The Aim of the Project

The aim of this project is to elucidate mechanisms of the complicated photochemical reactions, initiated by the exposure of molecules to sunlight, which we have reasons to believe could have contributed to the chemical synthesis of the molecular building blocks of the first living organisms on Earth. Although the origins of life on Earth remain unknown, the most plausible hypotheses are being tested in many laboratories worldwide, struggling to elucidate the complicated synthetic routes from simple prebiotic feedstock molecules to the biological macromolecules of complicated architecture (nucleic acids, proteins and lipids). Such studies are the domain of the prebiotic chemistry – rapidly developing branch of chemistry that is currently in the limelight of the scientific community.

The earliest signs of life are dated to the Archean Eon (from 4 to 2.5 billion years ago) a period of time shortly after the formation of the Earth's crust when the conditions on the surface of Earth were extremely harsh for organic molecules which constitute all living organisms. The Earth's internal heat flow and volcanic activity were considerably higher than today and the sunlight, including the harmful ultraviolet (UV) radiation, was reaching the surface of Earth unshielded by the ozone layer which formed much later (about one billion years ago), when the early aquatic organisms called blue-green algae began using energy from the Sun to split water and carbon dioxide molecules and recombining them into organic compounds and molecular oxygen.

According to the so-called "RNA world hypothesis", the first living organisms were based on the RNA molecules which are able to store and replicate the genetic information and catalyze metabolic processes. The RNA molecules are built of a chain of smaller organic molecules called nucleotides which are very resilient to UV light, even though most organic molecules are prone to UV-induced damage. Therefore, we believe that sunlight was a strong selection factor, favouring more photostable molecules at the early stages of chemical evolution which finally led to the emergence of life. On the other hand, UV radiation was also an extremely efficient and concentrated source of energy, allowing for otherwise inaccessible chemical reactions to occur.

The primary goal of this project is to explore the molecular mechanisms of photostability of the selected molecules which are the credible prebiotic precursors of the nucleotides and amino acids. We also plan to elucidate the mechanism of the photoreduction reaction which was suggested as the prebiological synthetic link between RNA and DNA which is responsible for the storage of genetic information in contemporary living organisms. Although the project is based on the results of planned computational simulations, it will be carried out in close collaboration with the experimental group of prof. Dimitar Sasselov from Harvard University, which will allow for experimental verification of our theoretical predictions. It should be noted, though, that currently there are no experimental techniques that would allow detailed mechanistic insight into chemical reaction mechanisms. Such an insight is only possible by using various experimental techniques in combination with theoretical calculations.

The Outline of the Project

We plan to use the state-of-the-art methods of molecular quantum mechanics, which were developed from the first principles and have a sufficient accuracy to provide valuable insights into molecular mechanisms of photochemical processes occurring at ultrafast, sub-picosecond timescale. The results of theoretical calculations can help in the interpretation of sophisticated femtosecond transient absorption spectra, recorded by our colleagues from Sasselov group, which allow to track in time the changes of the electronic structure of UV-excited molecules. This joint effort should allow us to identify the possible fates of the selected molecules, chosen for our studies due to their relevance to plausible prebiotic chemistry scenarios when exposed to intense UV radiation.

The primary objectives of this project are of the fundamental character, that is to deepen our understanding of the photochemical processes which might be relevant to the origins of life. However, the expected results should also broaden our general understanding of photochemistry and photophysics of thiated unsaturated organic compounds (that is compounds containing the sulfur atom in their molecular structure). Last but not least, we hope to elucidate the supposedly active role of solvent molecules, which we have reasons to believe could enable the otherwise inaccessible channels of photochemical reactions.