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Shifting photo-stationary light-induced excited spin state trapping equilibrium towards higher temperature by increasing light fluence

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Abstract: The Light-Induced Excited Spin-State Trapping (LIESST) process allows tuning the electronic state of spin-crossover materials from low (LS) to high spin (HS) states. The photoinduced HS state is long-lived, up to a characteristic temperature, $T(\text{LIESST})$, above which the system relaxes rapidly to the LS state. We study the effect of light irradiance on competing LS→HS up-conversion and HS→LS thermal relaxation on the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ system. Raman spectroscopy and magnetic measurements are used to investigate this phenomenon. An empiric model describes the competition between up conversion and thermal relaxation mechanisms and the stabilization of photo-stationary state towards higher temperature.

Introduction

Light is a tool to access states of matter, sometimes hidden at thermal equilibrium, which provides opportunities for photonic technologies. Spin Crossover materials (SCO) are textbook examples of bistable systems, which undergo spin-state conversion from low-spin (LS) to high-spin (HS) state.¹⁻³ The relative stability of HS and LS states is balanced under the effect of various external parameters, including temperature and pressure. For example, the LS to HS conversion at thermal equilibrium comes from the entropy change between LS and HS phases.⁴⁻¹³ This includes both the spin multiplicity contribution and the vibrational entropy contribution due to the shift of vibrational frequencies.³ In addition, optical excitation involving electronic transition around metal center can lead to LS→HS spin-state switching as a result of the Light-Induced Excited Spin-State Trapping (LIESST) process.¹⁴ A crucial point for observing transient LIESST, or reverse-LIESST, is the lifetime of the photoinduced state. In the first study of the LIESST effect, performed in solution, McGarvey et al. used nanosecond laser excitation and flash photolysis to induce and probe the dynamics of the spin equilibrium on the hundreds of ns timescale.¹⁵ Decurtins et al. investigated the LS→HS solid-state photoswitching in crystals at low temperatures (below 50 K)¹⁴ where the long-lived photoinduced HS state can be probed by more conventional techniques such as optical spectroscopy. During the last decade, ultrafast spectroscopic techniques have been intensively used to study the LIESST effect on few Fe(II) compounds. LIESST occurs typically within 150 fs for metal-to-ligand charge-transfer excitation and within 70 fs for d-d excitation,¹⁶⁻²⁵ and is driven by the activation and damping of the molecular breathing mode that elongate the Fe-ligand bonds.^{16-17, 19-21, 26} The reverse LIESST process is much slower and occurs within 40 ps.²⁷ Ultrafast techniques allow probing relaxation from photoinduced HS to ground LS states, but more interestingly also allow probing the multi-step conversion process in solid states where, in addition to sub-ps molecular photo-switching, delayed cooperative elastic conversion and thermal conversion also occur.²⁸⁻³⁴

The lifetime of the photo-induced state and the temperature at which photoswitching occurs are crucial aspects for various applications.³⁵⁻³⁶ In this way, for spin-crossover materials, the T(LIESST) temperature corresponds to a characteristic relaxation temperature, where the lifetime of the metastable photoinduced state, which is photoinduced at low temperature, becomes short in the dark. For comparing the lifetime of the photoinduced HS state in various systems, the T(LIESST) temperature was defined as the inflexion point of the relaxation from the HS state, photoinduced at 10 K, upon slow warming in the dark with a heating rate of 0.3 K/min.^{35, 37} It is important to find techniques that can evidence LIESST, without requiring ultrafast techniques or very low temperature measurements (below liquid Nitrogen), and which can be used on μm -sized single crystals, since the amount of sample is sometimes limited. In the present work, instead of studying the evolution of the sample in the dark, we use continuous light irradiation to study its photo-stationary evolution. Here we show that micro-Raman spectroscopy allows observing LIESST above T(LIESST) and that the laser fluence is a control parameter for observing this phenomenon. Indeed, the competition between photoinduced LS→HS conversion and thermal HS→LS relaxation allows reaching a photo-stationary state with appropriate laser fluence.

