2.5.5   Research Area "Photoinduced Processes in Organic Molecules" (M. Barbatti)

Involved: R. Crespo-Otero, D. Asturiol, D. Mancini

Objective: After UV photoexcitation, organic molecules relax through a manifold of excited states, dissipating the absorbed energy either by photoemission or by vibrational excitation. The objective of this research area is to determine the relaxation mechanisms in two classes of organic systems: a) molecules playing roles in living organisms and b) molecules with potential application as photo-triggers. This goal is accomplished by computational simulations of excited-state dynamics, of potential-energy pathways, and of absorption and emission spectra.

Results:

a) Photophysics of life

Over the past few years, we have investigated the effect of UV radiation on nucleic acid fragments (nucleobases and backbone models) using computational chemistry. This is a topic of major interest as it allows understanding the role played by photochemistry in the biosphere and how carcinogenic and mutagenic effects are induced by radiation. Between 2011 and 2013, we have completed the mapping of the excited-state reaction pathways of cytosine, guanine and uracil (collaboration with H. Lischka). Dynamics simulations for these nucleobases on the ultrafast time-scale revealed that several reaction paths are activated and compete with each other to determine the fate of the reaction. Additionally, we showed that the ionization potentials of adenine along the main reaction paths undergo strong variations that are usually not taken into account either in experimental or in computational analysis (collaboration with S. Ullrich).
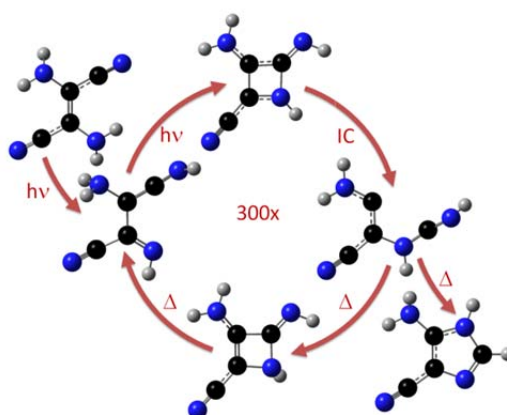

Figure 7. Photochemical steps for synthesis of an imidazole derivative from HCN.

We also investigated the photochemical step of one of the most likely pathways explaining the prebiotic origin of nucleotides on Earth (collaboration with W. Thiel and A. Anoop). This step consists of the photoinduced conversion of a HCN oligomer into an imidazole derivative. Although this photoreaction is known since the 1960s and most current prebiotic models are based on it, the exact reaction mechanism had still not been elucidated. Using dynamics, chemical kinetics, and thermodynamics, we showed that the reaction happens through a long sequence of excitations and de-excitations of an azetene derivative (Fig. 7).

Besides DNA, one of the most important UV chromophores in the skin of mammalians is urocanic acid (UA). The photophysics of this molecule is especially relevant because its *trans-cis* photoisomerization is a main factor inducing skin cancer. Another remarkable feature of UA is that its photoisomerization quantum yield decreases at short wavelengths. Although a number of models based on the topography of the excited-state potential energy surfaces have been proposed to explain this anomalous photophysics, none of them is completely satisfactory. We approached the problem in a distinct way, working under the hypothesis that the anomalous photophysics is caused by tautomeric effects. In fact, spectrum simulations of the tautomers allowed us to show that their relative spectral shift could be the cause of the anomalous photophysics.

A central process in photodynamic therapy is the generation of singlet oxygen ($^1O_2$) by a photosensitizer bound to a carcinogenic cell. Since the 1980s, porphycene (P_C) has been examined as a potentially efficient photosensitizer. We have investigated the UV absorption of P_C and the photophysics of $^1O_2$ generation via P_C sensitization. We showed that 1) there are several $^1O_2$-generation mechanisms available; that 2) the dominant mechanism is dependent on the O_2 concentration; and that 3) highly efficient $^1O_2$ generation could be obtained by encapsulating P_C and O_2 together, opening new conceptual perspectives for photodynamic therapy based on P_C.

As a last point in this research topic, we investigated the photodynamics of two simple models of molecules relevant for biological processes: the N-methyl-formamide (NMF), a model for peptide bonds; and methyl-pentadieniminium cation (Me-PSB3), a model for retinal. In both cases, ultrafast dynamics was simulated using QM/MM methods to incorporate environment effects. In the case of NMF, we showed that a caging effect enables the occurrence of reactions such as proton transfer, which are absent in the gas phase (collaboration with W. Sander). In the case of Me-PSB3, we showed that interaction with a polar solvent changes the orientation of the potential-energy

intersection cone from sloped to peaked, considerably enhancing the speed of deactivation to the ground state.

