



	Experiment title: Systematic mapping of the excited quintet state potentials in model Fe-based molecular photoswitches	Experiment number: CH-5824
Beamline:	Date of experiment: from: 12 May 2021 to: 18 May 2021	Date of report: 27/02/2023
Shifts:	Local contact(s): Matteo Levantino and Serhane Zerdane.	<i>Received at ESRF:</i>
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Summary:

We have performed X-ray Solution Scattering (XSS) on 7 different photoexcited $[\text{Fe}(4'\text{-R-terpy})_2]^{2+}$ complexes in aqueous solution. The energy of the quintet state in these complexes was tuned using different electron donating/withdrawing (ED/EW) groups at the 4' position. The quintet structures estimated from the experimental data show good agreement with the calculated DFT structures. Also, the measured relaxation times match the transient optical absorption spectroscopy (TOAS) measurements. However, the energy differences derived from the time-dependent temperature change of the solvent seems unreliable, which is linked to the probably ambiguous excitation yield. We tried to apply X-ray emission spectra (XES) using the von Hámos spectrometer of the beamline to follow the quintet population, however, that instrument turned out not efficient enough under the conditions of our experiment.

The analysis of the data has resulted in two M.Sc. thesis:

- B.L. Hansen: Ultrafast X-ray investigations of the excited state potential energy levels in a series of modified $[\text{Fe}(\text{terpy})_2]^{2+}$ systems, DTU, Lyngby, Denmark, 2022, and
- A.J. Mikeházi: Pump-probe scattering experiments on the ultrafast time scale, BME, Budapest, 2022.

Moreover, we are preparing a manuscript, in which we contrast the observed structural variations to theory, and compare the lifetimes observed in XSS with those obtained from TOAS.

However, to arrive at conclusions on the quintet energies, a more complete set of experimental data is needed, which also includes XES for a precise determination of the quintet population. For this we plan to submit a continuation proposal.

Detailed Report:

We have performed a preliminary time resolved and structural analysis on the aqueous solution of the 7 sample derivatives of the $[\text{Fe}(4'\text{-R-terpy}_2)]^{2+}$ (with R = SO₂Me, COOH, H, Cl, SMe, OMe, and OH) measured with X-ray Solution Scattering (XSS, i.e. liquid-phase WAXS). The experiments were conducted with an excitation wavelength of 560 nm, laser flux on the sample of 9.5 um, X-ray energy of 18 keV and sample concentration of 5-10 mM. Water was chosen for a solvent from handling and safety considerations, as the experiment was performed with limited manpower: this was done in COVID-afflicted times, when from the group in the Wigner Center only a single person was qualified to participate on site, having doubly vaccinated. The two main objectives of the experiment were to test the structure of the quintet states and measure the energy difference between the quintet-singlet states. The preliminary study shows publishable results for the systematic analysis of the quintet structure but not for the calorimetry study of the singlet-quintet energy.

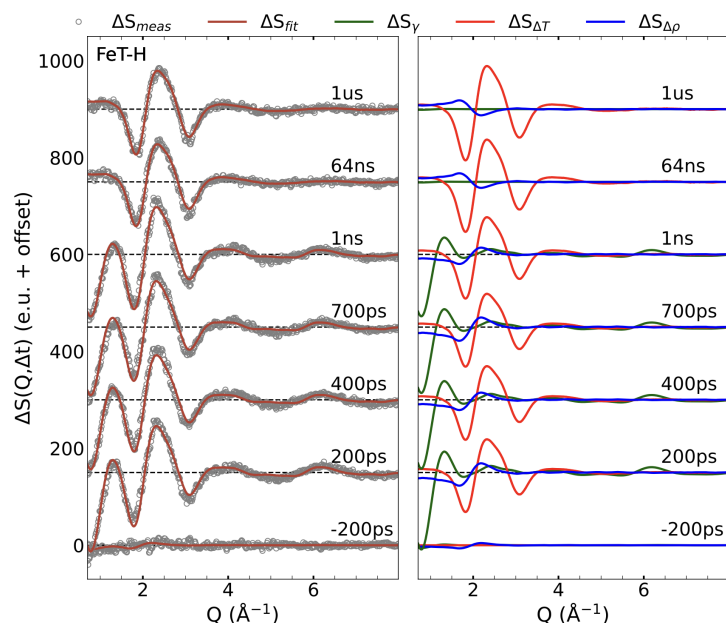
X-ray Solution Scattering (XSS)

