Photophysics of Adenosine Derivatives as Revealed by Liquid Flat Jet Extreme Ultraviolet Time-Resolved Photoelectron Spectroscopy

([1]*Institute of Molecular Science*, [2]*UC Berkeley*) ○Masafumi Koga,[1] Do Hyung Kang,[2] Zachary N. Heim,[2] Daniel M. Neumark[2]

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Photophysics and photochemistry of nucleic acid constituents are of fundamental interest in understanding how genetic codes are protected from ultraviolet (UV) light irradiation. The underlying mechanisms of photostability, i.e., the non-destructive dissipation of the excess energy imposed by the UV light absorption, remain elusive even at the single nucleobase level. In this study, femtosecond extreme ultraviolet time-resolved photoelectron spectroscopy (XUV-TRPES) was employed to investigate the relaxation dynamics of adeninosine in aqueous solution. An XUV probe pulse at 21.7 eV can ionize all excited states of a molecule, allowing for full relaxation pathways to be addressed after excitation at 4.66 eV. We also incorporated a gas-dynamic flat liquid jet, which significantly enhanced the pump-probe signal intensity due to the large exposure area (200 μm) of liquid to the incident laser beams compared to a conventionally used cylindrical jet (ca. 30 μm). The obtained TRPE spectra in all systems exhibited signals between 3 and 7 eV electron binding energies. The ultrafast decays within 1 ps were accurately reproduced by the global lifetime analysis under a bi-exponential function with time constants around 100 fs and 500 fs. The decay- associated spectra with a ~500 fs time constant showed distinct peaks 1-eV separated from those at ~100 fs, suggesting that the different electronic state, namely the $n\pi^*$ state, was involved in the relaxation from the initially populated $\pi\pi^*$ state.[1] At the conference site, the ultrafast stepwise relaxation mechanisms depending on the sugar and phosphate groups, and dynamics in adenosine dimer will be discussed.

1) M. Koga, D. H. Kang, Z. N. Heim, P. Meyer, B. A. Erickson, N. Haldar, N. Baradaran, M. Havenith, D. M. Neumark, *Phys. Chem. Chem. Phys.*, **2024**, *26,* 13106.