

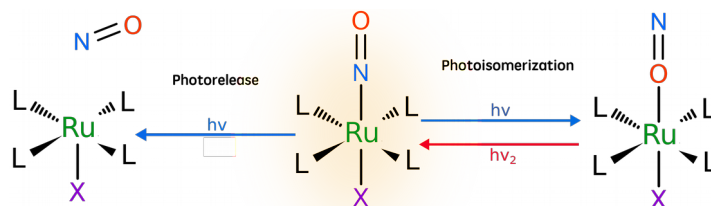
# A THEORETICAL INVESTIGATION OF THE TRANS-[RuCl(NO)(py)<sub>4</sub>]<sup>2+</sup> PHOTOCHEMISTRY

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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)<sub>4</sub>]<sup>2+</sup> 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. Further ab initio CASSCF/CASPT2 calculations performed during last year, supported and completed the DFT and experimental findings. In particular, the spin-orbit coupling outcomes helped to uncover the first steps of the photoisomerization process, suggesting an efficient singlet to triplet intersystem crossing after light absorption. At the same time, the topology of the CASPT2 potential energy surfaces highlighted the possibility of several photoisomerization pathways. It would therefore be desirable to verify these hypotheses, by determining the most probable pathways along with the spin-orbit couplings responsible for radiationless transitions. In addition, the role of the excited states in the NO photorelease process has not been investigated so far, and it is interesting to know what is their potential role. 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 my presentation I will present the results of ab initio and DFT calculations on the trans-[RuCl(NO)(py)<sub>4</sub>]<sup>2+</sup> complex that describe i) the absorption spectra of the involved isomers. ii) the complete ab initio photoisomerization pathways. iii) the preliminary results for the NO photorelease mechanism. iv) the assessment of the DFT and TD-DFT results.



## References

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- [4] L. Freitag *et al.*, *Phys. Chem. Chem. Phys.*, **2015**, 17, 14383.