PhD 2020-2023

**MOLECULAR MODELING: FROM PHOTOCHEMISTRY TO ATTOCHEMISTRY**

**DESCRIPTION:** PhD position in theoretical chemistry: 3 years from Oct. 2020. Financed by the University of Nantes.

**LOCATION:** Team **ModES: Modélisation Et Spectroscopie**
Lab: CEISAM, UMR CNRS 6230 Université de Nantes

**CONTACTS:** Morgane Vacher [morgane.vacher@univ-nantes.fr](mailto:morgane.vacher@univ-nantes.fr)
Denis Jacquemin [denis.jacquemin@univ-nantes.fr](mailto:denis.jacquemin@univ-nantes.fr)

**CONTEXT**

The applications of photochemical processes are very important (molecular switches, fluorescent probes, etc.). However, they are limited by the quantum yield of the desired process, the latter being almost always in competition with other processes. A challenge for chemists is therefore to design more efficient molecular systems as well as controlling methods for each of the applications. In this context, it is necessary to rely on a thorough knowledge of the photochemistry of the system. Time-resolved experiments with a femtosecond resolution (1 fs = 10^-15 s) played a major role in understanding chemical reactions by probing the motion of nuclei in real time. Recent advances in attosecond science (1 as = 10^-18 s) open the possibility of observing the motion of electrons on their intrinsic timescale. In this field where the experimental results are still very piecemeal, theoretical studies allow not only to propose reaction mechanisms rationalizing the low quantum yields observed but also to suggest better candidates as well as new means of control.

**RESEARCH PROGRAM**

The objective of this thesis is to understand the photochemical and photophysical processes of organic molecules using the tools of theoretical chemistry and to use attochemistry to effectively control photoreactivity. Due to the time-energy uncertainty principle, extremely short (attosecond) pulses have a large spectral width and populate coherently several excited electronic states. These coherent electronic wave packets can thus be considered as a new type of initial electronic state, having a new electronic distribution.

During this thesis, the student will simulate the non-adiabatic dynamics after photoexcitation (or photionization) by populating either a pure adiabatic electronic state (as in traditional photochemistry) or a coherent superposition of several electronic states (attochemistry). To this end, semi-classical and quantum on-the-fly ab initio molecular dynamics methods, such as the surface hopping method and the DD-vMCG method, will be used and their results will be compared. The methodological strategy will first be applied to prototype photochromic systems such as azobenzene and its derivatives based on five-membered cycles. Then, multi-photochromic systems will be studied. The association of several photochromes potentially leads to emergent properties but the photoreaction yield is often greatly reduced. The challenge will be to propose an initial electronic wave packet which makes it possible to recover sufficient photochemical efficiency for practical applications while maintaining a non-zero coupling between the two photochromes.

This thesis will also include the development and use of modern machine learning analysis methods. To date, simulations of quantum dynamics taking into account all dimensions remain difficult to reach for large systems. The selection of important nuclear coordinates by machine learning algorithms will be carried out.

In addition, the successful candidate will be required to have direct interactions with various experimental and theoretical teams collaborating with the supervisors.

**PROFILE OF THE CANDIDATE**

The candidate should have a Master degree in chemistry, chemistry-physics, theoretical chemistry or physics, or equivalent obtained in 2019 or in 2020 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 and a cover letter to [morgane.vacher@univ-nantes.fr](mailto:morgane.vacher@univ-nantes.fr).