Exploring excited state potential energy profile and luminescence properties of uranyl complexes by combination of TRLFS and *ab initio* methods

Hanna Oher, Florent Réal, Thomas Vercouter, Valérie Vallet

Exploring excited state potential energy profile and luminescence properties of uranyl complexes by combination of TRLFS and *ab initio* methods

H. Oher,[1,2] F. Réal,[1] T. Vercouter[2], V. Vallet[1]

[1] Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France
[2] DEN – SEARS, CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France

☐ oral ■ poster

Uranyl complexes have been the subject of many research works for fundamental chemistry of actinides, environmental issues, or nuclear fuel cycle processes. The formation of various uranyl complexes, with organic and inorganic ligands in solution must be characterized for a better understanding of uranium speciation. Because uranyl-ligand interactions and symmetry of the complexes affect the electronic structure of U(VI) and thus its luminescence properties, time-resolved laser induced fluorescence spectroscopy (TRLFS) is one of the major techniques for speciation analysis, with high sensitivity and selectivity to U(VI).

However, most of the relevant systems have complex chemical composition in solution and the identification of each species from spectroscopic data remains a tricky issue. Nowadays, combination of experimental and theoretical methods of investigation became quite effective and progressive. In our study, the balance of highly sensitive and selective to heavy metals method such as TRLFS and *ab initio* based interpretation allows a better description of the complexation data.

Luminescence spectra of uranyl complexes in solution show in general a narrow energetical range about 6000 cm^{-1} and we can identify mainly a single electronic transition between the initial and target states with the vibrationally resolved band [1].

The main challenge consists in exploring a computationally cheap, fast and effective theoretical approach, in a relativistic context, to characterize the first excited state of uranyl compounds (*i.e.* $UO_2Cl_4^{2-}$) after the photo-excitation and compute with high accuracy vibronic progression observed in experiments. First results obtained at different levels of DFT methods, with or without spin-orbit coupling, will be presented.
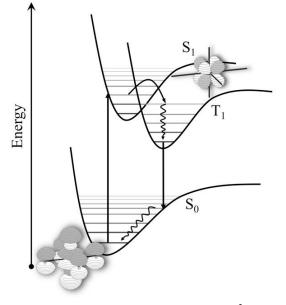

Figure 1 Energy transfer in $UO_2Cl_4^{2-}$ between ground and excited states during excitation and emission processes.

[1] J. Visnak and L. Sobec (2016) EPJ Web of Conferences.