Excited states relaxation dynamics of protonated DNA/RNA bases: isolated and monohydrated complexes studied in a cryogenic ion trap

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Charge transfer reactions are ubiquitous in chemical reactivity and often viewed as ultrafast processes. For DNA, femtochemistry has undeniably revealed the primary stage of the deactivation dynamics of the locally excited state following electronic excitation. We have demonstrated that the full timescale excited state dynamics can be followed up to milliseconds through an original pump-probe photodissociation scheme applied to cryogenic ion spectroscopy. The experimental results are assigned with the help of *ab initio* calculations at the spin-component scaled coupled-cluster level (SCS-CC2/aug-cc-pVDZ level) including singlet, triplet excited state geometry optimizations and frequency calculations.

Protonated cytosine [1] is a benchmark system in which the locally excited state $^1\pi\pi^*$ state decays in the femtosecond range without barrier towards long-lived charge transfer (CT), $^1n_O\pi^*$ for the keto form and $^1n_{NH2}\pi^*$ for the enol form. A much longer-lived component has been evidenced which has been assigned to the relaxation of the charge transfer states through intersystem crossing to the lowest $^3\pi\pi^*$ triplet state with lifetime in the order of 10 ms for both tautomers. The fragmentation signals following UV excitation proceed from repopulation of the ground electronic state. A three-step mechanism ($^1\pi\pi \rightarrow {}^1CT \rightarrow {}^3\pi\pi$) is proposed where internal conversion from each state can occur leading ultimately to fragmentation in the ground state. Direct internal conversion from the locally $^1\pi\pi^*$ state is evidenced and account for half of the fragmentation signal. Interestingly, Inter System Crossing from the $^3\pi\pi^*$ state accounts for about 50% of the fragmentation signal

In the case of protonated keto uracil, [2] time-resolved photodissociation spectroscopy reveals the complex non-radiative decay processes that occur in this RNA base. The UV photofragments are issued from unimolecular dissociation in the ground state after internal conversion. A multiscale dynamics ranging from nanosecond lifetime of the locally excited state up to the microsecond and millisecond lifetimes of the $^1n_O\pi^*$ state and $^3\pi\pi^*$ state, respectively has been observed. State-dependent photofragments are observed through absorption of probe photons from these specific electronic states. At the band origin, the analysis of the kinetics of appearance of these photofragments suggests that return to the ground state occurs both from the $^1n_O\pi^*$ state and through intersystem crossing from the lowest $^3\pi\pi^*$ state.

The pathway through the $^1n_O\pi^*$ state closes within less than 300 cm^{-1}, energy at which the excited state population decays through a region of close degeneracy between the singlet, triplet $\pi\pi^*$ states and the ground state.

We have also been interested in environmental effects on the intrinsic properties of protonated DNA/RNA bases. The experimental approach [3] is based on two separate cryogenic ion traps to form weakly bound solvent clusters around the electrosprayed ions. Prior to studying the relaxation dynamics of the microhydrated protonated species, it is mandatory to determine the structures of the low-lying conformers that could be present in the cryogenic ion trap. Recently, we revisited the photodynamics of protonated tryptophan [4] and its monohydrated complexes. The striking result arises from the conformer-selective photodynamics in which a single water molecule inserted in between the ammonium moiety and the indole ring hinders the barrierless ESPT reaction responsible for the ultra-fast deactivation process observed in the other conformers and in bare protonated tryptophan. The structures of the monohydrated DNA/RNA bases have been characterized using infrared photodissociation spectroscopy and IR-UV and UV-UV double resonance spectroscopy.

Index Terms: cryogenic IR and UV photodissociation spectroscopy, pump-probe photodissociation spectroscopy, excited states relaxation dynamics, biomolecules, hydration.

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