



# Light-induced spin transition in the spin-crossover complex $\text{FePt}_2$ detected by optical pump-coherent resonant nuclear elastic scattering

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## Abstract

We report the results of optical pump-nuclear resonance probe experiments on the SCO complex  $[\text{Fe}^{\text{II}}(\text{L}-\text{Pt}^{\text{II}}(t\text{-but-tpy}))_2](\text{BF}_4)_2$  with L being 2,6-di(pyrazol-1-yl)-4-(trimethylsilylethynyl)pyridine and *t-but-tpy* being 4,4',4''-Tri-tert-Butyl-2,2':6,2''-terpyridine using a novel experimental set-up at the beamline P01, Petra III, DESY Hamburg. We investigate the changes in the spin state of the complex when it is excited by laser pulses of 766 nm wavelength and pulse width < 100 ps. Our simulations of the nuclear forward scattering data indicate a dominant low spin state along with some high spin fraction in the absence of laser pulses. We observe clear changes in the time-spectrum following the instant at which the laser pulse hits the sample. Furthermore, these alterations are recorded as the relative timing of the laser pulses with respect to the synchrotron pulses is varied.

**Keywords** Nuclear forward scattering · NRS pump-probe experiments · Spin crossover

## 1 Introduction

Molecular complexes of 3d-transition metals such as Fe(II), which undergo the high spin (HS) – low spin (LS) phase transition are known as spin crossover (SCO) complexes. The variety of physical properties that change upon the phase transition makes them attractive for applications as sensors and memory devices [1, 2]. Although they are studied extensively by pump-

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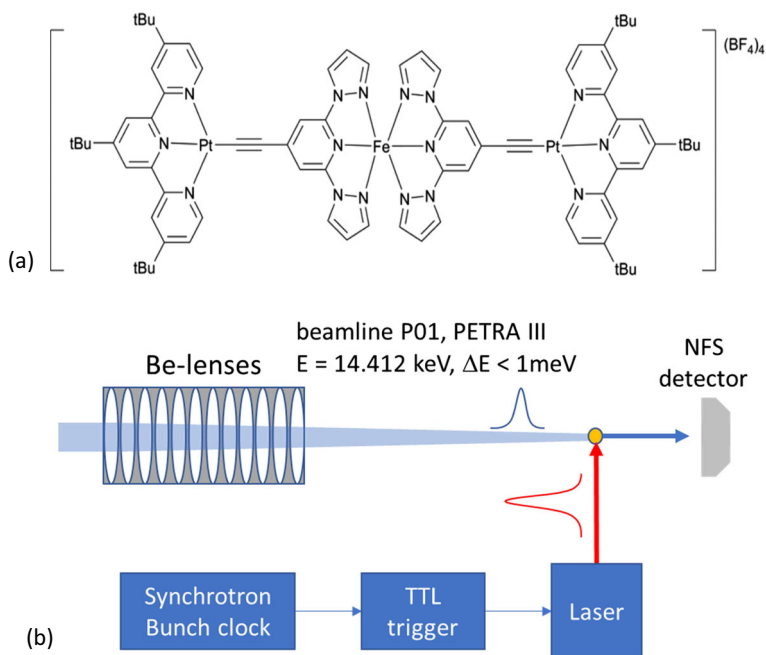
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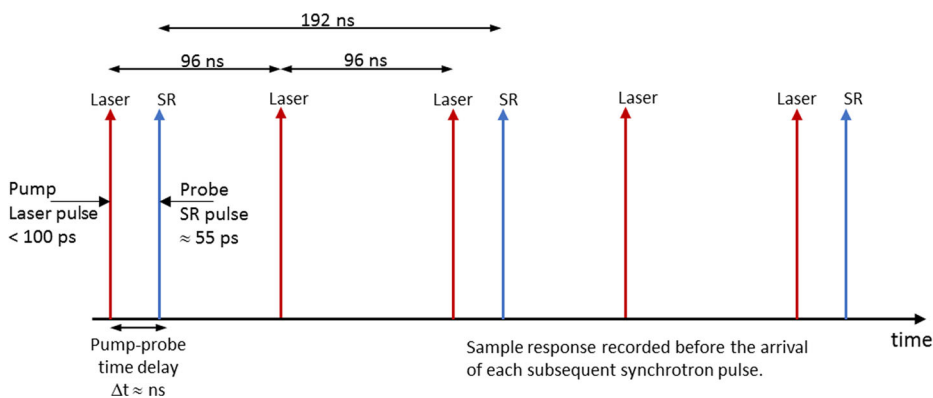
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probe spectroscopy using reflectivity, Infrared and Raman scattering as a probe of the spin state [3–5], such studies that use visible light as an optical probe suffer from several limitations due to the mixing of dynamics of the spin center along with other contributions [6], the optical selection rules and other effects such as fluorescence [6, 7]. On the other hand, techniques such as Nuclear resonance scattering (NRS) using  $^{57}\text{Fe}$  inherently overcome these limitations [8]. Therefore, it is of advantage to study the dynamics of the spin crossover phenomenon using NRS as a probe of the spin state [6].

