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Photo-isomerization in a model of ruthenium nitrosyl compound: two-step photon absorption process

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By means of visible absorption spectroscopy and X-Ray diffraction the photo-switching between the ground state nitrosyl (GS), isonitrosyl (SI) and side-on (SII) configurations under continuous light irradiation is studied in the $\text{PF}_6\text{-Ru}(\text{py})_4\text{Cl}(\text{NO})_2 \cdot 1/2\text{H}_2\text{O}$ system^[1]. It is a remarkable model compound in the family of systems containing $[\text{ML}_5\text{NO}]$ molecule, where $\text{M}=\text{Fe}, \text{Ru} \dots$ and $\text{L}=\text{F}, \text{Cl} \dots$ and usually only few percent of metastable populations^[2], as its GS to SI transformation efficiency is close to 1^[3]. This makes ruthenium nitrosyl system a perfect candidate for the photoisomerization studies. Moreover, study of this compound could also help in understanding another photo-chemical process, such as NO release, where SI and SII metastable states are suggested to be the intermediate steps before the formation of NO radical^[2].

A predominant two-step photon absorption process during GS to SI switching under blue light is shown. During the depopulation of SI, both two-step and direct processes are evidenced under red light. With infra-red excitation, SII is significantly populated before a thermal relaxation to GS, as shown by specific structural and optical signatures. In addition, different optical spectra associated with transient species (SII) during GS to SI and reverse processes will be discussed in relation with SII properties.

[1] L. Khadeeva et al, submitted

[2] R.v. Eldik, J.A. Olabe, *NOx Related Chemistry*, Ac. Press, Waltham, 2015.

[3] B. Cormary et al, *Acta Cryst.*, 2009, B65, 612-623.

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