MULTIREFERENCE-AB INITIO DYNAMICS SIMULATIONS OF THE PHOTOSTABILITY OF DNA BASES AND RELATED AROMATIC HETEROCYCLES.

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The explanation of the photostability of DNA bases is a very interesting and challenging topic. The main questions of interest concern the reaction pathways and life times of the molecular systems after electronic excitation. For the ultrafast radiationless decay nonadiabatic effects and conical intersections play a crucial role. In order to explain the entire photodynamical process several mechanisms for ultrafast decay have been proposed. High-level quantum chemical methods are required for the reliable calculation of electronically excited states and special methods are necessary for the computation of nonadiabtic couplings. In the present work we have used multireference configuration interaction (MRCI) and state-averaged complete active space self-consistent field (SA-CASSCF) methods for which analytic energy gradients and nonadiabatic coupling vectors are available in the program system COLUMBUS [1]. The dynamics calculations have been performed in the framework of on-the-fly nonadiabatic surface hopping using the program system NEWTON-X [2] based on the analytic vector features of COLUMBUS.
The investigation of two cases will be reported: (i) aminopyrimdine as model for adenine and (ii) adenine itself. A large variety of qualitatively different conical intersections, the branches of the crossing seam connecting them and the reaction paths from the Franck-Condon region have been characterized.The importance of ring puckering modes is discussed and lifetimes are presented. When starting in the $S_3(\pi - \pi^*)$ state of adenine the results show a two-step process consisting of ultrashort deactivation from S_3 to S_1 and a longer exponential decay step corresponding to the conversion from S_1 to S_0.

[1] H. Lischka, R. Shepard, I. Shavitt, R. M. Pitzer et al., COLUMBUS, an ab initio electronic structure program, release 5.9.1, 2007, www.univie.ac.at/columbus.
[2] M. Barbatti, H. Lischka et al., NEWTON-X: a package for Newtonian dynamics close to the crossing seam, version 0.14b, 2007, www.univie.ac.at/newtonx.