In this report, we describe the results of the optical pump- NRS probe experiments performed at the beamline P01, PETRA III (DESY, Hamburg) on  $[\text{Fe}^{\text{II}}(\text{L}-\text{Pt}^{\text{II}}(t\text{-but-tpy}))_2](\text{BF}_4)_2$ , which is a trinuclear iron-platinum complex containing one Fe(II) and two Pt(II) ions. It is referred to henceforth as  $\text{FePt}_2$ . The structural formula of the complex with the coordinated ligand L being 2,6-di(pyrazol-1-yl)-4-(trimethylsilylethynyl)pyridine and *t-but-tpy* being 4,4',4''-Tri-tert-Butyl-2,2':6',2''-terpyridine [9] is shown in Fig. 1a. The central iron ion is coordinated by six nitrogen atoms with the ligands and is thus located in an octahedral ligand field. As obtained from synthesis, this complex reveals two different conformers, resulting in two different molecular structures [9]. Crystallographic studies displayed the presence of two polymorphs in the synthesized complex. The bent polymorph (A) with *P* symmetry, containing 3.5 molecules of  $\text{CH}_2\text{Cl}_2$ , remains in the high spin state. The other linear polymorph (B) with *C2/c* symmetry, containing 10 molecules of  $\text{CH}_2\text{Cl}_2$ , exhibits a reversible spin-crossover with  $T_c = 268\text{ K}$  [9, 10]. Graphic representations of the complex in both modifications are given in Fig. 2 of ref. [9]. In this communication, we demonstrate the detection of the HS states created by laser-excitation of the SCO complex using nuclear forward scattering (NFS) as a probe.



**Fig. 1** **a** Structural formula of the  $\text{FePt}_2$  SCO complex used in this study. **b** A scheme of the optical pump – NRS probe experiment. A 100 ps pulsed laser that is triggered by the bunch clock of the synchrotron is used as a pump to optically excite the SCO complex. Monochromatized synchrotron pulses with an energy of 14.4 keV are used to probe the resulting spin state of the sample by recording the NFS spectra



**Fig. 2** Timing scheme of the experiment

Additionally, we study the effect variation of the time-delay of the laser pulses with respect to the synchrotron pulses.

## 2 Materials and methods

A schematic view of the experiment is shown in Fig. 1b. The  $^{57}\text{Fe}$  nuclear transition has a nuclear life time of approximately 141 ns. Thus, the synchrotron operated in the 40-bunch mode, corresponding to a time-interval of 192 ns between adjacent pulses of synchrotron radiation (SR) is well-suited for pump-probe experiments. A high heat load monochromator helps to reduce the bandwidth of the SR to 1 eV. A subsequent high-resolution monochromator reduces the bandwidth to approximately 1 meV. Subsequently, the SR beam was focused to a size of  $500\ \mu\text{m} \times 200\ \mu\text{m}$  at the sample position using a Be lens system. The elastically scattered coherent radiation was detected using a silicon avalanche photodiode (APD), placed 1.5 m from the sample position in the direction of propagation of the radiation. The coherent nature of the scattered radiation results in a time-spectrum with a quantum beat structure that can indicate the spin-state of the spin-crossover complexes and was detected using NFS, recorded in time-domain. It must be noted that the first 25 ns of the data is blocked due to the veto signal that screens the prompt signal. Additionally, the data acquisition window was limited to 155 ns.

For optical excitation, we used a pulsed laser source manufactured by Picoquant GmbH, Berlin, whose wavelength was 766 nm with a variable repetition rate (up to 80 MHz) and pulse width  $< 100\text{ ps}$ . A multimode optical fiber was used to guide the laser beam to two mirrors. An adjustable collimator at the termination of the fiber was used to realize different spot sizes. It was subsequently positioned onto the sample using the two mirrors, so that the angle between the laser beam and the synchrotron radiation was  $90^\circ$ , while the laser spot diameter was 3 mm. The laser head could be externally triggered using TTL pulses that are generated by electronically delaying the synchrotron bunch clock signal. The number of pulses emitted at each instance of triggering was adjusted in a way to achieve twice the repetition rate of the SR pulses.