b) Molecular photo-triggers

Photo-triggers are often used for activation of molecular machines and electronic devices. They work in different ways, for instance, by inducing structural changes via isomerization or dissociation, or by promoting electronic changes via charge transport. We have been investigating a number of different photo-triggers from these two classes. Azobenzene, azomethane, ethylene, and $Cr(CO)_6$ are examples of the first class of photo-triggers. After irradiation, these molecules undergo strong structural changes, which may be communicated to neighboring molecular groups to trigger a reaction. We have simulated the photoinduced ultrafast dynamics of these molecules. In the case of azobenzene, where two nonequivalent rotational pathways corresponding to clockwise or counterclockwise rotations are available, we determined that the course of the rotational motion is strongly dependent on the initial conditions. In fact, we could even demonstrate that the occurrence of one or another pathway can be completely controlled by selecting adequate initial conditions (collaboration with J. Pittner). In the case of $Cr(CO)_6$, dynamics results were used to assign experimental time-constants corresponding to the dissociative motion through the manifold of excited states.
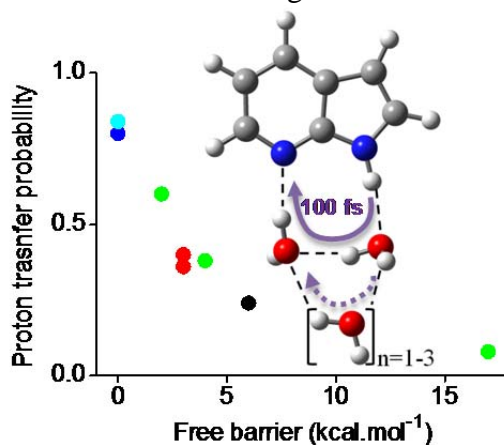

Figure 8. Excited-state intramolecular proton transfer in 7AI-water clusters.

Photoinduced excited-state intramolecular proton transfer in 7-azaindole (7AI), 2-(2´-hydroxyphenyl)benzothiazole and 1H-pyrrolo[3,2-h]quinoline are examples of the second class of photo-triggers. We have simulated the excited-state ultrafast dynamics of these three molecules within small clusters of water and methanol (collaboration with N. Kungwan). While in the gas phase the proton transfer occurs directly between the donor and acceptor groups of the molecule, within clusters the proton is transferred through the network of hydrogen bonds. For all these cases, we showed that the process

is completed within 100 fs. We also mapped the relative importance of several possible reaction pathways. In 7AI-water clusters, for instance, only the nearest two water molecules participate in the proton transfer, while the others play a passive role (Fig. 8).

Outreach: We have made an effort to communicate our results to a more general public through diverse media. Description of our research lines, main results, and new publications are constantly updated on the group homepage (sgk.mpg.de/private/barbatti). A YouTube channel dedicated to movies showing the results of dynamics simulations is also available (youtube.com/user/mbarbatti). News on our work and other relevant information for our field are delivered through our Twitter account (twitter.com/MarioBarbatti). Outstanding results from our research are communicated to general science popularization media. For this last point, we are supported by Sarah-Lena Gombert, from the press-office of our Institute.

2.5.6   Research Area "Development and Assessment of Methods" (M. Barbatti)

Involved: R. Crespo-Otero, T. Cardozo

Objective: Whereas state-of-the-art computational methods allow reaching chemical accuracy for the ground state, simulations of excited states bear a high level of uncertainty. This is due to the many approximations required to deal with the large density of states and the complicated electronic structures of excited states, while still keeping the simulations computationally affordable. The objectives of this research area are a) to implement new methods and algorithms to improve excited-state simulations within the Newton-X platform and b) to critically assess the quality of the calculations.

Results:

a) The Newton-X platform

Since 2005, we have been designing and developing the Newton-X platform. Newton-X is a collection of programs to perform all steps of excited-state nonadiabatic dynamics simulations, from the generation of initial conditions to the statistical analysis. The project involves collaborations with H. Lischka, J. Pittner, G. Granucci, and M. Persico. Newton-X is an open-source platform distributed free of charge. Within the last 12 months (as of October 15, 2013), 150 new downloads have been registered.

Most of new methodologies developed in our group are incorporated into Newton-X. Between 2011 and 2013, we implemented a general hybrid-gradient interface allowing dynamics with QM/MM and ONIOM approaches. We developed a general method for efficient numerical computation of nonadiabatic couplings and for dynamics using the Local Diabatization method. We also developed new interfaces for nonadiabatic dynamics with MCSCF wavefunctions using GAMESS (collaboration with T. Windus); CC2 and ADC(2) using Turbomole; and TDDFT and TDA using Gaussian 09.
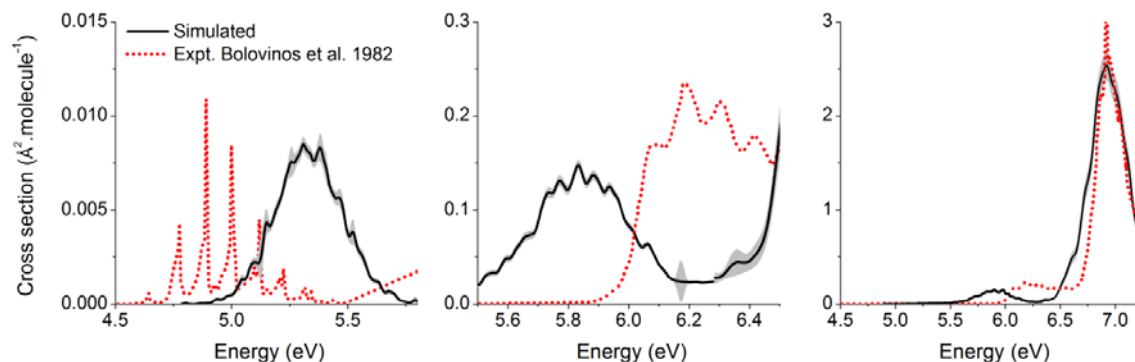

Figure 9. Simulated UV-absorption cross section of 2-phenylfuran compared to experimental results.