The XSS analysis assumes a model of three contributors:

$$\Delta S_{meas} = \gamma \cdot \Delta S_{\gamma} + \Delta T \cdot \Delta S_{\Delta T} + \Delta \rho \cdot \Delta S_{\Delta \rho}$$

where ($\Delta S_{\gamma} = \Delta S_{solute} + \Delta S_{cross}$) is DFT-derived difference scattering signal from solute-only contribution and solute-solvent contribution (cross). $\Delta S_{\Delta T}$ and $\Delta S_{\Delta \rho}$ are measured reference solvent differentials from earlier

ID09 pink beam measurements (K. Kjær et al., *Physical Chemistry Chemical Physics*, 2013). The following figure shows a representative set of measured difference signal curves for the $[\text{Fe}(4'\text{-H-terpy}_2)]^{2+}$ system (denoted FeT-H) with fits and corresponding signal strengths of the three contributions. The fit is performed in a Q-range of 0.7 to 8 Å⁻¹. Generally, good fits can be seen for all time delays. The fit captures the relaxation of the quintet state (decline of the ΔS_{γ} signal magnitude) and how the relaxation energy is transformed to heating of the solvent (increase in $\Delta S_{\Delta T}$ signal magnitude). The parameters of the quintet structures providing the best fit are listed in Table1 and compared to the DFT relaxed structure parameters.



The time evolution of the magnitude of each of the three model contributions is illustrated in the figure below together with a model fit for the excitation fraction γ and change in temperature ΔT . The γ -model is given by:

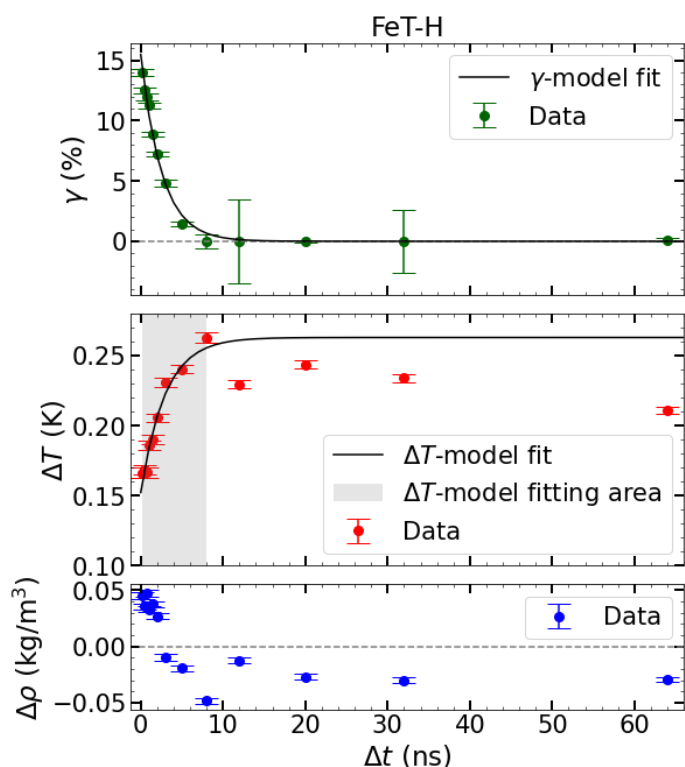
$$\gamma_{Model} = \gamma_0 \cdot \exp(-\Delta t/\tau)$$

with γ_0 denoting initial excitation fraction and τ the relaxation time between quintet and singlet state. The