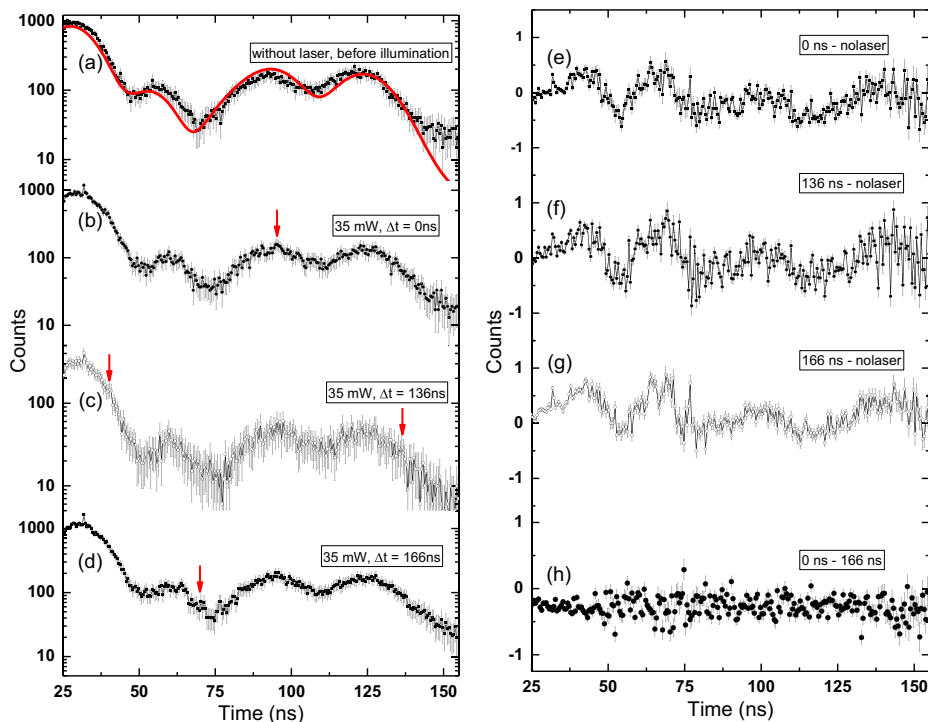
The relative time delay ( $\Delta t$ ) between the laser and the SR pulses was electronically adjusted by controlling the timing of the trigger pulses to the laser. In order to calibrate the time delay, the signals arising out of an APD (sensitive to both types of radiation), placed sufficiently close

to the sample, are monitored using a multichannel analyzer (MCA). We could vary  $\Delta t$  with an accuracy of 0.5 ns.

The timing scheme of the experiment is shown in Fig. 2. The laser excitation of the sample could be adjusted to occur at a certain time before (or after) the arrival of the SR pulse. The NFS response of the sample after arrival of the corresponding SR pulse is recorded during the subsequent 192 ns. Thus, the sample is excited once in every 96 ns.

The title complex was prepared using methods discussed elsewhere, by starting from  $^{57}\text{Fe}$  enriched (98%) salts [9]. The powder sample was attached using silicon high-vacuum grease at the tip of a glass rod. The rod is mounted on top of a goniometer and is continuously rotated about its axis to minimize heating of the sample by the laser beam on any one part of the sample. In addition, it helps to average any non-uniformities of penetration of the x-ray beam through the sample. Cold nitrogen gas flowing out of a liquid nitrogen cryostream (Oxford Cryosystems) maintained the sample at 80 K, so the part of the sample, which has the molecular structure **A** is in the LS state during the experiment. The set-up is arranged in a similar way as in Reference [11].

The NFS spectra were analyzed using a theoretical simulation of the forward scattering amplitudes, as implemented in the CONUSS software [12]. The hyperfine parameters, the



**Fig. 3** NFS spectra recorded for  $\text{FePt}_2$  at 80 K at different time-delays of the 766 nm laser pulses with respect to the synchrotron radiation. The laser power was 35 mW and repetition rate was 10.4 MHz. **a** Before laser illumination. The black spheres represent the data and the red line represents the CONUSS simulations [12]. **b**  $\Delta t = 0$  ns, **c**  $\Delta t = 136$  ns, **d**  $\Delta t = 166$  ns. The difference of spectra acquired under laser illumination with respect to that before illumination are shown on the right. **e** spectrum at  $\Delta t = 0$  ns-spectrum before laser illumination. **f** spectrum at  $\Delta t = 136$  ns-spectrum before laser illumination. **g** spectrum at  $\Delta t = 166$  ns-spectrum before laser illumination. **h** spectrum at  $\Delta t = 0$  ns-spectrum at  $\Delta t = 166$  ns

fraction of the sample excited to the HS state, as well as the effective thickness of the samples were extracted from the simulation parameters.