State classifications based on CI-type electronic densities were implemented, allowing automatic characterization of the electronic states in terms of local excitations, charge-transfer and delocalized excitations during the dynamics.

Newton-X allows spectrum simulation using ensembles of nuclear geometries. The method can provide absolute intensities, effective parameter-free band widths, and dark vibronic bands (Fig. 9). We presented a formal derivation of the method, which, although popular among several groups, had up to that point only been based on qualitative arguments. This derivation will also allow the development of new algorithms in the future.

b) Method assessment and benchmarks

To understand the impact of the active and reference spaces, we systematically investigated the dynamics of 2-aminopyrimidine at the CASSCF level and of ethylene at the MRCI level (collaboration with H. Lischka). In the first case, we found that the selection of orbitals for the active space has a strong effect on the dynamics output, up to a point where the space is saturated. Before saturation, even with the same nominal number of electrons and orbitals, the dynamics results can be very different for distinct sets of orbitals. After saturation, the results are not affected significantly even when the space is increased. In the case of ethylene, we concluded that the dynamics are influenced not only by the dynamic electron correlation within the π-system, but also within the σ-σ* subsystems and between the σ- and the π-systems. This finding allowed us to explain most of the divergences between simulated and experimental results for the excited-state lifetime of ethylene.

Dynamics simulations for adenine performed with semi-empirical and *ab initio* MRCI predicted similar lifetimes, but deactivation through different pathways. In collaboration with W. Thiel, we systematically repeated these simulations under very controlled conditions. An imbalance in the barriers along two different reaction pathways was found to be the reason for the divergence. Curiously, the imbalance was found in both methods with opposite trends. Under the same conditions, we also tested the dynamics of adenine at the TDDFT level using several functionals. All of them failed to describe the ultrafast dynamics of this molecule. Right now, we are extending these simulations to the ADC(2) level. The collection of all these simulations will provide a useful benchmark of dynamics results for small hetero-aromatic molecules.

We have also validated TDDFT for simulations of donor-acceptor (D-A) interfaces for photovoltaics (collaboration with W. Thiel). Using dimers of thiophene oligomers (D) and fullerene C_{60} (A) as prototypes, we benchmarked the vertical electronic spectra by

systematically changing a number of variables, including oligomer size, density functional (Fig. 10), polarization medium, D-A distance, and chemical functionalization of the monomers. This benchmark will guide the selection of models and computational levels in our future investigations in this field.
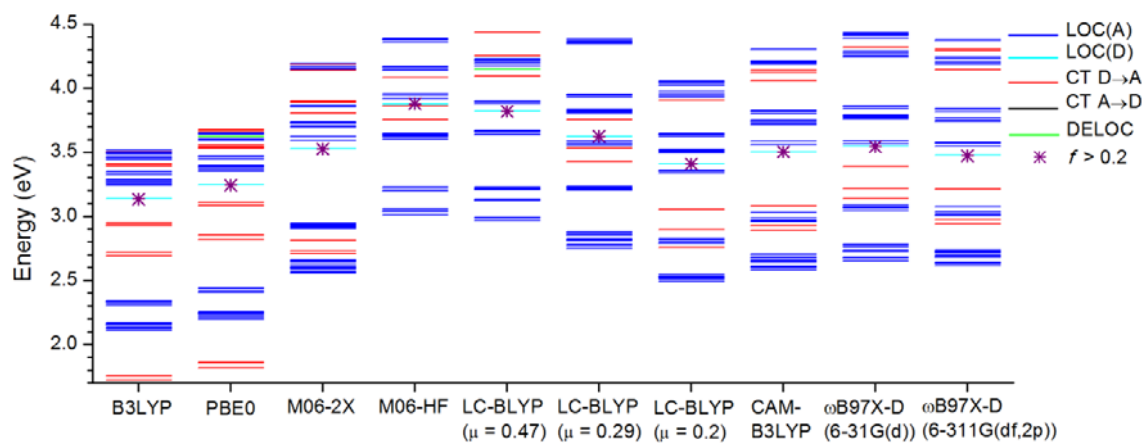

Figure 10. Benchmark of vertical excitations for a thiophene-oligomer/fullerene interface at different levels.

Outreach: Our group supervises the release and distribution of the Newton-X platform. This is done via the Newton-X webpage (www.newtonx.org), where full documentation and tutorials can be accessed. Moreover, we moderate a discussion list at goo.gl/G0H9fg, where a knowledge database is built from users and developers contributions.