

Abstract

The photochemistry and photophysics of the canonical guanine-cytosine (G-C) and adenine-thymine (A-T) nucleobase pairs have been the subject of intensive research by numerous experimental and theoretical groups. However, there is still no consensus in the literature regarding the nature of the relaxation processes that occur after the absorption of UV radiation. Theoretical studies on the behavior of canonical Watson-Crick (WC) base pairs under photoexcitation have led to the suggestion that proton-coupled electron transfer (PCET), also known as electron-driven proton transfer (EDPT), processes seem to play a significant role in the radiationless deactivation of photoexcitation through the intersection of the dark repulsive $^1\pi\pi^*$ charge-transfer (CT) state with a locally excited bright state (LE) and subsequently with a ground state.

Although much is already known about these processes, the proposed proton transfer mechanism as a result of electron transfer has not been confirmed experimentally for the WC-A-T canonical base pair. It could be a result of spectroscopic failure to measure the ultra-short lifetimes (<100 fs) or wrong assumptions about the nature of this process. The computational studies carried out within this thesis have led to the research hypothesis that **there are several alternative relaxation channels through charge and electron transfer due to interaction between nucleobases**. The latter not only enables EDPT or PCET processes but also alters the intramolecular photoexcitation decay pathways through heterocyclic ring deformation or bond stretching. The processes involving intersections of the LE $^1\pi\pi^*$ bright states with the dark $^1n\pi^*$ states and the alternative EDPT channel through the population of $^1n\pi_{CT}^*$ states were identified and described here for the first time.

Simultaneously, a significant part of the research is devoted to alternative non-canonical base pairs. Comparative analysis and verification of the mechanisms of nonradiative deactivation of excited states in canonical and non-canonical nucleobases paired in the WC scheme deepen the insight into the role of photoinduced charge transfer processes in nucleic acids after UV absorption. They also contribute to a better understanding of why living organisms use such a narrow set of building blocks of genetic material, which interestingly share a common feature of high photostability.

Scientific research conducted within the confines of this thesis is divided into several stages. First, the research on the photophysics and photochemistry of the canonical and noncanonical nucleobases, both isolated and paired in the WC scheme, is reviewed. The selection of non-canonical nucleobases was inspired by research reports on the synthesis of nucleotides and their prebiotic precursors under reliable abiotic conditions. The analysis of the potential energy surface profiles for low-lying excited states of the systems studied along the proton transfer coordinates is discussed and the role of $^1n\pi^*$ states in these processes is established. Theoretical studies of potential energy surfaces (PESs) and conical intersections between them were performed using state-of-the-art single- and multireference ab initio methods.

This dissertation describes for the first time the conical intersections of intermolecular CT $^1n\pi^*$ with the ground state in canonical and alternative base pairs, which may allow efficient deactivation through a new type of EDPT mechanism. This indicates that long-lived, reactive $^1n\pi^*$ states, previously considered as potential sources of photodamage in isolated pyrimidine nucleosides, may actually facilitate efficient photodeactivation.

Two possible types of nonradiative deactivation channels have been identified and described occurring on the potential energy surfaces of $^1n\pi^*$ states. It may be a one-step process in which the pyrimidine ring is deformed after photoexcitation and, as a result, the conical intersection with a ground state is reached. The population of the $^1n\pi^*$ states may also initiate a two-step EDPT process in some WC-type base pairs, in particular the G-C, H-C and oxoG-C pairs. It was also noticed that in all systems studied, the population of the $^1\pi\pi^*$ charge transfer state should lead to effective photorelaxation through the EDPT process.