

Photodynamical Simulations Using On-the-Fly Surface Hopping Methods

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The simulation of photochemical processes is an extremely fascinating and challenging field. Very high demands are posed on the quantum chemical methods to be used since the energy surfaces of several electronic states have to be computed including nonadiabatic coupling between different states. The present work is based on the MCSCF and MRCI methods as implemented in the program package COLUMBUS¹ using analytic energy gradients and nonadiabatic couplings and on Tully surface hopping by means of the program system NEWTON-X.² The presented work concentrates on the ultrafast photodynamics of heteroaromatic rings with the main focus on DNA bases. Ring puckering and NH dissociation processes will be discussed. The dynamics simulations show the predominance of ring puckering in the investigated cases adenine, thymine and aminopyrimidine when excited into the bright $\pi\pi^*$ band. On the other hand, due to the reversed order of $\pi\pi^*$ and $\pi\sigma^*(R3s)$ states, NH dissociation is dominating in the photodynamics of pyrrole.

Calculations including solvent effects will be presented as well. These have been performed at two levels. At the first one a microsolvation model is used including a few water molecules in the quantum chemical model. The second approach utilizes the newly developed QM/MM feature of NEWTON-X. First results for the dynamics of solvated protonated Schiff bases will be shown.

Literature

¹ <http://www.univie.ac.at/columbus/>

² <http://www.univie.ac.at/newtonx/>