

## 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

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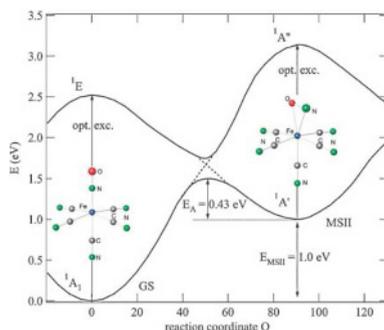
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**Abstract.** A femtosecond visible pump - infrared probe time resolved absorption experiment makes it possible to reveal the ultrafast vibrational kinetic associated to formation of light-induced linkage isomers in  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  (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  $90^\circ$  yields the side-on configuration of  $\text{Fe}-\text{O}-\text{N}$  (metastable state MS2) while a rotation of  $180^\circ$  results in the isonitrosyl configuration  $\text{Fe}-\text{O}-\text{N}$  (metastable state MS1). The transition from the excited ground state  ${}^1E$  towards MS2 occurs radiationless in about  $300 \pm 30$  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  $1961 \text{ cm}^{-1}$  (5100 nm),  $1831 \text{ cm}^{-1}$  (5460 nm) and  $1631 \text{ cm}^{-1}$  (6130 nm) respectively [7]. Hence optical

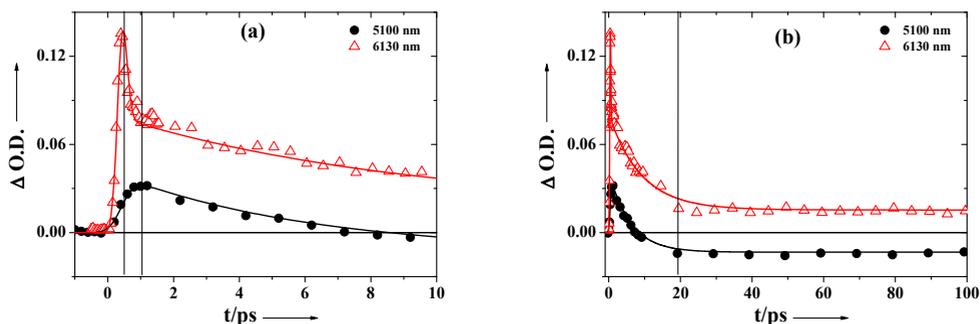
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pump and infrared probe time resolved absorption spectroscopy offers to the possibility to monitor the vibrational kinetic during photo-induced isomerization and makes an unambiguous identification of the corresponding relaxation pathways possible.



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

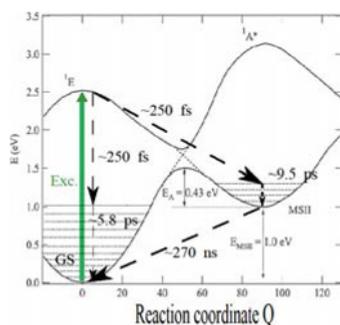
Our experimental set-up is based on a 1 kHz Ti:Sapphire regenerative amplifier system producing 50 fs, 4.5 mJ laser pulses centered at 800 nm (Coherent Legend USP + Legend Duo Elite). The output of the laser system was split in two 1 mJ laser pulses which pumped two Optical Parametric Amplifiers (OPA, 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  $\mu\text{J}$  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  $\mu\text{J}$  in the 4000 nm ( $2500\text{ cm}^{-1}$ ) to 6000 nm ( $1666\text{ cm}^{-1}$ ) 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  $200 \pm 50$  fs respectively. The used sample is a 270  $\mu\text{m}$  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  $1961\text{ cm}^{-1}$  (●) and  $1631\text{ cm}^{-1}$  (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 ( $1961\text{ cm}^{-1}$ ) and MS2 ( $1631\text{ cm}^{-1}$ ) states after

pump excitation. In all cases, the absorption increases during  $\sim 300$  fs, that is about the pump-probe temporal overlap. The increase of the  $\nu(\text{NO})$ -vibrations at  $1631\text{ cm}^{-1}$  indicates the destabilization linear Fe-N-O arrangement in the  ${}^1\text{E}$  excited state. The increase of the  $\nu(\text{NO})$ -vibrations at  $1961\text{ cm}^{-1}$  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  $1631\text{ cm}^{-1}$  (MS2) as well as the increase of the absorption at  $1961\text{ cm}^{-1}$  (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  $5.8 \pm 0.4$  ps. About 5% of the N-O ligand of the photo-excited complexes rotates by  $90^\circ$ . Once in the MS2 potential well, they are in a vibrationally excited state that is thermalized in about  $9.5 \pm 0.5$  ps. The positive and negative absorption recorded at the nanosecond time scale at  $1631\text{ cm}^{-1}$  and  $1961\text{ cm}^{-1}$  is the fingerprint of the MS1 photo-induced linkage isomer. This isomer has been shown to relax in  $\sim 270$  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

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