

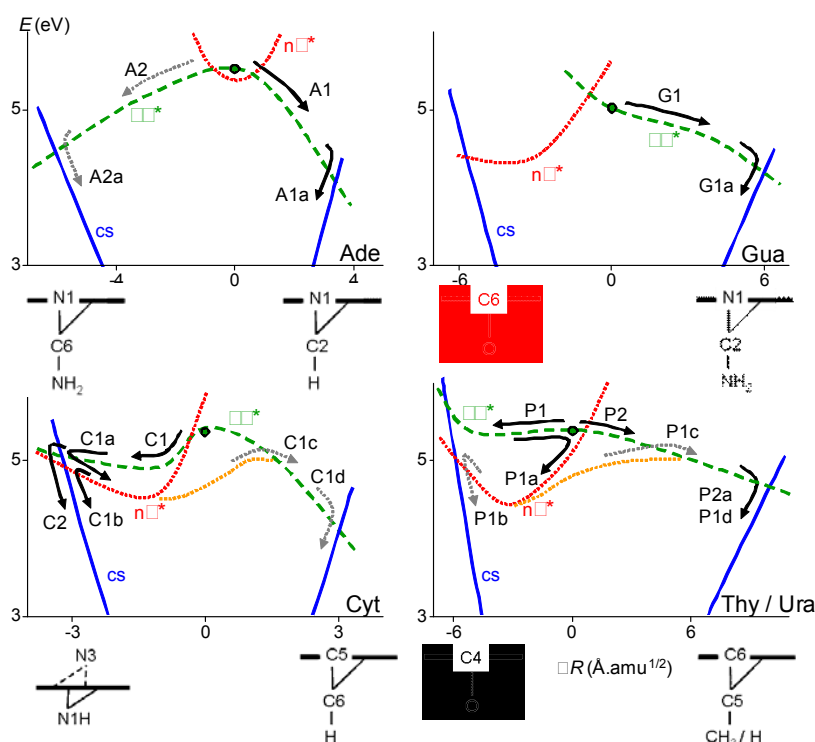
2.5.5 Research Area “Simulations of Photoexcited Molecules and Dynamical Processes” (M. Barbatti)

Involved: R. Crespo-Otero

Objective: Determination of steady and time-dependent properties of UV/vis excited molecules by means of semi-classical simulations based on ab initio quantum chemical methods.

Results:

1. *Photodynamics of nucleobases and nucleobase models:* We have performed excited-state dynamics simulations for all five naturally occurring DNA/RNA bases after UV-excitation. This research, carried out with our collaborators in Prague and Vienna, has allowed us to propose a very complete scenario for the mechanisms driving the internal conversion of the nucleobases. These mechanisms are schematically illustrated in the figure below.



Deactivation mechanisms in UV-excited nucleobases as determined by dynamics simulations. Purine bases (ade, gua) follow homogenous pathways along the $\pi\pi^*$ state. Pyrimidine bases (cyt, thy, ura) follow inhomogeneous pathways composed by several steps.

Besides the nucleobases themselves, we have also investigated the nonadiabatic dynamics of the nucleobase models aminopyrimidine and diaminopyrimidine. The investigation of such models aims at determining the role of specific site restrictions to the internal conversion. First, we have systematically changed the substitutions in aminopyrimidine so as to understand how the imidazole group affects the out-of-plane modes of the pyrimidine ring in adenine during the dynamics. Moreover, we

investigated how the out-of-plane modes responsible for the internal conversion are affected by the stacking interactions in DNA strand geometry.

2. Simulations of UV spectra of organic molecules: We have recently developed a Monte-Carlo semi-classical method for simulation of UV/vis spectra. The quality of the method has been assessed by direct comparison to full quantum chemical approaches in simulations of azomethane. We have shown that the semi-classical approach predicts band shapes and intensities, including those resulting from weak vibronic couplings, of quality similar to the full quantum chemical approach if vibrational progressions are neglected.

3. Methods for photodynamics simulations: In the last years, we have developed the NEWTON-X program (www.newtonx.org) for excited-state semi-classical dynamics simulations. Giving continuity to the program development, we have implemented routines for excited-state QM/MM simulations, which have been tested with dynamics of UV-excited formamide in Ar matrix. We have also implemented routines to compute time-dependent non-adiabatic coupling vectors at the time-dependent DFT level. Dynamics of pyrrole was studied as a test case.

A central problem in dynamics simulations based on the complete active space self-consistent field (CASSCF) method is to determine how the results depend on the active space. Taking aminopyrimidine as a test case, we have systematically investigated the influence of the active space in the simulations. The results shed light on how different active spaces affect the results and how one should proceed to select adequate spaces.

Publications resulting from this research area: 291, 292, 304, 365, 366, 392, 406

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