

2.5.5 Research Area “Photoinduced processes in organic molecules” (M. Barbatti)

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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 objectives of this research area are 1) to characterize these relaxation mechanisms through excited-state computational simulations; and 2) to implement new methods and algorithms to improve these simulations.

Results:

a) Fundamental processes

Photoexcitation may induce electron and proton transfers within the molecule or between neighbor molecules. We have investigated several cases to understand how this transfer process occurs, how it is triggered, and on which time scale it proceeds [93, 95, 96, 103].

In collaboration with E. Sánchez-García and W. Sander, we investigated the formation of weakly bound dimers of N-methylformamide (NMF) and their photochemistry after UV irradiation [95]. The aim was to understand the effect of UV radiation on peptide bonds. Starting from trans(donor)-trans(acceptor) dimers, the experiments carried out in the Sander group showed that the main products formed upon irradiation are the trans(donor)-cis(acceptor) dimers. Moreover, in contrast to the photochemistry of the NMF monomers, no dissociative products were observed upon 248 nm irradiation of the NMF dimers. On the basis of nonadiabatic dynamics simulations, we could explain the absence of dissociative products. The simulations showed that the NMF dimers are protected by a proton-transfer mechanism in the excited state that is faster than the photodissociation.

In another case study, I showed that an electron transfer from solvent molecules to the photoexcited chromophore can also induce internal conversion with little geometric distortion [93]. Using dynamics simulations, I found out that when a specific tautomer of adenine (7H-adenine) in water absorbs UV radiation, it dissipates the photo-energy as heat after receiving an electron from a nearby water molecule. This result revealed an

unknown internal conversion pathway, with implications for the assignment of photoreactions in biological environments and for the design of organic photodevices.

In a recent case study, we addressed the double proton transfer in 7-azaindole (7AI) dimers [103]. Two decades ago, A. Zewail and his team, using time-resolved spectroscopy, proposed that photoinduced double proton transfer in 7AI dimer is a stepwise process. Since then, this conclusion has motivated an uncommonly fierce debate on the nature of this transfer – whether it is really stepwise or alternatively concerted. Using high-level computational simulations of static and dynamic properties, R. Crespo-Otero, N. Kungwan, and I found out that much of these earlier discussions were induced by inappropriate theoretical modeling, which led to a biased interpretation of the experimental results. We showed that earlier models provided either a wrong or incomplete topographic description of the excited-state potential energy surface of the 7AI dimer. They delivered an inadequate balance between the energies of the local-excitation and charge-transfer regions, and completely missed the possibility of internal conversion to the ground state (Figure 12). We concluded that stepwise transfer is thermodynamically and kinetically disfavored and only concerted transfer takes place.

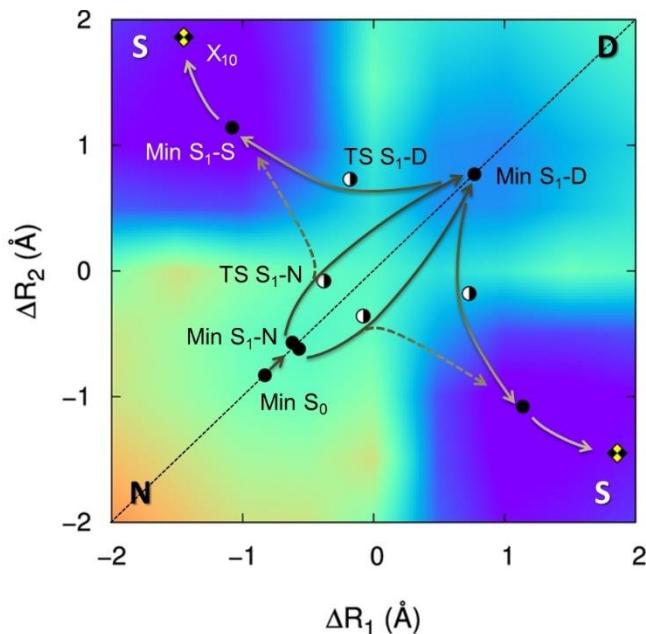


Fig. 12. Potential energy surface of the first excited state of the 7AI dimer. The presence of a conical intersection (X_{10}) blocks the occurrence of stepwise double proton transfer.

b) Applied photophysics

Photophysical and photochemical processes are core phenomena in diverse aspects of life on Earth. In the 2014-2016 period, we continued a long-term research program addressing such processes from a computational standpoint [13, 19, 31, 42, 62, 91, 94, 97, 100-102, 104, 107].

