Anion Photoelectron Spectroscopy of Deprotonated Cytosine and Thymine at 5.826 eV

TERRY YEN, BRADLEY F. PARSONS, SEAN M. SHEEHAN, DANIEL M. NEUMARK, University of California, Berkeley — UV radiation from sunlight is one of the most ubiquitous and lethal forms of environmental carcinogens. Luckily, perhaps as a result of selective pressure by molecular evolution, DNA is remarkably stable to photochemical decay. The solar UV photons are absorbed primarily by the building blocks of DNA, the nucleobases, which undergo ultrafast nonradiative relaxation processes back to the ground state by internal conversion. It has been suggested that the nucleobases’ excited singlet states of pi-sigma-star character, which are dissociative along the NH stretch coordinate, play a key role in the relaxation pathways. Studying the dynamics of the excited states of deprotonated nucleobases is therefore of great importance in understanding the photostability of DNA. Excited state dynamics of the deprotonated nucleobases cytosine and thymine has been investigated using anion photoelectron spectroscopy at 5.826 eV. In the experiments, a laser is used to detach an electron from a mass selected deprotonated nucleobase anion and the electron kinetic energy (eKE) is measured using velocity-map imaging (VMI). Through VMI, information is obtained on the nature of the excited states involved in the non-radiative processes of DNA.

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