

# 生体関連分子の多段階無輻射失活過程

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Nonradiative decay (NRD) processes such as internal conversion (IC) and intersystem crossing (ISC) govern photo-functionality of living systems such as the photostability of the DNA, phototaxis, visual perception *etc.* The NRD processes of biomolecules often take places in multistep way due to their many-body nature of molecular and electronic structures. Understanding the complex NRD pathways of biomolecules should help us develop bio-inspired photo-functional molecular materials. In this talk, we will discuss our recent theoretical works on the multistep NRD pathways of biomolecules in gas phase with the aides of pump-probe experiments:

## (1) Structure dependent photoisomerization routes of cinnamate based sunscreens<sup>1-4</sup>

We found that the cinnamate based sunscreens undergo *trans* → *cis* photo-isomerization under UV irradiation but differ in the isomerization pathway<sup>1,2</sup> *Para*-substituted cinnamates are isomerized *via* ISC from the bright  $^1\pi\pi^*$  state to the  $^3\pi\pi^*$  state mostly *via* stepwise ISC followed by the IC from  $^1\pi\pi^*$  to the dark  $^1n\pi^*$  state<sup>1-3</sup>. On the other hand, *ortho*- and *meta*- substituted cinnamates are directly isomerized by twisting along the C=C double bond to 90° on the  $^1\pi\pi^*$  state and subsequent IC to the electronic ground state<sup>2</sup> We also found that substitution on the benzene ring of cinnamates governs this NRD mechanism switching *via* the moderation of the  $^1\pi\pi^*$  energy level<sup>4</sup>. These results suggest that controlling the substitution position is essential to design the cinnamate based photo-functional materials.

## (2) Ultrafast nonadiabatic cascade of XUV excited caffeine molecule<sup>5</sup>

We next extend our study to the XUV driven femtosecond dynamics of caffeine as a model of prebiotic molecule. We observed a decay of excited cationic states with a time constant of 40 fs *via* femtosecond XUV-pump-IR-probe experiments. Guided by *ab-initio* many-body theory, this timescale is interpreted in terms of a non-adiabatic cascade *via* 10<sup>2</sup> highly correlated states. These results show that both nonadiabatic coupling and electron correlation are the keys for ultrafast reaction dynamics in the highly-correlated electronic excited states.

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