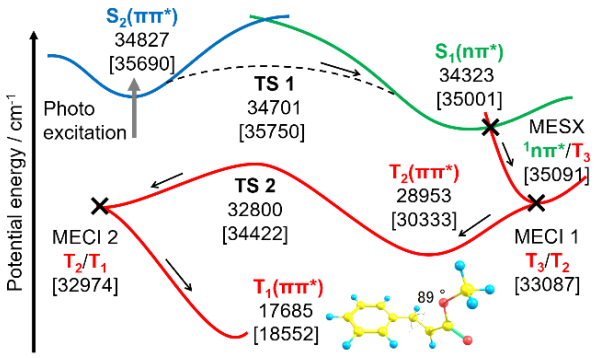


Fig. 2 Photoisomerization route of MC

Fig. 2 shows the photoisomerization route obtained by GRRM/TD-DFT calculation. The values with zero-point energy corrections are also shown in parentheses. $S_2(\pi\pi^*)$ of MC decays to $S_1(n\pi^*)$ by IC through the transition state (TS 1). After IC, it finally decays to $T_1(\pi\pi^*)$ state by consecutive ISC and IC through the minimum energy seam crossing (MESX) and the minimum energy conical intersections (MECI 1 and MECI 2). The C=C bond of $T_1(\pi\pi^*)$ is twisted by ~ 90°, and it looks like a transient state between *trans* and *cis* isomer. The energy level of $T_1(\pi\pi^*)$ was calculated at 18685 $cm^{-1}$, showing reasonable agreements with the experimental value (21790 $cm^{-1}$). From these results, it was concluded that the photoisomerization route of MC is as follows, "$S_2(\pi\pi^*) \rightarrow S_1(n\pi^*) \rightarrow T_1(\pi\pi^*)$". This is same with other *para*-substituted cinnamates.

【**Reference**】 [1] S. Kinoshita *et al*. *Phys. Chem. Chem. Phys.* 2018, **20**, 17583-17598. [2] S. Kinoshita *et al*. *Phys. Chem. Chem. Phys.* 2019, **21**, 19755-19763.