The $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ material studied here is a well-known prototypical SCO system.^{4, 17, 31, 38-40} At atmospheric pressure it undergoes a weakly first-order phase transition around ≈ 173 K from LS ($S=0$, $t_{2g}^6 e_g^0$) to HS ($S=2$, $t_{2g}^4 e_g^2$) states, where t_{2g} and e_g orbitals refer to Fe d-orbitals. As it is the case for many SCO materials, $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ exhibits photomagnetic and photochromic properties upon optical excitation around 650 nm, where d-d and MLCT bands are found.^{16-17, 31, 39-43} Herber et al. used variable-temperature infrared spectroscopy to follow the thermal evolution of the metastable photoinduced HS state of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, by using the IR spectroscopic fingerprints of the HS and LS states. In this way, they found that the photoinduced HS state relaxes around $T(\text{LIESST})=63$ K.⁴⁴ The spin-state switching is associated with important structural reorganizations,^{17, 39, 45} as the less bonding HS state leads to the expansion of the Fe-ligand distance, from $\langle Fe-N \rangle_{LS} = 1.97 \text{ \AA}$ to $\langle Fe-N \rangle_{HS} = 2.16 \text{ \AA}$, as reported for many Fe^{II} SCO materials.⁴⁶ This structural reorganization gives rise to an energy barrier between the HS and the ground LS state, which stabilizes the photoinduced state at low temperature.^{17, 39, 45} An important signature of the spin-state switching is the frequency shift of the different N–CS stretching modes, which can be probed by Raman or IR spectroscopies.^{4, 7, 47-48}

Experiment

We performed Raman Spectroscopy with an Invia Spectrometer from Renishaw. We used two different laser wavelengths: 633 nm obtained from a HeNe laser and 785 nm with a laser diode. The temperature was controlled by a HFS600E-PB4 stage from Linkam. Incident excitation light was linearly polarized along the b axis of the crystal, which corresponds to the C_2 molecular axis.³⁸ In the backscattering configuration of the microscope, only the parallel polarization of backscattered Raman signals was recovered using a linear analyzer for the output. Since the unit cell in the crystal contains 4 molecules, there are 8 N–CS stretching modes of symmetry A_g , A_u , B_{1g} , B_{2g} , B_{3g} , B_{1u} , B_{2u} or B_{3u} (mmm point group).³⁸ Only the g modes are Raman-active and in the single crystal. The bb polarizations of the selected fields allow probing the A_g mode only, avoiding the superposition of signals from other modes of different symmetries. For both measurements performed at 633 nm and 785 nm we used a microscope objective to focus the laser on a $\approx 4 \mu\text{m}^2$ spot on a single crystal.

The photomagnetic measurements were carried out on a thin layer of polycrystals of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, using a laser diode coupled to an optical fiber through the cavity of a MPMS-5 Quantum Design SQUID magnetometer. The standardized procedure for registering the $T(\text{LIESST})$ properties was as previously published.^{35,37} After slow cooling to 20 K (in the LS state), the sample was irradiated at 650 nm, at various fluences (from 10 to 80 mW/cm²). The magnetization change was followed until the photo-saturation point was reached. The temperature was then increased at a temperature scan rate of 0.5 K/min, keeping the light irradiation on, until the compound fully relaxes to the LS state. In the absence of irradiation, the magnetization was also measured from 10 to 300 K to follow the thermal spin transition and obtain a reference curve.

Results and discussion

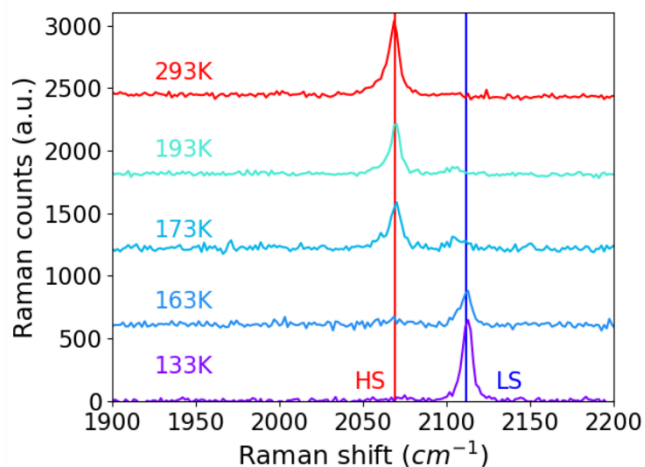


Fig. 1. Temperature dependence of bb polarized Raman spectra measured on a $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ single crystal with 633 nm excitation. The frequency shift of the A_g Raman N–CS stretching modes is characteristic of the transition between the HS and LS phase.

