Photochemical Selection in Prebiotic Chemistry of Nucleobases

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From a chemical perspective one may define the origin of life as the synthesis of the first macromolecule with a replication scheme, such as RNA. Once such a replicating, or autocatalytic, macromolecule exists, evolution can be called on as the model for further development of life. Today such synthesis is mediated by an extensive biochemical machinery, involving complex proteins and enzymes, which however would not have existed on a prebiotic earth. Therefore we investigate the fundamental properties of nucleobases without the contemporary biological environment by studying them as *isolated* molecules and clusters, in the gas phase.

Most of the heterocyclic compounds that today are involved in replication exhibit UV photochemical stability, due to fast internal conversion, while other derivatives of *the same compounds* often do not. This diffusion of electronic energy is mediated by conical intersections, as modeled by a growing number of quantum calculations. Yet more surprisingly, in many cases the biologically most relevant tautomeric form or even specific base pair structure exhibit this mechanism, while other tautomers or structures of the same base pair are vulnerable to UV radiative damage.

We study the excited state dynamics of isolated nucleobases and their clusters by a combination of double resonant spectroscopy, pump-probe measurements and detection of hot ground state molecules that result from rapid internal conversion. For comparison we also study these properties in alternate bases that could potentially have led to alternate genetic alphabets to evaluate if UV photochemical selection could have played a role in arriving at the biochemistry of life as we know it today.