In collaboration with W. Thiel and T. C. Ramalho, we showed that excited-state proton transfer may give rise to new diagnostic tools to follow the clinical evolution of cancer patients [42]. It is well-known that a number of phenylbenzothiazole (PBT) compounds exhibit antitumor activity. Certain PBTs are also well-known for their very large Stokes shifts caused by excited-state intramolecular proton transfer (ESIPT). Aiming at connecting tumor selectivity and proton-transfer properties, we have theoretically designed and studied a new PBT compound, named HABT. Our hypothesis, confirmed by the simulations, is that the proportion and intensity of violet and green emissions from HABT depend on the protein active-site conformation, which modulates the rates of proton transfer, and of radiative and nonradiative decays. Thus, changes in the fluorescence spectrum of HABT bound to tyrosine kinases could be the basis for a new method to detect mutations in cancer cells, usually associated to development of drug resistance.

Still in the health field, I have completed a comprehensive map of processes that produce or cleave pyrimidine dimers (Figure 13) [94]. Cyclobutane pyrimidine dimers (CPD) are closely related to mutagenesis and carcinogenesis; they are formed when UV radiation induces dimerization of adjacent pyrimidine nucleobases. To understand how the dimerization and the repair process happen, I built a benchmark of computational results based on different methods. For these simulations, I used a thymidine-dimer model in the gas phase and explored the ground- and excited-state potential energy surfaces of neutral (singlet and triplet), cationic, and anionic species. The analysis of these surfaces allowed me to describe several reaction pathways for dimerization and repair, some of them completely unknown so far.

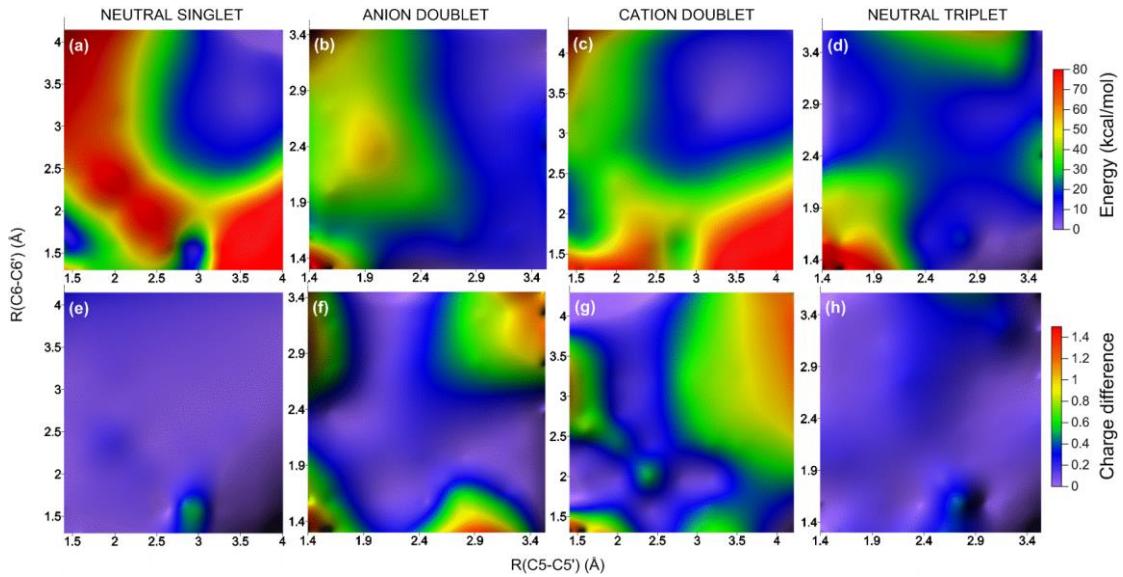


Fig. 13. Potential energy surface and charge distribution in the ground state of neutral and charged thymine dimers.