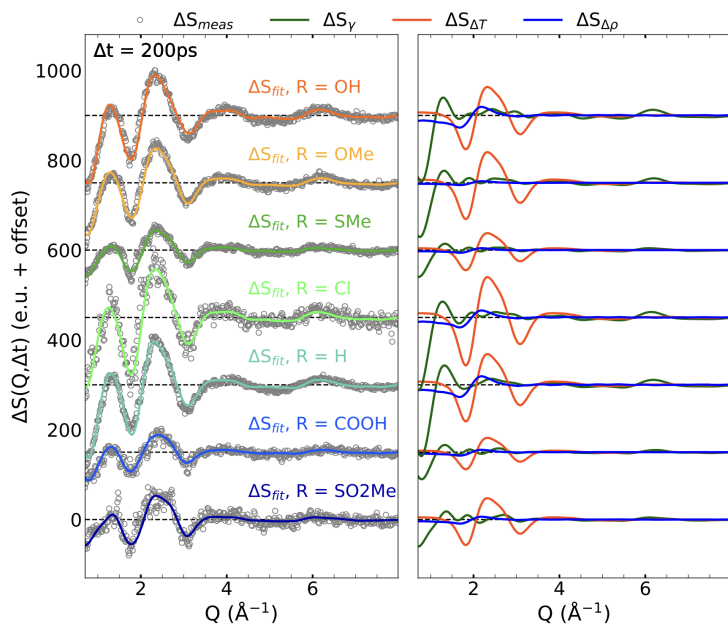
ΔT -model is given by:

$$\Delta T_{Model} = C \cdot (1 - \exp(-\Delta t/(\tau^*))) + \Delta T_{offset},$$

where C is a constant describing the amplitude of the asymptotic increase. τ^* is a time constant describing how fast the temperature in the solvent is increasing, and ΔT_{offset} is the initial temperature of the system when it is relaxed to the quintet state. The two models fit the data nicely with fitting parameters illustrated in Table 2. In Table 2 the TOAS relaxation time measurements (D. Sárossiné Szemes *et al.*, *Chem. Commun.* **56** (2020) 11831) are also shown for comparison.



The figure below shows the experimental XSS data and fit for all seven derivatives for one time delay $\Delta t = 200$ ps together with the strength of the model contributors.



The data is fitted nicely across the different systems. The systems $R=SO_2Me$, $R=COOH$ and $R=Cl$ experience more noisy data compared to the others which is caused by lower repetitions due to prioritisation of the beam time.

Table 1: The change of a selected structural parameters between the DFT-calculated LS structure and the calculated and measured HS structure of the different derivatives of $[\text{Fe}(4'\text{-R-terpy})_2]^{2+}$.

Parameter	R (Subst.)						
	FeT-SO2Me	FeT-COOH	FeT-H	FeT-Cl	FeT-SMe	FeT-OMe	FeT-OH
Calculated - DFT 5 ^B							
$\Delta d_{\text{FeN},\text{Ax}}$ (Å)	0.24	0.22	0.22	0.26	0.24	0.24	0.25
$\Delta d_{\text{FeN},\text{Eq}}$ (Å)	0.21	0.22	0.22	0.21	0.21	0.21	0.21
$\Delta N_{\text{ax-Fe-N}_{\text{eq}}}$ (same tpy) (°)	-6.33	-5.83	-5.87	-6.88	-6.57	-6.61	-6.69
$\Delta N_{\text{ax-Fe-N}_{\text{eq}}}$ (cross tpy) (°)	6.22	5.83	5.87	6.88	6.57	6.61	6.69
$\Delta N_{\text{ax-Fe-N}_{\text{ax}}}$ (same tpy) (°)	5.46	5.84	5.94	5.14	5.57	5.54	5.45
Measured							
$\Delta d_{\text{FeN},\text{Ax}}$ (Å)	0.21 ± 0.04	0.17 ± 0.07	0.20 ± 0.01	0.29 ± 0.05	0.23 ± 0.02	0.22 ± 0.02	0.22 ± 0.01
$\Delta d_{\text{FeN},\text{Eq}}$ (Å)	0.19 ± 0.04	0.17 ± 0.07	0.20 ± 0.01	0.23 ± 0.05	0.20 ± 0.02	0.18 ± 0.02	0.19 ± 0.01
$\Delta N_{\text{ax-Fe-N}_{\text{eq}}}$ (same tpy) (°)	-6.05	-4.62	-5.39	-7.49	-6.28	-5.94	-6.12
$\Delta N_{\text{ax-Fe-N}_{\text{eq}}}$ (cross tpy) (°)	5.94	4.62	5.39	7.49	6.27	5.94	6.11
$\Delta N_{\text{ax-Fe-N}_{\text{eq}}}$ (same tpy) (°)	5.20	4.57	5.42	5.63	5.30	4.95	4.95

