
PhD 2022-2025

DYNAMICS SIMULATIONS OF PHOTOCHEMISTRY AND ATTOCHEMISTRY

DESCRIPTION: PhD position in theoretical chemistry: 3 years from Oct. 2022.
Doctoral contract financed by the EUR LUMOMAT.

LOCATION: Team: **ModES** (Modeling & Spectroscopy)
Lab: CEISAM, UMR 6230, Nantes Université, CNRS
<https://ceisam.univ-nantes.fr/en/>

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CONTEXT

One of the most fundamental and widespread processes in chemistry is the absorption of light to excite electrons of molecules and potentially induce a chemical reaction. As a result of excitation into an electronic excited state, the distribution of electrons and thus the reactivity of the molecule differ significantly from the ones in the ground state. Thanks to this conceptually simple yet complex process, photochemistry has considerably broadened the spectrum of possible reactions, as compared to thermal chemistry. The applications of photo-induced processes cover almost all fields from medicine to computer science and energy conversion. However, the practical use of photoinduced processes is limited by the quantum efficiency of the desired process, the latter being almost always in competition with other processes. A challenge for chemists today is therefore to design more efficient molecular systems and optical control methods for each desired application. In this context, it is necessary to rely on an in-depth knowledge of the photochemistry of the system of interest. Theoretical studies complementary to the experimental measurements are often necessary.

RESEARCH PROGRAM

The goal of this thesis is to study photochemical and photophysical processes of organic molecular compounds using theoretical approaches to learn how to control their photoreactivity in a more efficient way. The first objective is to gain deep knowledge about photochemical processes. To connect with experimental observables, we will resort to two powerful tools: isotope labelling and X-ray spectroscopy used as a probe. Using these tools in combination with non-adiabatic molecular dynamics simulations, we will study the photochemistry of ethylene cation and spyropyran. Our second objective is to affect photoreactivity using attosecond pulses thanks to the knowledge gained with the above simulations. Because of the time-energy uncertainty principle, pulses of extremely short duration have a large spectral bandwidth, potentially larger than the energy difference between electronic excited states. Such attosecond pulses can therefore populate several electronic excited states in a simultaneous and coherent manner; this is referred to as an “electronic wavepacket”. Because of interference phenomena between the populated states, the electronic distribution of the wavepacket is not the simple average of the electronic distributions of the individual states: a coherent electronic wavepacket has a new electronic distribution – a new chemical bonding – and thus can be considered as a new type of initial electronic state. The key concept is to induce a chemical reaction not with a single electronic excited state as in “traditional” photochemistry, but with an electronic wavepacket and thus to control the outcome of a photochemical reaction by manipulating directly the particles that form the chemical bonds, i.e., the electrons.

This thesis will include direct interactions with experimental collaborators based at Institut Lumière Matière (Lyon, France) working on the same photochemical reactions.

PROFILE OF THE CANDIDATE

The candidate should have a Master degree in chemistry, chemistry-physics, theoretical chemistry or physics, or equivalent obtained in 2021 or in 2022 and must have a solid training in physical and theoretical chemistry. Experience in *ab initio* molecular calculations as well as programming skills (Fortran, Python...) are assets.

Applicants must send a CV, a cover letter to morgane.vacher@univ-nantes.fr, and the names of two reference persons.