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# Optical pump - nuclear resonance probe experiments on spin crossover complexes

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**Abstract** A novel sample environment enabling optical pump – nuclear resonance probe experiments has been installed at the beamline P01, Petra III, DESY Hamburg. This set-up has been used to investigate optically induced spin state changes of spin crossover (SCO) complexes by nuclear resonant scattering immediately after excitation by an optical laser pulse. Here, we report the technical details as well as first results of the experiments performed at 290 K and 80 K on the SCO complexes [Fe $(NH_2trz)_3]Cl_2$ and [Fe(PM-BiA)$_2$(NCS)$_2$], respectively. The $^{57}$Fe-enriched SCO complexes were excited by a 531 nm laser with a pulse length $<$100 ps. Evaluation of the nuclear forward scattering data clearly indicate the presence of high spin (HS) states when the complexes are excited by laser pulses and a pure low spin (LS) state in the absence of any laser pulse. Furthermore, the dependence of the optically excited HS-fraction has been determined as a function of the average optical power.

**Keywords** Nuclear forward scattering · Time-resolved spectroscopy · Pump-probe experiments · Spin crossover · [Fe(PM-BiA)$_2$(NCS)$_2$] · $[Fe(NH_2trz)_3]Cl_2$

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## 1 Introduction

The high spin (HS) – low spin (LS) phase transition in spin crossover (SCO) complexes makes them attractive for applications in sensor and memory devices [1]. This transition has been studied extensively by pump-probe spectroscopy using reflectivity, Infrared and Raman scattering as a probe of the spin state [2–4]. Such studies cannot reveal dynamics specific to the spin center, rather the dynamics is often mixed with other contributions [5]. In addition, Raman spectroscopy is only sensitive to the modes allowed by the optical selection rules. Moreover, fluorescence can mask the (weaker) Raman signals [5, 6]. On the other hand, nuclear resonance scattering (NRS) using $^{57}$Fe reveals dynamics specific to the spin center and is not bound by the optical selection rules [7]. Therefore, it is of advantage to study the dynamics of the spin crossover phenomenon using NRS as a probe of the spin state [5]. However, so far, there have been no reports of optical pump-NRS probe experiments.

In this report, we describe an optical pump – NRS probe experiment that was set up at the Dynamics Beamline P01, PETRA III, DESY, Hamburg. We report on the optical excitation of $[Fe(NH_2trz)_3]Cl_2$ and $[Fe(PM\text{-}BiA)_2(NCS)_2]$, both being SCO materials. $NH_2trz$ is the abbreviation for 4-amino-1,2,4-Triazole, while PM-BiA is the abbreviation for (2-pyridylmethylene)aminobiphenyl). $[Fe(NH_2trz)_3]Cl_2$ is a polymer complex consisting of a chain of Fe(II) atoms, bridged through the nitrogen atoms of two triazole units [8]. It shows an abrupt LS-HS transition occurring at 340 K with a thermal hysteresis of 40 K. $[Fe(PM\text{-}BiA)_2(NCS)_2]$ is a mononuclear Fe(II) complex with the central Fe atom being coordinated to two N-(2-Pyridylmethylen) ligands, two 4-aminophenyl ligands and two thiocyanate anions. This sample consists of a mixture of two polymorphic crystalline phases. For one of the phases, the LS-HS transition occurs around 165 K, with a 5 K thermal hysteresis [9]. In this communication, we show that it is possible to drive the transition of laser-excited SCO complexes from their LS to their HS state and to use nuclear forward scattering (NFS) as a probe of the spin state. In addition, spectral analysis has been performed to extract the hyperfine parameters and identify the fraction of the complexes excited to the HS state.

## 2 Materials and methods

A schematic view of the experiment is shown in Fig. 1. The synchrotron was operated in the 40-bunch mode. This corresponds to a time-interval of 192 ns between adjacent pulses of synchrotron radiation (SR), which is sufficient to measure the $^{57}$Fe nuclear transition ($\Delta t_{Fe} \approx 141$ ns) and suited for pump-probe experiments. The SR pulses were monochromatized using a high heat load monochromator and a high-resolution monochromator to a bandwidth of 1 meV. Subsequently, the SR beam was focused to a size of 500 $\mu$m $\times$ 200 $\mu$m at the sample position. A silicon avalanche photodiode (APD), placed 1.5 m from the sample position, was used to detect the scattered SR. The spin-state of the spin-crossover complexes was detected using the NFS time-spectra.