The thermal dependence of the vibrational modes of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ has already been presented in the literature,^{4, 7, 38} and there are many modes exhibiting frequency shifts between LS and HS states. Here we focus our attention on the high frequency range ($1900\text{--}2200\text{ cm}^{-1}$) in order to probe modes involving essentially the $\text{C}\equiv\text{N}$ bonds. Moreover, we take advantage of light polarization for probing the single $\text{N}\leftrightarrow\text{CS}$ stretching mode of A_g symmetry. Fig. 1 displays Raman spectra recorded for A_g symmetry (bb polarization) at different temperatures above and below the spin transition temperature. At 293 K, the system is fully in the HS state, as characterized by the $\text{N}\leftrightarrow\text{CS}$ stretching mode at $\approx 2070\text{ cm}^{-1}$. At 133 K, the system is fully in the LS state, as characterized by the A_g $\text{N}\leftrightarrow\text{CS}$ stretching mode at $\approx 2114\text{ cm}^{-1}$. Just above the phase transition, at 193 K and 173 K, a small fraction of the molecules converts to the LS state, while at 163 K a weak signal of HS molecules is also observed. All these features are in good agreement with magnetic susceptibility data providing a phase transition temperature $T_{1/2} \sim 173\text{ K}$ with partial conversion on each side.⁴⁰ This confirms the sensitivity of Raman spectroscopy to probe the spin state reported in various systems,^{6, 49–50} even though the measurement may be affected by a weak heating from the laser, lower than 5 K.

Figure 2 shows Raman spectra excited at 633 nm with irradiances of 100 W/cm^2 and 200 W/cm^2 in the lower temperature range. For both fluences, a single Raman peak is observed around 2114 cm^{-1} at 123 K, which corresponds to the LS mode. However, at 113 K, while the main peak is centered at 2114 cm^{-1} , another weak peak appears at 2070 cm^{-1} , which corresponds to the HS state. As temperature is lowered to 103 K and 93 K, there is a spectral weight transfer from the LS signal to the HS signal. At 88 K, the LS signal has almost disappeared for a fluence of 200 W/cm^2 , while it is still present at 100 W/cm^2 . For both laser fluences the system is mainly in the HS state at 83 K under the 633 nm excitation of the Raman set-up.

The black spectra at the bottom of Fig. 2 show Raman measurements performed at 785 nm excitation at laser fluences similar to 633 nm excitation (100 W/cm² and 200 W/cm²). At 785 nm excitation, only the LS peak is present at 83 K, and there is no conversion towards the HS state, in opposition to the observation made at 633 nm. The HS state observed for 633 nm excitation is therefore photoinduced. Indeed, the d-d and MLCT bands driving LIESST for [Fe(phen)₂(NCS)₂] are around 650 nm.¹⁶⁻¹⁷ However, 785 nm excitation cannot induce electronic transition: the photon energy is lower than the gap of the LS state found by theoretical calculations,¹⁶⁻¹⁷ which is characterized by a lack of absorption above 750 nm.^{40,51} At last, since the observed effect decreases as temperature increases (Fig. 2) we can underline that the photoinduced HS state observed here upon 633 nm excitation is not due to laser heating. Kato *et al* reported similar phenomena by using x-ray diffraction for monitoring the effect of light excitation. They demonstrated the on-off optical control of spin-state switching and excluded laser heating effect.⁵²

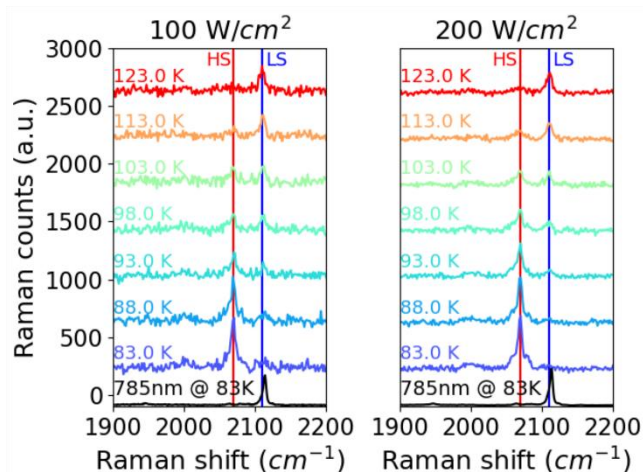


Fig. 2. Temperature dependence of the frequency of the A_g Raman N↔CS stretching mode in low temperature region and measured at 633 nm (colored) and 785 nm (black).