In collaboration with S. do Monte and R. Hilal, I have investigated the photochemistry of a series of halogen compounds, whose photoproducts may impact atmospheric chemistry [97, 104, 107]. One example is HCFC-132b ($\text{CF}_2\text{ClCH}_2\text{Cl}$), which is the major compound used for replacing CFC-113 ($\text{CF}_2\text{ClCFCl}_2$) in different industrial applications [107]. These simulations revealed how the radiation from different UV-wavelength regions interacts with these compounds and leads to formation of diverse products.

In recent years, the research on organic photovoltaics has become central in the field of photochemistry due to its high technological potential. Between 2014 and 2016, we investigated the fundamental properties of diverse organic compounds of interest for photoenergy conversion [13, 19, 31, 62, 102], including oligothiophenes (collaboration with W. Thiel) [31, 62], squaraine-fullerene complexes (also with W. Thiel) [19], and poly-(p-phenylene vinylene) (PPV) oligomers (with H. Lischka) [102]. In all these studies, our focus was the development of analytical tools to characterize charge and energy transport processes. In the case of oligothiophenes, for instance, we developed a new computational approach, in which the energy, relative ordering, and population of productive and unproductive electronic states of a molecular aggregate are monitored during the dynamic relaxation following photoexcitation. Applying this approach to a particular system – the photoexcited bi-thiophene dimer – we showed that few femtoseconds after light absorption, the dimer has two electronic energy bands separated by a sizable energy gap [62]. The high-energy band has a productive state lying on its bottom, while the low-energy band is composed of unproductive states only.

As the dimer relaxes, it populates the productive state on the bottom of the high-energy band. If the gap separating the bands remained constant, this productive state would survive for a long time, contributing to current generation. However, induced by molecular vibrations, the energy gap fluctuates and, when it gets to a minimum, the population is transferred to the low-energy unproductive band. As a result, the productive state survives for not more than 100 fs, rendering poor power conversion performance.

c) Method and program development

Since 2005, we have been designing and developing the Newton-X platform [92]. 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, and others. Newton-X is an open-source platform distributed free of charge. Between 2014 and 2016, we finished the development of new interfaces for nonadiabatic dynamics using different wavefunctions and codes: MCSCF / GAMESS (collaboration with T. Windus) [99]; CC2 and ADC(2) / Turbomole; and (U)TDDFT, (U)TDA, and (U)CIS / Gaussian 09 [98, 106].

We have additionally implemented a new method for simulating steady and time-resolved photoelectron spectra based on nuclear ensembles (Figure 14) [105].

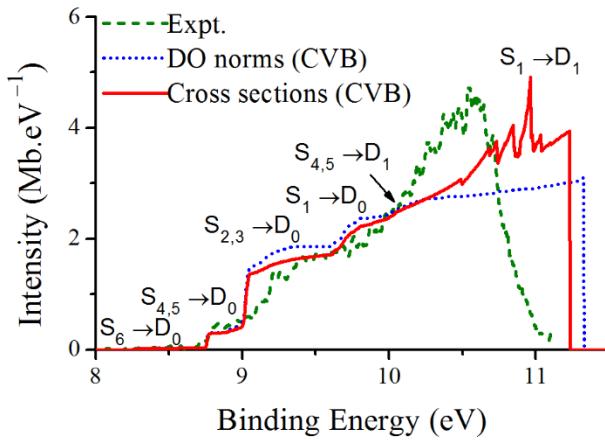


Fig. 14. Simulated time-resolved (0-25 fs) photoelectron spectrum of imidazole compared to experimental results.

Future directions: I was appointed professor of the chair of excellence A*MIDEX at the University Aix-Marseille, where I am since September 2015. A productive

collaboration with W. Thiel's group is still in place. We have been working on the characterization of exciton formation in an ensemble of organic heterojunctions for organic photovoltaics (collaboration with D. Fazzi) and on the development of a new program for computing spin-orbit couplings based on DFT methods (collaboration with X. Gao).

Outreach: Access to the Newton-X platform is gained via the Newton-X webpage (www.newtonx.org), where a full documentation and tutorials are available.

Publications resulting from this research area: 13, 19, 31, 42, 62, 91-107

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