Table 2: Best-fit parameter values from kinetic models fits along with Transient Absorption Spectroscopy measurements from [8].

	FeT-SO2Me	FeT-COOH	FeT-H	FeT-Cl	FeT-SMe	FeT-OMe	FeT-OH
Gamma model							
τ (ns)	2.8 ± 0.9	1.1 ± 0.3	2.9 ± 0.3	2.8 ± 0.7	8.2 ± 1.2	13.2 ± 0.9	14.9 ± 0.7
γ_0 (%)	9.6 ± 1.3	21.2 ± 3.4	11.1 ± 0.5	32.7 ± 3.6	17.0 ± 0.9	27.9 ± 0.8	26.4 ± 0.5
Temperature model							
τ^* (ns)	1.17 ± 1.11	0.23 ± 0.51	1.91 ± 1.29	0.57 ± 0.35	4.7 ± 9.38	14.2	16.45
T_{offset} (K)	0.17 ± 0.01	0.2 ± 0.08	0.16 ± 0.01	0.51 ± 0.07	0.28 ± 0.01	0.38	0.34
C	0.03 ± 0.01	0.03 ± 0.07	0.03 ± 0.01	0.07 ± 0.07	0.01 ± 0.01	0.0	0.0
Transient Absorption measurement from [8]							
τ_{TAS} (ns)	1.3	2.0	2.7	4.2	5.9	10.7	12.8

[8] refers to D. Sárosiné Szemes *et al.*, *Chemical Communications* **56** (2020) 11831, <http://doi.org/10.1039/D0CC04467A>.

The energy difference ΔE between the quintet and singlet state is calculated by:

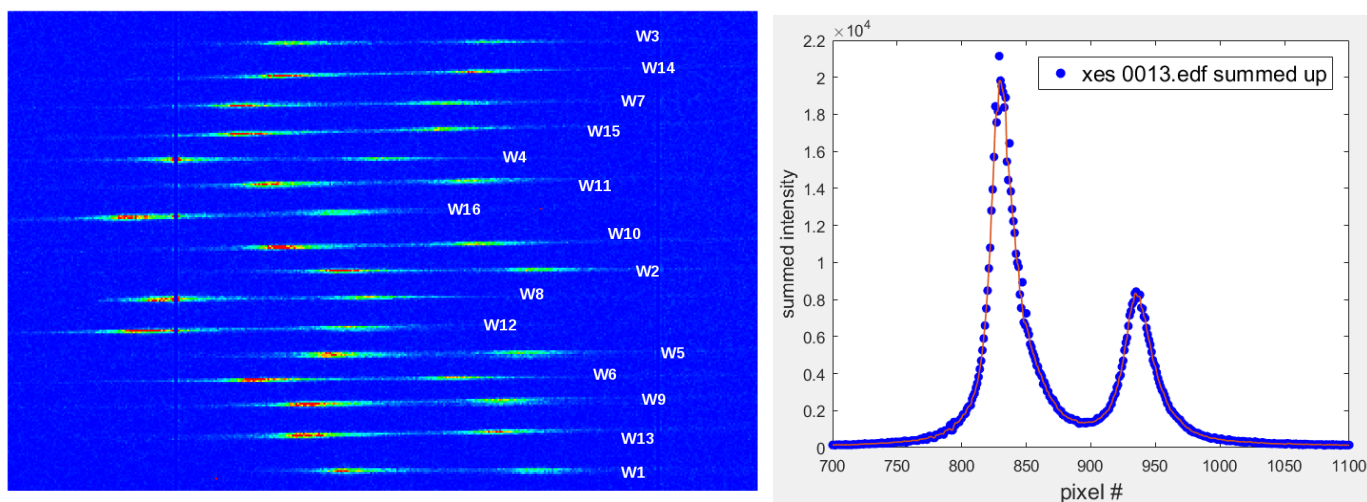
$$\Delta E = C_V \cdot \Delta T \cdot N_{\text{LUC}} / (\gamma_0 \cdot N_A),$$