As the impact of light fluence on the Raman spectra was important, we conducted SQUID measurements under light for different light fluences. Fig. 3 shows the evolution with temperature and under continuous light excitation of the fraction γ of molecules in HS state, extracted from magnetic susceptibility. Even though the laser fluence is much lower than for micro-Raman, it is clear that the photo-stationary HS fraction is stabilized towards higher temperature as laser fluence increases. The photo-stationary half conversion temperature $T_{\frac{1}{2}}^{hv}$, where $\gamma = \frac{1}{2}$ under light irradiation, shifts from 59 K (0.01 W/cm²) to 62 K (0.08 W/cm²).

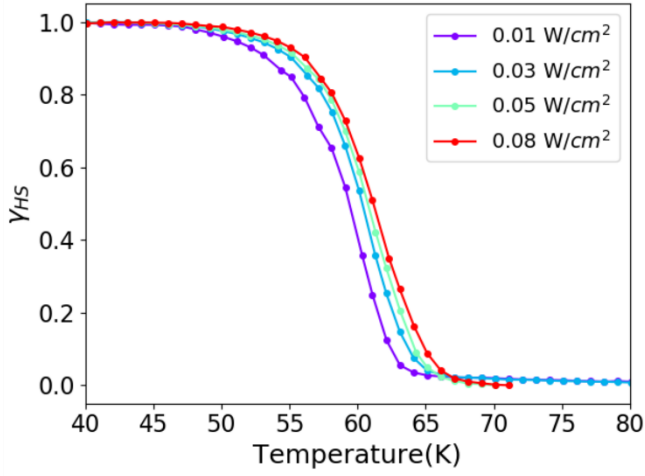


Fig. 3. Temperature dependence of the photo-stationary HS fraction γ extracted from SQUID measurements.

The observed photo-stationary population of the HS state is due to the well-known competition between the photoinduced LS→HS photo-conversion and thermally-activated HS→LS relaxation. In order to discuss this phenomenon, we use a simplified version of the model introduced by Desaix *et al.*,⁵³ which describes the competition between photoexcitation driven by permanent light irradiation and relaxation towards the non-excited state. These authors considered a relaxation rate depending on the HS fraction γ , due to cooperative interactions, which modulate the energy barrier. The following master equation from Desaix *et al.*, describes the evolution of γ under competing photoinduced LS→HS conversion and thermally-activated HS→LS relaxation:

$$\frac{d\gamma}{dt} = \Phi_{LS \rightarrow HS} - \Phi_{HS \rightarrow LS} = I_0 \omega (1 - \gamma) - \gamma k_{\infty} \exp\left(-\frac{E_a(0)}{kT}\right) \exp(-\alpha\gamma)$$

Where $I_0 \omega$ is the probability per time unit for a LS molecule to absorb a photon and switch to the HS state, with I_0 the beam fluence (in photons/s/cm²) and ω a proportionality factor, which includes the absorption cross-section of the optical transition driving LIESST. α is the self-acceleration factor, which is important for describing non-exponential relaxations. In the case of the [Fe(phen)₂(NCS)₂] system investigated here, the cooperative interactions are not so strong: the thermal conversion exhibits pretransitional conversion and at high temperature the relaxation curves from the photoinduced HS state are close to exponential.⁵⁴ In this case, we can simplify Desaix's model and neglect the self-acceleration factor in a first approximation and for a non-cooperative system, the equation can be reduced to

$$\frac{d\gamma}{dt} = I_0 \omega (1 - \gamma) - \gamma k_{\infty} \exp\left(-\frac{E_a}{kT}\right)$$

The photo-stationary state is then found for

$$\begin{aligned} \frac{d\gamma}{dt} &= 0 \\ I_0 \omega (1 - \gamma) &= \gamma k_{\infty} \exp\left(-\frac{E_a}{kT}\right) = \gamma k(T) \end{aligned}$$