For optical excitation, we used a pulsed laser source manufactured by Picoquant GmbH, Berlin, whose wavelength was 531 nm with a variable repetition rate (up to 80 MHz) and pulse width $< 100$ ps. The set-up is also equipped with a second laser providing 785 nm radiation. The laser beam was passed through a multimode optical fiber coupled to an adjustable collimator to realize different spot sizes. It was subsequently positioned onto the sample using two mirrors, so that the angle between the laser beam and the synchrotron radiation was 90°, while the laser spot diameter was 3 mm. The laser head was externally triggered using clock pulses that are generated by electronically delaying the synchrotron

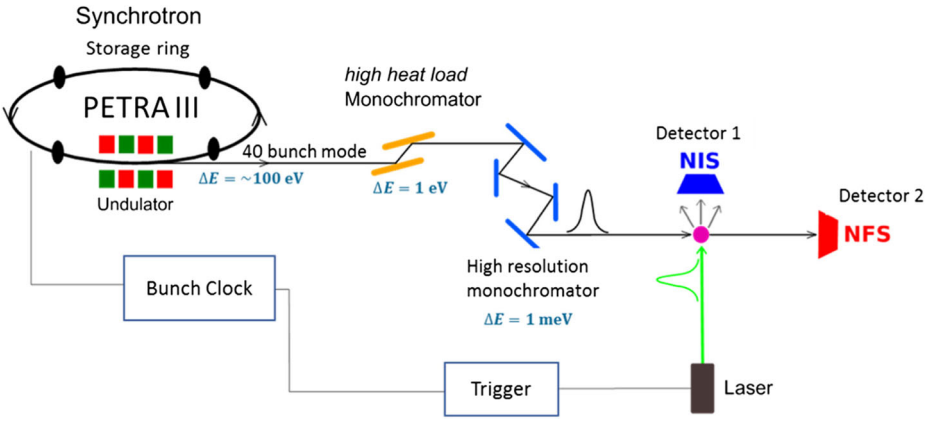


**Fig. 1** A schematic of the optical pump – NRS probe experiment. A 100 ps pulsed laser that is triggered by the bunch clock of the synchrotron is used as a pump to optically excite the spin-crossover complex. Monochromatized synchrotron pulses at 14.4 keV are used to probe the resulting spin state of the sample by recording the NFS spectra

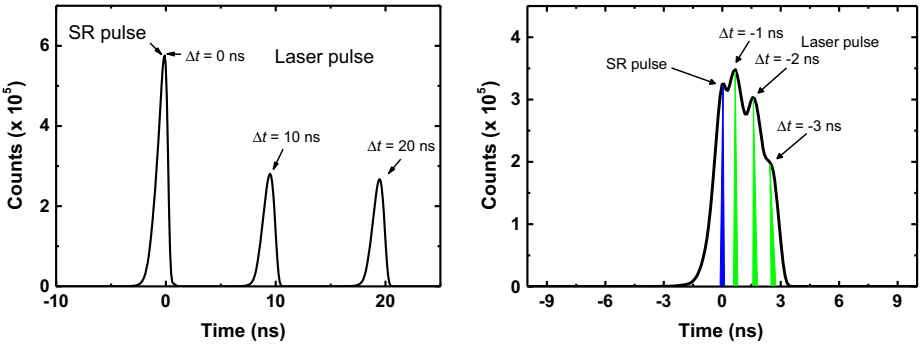


**Fig. 2** Time spectra to verify the relative timing of the laser pulses with respect to the SR pulses. The picture on the left corresponds to time delays between the incoming SR and laser pulse at Δt=0, 10 and 20 ns. The picture on the right corresponds to smaller delays of Δt=0, 1, 2 and 3 ns

bunch clock signal. The number of pulses emitted at each instance of triggering was varied to achieve different average optical powers of the laser.

In order to verify the relative time delay (Δt) between the laser and the SR pulses, an APD (sensitive to both types of radiation) was arranged close to the sample so that both the beams would hit it. The APD signals were then analyzed using a multichannel analyzer (MCA), which is also used to record the NFS spectra. The SR or laser pulses are observed as peaks whose full width at half maximum $\approx 1$ ns due to the electronic evaluation of the MCA (see Fig. 2). At $\Delta t = 0$ ns, a single peak of the highest intensity was detected because both the SR and the laser pulses are recorded in the same channel of the MCA. At $\Delta t \geq 10$ ns, two peaks of lower amplitude were detected (SR and the laser). At small delays 1 ns $< \Delta t < 4$ ns, the detected peak is distorted depending on the actual time delay. For clarity, the laser pulse is shown as green peaks at different time delays, while the SR is shown as the blue peak. The detected distorted peak is shown as the envelope. Thus, we could vary Δt with an accuracy of 0.5 ns.