where C_V is the specific heat capacity of water, γ_0 the initial excitation fraction, N_A avogadros constant, N_{LUC} the number of solvent molecules for each solute molecule calculated from the concentration of the solution, and $\Delta T = \Delta T(\Delta t = 3\tau) - \Delta T(\Delta t = 100 \text{ ps})$. The estimated energy difference for the different modified systems is listed in Table3. The energy differences are in general a factor two larger than the DFT predicted values, and the energy differences are not estimated for FeT-OMe and FeT-OH since the temperature models could not fit the data. ΔE_{offset} is the estimated energy of the quintet state. Since the pump energy is 2.2 eV (560 nm) the estimated quintet energy is clearly determined to be too high.

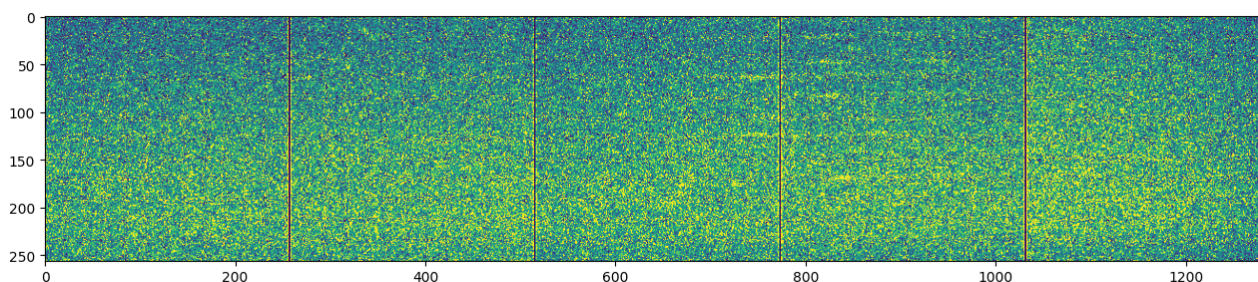
Table 3: Best-fit parameter values from energy model along with predicted DFT values from [8]. $\Delta E_{\text{singlet-quintet}}$ is the energy difference between the HS quintet and LS singlet state. ΔE_{offset} is the energy of the quintet state.

