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To cite this version:
M Galle, M Nicoul, Theo Woike, Dominik Schaniel, E Freysz. Monitoring of the ultrafast vibrational kinetic during formation of photo-induced linkage isomers in Na₂[Fe(CN)₅NO]. 2H₂O single crystal. XVIIIth International Conference on Ultrafast Phenomena, Jul 2012, Lausanne, Switzerland. pp.05005, 10.1051/epjconf/20134105005. hal-01522054

HAL Id: hal-01522054
https://hal.univ-lorraine.fr/hal-01522054
Submitted on 12 May 2017

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

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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 Na$_2$[Fe(CN)$_5$NO]$_2$H$_2$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 [Fe(CN)$_5$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 $\delta$(Fe-N-O) can induce a rotation of the NO ligand. The rotation of about 90° yields the side-on configuration of Fe-$^N$O (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 $\nu$(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

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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 [Fe(CN)₅NO]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 λ~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 ~100 ±20 fs and 200±50 fs respectively. The used sample is a 270
µm thick single crystals of Na₂[Fe(CN)₅NO]·2H₂O. It is orthorhombic (Pnnm) 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 ν(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 ν(NO)-vibrations at 1631 cm$^{-1}$ indicates the destabilization linear Fe-N-O arrangement in the $^1$E excited state. The increase of the ν(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 $^1$E excited state is found to last ~250±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: Vibrationnal kinetic of the of SNP single crystals after a pulsed excitation centered at 500 nm

References