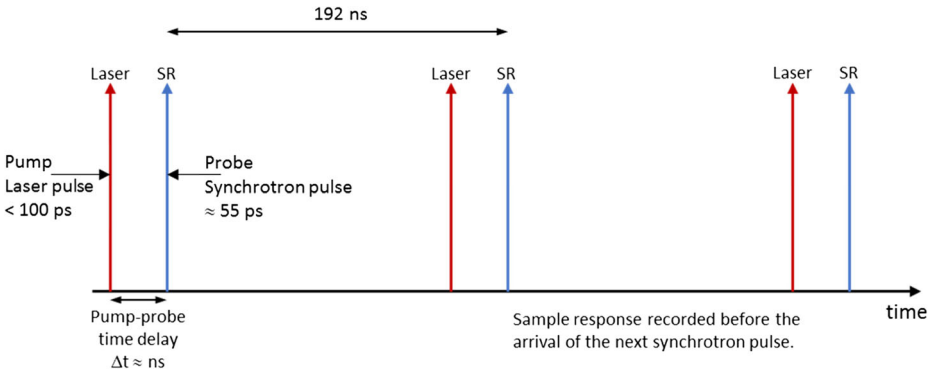


**Fig. 3** Timing scheme of the experiment

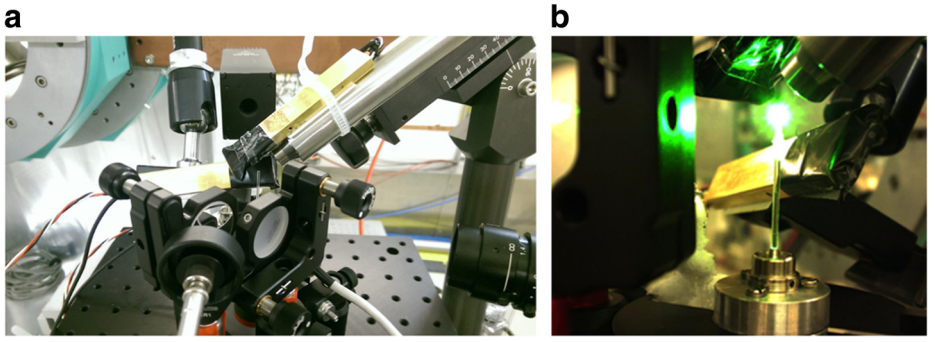


**Fig. 4** Picture of the pump-probe experiment. **a** The sample holder, along with the *cryostream*, collimator and mirrors that guide the laser beam. **b** A mounted sample, which is illuminated using a 531 nm laser beam

The timing scheme of the experiment is shown in Fig. 3. 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. It should be mentioned that it is also possible to perform optical pump nuclear inelastic scattering (NIS) probe experiments with this set-up. For such an experiment, the APD which is close to the sample and registers the NIS signal should be covered by a Kapton® black foil.

The $[Fe(NH_2trz)_3]Cl_2$ and $[Fe(PM\text{-}BiA)_2(NCS)_2]$ complexes were prepared by starting from $^{57}Fe$ enriched (98%) salts and following published procedures [8, 10]. Before performing the experiments, $[Fe(NH_2trz)_3]Cl_2$ was dehydrated [8]. The samples were mounted as powders, using silicon high-vacuum grease, at the tip of a glass rod, which is mounted on top of a goniometer and is continuously rotated about its axis to minimize heating of the sample due to concentration of the laser beam on any one part of the sample. In addition, any non-uniformities of penetration of the x-ray beam through the sample are averaged out. The samples were cooled to temperatures corresponding to the LS state during the experiment using a liquid nitrogen cryostream manufactured by Oxford Cryosystems. A CCD camera was used to monitor the sample environment during the experiment. Figure 4a shows the sample holder and mirrors, placed on an optical breadboard. A picture of an illuminated sample is shown in Fig. 4b.