	FeT-SO2Me	FeT-COOH	FeT-H	FeT-Cl	FeT-SMe	FeT-OMe	FeT-OH
$\Delta T(100 \text{ ps})$ (K)	0.17 ± 0.01	0.21 ± 0.01	0.17 ± 0.0	0.52 ± 0.03	0.28 ± 0.01	0.38 ± 0.03	0.34 ± 0.02
$\Delta T(3\tau)$ (K)	0.2 ± 0.01	0.23 ± 0.01	0.2 ± 0.0	0.58 ± 0.03	0.29 ± 0.01	0.38 ± 0.03	0.34 ± 0.02
ΔE_{offset} (eV)	7.78 ± 0.28	8.7 ± 0.31	6.31 ± 0.15	13.63 ± 0.73	14.02 ± 0.4	11.68 ± 0.92	11.17 ± 0.58
$\Delta E_{\text{singlet-quintet}}$ (eV)	1.12 ± 0.39	0.82 ± 0.43	1.16 ± 0.22	1.51 ± 1.03	0.54 ± 0.57	0.0 ± 1.3	0.0 ± 0.82
DFT calculation in [8]							
ΔE_{DFT} (eV)	0.525	0.550	0.505	0.482	0.439	0.385	0.404

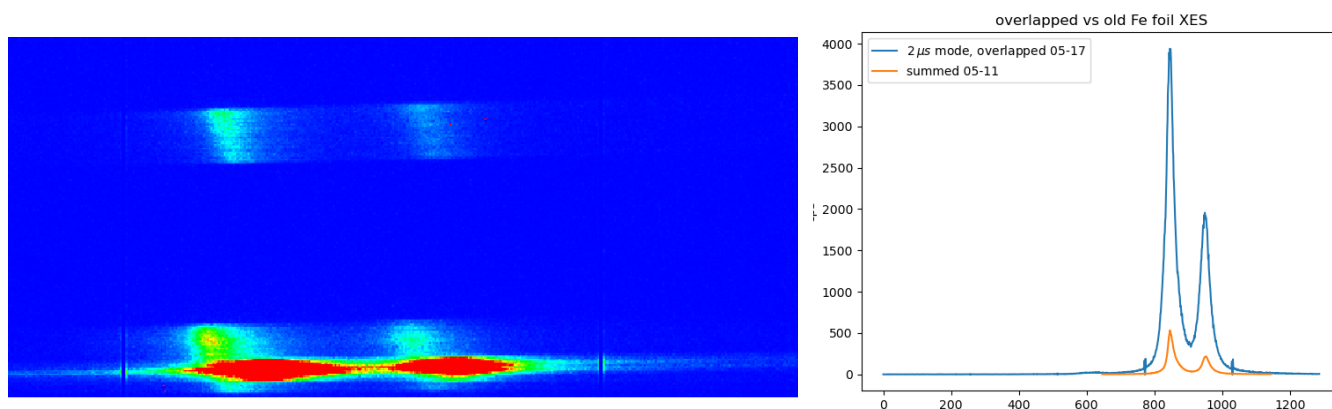
X-ray Emission Spectroscopy (XES)



The 16-crystal von Hámos spectrometer was aligned on an iron foil, and the Fe K α spectrum was taken in stationary conditions; the reflections on the detector and the spectra obtained in from a 30 s acquisition is shown above. However, with the kHz repetition rate on a 10 mM solution the K α signal is barely visible on the detector (in the range of pixel #750-950) after 15 minutes acquisition, although the background was rather low due to careful shielding applied.



We managed to merge the signal of 9 analyzers together on the detector to improve S/N. This has improved the count rate on the iron foil (the spectra below are taken in 5 s, with the chopper lowered to allow 20 μ s duration for the pulses in order to increase the flux by a factor of 30), but the improvement was still far from being efficient for the solution under the conditions of the pump-probe experiment.



From the XES signal we estimated that it would take about a day to get a reasonable pump-probe spectrum at a single time delay. Therefore, after verifying the experimental conditions, possible mistakes with the setup, and count rates, as well as comparing the numbers to those in our previous experiments with practically identical spectrometers (e.g. <http://doi.org/10.1021/acs.jpcc.6b12940> : A.M. March *J. Phys. Chem. C* **121** (2017) 2620), we decided to give up the idea of recording XES, and focus on X-ray scattering only.

We note that a scanning Rowland-circle spectrometer, where the whole analyzer reflects the same single wavelength, has been used successfully in earlier pump-probe experiments at ID09.