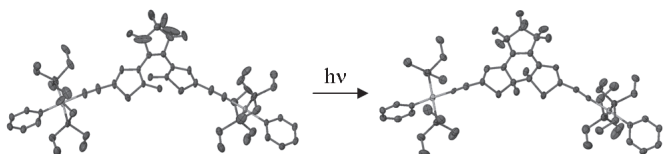


activation, the activated species returns to its original state or, (ii) irreversible processes where a new species is obtained. We have been investigating both types of process.

A series of octahedral nickel(II) nitro complexes display high levels of conversion from the nitro linkage isomer to the nitrito linkage isomer when photoactivated with blue or UV light, at low temperatures, in the single crystal. The nitrito isomers are metastable, and if the temperature is raised above 200 K, the structures revert to the nitro isomer. Examples of systems that display this phenomenon include $[\text{Ni}(\text{dppe})(\text{Cl})(\text{NO}_2)]$ [1] and $[\text{Ni}(\text{Et}_4\text{dien})(\text{NO}_2)_2]$ ($\text{Et}_4\text{dien} = N,N,N',N'$ -tetraethyldiethylenetriamine) [2].

In our studies of irreversible processes, we have established that high conversions of the open form to the closed form of dithienylethene (DTE) ligands in platinum and gold diyne complexes. The ring closing photoconversion in a single crystal of $[\text{Pt}(\text{PEt}_3)_2(\text{C}\equiv\text{C})(\text{DTE})(\text{C}\equiv\text{C})\text{Pt}(\text{PEt}_3)_2\text{Ph}]$ occurs with the extremely high yield of 80% [3].



[1] M.R. Warren, S.K. Brayshaw, A.L. Johnson, S. Schiffers, P.R. Raithby, T.L. Easun, M.W. George, J.E. Warren, S.J. Teat, *Angew. Chem.-Int. Edit.* **2009**, *48*, 5711-5714. [2] L.E. Hatcher, M.R. Warren, D.R. Allan, S.K. Brayshaw, A.L. Johnson, S. Fuertes, S. Schiffers, A.J. Stevenson, S.J. Teat, C.H. Woodall, P.R. Raithby, *Angew. Chem.-Int. Edit.* **2011**, in press. [3] S.K. Brayshaw, S. Schiffers, A.J. Stevenson, S.J. Teat, M.R. Warren, R.D. Bennett, I.V. Sazanovich, A.R. Buckley, J.A. Weinstein, P.R. Raithby, *Chem. Eur. J.* **2011**, *17*, 4385-4395.

Keywords: photochemistry, metastable, isomerism

MS.80.3

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Real Time Dynamics of Solid Molecular Switches and "Machines" Investigated with Ultrafast Pulsed X-ray Radiation

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Common for all our time-resolved x-ray experiments is the applied pump/probe scheme, where an optical pump-laser initiates a reaction whose structural time evolution is then investigated by x-ray probe pulses at various time delays. In the present contribution we will refer to our work in time-resolved x-ray diffraction of organic solids. We will reflect capabilities and limitations of state-of-the-art time resolved x-ray diffraction for the investigation of different kind of molecular switches and motors in the crystalline phase. Besides our time-resolved Laue and diffuse scattering work, we will discuss our current status in reaching this goal (proof-of-principle experiments) with free electron laser radiation and how the investigation of chemical reactions benefits from pulsed synchrotron radiation and free electron laser science as they have been performed at the FLASH facility and at LCLS.

The data will be compared to recent results collected at ultrafast pulsed table-top x-ray sources. General features of structural dynamics in solid molecular switches and motors will be presented.

Keywords: time-resolved diffraction, laue diffraction, free electron laser radiation

MS.80.4

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Time-resolved photo-crystallography of ruthenium sulfur-dioxide complexes

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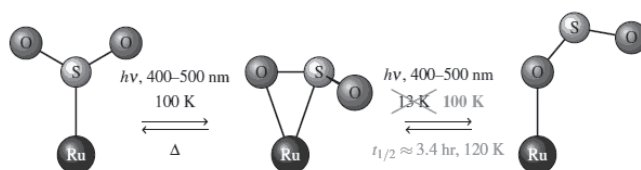
Time-resolved solid-state photo-isomerism is presented in a ruthenium (II) sulfur dioxide based complex, $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4(\text{H}_2\text{O})][\text{C}_{10}\text{H}_{15}\text{O}_4\text{S}]_2$, using the developing technique, photo-crystallography [1-4]. Such materials are of interest due to their potential for optical data storage applications.

Previously, single-crystal to single-crystal photo-isomerism of the SO_2 ligand has been demonstrated in these complexes whereby the original ground-state, $\eta^1\text{-SO}_2$ (Fig. 1, left) photo-converts to form metastable species: side-bound coordinated $\eta^2\text{-SO}_2$ at 100K (Fig. 1, centre) [5] and, additionally, O-bound $\eta^1\text{-OSO}$ when at 13K (Fig. 1, right) [6].

Here, it is shown, for the first time, that the $\eta^1\text{-O}$ -bound OSO photo-isomer can exist above liquid nitrogen temperatures [7]. We show that this $\eta^1\text{-O}$ SO photoisomer is not metastable at 100K; rather, it has a finite lifetime and decays to the more stable $\eta^2\text{-S-O}$ O photoisomer, in a fashion that is consistent with first-order kinetics. While hints of $\eta^1\text{-OSO}$ have been noted in photo-induced FTIR studies [5], our photo-crystallography studies provide the first clear evidence of its existence. The thermodynamic quantification of its decay, monitored by time-resolved photocrystallography, is the first of its kind; it has the particular merit that it grounds the topic on a thermodynamic crystallographic footing.

New paradigms to describe these 4-D (space-time) photo-induced transformations are presented as an alternative to the more conventional thermodynamic equilibria description. The need for this new schematic descriptor for time-resolved photo-crystallography is explained in the context of the subject example as well as other studies.

The paper concludes with the exposition of new computational work with aims to rationalize the distribution of the various photo-converted species and investigates possible photo-induced cooperativity mechanisms. This leads to the 'smart material' design and prediction of new ruthenium sulfur dioxide complexes with improved and more controlled photo-conversion efficiencies and wider optical applications.



[1] J.M. Cole, *Chem. Soc. Rev.* **2004**, *33*, 501-513. [2] J.M. Cole, *Analyst*, **2011**, *136*, 448-455. [3] J.M. Cole, *Acta Crystallogr. A* **2008**, *64*, 259-271. [4] J.M. Cole, *Zeit. Krist.* **2008**, *223*, 363-369. [5] A.Y. Kovalevsky, K.A. Bagley, J.M. Cole, P. Coppens, *Inorg. Chem.* **2003**, *42*, 140-147. [6] K.F. Bowes, J.M. Cole, S.L.G. Husheer, P.R. Raithby, T.A. Savarese, H.A. Sparkes, S.J. Teat, J.E. Warren, *Chem. Commun.* **2006**, 2448-2450. [7] A.E. Phillips, J.M. Cole, T. d'Almeida, K.S. Low, *J. Am. Chem. Soc.* **2011** (in preparation).

Keywords: photochemistry, kinetics, photostimulated