

Monitoring of the ultrafast vibrational kinetic during formation of photo-induced linkage isomers in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ single crystal

G. Galle¹, M. Nicoul², Th. Woike³, D. Schaniel⁴ and E. Freysz¹

¹University of Bordeaux, CNRS-UMR 5798, LOMA, 351 cours de la Libération, Talence 33405, France

²Physikalisches Institut, Universität zu Köln, Zùlpicherstr. 77, 50937 Köln, Germany

³Institut für Strukturphysik, TU-Dresden, Zellescherweg 16, Dresden, Germany

⁴CRM2, Institut Jean Barriol, Nancy Université, 54506 Vandoeuvre-les-Nancy, France

Abstract. A femtosecond visible pump - infrared probe time resolved absorption experiment makes it possible to reveal the ultrafast vibrational kinetic associated to formation of light-induced linkage isomers in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ (SNP) single crystals.

Time-resolved spectroscopy on a femtosecond scale makes it possible to observe and to record photochemical processes [1-2]. The ultrafast study of electronic, vibrational and structural changes during light-induced isomerization reveals the correlation between the changes of the electron density and the structural response of matter. Consider an electronic transition that excites a molecule from a (bonding) ground state to an (reactive) excited state that is the starting point for, e.g., the rotation of a ligand in a molecule. According to the Born-Oppenheimer approximation the direct electronic excitation in the sub-femtosecond range is followed by a slower nuclear response in the fs-ps range. The nuclear motion (e.g. rotation) of the ligand starts in a highly excited state and in the absence of luminescence will end in highly excited vibrational-rotational states of the novel geometry. The excess energy will be dissipated during the thermalization of this highly excited vibrational-rotational state towards its ground state. A typical example for such ultrafast photochemical processes is the photo-induced linkage isomerism of the nitrosyl ligand in coordination complexes [3]. Here we study the prototypic case of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ anion. As shown in Figure 1 the ground state (GS) is characterized by a linear Fe-N-O coordination. The irradiation with light in the blue-green spectral range (e.g. $\lambda \sim 500$ nm) induces a charge-transfer transition. Thereby the system changes symmetry from a 1A_1 state to a 1E doubly degenerate state. As a consequence the doubly degenerate deformational mode $\delta(\text{Fe-N-O})$ can induce a rotation of the NO ligand. The rotation of about 90° yields the side-on configuration of $\text{Fe}-\text{O}^{\leftarrow\text{N}}$ (metastable state MS2) while a rotation of 180° results in the isonitrosyl configuration Fe-O-N (metastable state MS1). The transition from the excited ground state 1E towards MS2 occurs radiationless in about 300 ± 30 fs [3]. In the case of the NO ligand the structure of GS and the metastable states MS1 and MS2 is known from X-ray and neutron diffraction measurements at low temperatures in the static regime [4,5,6]. Moreover, the GS, MS1, and MS2 have clearly distinguished $\nu(\text{NO})$ vibration frequency centered at 1961 cm^{-1} (5100 nm), 1831 cm^{-1} (5460 nm) and 1631 cm^{-1} (6130 nm) respectively [7]. Hence optical

This is an Open Access article distributed under the terms of the Creative Commons Attribution License 2.0, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

pump and infrared probe time resolved absorption spectroscopy offers to the possibility to monitor the vibrational kinetic during photo-induced isomerization and makes an unambiguous identification of the corresponding relaxation pathways possible.

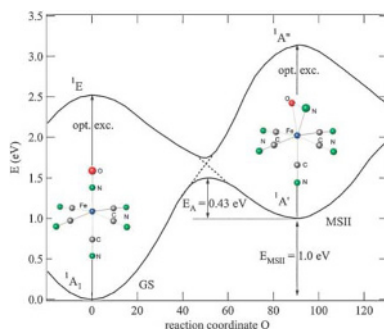


Fig. 1: Potential scheme for the formation of the side-on bound isomer MS2 in $[\text{Fe}(\text{CN})_5\text{NO}]^2$

Our experimental set-up is based on a 1 kHz Ti:Sapphire regenerative amplifier system producing 50 fs, 4.5 mJ laser pulses centered at 800 nm (Coherent Legend USP + Legend Duo Elite). The output of the laser system was split in two 1 mJ laser pulses which pumped two Optical Parametric Amplifiers (OPA, Model TOPAS from Light Conversion). The pump beam generated by the first OPA centered at $\lambda \sim 500$ nm and of energy of about 9 μJ was focused in the sample. The second OPA was equipped with a Degenerate Frequency Generation (DFG) module for the generation in the spectral range in between 2500 nm -10.000 nm. The output energy is at maximum about 4 μJ in the 4000 nm (2500 cm^{-1}) to 6000 nm (1666 cm^{-1}) spectral range. The probe pulse energy used in our experiment was at least ten times lower than the pump pulse energy. The pump and probe pulses have duration of $\sim 100 \pm 20$ fs and 200 ± 50 fs respectively. The used sample is a 270 μm thick single crystals of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. It is orthorhombic (Pnmm) and was b-cut. We set the pump-polarization parallel c-axis while the probe polarization is parallel to a axis. All measurements were performed at room temperature.

