

## ELECTRONIC RELAXATION MECHANISM OF GUANINE DERIVATIVES IN SOLUTION

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The natural RNA and DNA nucleobases absorb harmful ultraviolet radiation but the ability to dissipate this excess electronic energy efficiently to the ground state makes them highly photostable. Understanding how minor structural modifications affect their photochemical properties is important for advancement in biological applications. For example, 7-deazaguanosine (7dza) has been used for decades to probe the charge transfer dynamics in DNA, due to its lowered oxidation potential relative to guanosine. However, the electronic relaxation mechanism of 7dza has not been investigated until recently.

Using steady-state and time-resolved electronic spectroscopic techniques, combined with quantum-chemical calculations, we have investigated the excited-state dynamics of guanosine 5'-monophosphate (GMP) and 7dza in aqueous solution and in a mixture of methanol and water following excitation at 267 nm. The following relaxation mechanism has been proposed for both molecules:  $L_b \Rightarrow L_a \Rightarrow {}^1\pi\sigma^*(\text{ICT}) \Rightarrow S_0$ , where the  ${}^1\pi\sigma^*(\text{ICT})$  stands for an intramolecular charge transfer excited singlet state with significant  $\pi\sigma^*$  character. In 7dza, however, the relaxation dynamics is slightly slowed compared to GMP, which adjudicate to stabilization of the two lowest-energy singlet states and to the alteration of the topology of the excited state potential energy surfaces.

The authors acknowledge the National Science Foundation (Grant No. CHE-1800052) for financial support and the High-Performance Computing Resource in the Core Facility for Advanced Research Computing at Case Western Reserve University.