CONFORMER SPECIFIC METHYL INTERNAL ROTATION AND OBSERVATION OF PHOTODISSOCIATION DYNAMICS: IS METHYL INTERNAL ROTATION COUPLED WITH TORSIONAL VIBRATION?

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The spectroscopic peak assignment gives barrier height of internal rotation as well as minimum angle displacement between S_1 and S_0 electronic states. The most well-known type is methyl internal rotation because most organic molecules have it. Conventional way to assign the spectra uses 1D hindered rigid rotor model. The model system is thioanisole because it engendered mode specific nonadiabatic photofragment in previous experiment[a]. Resonance enhanced multiphoton ionization (REMPI) followed by velocity-map imaging (VMI) made us be possible to assign the methyl internal rotation peaks and to see the dynamics of the photodissociation. Conformers were selectively sampled using different carrier gases in supersonic jet-expansion and their electronic transitions were confirmed by UV-UV hole-burning spectroscopy equipped with Stark-Deflector. In this presentation, *trans* ***meta***-methylthioanisole (***m***MTA) manifests active progressions of methyl internal rotation ($0a_1$, 1e, 2e, $3a_1$, 4e, 5e, $6a_1$), whereas a few of them ($0a_1$, 1e, $3a_1$) for *cis* ***m***MTA are tangible. For *cis* ***m***MTA, the rotor progressions are combined with the torsional vibration. In case of *trans* ***ortho***-methylthioanisole (***o***MTA), not only active combinations of methyl internal rotation and torsional vibration but also couplings of them seem to be exist in S_1-S_0 transitions[b]. VMI studies imply two distinguished photodissociation dynamics of ***o***MTA and ***m***MTA, respectively. The detailed comparison of them is to be presented.

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[a] Jeong Sik Lim, Sang Kyu Kim, Nat. Chem. 2, 627-632(2010)

[b] *trans* ***m***MTA also shows a coupling of **e** transition of methyl rotor and the vibronic transition of methylthio group at around 200 cm^{-1} above S_1 origin.