### 3 Results and discussions

Figure 3a-d depicts the NFS spectra recorded for the SCO complex at 80 K, under various laser-illumination conditions. The spectrum recorded before illuminating the sample with the laser – (Fig. 3a) shows a complex quantum beat pattern with different periodicities, indicating multiple components in the sample. This is expected because our sample consists of a mixture of **A** and **B**, which have slightly different structures. To simulate the time spectrum, we used a model with three components: (i) The first component refers to the part of the sample with structure **B**, using a fixed isomer shift of  $1.1 \text{ mms}^{-1}$ . (ii) The second and third components refer to the part of the sample with structure **A** with set isomer shifts of  $0.28 \text{ mms}^{-1}$  and  $1.39 \text{ mms}^{-1}$ . The simulations yielded a quadrupole splitting  $\Delta E_Q$  of  $3.47 \text{ mms}^{-1}$  for the first component, indicating the HS state. The contribution was 16% by weight. For the second component, the simulations yielded a  $\Delta E_Q$  of  $0.27 \text{ mms}^{-1}$ . This is typical of the Fe(II) low spin state. The contribution was found to be 60%. For the third component,  $\Delta E_Q$  was found to be  $2.47 \text{ mms}^{-1}$ , indicating a high spin state with a contribution of 24%. The hyperfine values are in good agreement with known values from literature [9]. The simulation is indicated as a red solid line in Fig. 3a.

Figure 3b-d depict the NFS spectra acquired while the sample was illuminated by the laser pulses with different time-delays with respect to the SR pulses. The delays are  $\Delta t = 0 \text{ ns}$ , 136 ns and 166 ns in Fig. 3b, c and d respectively. The small red arrows indicate the temporal positions of laser pulses with reference to the acquisition of the NFS spectra. Due to time-window during which the data is acquired, the arrows only appear once in Fig. 3b and d, but twice in Fig. 3c. In each case, it can be observed that there is a small difference with respect to the reference spectrum of Fig. 3a. The minima of the quantum beat pattern are shifted to later times. This indicates that there is a change of the hyperfine contributions to the signals, indicating a change of the high spin fraction in the sample. However, the newly created high spin state relaxes to the low spin state at a time scale which could be comparable to (or larger than) the periodicity of the quantum-beat pattern in the NFS spectra. Therefore, the resulting signal is a complicated convolution of the time-dependent change of the hyperfine states and the change of intensity due to the quantum interference of the photons emitted from instantaneous spin-state. Thus, a modelling from established routines such as using CONUSS would not be applicable.

Figure 3e-g indicate the difference of the spectra in Fig. 3b-d with respect to that in Fig. 3a. It shows the changes in the NFS spectra caused by the laser illumination. Although there is a definite change in the spectra with respect to the non-illuminated case of Fig. 3a, the changes caused by the laser illumination don't seem to depend on the specific laser-SR delay  $\Delta t$ . This is further confirmed by taking a difference of the NFS spectra corresponding to the laser-illuminated cases with each other, as shown in Fig. 3h. This could be understood on the basis of the relative dynamics of relaxation of the high spin state created by each laser pulse with respect to the excitation by the subsequent laser pulse. In our experiment, the laser pulses occur with a repetition rate of 10.4 MHz, corresponding to a separation of 96 ns between subsequent laser pulses. In earlier LIESST experiments, it has been shown that the laser-excited SCO molecules relax from the HS to the LS state at a rate dependent on the sample temperature [13].

In our experiments the sample temperature is 80 K. The relaxation rate is in the range of 10–100 ns. Thus, the laser-excited HS state might not yet be completely relaxed into the low spin state. Therefore, the measured state could be a dynamical equilibrium state. In addition, we cannot exclude the presence of the heating effect that might cause a reduction of the Lamb-Mössbauer factor, which could be responsible for the shift of the minima of the NFS spectra in Fig. 3b-d. Therefore, further investigations in which the laser pulses are well separated with respect to the relaxation rate of the HS state, as well as an inherent measurement of the sample temperature such as using nuclear inelastic scattering are required to resolve the issue.

## 4 Conclusions

We report the results of the optical pump-nuclear resonance probe experiments performed on a FePt<sub>2</sub> spin crossover complex. The sample consists, in the initial state at 80 K, of two molecular structures **A** and **B**. Our analysis of the NFS data indicates that the sample consists of 60% low spin state and 24% high spin state with the structure **A**. The remaining 16% is comprised by the structure **B**, entirely in the high spin state. The optical pump laser was triggered in synchronisation with the synchrotron at DESY to emit two pulses for each synchronization x-ray pulse. This causes definite changes in the recorded NFS spectra. However, since the signal is a complicated convolution of the dynamical state and the time-dependent signal that results from the quantum interference of the nuclear resonant photons, we cannot simulate it using known algorithms and software such as CONUSS. No influence of the exact time-delay between the laser pulses and the synchrotron pulses was perceptible probably because the relaxation rates of the high spin state are comparable to the time-separation between subsequent excitations by the laser pulses. Further investigations are necessary with significantly lower laser repetition rates to identify the contribution of the optical field alone of the laser pulses in the excitation of the SCO complex to the HS state.

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