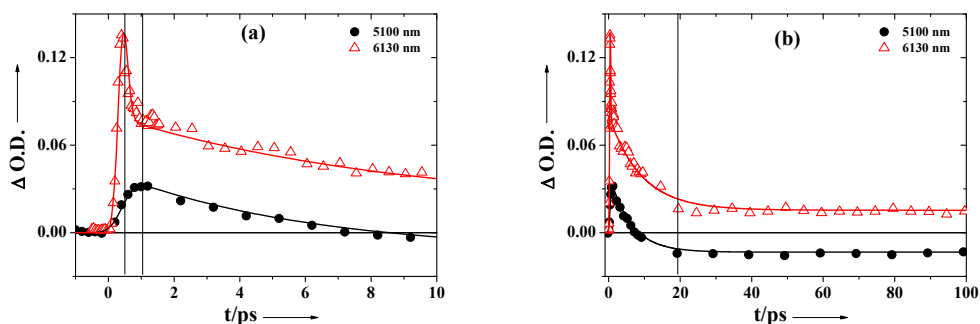


Fig. 2: Transient change of the optical density of the sample recorded for 1961 cm^{-1} (●) and 1631 cm^{-1} (Δ) as a function of the pump-probe delay. The solid lines are fits of the experimental data.

Figure 2 shows the temporal evolution of the optical density of the sample measured for the probe pulses centered along the $\nu(\text{NO})$ -vibration of GS (1961 cm^{-1}) and MS2 (1631 cm^{-1}) states after

pump excitation. In all cases, the absorption increases during ~ 300 fs, that is about the pump-probe temporal overlap. The increase of the $\nu(\text{NO})$ -vibrations at 1631 cm^{-1} indicates the destabilization linear Fe-N-O arrangement in the ${}^1\text{E}$ excited state. The increase of the $\nu(\text{NO})$ -vibrations at 1961 cm^{-1} also reveals the higher cross section absorption of this vibration in this state. In good agreement with previous work, the ${}^1\text{E}$ excited state is found to last $\sim 250 \pm 30$ fs. This accounts for the rapid decrease of the recorded absorption at 1631 cm^{-1} (MS2) as well as the increase of the absorption at 1961 cm^{-1} (GS). The latter increase is due to the fact that 95% of the photo-excited complexes relax back to the fundamental state where they are lived in a highly vibrationally excited state [3]. Then, they relax vibrationally towards the minimum of the potential well with a constant time of 5.8 ± 0.4 ps. About 5% of the N-O ligand of the photo-excited complexes rotates by 90° . Once in the MS2 potential well, they are in a vibrationally excited state that is thermalized in about 9.5 ± 0.5 ps. The positive and negative absorption recorded at the nanosecond time scale at 1631 cm^{-1} and 1961 cm^{-1} is the fingerprint of the MS1 photo-induced linkage isomer. This isomer has been shown to relax in ~ 270 ns [3]. As shown in Figure 3, these time-resolved measurements make it possible to picture the electronic and vibration evolution during formation of photo-induced linkage isomers in this crystal.

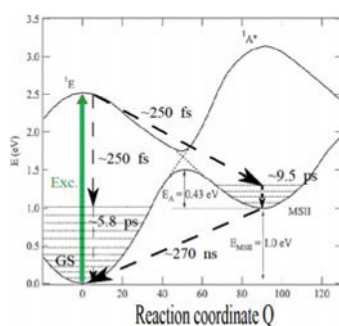


Fig. 3: Vibrational kinetic of the of SNP single crystals after a pulsed excitation centered at 500 nm

References

- [1] A. H. Zewail, *J. Phys. Chem.* 97, 12427 (1993)
- [2] F. C. de Schryver, S. de Feyter, G. Schweitzer, *Femtochemistry*, (Wiley-VCH, Weinheim 2001).
- [3] D. Schaniel, M. Nicoul, Th. Woike, *Phys. Chem. Chem. Phys.* 12, 9029 (2010).
- [4] M. D. Carducci, M. R. Pressprich, P. Coppens, *J. Am. Chem. Soc.* 119, 2669 (1997).
- [5] D. Schaniel, Th. Woike, J. Schefer, V. Petricek, *Phys. Rev. B* 71, 174112 (2005).
- [6] D. Schaniel, Th. Woike, J. Schefer, V. Petricek, K. W. Krämer, H. U. Güdel, *Phys. Rev. B* 73, 174108 (2006).