$k(T)$ is the temperature dependence of the HS→LS relaxation rate for an exponential decay. This is reasonable since Badle *et al* have reported an almost linear evolution of $\ln(k(T))$ with $\frac{1}{T}$ for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.^{40, 54} In this way, the photo-stationary HS fraction depends on the thermal relaxation rate and on the laser fluence, which rescales $k(T)$ to $r(T)$

$$\gamma(T) = \frac{1}{1 + \frac{k(T)}{I_0\omega}} = \frac{1}{1 + r(T)}$$

The half-conversion photo-stationary equilibrium, $\gamma = \frac{1}{2}$, occurs when $k(T) = I_0\omega$, *i.e.* when the LS→HS conversion and HS→LS relaxation rates are equal. We define $T_{\frac{1}{2}}^{hv}(I_0\omega)$ as the temperature for which half-conversion is reached under laser fluence I_0 for a non-cooperative system, with known $k(T)$ and ω . In this way, the light fluence I_0 is the control parameter for reaching photostationary equilibrium.

Fig. 4a shows the calculated dependence of the photo-stationary HS fraction with temperature, using the $k(T)$ values reported by Baldé *et al*.⁵⁴ Since the relaxation rate in SCO materials is known to change by 12 orders of magnitude with temperature,⁵⁵ the laser fluence also has to change by orders of magnitudes to shift $T_{\frac{1}{2}}^{hv}$. For example, Baldé *et al* measured $k(85 \text{ K}) = 1$.⁵⁴ Photo-stationary half-conversion at $T_{\frac{1}{2}}^{hv} = 85 \text{ K}$ is then possible when $I_0\omega = 1$, which corresponds to 1 photon absorbed per molecule and per second, as the quantum efficiency of LS→HS photoconversion is close to 1. For reaching photo-stationary half conversion at $T_{\frac{1}{2}}^{hv} = 60 \text{ K}$, where $k(60 \text{ K}) = 0.0002$,⁵⁴ the laser fluence should therefore be reduced by almost 4 orders of magnitude compared to 85 K. This agrees with light fluence used for Raman experiments (100 W/cm^2) where $\gamma = \frac{1}{2}$ at $T_{\frac{1}{2}}^{hv} = 90 \text{ K}$ and SQUID experiment (0.01 W/cm^2) where $\gamma = \frac{1}{2}$ at $T_{\frac{1}{2}}^{hv} = 60 \text{ K}$. The model, considering the $k(T)$ data reported for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$,⁵⁴ predicts a shift of $T_{\frac{1}{2}}^{hv}$ from ≈ 55 to $\approx 90 \text{ K}$ if the light fluence increases by 4 orders of magnitude (Fig. 4b). During the SQUID experiment, the limited increase in light fluence from 0.01 to 0.08 W/cm^2 allows for a small shift of $T_{\frac{1}{2}}^{hv}$ of about 3 K.

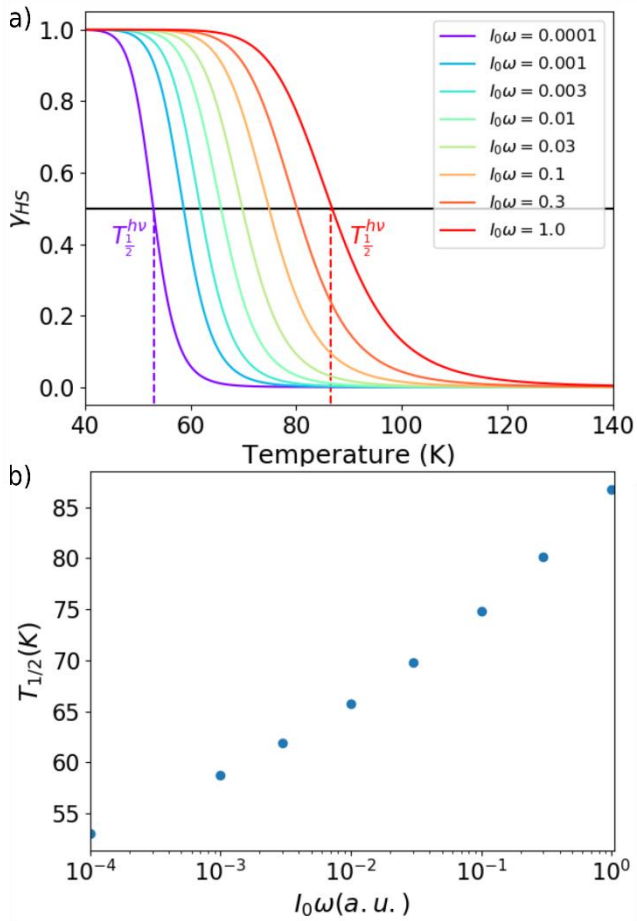


Fig. 4. a) Calculated temperature dependence of the photo-stationary HS fraction. b) Evolution of $T_{1/2}^{hv}$ with $I_0\omega$.

