

AIMD study on $\pi\pi^*$ -excited substituted-stilbene

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Stilbene (SB) is a typical molecule to exhibit cis-trans photoisomerization, and the photocyclization from cis-SB to 4,4-dihydrophenanthrene (DHP) is an important model for diarylethene derivatives as optical switching molecules. Experimentally $\pi\pi^*$ -excited cis-SB showed ultrafast decay to the ground state with a lifetime of 1 ps, and the branching ratio was reported as cis : trans : DHP = 55 : 35 : 10. We examined reaction mechanism and dynamics for $\pi\pi^*$ -excited cis-SB and cis-dimethyl-stilbene (cis-dmSB) by reaction path calculations and ab initio molecular dynamics (AIMD) simulations at the SF-TDDFT level [1,2]. The branching mechanism into trans-form and DHP, and the origin of the short lifetime of CIS* (minimum in cis-dmSB* region) and the long lifetime of P* (perpendicular-structure state) for dmSB were well explained. The meta-IRC path from the Franck-Condon structure of cis-SB is oriented toward the twist-side in the initial stage, while the meta-IRC pathway for cis-dmSB is oriented toward the DHP-side. The geometries of minima and minimum energy conical intersection (MECI) for dmSB suggested that molecules in the DHP region could easily decay to the ground state, while molecules in the twist region should accompany a relatively long lifetime since the pyramidalization as to the central C=C bond in the minimum geometry is weakened compared to the MECI geometry. AIMD simulations indicated that, after entering and leaving the cis-region, more trajectories enter the DHP region than the twist region for $\pi\pi^*$ -excited cis-dmSB, which is opposite to the case of SB. The calculated S_1 -population decay qualitatively reproduced the experimental lifetimes of the CIS* and P* bands, as well as the finite rise time in the growth of the P* band. The same computational approach was employed to examine the reaction pathway and dynamics for monomethyl SB, and the results will be discussed in the presentation.

[1] Y. Harabuchi, K. Keipert, F. Zahariev, T. Taketsugu, M.S. Gordon, *J. Phys. Chem. A* **118**, 11987 (2014).

[2] Y. Harabuchi, R. Yamamoto, S. Maeda, S. Takeuchi, T. Tahara, and T. Taketsugu, *J. Phys. Chem. A* **120**, 8804 (2016).