AB INITIO INVESTIGATION OF trans-[RuCl(NO)(py)$_4$]$^{2+}$ PHOTOCHEMISTRY

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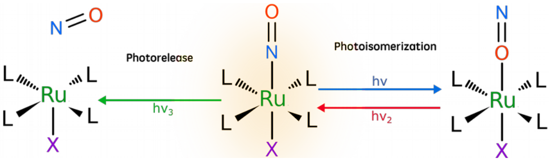
Ruthenium nitrosyl complexes have found utility in a variety of applications, such as optical switches, data storage, and medicine. Depending on the ancillary ligands, environment, and irradiation wavelength, these complexes can undergo either intramolecular NO linkage photoisomerization or NO photorelease (Figure 1). In the last two years, DFT studies of both the NO linkage photoisomerization and photorelease process in the trans-[RuCl(NO)(py)$_4$]$^{2+}$ complex revealed a complex two-step photoisomerization mechanism involving a sequential two-photon absorption.[1,2] This mechanistic picture has been confirmed experimentally recently.[3] The DFT study was based on the exploration of the lowest singlet and triplet potential energy surfaces, assuming efficient decay via intersystem crossing (ISC) from the first singlet excited state to the lowest triplet state. It would therefore be desirable to verify this hypothesis by determining the possible pathways for ISC along with the spin-orbit couplings responsible for such radiationless transitions. In addition, the role of other excited states has not been investigated so far and it is interesting to know what are their potential roles in the photoisomerization mechanism. It is important to verify that a single-configuration-based method such as DFT can be reliable to describe complex photochemical mechanisms such as the ones studied here.[4] Thus, in this seminar I will present the results of accurate ab initio MS-CASPT2 calculations and TD-DFT method on the trans-[RuCl(NO)(py)$_4$]$^{2+}$ complex, obtained during the first year and a half of my PhD at LCPQ. The presentation will cover: i) the main ISC pathway after initial photoexcitation ii) the photoisomerization pathways iii) the assessment of different DFT functionals against CASPT2 results.



[1] J. S. Garcia et al. *J. Mol. Model.*, **2016**, 11, 284.

[2] J. S. Garcia et al. *Inorg. Chem.*, **2015**, 54, 8310.

[3] L. Khadeeva et al. *Inorg. Chem*, **2016**, 55, 4117.

[4] M. G. Delcey et al. *J. Chem. Phys.*, **2014**, 140, 174103.