Fig. 5 summarizes the experimental and theoretical results. In addition to Raman and SQUID data, we include reflectivity measurements published in ref. 16 with an intermediate fluence, more difficult to estimate since reflectivity mainly probes changes induced by a white light excitation close to surface, where optical excitation is higher than in the bulk. The fit of the experimental data with the model, provides some $I_0\omega$ values ($I_0\omega = 1$ for Raman $I_0\omega = 0.001$ for SQUID data) which confirms that for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ it is necessary to increase the laser fluence by 4 orders of magnitude to shift $T_{1/2}^{hv}$ 30 K above $T(\text{LIESST})$. The different shapes of the experimental data compared to the fit may come from the approximation that $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ is a non-cooperative system. However, the order of magnitude of the shift of $T_{1/2}^{hv}$ with $I_0\omega$ is in good agreement with experimental data.

Another study by Kato et al⁵² evidenced that the photoresponse of this materials is more important under excitation at 532 nm, which allows a 88% conversion at 92 K with $I_0 = 2 \text{ W/cm}^2$. The highest absorption at 532 nm translates in higher ω , compared to 633 nm in our experiment, and finally the products $I_0\omega$ are comparable in both experiments.

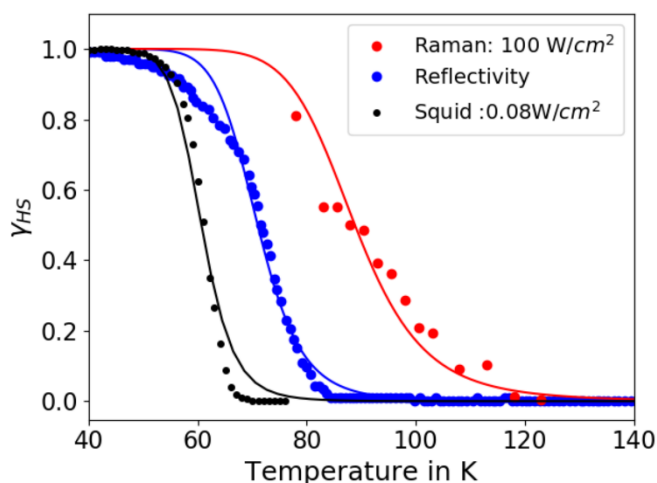


Fig. 5. Temperature dependence of the photo-stationary HS fraction from SQUID (black), reflectivity (blue) and micro-Raman (red) measurements. The continuous lines are a fit of the data with $I_0\omega$ as free parameter.

4 Conclusions

This paper discusses the possibility to investigate the LIESST processes in SCO materials well above $T(\text{LIESST})$ under high light fluence. A simple model explains that, for no or weakly cooperative systems, a photo-stationary half photo-conversion is observed when the when the number of absorbed photons per second equals the relaxation rate. With this respect, μ -Raman technique allows observing LIESST at lower cost by using liquid-nitrogen operating cryostats instead of He-operating ones, without using sophisticated time-resolved technique and with the possibility to investigate micro-crystals. Tracking how photo-stationary half-conversion evolves with temperature and light fluence is then another approach for measuring HS \rightarrow LS thermal relaxation rates.

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Author contributions

E.C., J.-Y.M., E.J., L.Gu, M.C. and B.H conceived and coordinated the project in the frame of the ANR ELECTROPHONE and MULTICROSS projects. L.Go., I.C., J.-Y.M. and B.H. performed the Raman experiment and analyzed the data. N.D. synthesized the samples. G.C. performed the SQUID measurements and analyzed the data. L. Go. and E.C. developed the photo-stationary model. E.C. and L. Go wrote the manuscript with significant contributions from B.H., J.-Y.M., E.J. and G.C.. All authors contributed to discussions and gave comments on the manuscript.

