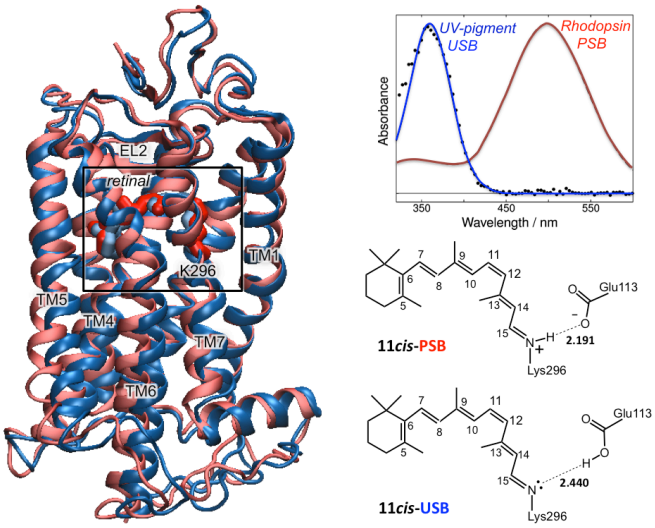
Understanding ultraviolet vision: tracking new photochemistry with ultimate ultrafast spectroscopy

Scientific context: The interest in photochemistry is triggered by the evolution of the nanotechnologies, which require smart, tunable and efficient devices. Understanding the behavior of natural organic chromophores is then crucial to be able to create and develop a new generation of devices. Retinal chromophores represent prototype chromophoric systems involved in several natural light-induced processes, with chromophores embedded via *protonated* Schiff base (PSB) links to transmembrane proteins, the visual pigments (called opsins). While the retinal photochemistry in rhodopsins, the family of opsin proteins found in the eye retinas and allowing color vision, has been widely studied and currently well understood [1], the photophysical properties of visual pigments allowing ultraviolet (UV) vision have recently attracted particular attention [2-3]. A distinct aspect of UV-sensitive pigments, when compared to visual rhodopsin, is that the chromophore is bound to the protein by an *unprotonated* Schiff base (USB) linkage in the dark-state. Elucidating the fundamental interactions responsible for regulating the protonation state of the retinyl chromophore in UV-pigments and the underling dynamics triggered by UV-photoexcitation is critical for understanding the photophysics of ancestral pigments as well as for the design of bio-mimetic UV photochromic switches.

Project objectives: The aim of the project is to study the UV-pigment photochemistry by means of various computational techniques, including classical molecular dynamics and hybrid QM/MM schemes involving wavefunction methods, and provide direct comparisons with experiments by simulating state-of-the-art time-resolved electronic spectroscopy. Two-dimensional electronic spectroscopy (2DES) based on ultrashort laser pulses is a cutting-edge technique to track electronic transitions in complex systems with unprecedented spectral and time resolution. The 2DES can be used to investigate energy transfer, structure, conformation dynamics and photochemical reactivity in a wide range of systems. The "Theory Axis of ENS Lyon" has recently developed a computational tool that can be routinely applied to accurately simulate 2DES spectra of multichromophoric systems including proteic systems in the ultraviolet (2DUV) [4]. The project will strongly benefit from important international collaborations with Prof. S. Mukamel, in University of California Irvine (USA) and with Prof. G. Cerullo in Politecnino di Milano (Italy).



Requested skills: For this project, we are looking for highly motivated students interested in a PhD thesis on computational chemistry, involving state-of-the-art modelling techniques applied to photophysical problems. The student will discover several aspects of theoretical chemistry, from classical dynamics to high-end quantum mechanics. The work will be performed in the Chemistry Laboratory of the ENS-Lyon.

Supervisors:
Ivan Rivalta ivan.rivalta@ens-lyon.fr
Marco Garavelli marco.garavelli@ens-lyon.fr

References

[1] Polli D, Altoè P, Weingart O, Spillane KM, Manzoni C, Brida D, Tomasello G, Orlandi G, Kukura P, Mathies RA, Garavelli M, Cerullo G, *Nature* **2010**, *467*, 440-443.
[2] Mooney VL, Szundi I, Lewis JW, Yan ECY, Kliger DS, *Biochemistry* **2012**, 51, 2630-2637
[3] Sekharan S, Mooney VL, Rivalta I, Kazmi MA, Neitz M, Neitz J, Sakmar TP, Yan ECY, Batista VS, *J Am Chem Soc* **2013**, *135*, 19064-19067
[4] Nenov A, Rivalta I, Cerullo G, Mukamel S, Garavelli M *J. Phys. Chem. Lett.* **2014**, 5, 767–771