ABSTRACT FOR THE GENERAL PUBLIC

(*the project goal, description of research, reasons for attempting a particular research topic and substantial results expected*)

Although the origins of life on Earth remain unknown, the most plausible hypotheses are being tested in numerous laboratories worldwide, struggling to elucidate the complicated pathways of forming complex biological macromolecules as proteins, lipids and nucleic acids from simple prebiotic feedstock molecules. The earliest signs of life are dated to the period of time when the conditions on the surface of Earth were extremely harsh for organic molecules, as surely the Earth's internal heat flow, the volcanic activity and the sunlight including the harmful ultraviolet (UV) radiation reaching the surface of Earth were considerably higher than today. In particular, the results obtained by many research groups indicate that UV radiation had a significant influence on synthesis and preselection of organic molecules. In fact, DNA and protein fragments constituting all living organisms as the final form of evolution taken place at that time, share the photostability feature. What it means is that single nucleobases, their dimers, nucleosides and even fragments of nucleic acid strands, as a carrier of genetic information, undergo a series of structural changes under the influence of UV light, leading to ultrafast deactivation of the excited states in which the molecules are more susceptible to structural damages. This remarkable attribute along with the recently discovered self-repairing mechanisms of short DNA fragments may underline the photostability as an important criterion for natural selection, and thus bring us closer to discovering the mechanisms of the origin of life on Earth. We do not really know whether RNA and DNA appeared in the Archean and remained unchanged since then or, what is more likely, their precursors underwent a sort of prebiotic evolution. However, the focus on the photostability feature seems valid irrespective of protonucleotides being assembled from nucleobases, ribose and phosphates or appearing in direct synthesis from prebiotic feedstock molecules. Experimentally, the direct combination of ribose and nucleobases failed. This is why we assume the non-inherited backbone heterogeneity could be supported by the presence of alternative nucleotides in nucleic acid polymers. Comparative analysis and verification of the mechanisms of non-radiative deactivation of excited states, either in canonical and non-canonical bases, may vividly contribute to determining the behavior of nucleic acids under UV irradiation, which is the main goal of the project.

Thanks to spectroscopic studies, we are ensured of existence of ultrafast deactivation of excited state in guanine-cytosine (G-C) basepair. In the years 2004-2006, Sobolewski and his colleagues proposed an explanation for this process, hypothesizing that the electron-driven proton transfer (EDPT) is largely involved in the non-radiative relaxation. This mechanism occurs via transfer of an electron under the influence of photoexcitation from one base to another, which is the driving force for proton transfer and consequently energy dissipation. A series of later papers, both experimental and theoretical, seemed to validate the Sobolewski's hypothesis. However, the proposed proton transfer mechanism as a result of electron transfer has not been experimentally confirmed for the canonical adenine-thymine (A-T) base pair, which leaves an open space for attempts to describe the nature of the mentioned process in this project. There are experimental indications that in the case of A-T dimer, after excitation of the lowest lying state, the internal conversion leads to the state having considerably longer lifetime, from which it is impossible to emit electromagnetic radiation (the so-called dark state). Studies performed in our group have led to the research hypothesis, that there may be several alternative relaxation channels driven by the intermolecular charge transfer as a result of interaction between nucleobases. We plan to characterize the deactivation via these competing channels. The research we propose may allow verification of described hypotheses and provide a better understanding of the nature and role of charge-transfer processes after photoexcitation of the base pairs of nucleic acids.