Theoretical spectroscopy of organic chromophores and their aggregates

ABSTRACT: The project aims at the computational characterization of steady-state and time-resolved optical spectroscopies of organic chromophores that are of great relevance from a biological and/or technological point of view. Since aggregation is the typical phenomenon that could modulate the optical spectroscopy in natural or artificial photo-sensitive systems composed of organic chromophores, particular attention will payed to this aspect among the complex and various effects involved in their photochemistry. Starting from the simulations of absorption electronic (linear) spectra, followed by investigation of vibrational effects (i.e. vibronic spectra), both pump-probe electronic and Raman types of nonlinear spectroscopies will be investigated. Computational method will involve MD simulations and both TD-DFT and MC-SCF QM methodologies to characterize the electronic structures of the target organic molecules, including DNA/RNA nucleobases, Rhodamine-like molecules and retinal chromophores.

ABSTRACT: Il progetto mira alla caratterizzazione computazionale delle spettroscopie ottiche sia stazionarie che risolte nel tempo di cromofori organici di grande rilevanza dal punto di vista biologico e/o tecnologico. Poiché l'aggregazione è il tipico fenomeno che può modulare la spettroscopia ottica in sistemi fotosensibili naturali o artificiali composti da cromofori organici, particolare attenzione sarà rivolta a questo aspetto tra i complessi e vari effetti coinvolti nella loro fotochimica. Partendo dalle simulazioni di spettri elettronici (lineari) di assorbimento, seguite dall'indagine degli effetti vibrazionali (es. spettri vibronici), verranno studiate spettroscopie non lineari sia di tipo pump-probe che Raman. La metodologia computazionale coinvolgerà simulazioni MD ed entrambi gli approcci QM di tipo TD-DFT e MC-SCF per caratterizzare le strutture elettroniche delle molecole organiche target, comprese basi azotate DNA/RNA, molecole simil-Rodamina e cromofori retinalici.

Research Project: Understanding the photo-reaction mechanisms of biological systems is of fundamental importance for a variety of technological applications, such as the design of photochromic molecular switches and photosynthetic systems, as well as in biosensing or in the evaluation of health risks, for instance related to skin damage upon irradiation. Due to the complexity of photo-induced phenomena, giving a coherent picture of the photoreaction pathways is challenging and the aggregation phenomena often play a vital role. Sometimes even the interpretation of conventional UV-vis absorption spectra is not as straightforward as expected.

The project, thus, will first investigate absorption spectra of the target organic chromophores and the role of aggregation. For a good accuracy of the simulated absorption spectra, beside the employment of various QM methodologies and extensive benchmark studies, it is quite important to include vibrational effects that play a key role on the spectral lineshapes.

Since the time scales of the photochemical phenomena are too fast for conventional spectroscopies, their study requires the implementation of nonlinear ultrafast techniques, such as time-resolved electronic and/or Raman spectroscopies. Generally, the interpretation of the experimental signals is not straightforward at all, as it originates from multiple concurring optical processes, which need to be disentangled and assigned to the corresponding out-of-equilibrium geometries. Theoretical simulations planned in this project will play, thus, a pivotal role for the detailed interpretation of the experimentally recorded responses.

Activity Plan:

1. Simulations (TD-DFT and MC-SCF) of linear absorption spectra of target organic chromophores
   1.1 DNA/RNA nucleobases
   1.2 Rhodamine-like molecules
   1.3 Retinal chromophores

2 Simulations of vibrational effects by means of vibronic modeling
3 Investigations on the role of aggregation by means of dimeric models
  3.1 MD simulations in solution
  3.2 QM/MM simulations of selected conformations
  3.3 Simulations (TD-DFT and MC-SCF) of linear absorption spectra of dimers
  3.4 Simulations of vibrational effects in dimers
4 Simulations (TD-DFT and MC-SCF) of time resolved spectra
  4.1 Simulations of pump-probe electronic spectra of monomers
  4.2 Simulations of pump-probe Raman spectra of monomers
  4.3 Simulations of pump-probe electronic spectra of dimers
  4.4 Simulations of pump-probe Raman spectra of dimers