

**Light-induced isomerization of a protonated Schiff base:
Study of the effects of photo-excitation and environment**

Three-year PhD position at the University Paris-Saclay (UPSay), Graduate School of Chemistry, in the group ThéoSim of the Institut de Chimie Physique (ICP).

Starting date: 01/10/2021.

Funding provided by the Doctoral School 2MIB of Paris-Saclay.

Supervisors: Dr. Federica Agostini (associate professor at UPSay, ICP), Dr. David Lauvergnat (researcher at CNRS, ICP).

Deadline for submission of applications: April 4th, 2021.

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Research topic

One of the fastest photochemical reactions known in nature is the 11-*cis* to *all-trans* isomerization of the retinal protonated Schiff base (rPSB11) of rhodopsin. The photo-isomerization is initiated by visible light and is complete within 200 fs, with an efficiency of more than 60% [4]. Microscopically, the photo-reaction consists of three main steps: (i) the initial electronic excitation, (ii) the subsequent ultrafast relaxation through conical intersections, and (iii) the formation of the *trans* photo-products in the ground state. It has been pointed out [4], that the ultrafast nature of the relaxation process, i.e., step (ii), critically relies on the concerted effect of three vibrational modes: the bond-length-alternation (BLA) stretching, the torsional deformation (TORS) along the reactive CC double bond, and the hydrogen-out-of-plane (HOOP) wagging.

Recently, the 2-*cis*-penta-2,4-dieniminium cation (*cis*-PSB3), which is a minimal model for rPSB11, has been employed as test case to study the microscopic details of the isomerization reaction [1] based on state-of-the-art techniques for quantum molecular dynamics simulations. In particular, analytical potential energy surfaces for the two essential singlet electronic states, i.e., S_0 and S_1 , involved in the process have been used, which have been developed by Olivucci and coworkers [5] based on ab initio multi-state multi-configuration electronic structure calculations. The preliminary study [1] proved that some features of the isomerization reaction, observed in experiments [6] and in atomistic QM/MM simulations [7], are retained in the isolated PSB3. For instance, sub-50 fs S_1 -to- S_0 relaxation, long-lasting vibrational coherence, and interplay of TORS and HOOP to favor/inhibit the photo-products formation have been confirmed. Nonetheless, the absence of relaxation channels provided by the “environment” is the source of some disagreement between the PSB3 simulated dynamics and the observed behavior in more realistic conditions, such as the incorrect equipartition of the ground-state and excited-state population at long times. The term “environment” used here refers to the additional internal degrees of freedom of PSB3 that are not considered in the model as well as protein and solvent degrees of freedom.

Summary

The proposed doctoral project aims to investigate the photo-isomerization process of the 2-*cis*-penta-2,4-dieniminium cation (*cis*-PSB3) in realistic – natural – conditions, taking into account various effects that drive the ultrafast relaxation process of the photo-excited species towards the *trans*-PSB3 photo-products (see details below). In particular, the focus will be put (1) on the initial electronic excitation, induced either by a laser pulse of finite duration or by incoherent light, and (2) on the effect of the environment, mimicked either as a bath of harmonic oscillators or as a fictitious stochastic force.

These two ingredients will help providing a general overall picture of the photo-isomerization process in PSB3, building upon the preliminary investigation performed by Dr. F. Agostini and Dr. D. Lauvergnat in collaboration with Prof. M. Olivucci (Univ. of Siena, Italy) [1].

The project relies on theoretical and computational developments of quantum molecular dynamics techniques.

Objectives

The ultimate goal of the project is to achieve a microscopic description of the *complete* light-induced isomerization process in PSB3, from the initial photo-excitation to the formation and stabilization of the photo-products. Intermediate objectives are more fundamental and general: constructing an

efficient simulation tool to include the effect of the environment in the quantum and trajectory-based techniques developed in the group ThéoSim; clarifying the differences in the relaxation pathways towards conical intersections due to laser pulse of finite duration and to an instantaneous excitation; applying novel theories, recently proposed [8], in the domain of trajectory-based methods to the techniques developed at ThéoSim.

Methods

The doctoral project is a theoretical and computational project. The successful candidate is expected to get acquainted with the codes for quantum and quantum-classical dynamics developed at ThéoSim. The issues that will be addressed in the course of the project, i.e., inclusion of light excitation and effects of environment, require theoretical and numerical developments. In particular, the exact factorization approach, together with its quantum-classical formulation, will be employed for the trajectory-based simulations. Alongside, more standard techniques, such surface hopping and Ehrenfest dynamics, will be used for test studies.

Bibliography

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- [3] D. Lauvergnat, A. Nauts, *J. Chem. Phys.* **116** (2002) 8560.
- [4] S. Gomez, H. L. Luk, I. Schapiro, M. Olivucci, *Chem. Rev.* **117** (2017) 13502.
- [5] E. Marsili, M. H. Farag, X. Yang, L. de Vico, M. Olivucci, *J. Phys. Chem. A* **123** (2019) 1710.
- [6] D. Polli, *et al.*, *Nature* **467** (2010) 440.
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Scientific conditions and funding

The successful candidate will join the group ThéoSim of the Institut de Chimie Physique at the University Paris-Saclay. Currently, the group is composed of 10 permanent researchers (UPSay professors and CNRS researchers), 2 postdoctoral researchers, and 7 doctoral students.

Every year the group hosts bachelor and master students for short-term research projects, supervised by the permanent staff members. The successful candidate will be invited to participate in and, possibly, partially supervise students in the course of such projects.

Funding will be provided upon acceptance at the doctoral school 2MIB of the University Paris-Saclay. After a first round of screening of the candidates by the supervisors of the project, the selected candidate will be interviewed by the scientific board of the doctoral school. The doctoral school will make the final decision on the successful candidates.

Profile of the candidate

Applications from candidates holding a master degree in Physics or Chemistry are now open.

Please send a CV, with a brief cover letter, and at least one reference letter to Dr. Federica Agostini federica.agostini@universite-paris-saclay.fr no later than April 4th, 2021.

We look for candidates strongly interested in theory and software developments. We expect the successful candidate to have experience in one of the following domains: theoretical chemistry, chemical physics, molecular physics, quantum chemistry, molecular dynamics.

Language level: French and English

Knowledge of English is essential, but we do not request a particular level or certificate.

Knowledge of French is not required, but it is indeed a plus.