Oral presentation

In-situ monitoring of structure and optical properties of molecular photoswitches

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Molecular photoswitches bear significant potential for designing functional materials whose properties can be controlled by optical stimulation (see e.g. [1,2]). It is important to understand the underlying switching mechanisms as well as the influence of the photoswitch's environment on the resulting material properties. Precise knowledge of the photochromic properties is essential for applications, and hence the measurement of the absorption spectra in parallel to the molecular structure of the photoswitchable material is necessary. We are particularly interested in photoswitches based on photoinduced linkage isomers (PLI) that can be generated in metal nitrosyl compounds, and which offer interesting photochromic and photorefractive properties [3].

We present a laboratory single-crystal X-ray diffraction (XRD) setup allowing for in-situ measurement of static and time-resolved absorption properties after continuous wave (cw) or pulsed Laser excitation of the sample. The time-resolution of the optical experiments is nanoseconds while the time resolution of the XRD is milliseconds. Using this setup, we can investigate the generation and relaxation of PLI, e.g., in a ruthenium nitrosyl compound we could monitor the two-step generation of one PLI via a second PLI (see Figure 1) [4]. While low-temperature static photocrystallography after cw or pulsed Laser excitation provides accurate structures for the different PLI configurations, time-resolved photocrystallography on the millisecond time scale gives access to transient or metastable species [5]. In combination with in-situ static and transient absorption spectroscopy, complemented by infrared spectroscopy, the two-step mechanism from the linear Ru-N-O ground state (GS) structure over the side-on MS2 structure to the linear Ru-O-N structure can be monitored optically and structurally.

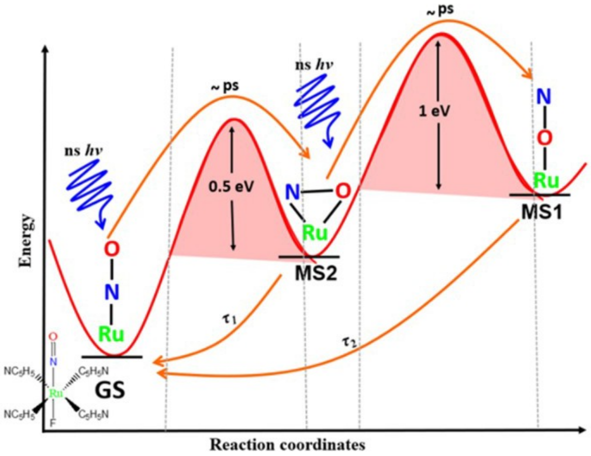

Figure 1. Two-step process for the generation of Ru-O-N (MS1) from Ru-N-O (GS) as monitored by XRD and optical spectroscopy

[1] Goulet-Hanssens, A., Eisenreich, F. & Hecht, S. (2020). *Adv. Mater.* **32**, 1905966.

[2] Zhao, J.-L., Li, M.-H., Cheng, Y.-M., Zhao, X.-W., Xu, Y., Cao, Z.-Y., You, M.-H., Lin & M.-J. Chupas, (2023). *Coord. Chem. Rev.* **475**, 214918.

[3] Schaniel, D., Imlau, M., Weisemoeller, T., Woike, T., Krämer, K. W. & Güdel, H.-U. (2007). *Adv. Mater.* **19**, 723.

[4] Hasil, A., Konieczny, K.A., Mikhailov, A., Pillet, S & Schaniel D. (2024). *ChemPhotoChem.* **8**, e202300149.

[5] Casaretto, N., Schaniel, D., Alle, P., Wenger, E., Parois, P., Fournier, B., Bendeif, E.-E., Palin, C. & Pillet S. (2017) *Acta Cryst. B***73**, 696.

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