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UV Photoprotection of Ammonia and Adenine Studied by Time-resolved Photoelectron and Photofragmentation Spectroscopy¹

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The UV photostability of molecules is determined by excited state electronic relaxation mechanisms that must operate on ultrafast time scales in order to dominate over competing photochemical processes that potentially lead to destruction of the molecule. Electronic excited states with notable σ^* character, centered at X - H (where X = O or N) bonds, may play a particularly important role in efficient photoprotection of many (bio)molecules. We have investigated the photophysics of UV excited ammonia and adenine using three complementary femtosecond (fs) pump-probe techniques: time-resolved photoelectron (TRPES), ion-yield (TRIY) and photofragment translational spectroscopy (TRPTS). Ammonia, a prototypical amine group which appears in a number of organic molecules, is resonantly excited to specific vibrational levels of its first electronic excited state of $n\sigma^*$ character. Three deactivation paths are available along the N-H stretching coordinate: Non-adiabatic crossing through a conical intersection leads to either repopulation of the NH_3 ground state or dissociation into ground state NH_2 and H photoproducts whereas adiabatic avoidance correlates with excited state NH_2 and ground state H. TRPES spectra give direct spectroscopic evidence of σ^* mediated relaxation in form of combination bands of the umbrella mode and symmetric stretch. TRPTS measurements of H-atom appearance times provide time constants of < 75 fs to 350 fs for the relaxation, which increase with the amount of internal energy partitioned into the NH_2 co-fragment. Adenine, a purine DNA base, is shown to undergo similarly efficient $\pi\sigma^*$ mediated relaxation in competition with a ring puckering pathway following 200nm photoexcitation to a bright $^1\pi\pi^*$ state. H-atom photoproducts from the NH-stretching pathway are observed within <200fs, whereas deactivation along the ring puckering pathway takes \sim 700fs.

N. L. Evans, H. Yu, G. M. Roberts, V. G. Stavros, S. Ullrich: Observation of Ultrafast NH_3 ($\tilde{\text{A}}$) State Relaxation Dynamics using a Combination of Time-resolved Photoelectron Spectroscopy and Photoproduct Detection, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10401

N. L. Evans, S. Ullrich: Wavelength Dependence of Electronic Relaxation in Isolated Adenine Using UV Femtosecond Time-Resolved Photoelectron Spectroscopy, *J. Phys. Chem. A*, 2010, **114**, 11225

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