



Innsbruck Physics Colloquium

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Ultrafast Nonadiabatic Photochemistry of Hydrogen Bonds in Biomolecules

High stability with respect to photochemical destruction by ultraviolet light is of utmost importance for biological molecules such as DNA bases, amino acids, saccharides or biological sunscreen molecules. Research over the past decades has provided evidence that ultrafast and highly efficient excited-state deactivation via so-called conical intersections of electronic potential-energy surfaces is the mechanism which endows many biomolecules with exceptionally high photostability. An overview of the role of conical intersections in photochemical reaction dynamics is provided. For example, the twisting of CC double bonds or CN bonds in $\pi\pi^*$ excited states of heteroaromatic molecules has been identified as a generic mechanism for ultrafast radiationless decay to the electronic ground state. In addition, optically dark and dissociative so-called $\pi\sigma^*$ states play a decisive role in the excited-state deactivation of aromatic chromophores with acidic groups (OH, NH, or NH_2). In nucleotides, such as adenosine, an ultrafast deactivation mechanism involving a hydrogen bond between adenine and ribose has been shown to lead to enhanced excited-state quenching. For the guanine-cytosine and adenine-thymine Watson-Crick base pairs, a proton-coupled electron-transfer mechanism of ultrafast excited-state deactivation has been identified by theory and experiments. A specific picture of ultrafast excited-state deactivation in biological molecules emerges: in multiply hydrogen-bonded biopolymers (e.g., DNA, proteins and cellulose), the energy deposited by an UV photon in one of the chromophores is first transferred to a hydrogen-bonded proton within about 50 fs and subsequently dissipated into the vibrations of the surrounding heavier atoms. This mechanism enhances the photostability of biological supramolecular structures. The photoreactivity of DNA bases with surrounding water molecules is another example of ultrafast nonadiabatic excited-state hydrogen-bond dynamics. We have recently discovered that photoexcited adenine can abstract hydrogen atoms from water molecules in hydrogen-bonded adenine-water clusters. Adenine may thus have been the photocatalyst for water splitting by UV light at the very beginning of photosynthesis.

Tuesday, 25.4.2017, at 17:15 h in lecture hall C

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