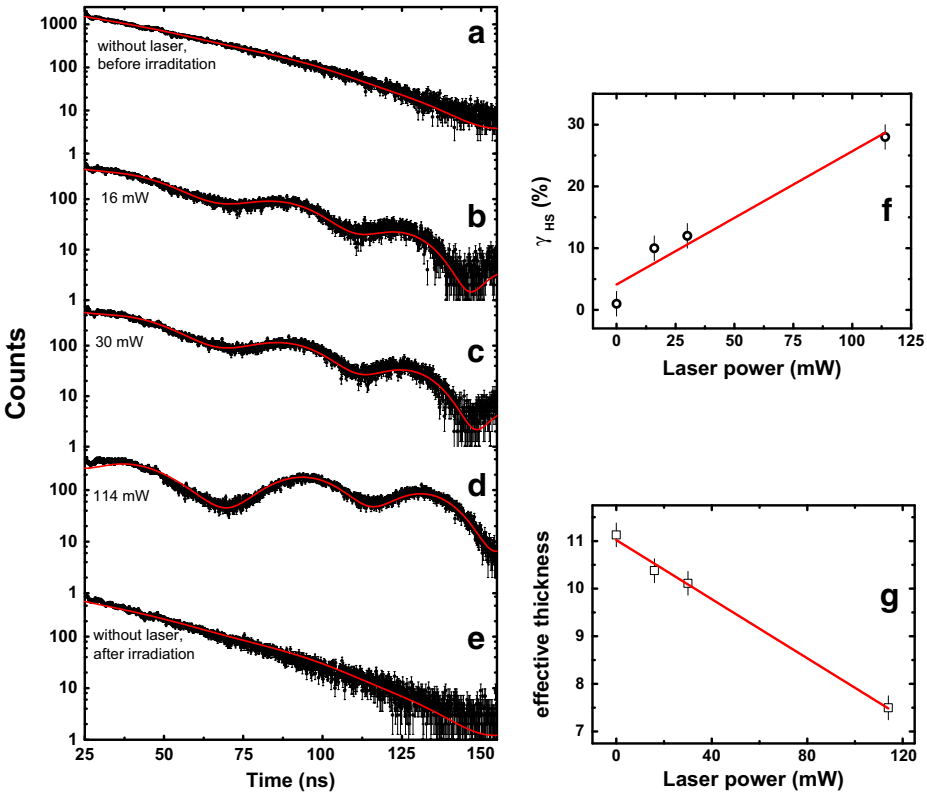


**Fig. 5** NFS spectra recorded for $[Fe(NH_2trz)_3]Cl_2$ at 290 K at different average laser power and repetition rates. **a** No laser, **b** 16 mW, 5.2 MHz, in phase with the SR, $\Delta$t=0 ns, **c** 30 mW, 10 MHz, **d** 114 mW, 40 MHz, **e** No laser, after illumination at the other power levels. The black spheres represent the data and the red lines represent the CONUSS simulations [11]. The figures on the right show the variation of: **f** $\gamma_{HS}$ and **g** $t_{eff}$ as a function of laser power used in (**a**–**e**). The green and blue lines represent straight line fits to the data shown as open symbols

The NFS spectra were analyzed using a theoretical simulation of the forward scattering amplitudes, implemented in the CONUSS software, to extract the hyperfine parameters, the fraction of the sample excited to the HS state $\gamma_{HS}$, as well as the effective thickness $t_{eff}$ of the samples [11].

## 3 Results and discussions

Figure 5 shows the NFS spectra recorded for the $[Fe(NH_2trz)_3]Cl_2$ complex at 290 K, under various illumination conditions. The spectrum recorded before laser – illumination (Fig. 5a) shows no quantum beat pattern, indicating that all Fe atoms were in the LS state. A simulation with a set value of the isomer shift $\delta$ of $0.43 \pm 0.02$ mms$^{-1}$ gives a quadrupole splitting $\Delta E_Q$ of $0.14 \pm 0.02$ mms$^{-1}$ (see Fig. 5a) consistent with the $Fe^{II}$ being in the LS state. The spectrum shown in Fig. 5b corresponds to the laser being triggered to obtain one pulse per SR pulse (5.2 MHz, average power 16 mW), $\Delta$t being 0 ns. It shows a quantum beat pattern with a period $\approx$40 ns. The corresponding simulation shows the presence of a HS component ($\gamma_{HS} = 10\%$) with $\delta = 1.02 \pm 0.02$ mms$^{-1}$ and $\Delta E_Q = 2.7 \pm 0.02$ mms$^{-1}$, typical of

