Photochemistry of alkaloids in the gas phase - Work plan.

This project focuses on the chirality and stereochemical effects on the structure and photostability of biomolecules in the gas phase, from both experimental and theoretical points of view. It is a three-years project led within the frame of the thesis of Feriel Ben Nasr, with co-mentoring by both the Orsay (Anne Zehnacker) and Tunis (Nejm-Eddine Jaïdane) groups. The experiments combines and UV or IR laser spectroscopy and supersonic expansions, in the Institut des Sciences Moléculaires d'Orsay or Infrared Multiple photons dissociation spectroscopy and mass spectrometry in collaboration with Debora Scuderi, Laboratoire de Chimie Physique and CLIO (IR Free Electron Laser in Orsay). The project involves an large contribution of quantum chemical calculations, for determining the most stable structures in the ground state and the nature of the electronic exited states which dictate the photoreactivity of the systems.

The first year, for which STSM is applied, is devoted to the photoreactivity of protonated cinchona alkaloids (Figure 1) for which a dramatic effect of chirality and of complexation with H_2SO_4 has been observed. Of special interest is the comparison of of quinine and quinidine, which are called "pseudo-enantiomers" because two of their chiral centers, C_8 and C_9, are of opposite chirality. The structure of their neutral and protonated form as well as that of their protonated dimer has been determined previously and is dependent, in case of the dimer, on stereochemistry[1,2] These molecules and their protonated dimers exhibit a very rich photoreactivity which also depend on the pseudo enantiomer[1,3]

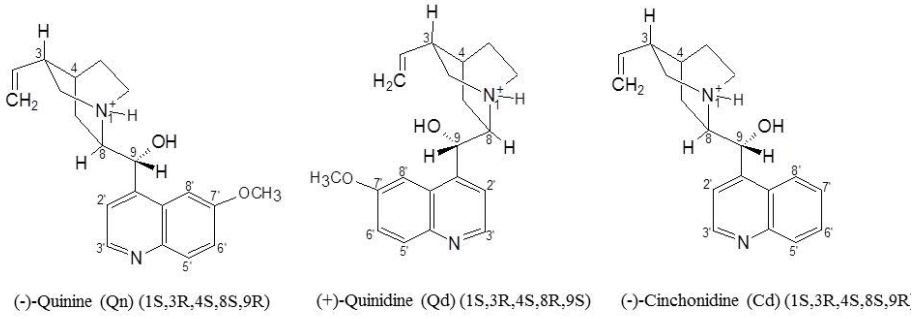

Figure 1: Cinchona alkaloid under study.

The structure of the model system cinchonidine/H_2SO_4 protonated complex is currently under theoretical investigation by the candidate during a six weeks internship in Orsay, to interpret the experimental vibrational spectrum. That of the $(cinchonidine)_2H^+/H_2SO_4$ ternary complex will be investigated during the next visit, for which funding is applied there. This first achievement should result in one publication in 2016. The visit is planned between 15th October 2015 and 15th January 2016 so that the candidate can also participate in experimental runs in the free electron laser facility in Orsay (CLIO) planned in October 2015. The second year of the project will focus on the description of the electronic excited states of the systems mentioned above, to explain the dramatic difference in photo-reactivity between protonated cinchonidine or its dimer when bare or complexed with H_2SO_4. The third year of this project will consist in extending the experimental studies to other cinchona alkaloid complexes, involving for example amino-acids and understand the strong chirality effects observed in these systems.

(1) Scuderi, D.; Maitre, P.; Rondino, F.; Le Barbu-Debus, K.; Lepere, V.; Zehnacker-Rentien, A. *Journal of Physical Chemistry A* **2010**, *114*, 3306.

(2) Sen, A.; Le Barbu-Debus, K.; Scuderi, D.; Zehnacker-Rentien, A. *Chirality* **2013**, *25*, 436.

(3) Zehnacker, A. *International Reviews in Physical Chemistry* **2014**, *33*, 151