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UV-Deep UV pump-probe spectroscopic study on nonradiative decay process of cinnamate derivatives

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In many aromatic molecules having C=O group or N atom(s) in the aromatic ring, there exists a $^1n\pi^*$ state. This state is thought to play an important role in nonradiative decay process as well as photochemistry. Cinnamate derivatives are such kind of molecules, which exhibit photoinduced *trans* → *cis* isomerization. However, the $^1n\pi^*$ state as well as triplet states are dipole-forbidden from S_0 and they are called "dark state".

In the present study, in order to detect the transient dark state, we developed UV-Deep UV pump-probe spectroscopy and applied it to detect the dark state of *para*-methoxy methylcinnamate (*p*-MMC) in a supersonic molecular beam. The energy level diagram and excitation scheme is shown in Fig.1. *p*-MMC is excited to the $S_1(\pi\pi^*)$ state by UV pump laser. After certain delay time (Δt), the deep UV (~ 210 nm) laser pulse is irradiated to ionize the molecule in the transient dark state. Fig.2 (a) shows an ionization efficiency curve of the dark state. The ionization threshold of the dark state is obtained as 46850 cm^{-1}. From this result, the energy level of dark state is estimated as 16577 cm^{-1} and is assigned to the $T_1(\pi\pi^*)$ state as shown in Fig.2 (b). Based on these experimental data and theoretical calculation, we discuss the nonradiative decay process of *p*-MMC.

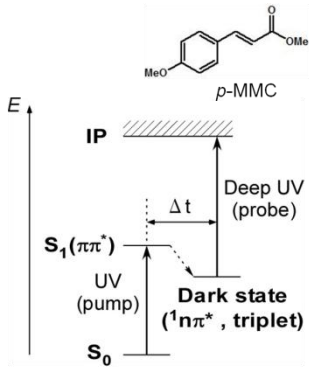


Fig.1 The energy level diagram and excitation scheme

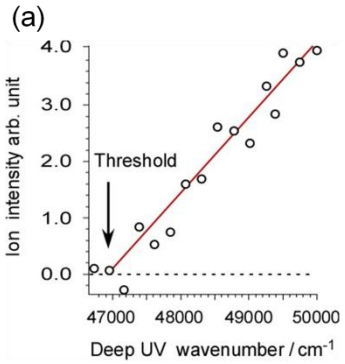
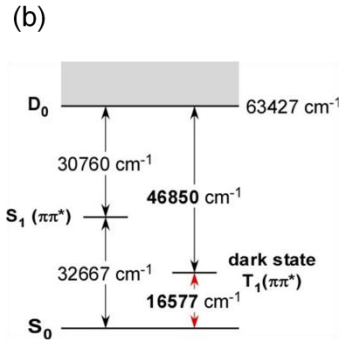


Fig.2 (a) Ionization efficiency curve from the dark state



(b) energy level diagram

［Reference］ *J. Phys. Chem. Lett.*, **2016**, *7* (19), 4001–4007