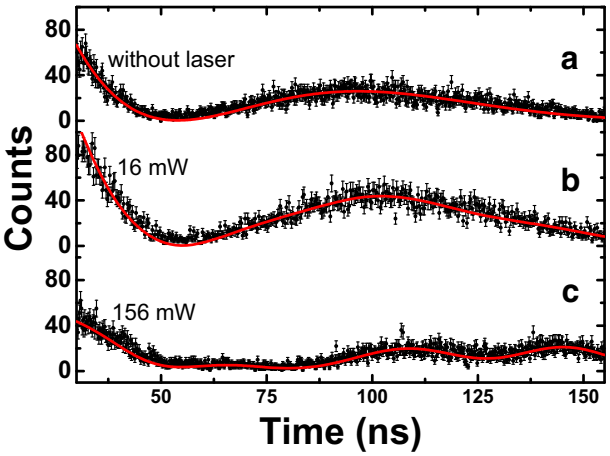


**Fig. 6** The NFS spectra of $[Fe(PM\text{-}BiA)_2(NCS)_2]$ at 80 K under illumination at different average power and repetition rates. **a** No laser, **b** 16 mW, 5.2 MHz, **c** 153 mW, 80 MHz. The red lines are fit to the black data points using CONUSS with parameters discussed in the text

$Fe^{II}$ atoms in the HS state, in addition to the LS component. When the average laser power was increased to 30 mW (repetition rate to 10 MHz), there was a slight change in the NFS spectra (see Fig. 5c). At a laser power of 114 mW (repetition rate 40 MHz, see Fig. 5d), the beat pattern changed prominently. $\Delta E_Q$ of the HS state reduced to $2.6 \pm 0.02$ $mms^{-1}$ and $\gamma_{HS}$ increased to 28%. Thereafter, we recorded an NFS spectrum after switching off the laser (see Fig. 5e). The absence of quantum beats indicates that the sample is back in the LS state, which is confirmed by the simulation performed with the same parameter set as that in Fig. 5a. This shows that $[Fe(NH_2trz)_3]Cl_2$ was not damaged by the laser beam during the optical pump - NFS probe experiments performed at 290 K.

The corresponding values of $\gamma_{HS}$ and $t_{eff}$ as a function of the average laser power is depicted in Fig. 5f–g. Since the number of excited spin centers increases linearly with the number of photons, $\gamma_{HS}$ increases linearly as a function of the laser power, as shown in Fig. 5f. $t_{eff}$, which is proportional to the Lamb-Mössbauer factor f, decreases with increased laser power (see Fig. 5g). Since f decreases with increasing temperature [12], it hints at the presence of a heating effect, in addition to the optical excitation by the laser. In addition, it is reasonable to assume that f is lower for the HS state than for the LS state. However, in the CONUSS program, only one value of $t_{eff}$ is used for simulating the NFS pattern of both phases to correct for the Bessel beats and speed up in the time spectrum. So, in this study, $t_{eff}$ cannot be directly correlated to an increase of sample temperature. Therefore, further investigations such as a measurement of the sample temperature through inelastic scattering methods are required to resolve this issue.

Figure 6 shows the NFS spectra recorded for the $[Fe(PM\text{-}BiA)_2(NCS)_2]$ complex at 80 K, under various illumination conditions. In the absence of a laser pulse, the quantum beat structure shows a separation $\approx 110$ ns between the minima (see Fig. 6a). This spectrum could be simulated with a single component in the LS phase ($\gamma_{HS} = 0\%$) with $\Delta E_Q$ of $0.6 \pm 0.02$ $mms^{-1}$, characteristic of the Fe(II) LS state. When the laser was switched on, triggered to emit one pulse at each SR pulse (5.2 MHz) and $\Delta t = 0$ ns, the beat structure changed slightly (see Fig. 6b). In our simulations, we had to introduce a second component with the HS phase ($\gamma_{HS} = 2\%$) along with the LS component. $\Delta E_Q$ of the HS component is

found to be $2.8 \pm 0.02$ mms$^{-1}$. This indicates that the laser pulse excited a small fraction of the sample into the HS state. When the repetition rate is set to approx. Sixteen laser pulses per SR pulse, the spectrum changed considerably (see Fig. 6c). $\gamma_{HS}$ increased to 17%. Thus, the laser pulses excite the complex to the HS state.

## 4 Conclusions

We report the results of the optical pump-nuclear resonance probe experiments performed on spin crossover complexes $[Fe(NH_2trz)_3]Cl_2$ and $[Fe(PM\text{-}BiA)_2(NCS)_2]$. The optical pump laser was triggered to emit at least one pulse in synchronization to the x-ray pulses. By analyzing the recorded NFS data using CONUSS we extracted the hyperfine parameters and estimated the HS fraction $\gamma_{HS}$ of the sample created by the laser pulses [11]. It was observed that as the number of laser pulses triggered at each SR pulse was increased, $\gamma_{HS}$ increased linearly and, simultaneously, the effective thickness decreased linearly due to the reduction of the Lamb-Mössbauer factor in the HS phase. Further investigations are underway to identify the contribution of the optical field alone of the laser pulses in the excitation of SCO complexes to the HS state.

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