References

1. Halcrow, M. A., *Spin-crossover materials : properties and applications*. Wiley: 2013; p xviii, 546 p.
2. Gutlich, P.; Hauser, A.; Spiering, H., Thermal and Optical Switching of Iron(II) Complexes. *Angewandte Chemie-International Edition in English* **1994**, *33* (20), 2024-2054.
3. Nicolazzi, W.; Bousseksou, A., Thermodynamical aspects of the spin crossover phenomenon. *Cr Chim* **2018**, *21* (12), 1060-1074.
4. Ronayne, K. L.; Paulsen, H.; Hofer, A.; Dennis, A. C.; Wolny, J. A.; Chumakov, A. I.; Schunemann, V.; Winkler, H.; Spiering, H.; Bousseksou, A.; Gutlich, P.; Trautwein, A. X.; McGarvey, J. J., Vibrational spectrum of the spin crossover complex [Fe(phen)(2)(NCS)(2)] studied by IR and Raman spectroscopy, nuclear inelastic scattering and DFT calculations. *Physical Chemistry Chemical Physics* **2006**, *8* (40), 4685-4693.
5. Buron-Le Cointe, M.; Hébert, J.; Baldé, C.; Moisan, N.; Toupet, L.; Guionneau, P.; Létard, J. F.; Freysz, E.; Cailleau, H.; Collet, E., Intermolecular control of thermoswitching and photoswitching phenomena in two spin-crossover polymorphs. *Physical Review B* **2012**, *85*, 064114
6. Tuchagues, J. P.; Bousseksou, A.; Molnar, G.; McGarvey, J. J.; Varret, F., The role of molecular vibrations in the spin crossover phenomenon. *Top Curr Chem* **2004**, *235*, 85-103.
7. Brehm, G.; Reiher, M.; Schneider, S., Estimation of the vibrational contribution to the entropy change associated with the low- to high-spin transition in Fe(phen)(2)(NCS)(2) complexes: Results obtained by IR and Raman spectroscopy and DFT calculations. *Journal of Physical Chemistry A* **2002**, *106* (50), 12024-12034.
8. Metatla, A.; Latelli, H.; Nicolazzi, W.; Bousseksou, A., Vibration-driven thermal transition in binuclear spin crossover complexes. *The European Physical Journal B* **2012**, *85* (6).
9. Sorai, M.; Seki, S., Phonon coupled cooperative low-spin 1A1high-spin 5T2 transition in [Fe(phen)2(NCS)2] and [Fe(phen)2(NCSe)2] crystals. *Journal of Physics and Chemistry of Solids* **1974**, *35* (4), 555-570.
10. Takemoto, J. H.; Streusan, B.; Hutchins, B., Far-Infrared Spectra of Some Fe(1,10-Phenanthroline)2x2 Complexes. *Spectrochim Acta A* **1974**, *30* (3), 827-834.
11. Watanabe, H.; Tanaka, K.; Bréfuel, N.; Cailleau, H.; Létard, J.-F.; Ravy, S.; Fertey, P.; Nishino, M.; Miyashita, S.; Collet, E., Ordering phenomena of high-spin/low-spin states in stepwise spin-crossover materials described by the ANNNI model. *Physical Review B* **2016**, *93*, 014419.
12. Collet, E.; Azzolina, G., Coupling and decoupling of spin crossover and ferroelastic distortion: Unsymmetric hysteresis loop, phase diagram, and sequence of phases. *Physical Review Materials* **2021**, *5* (4), 044401.
13. Azzolina, G.; Bertoni, R.; Collet, E., General Landau theory of non-symmetry-breaking and symmetry-breaking spin transition materials. *Journal of Applied Physics* **2021**, *129* (8), 085106.
14. Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A., Light-induced excited spin state trapping in a transition-metal complex: The hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system. *Chemical Physics Letters* **1984**, *105* (1), 1-4.
15. Lawthers, I.; McGarvey, J. J., Spin-State Relaxation Dynamics in Iron(III) Complexes - Photochemical Perturbation of the 2t Reversible 6a Spin Equilibrium by Pulsed-Laser Irradiation in the Ligand-to-Metal Charge-Transfer Absorption-Band. *Journal of the American Chemical Society* **1984**, *106* (15), 4280-4282.
16. Bertoni, R.; Cammarata, M.; Lorenc, M.; Matar, S. F.; Létard, J. F.; Lemke, H. T.; Collet, E., Ultrafast light-induced spin-state trapping photophysics investigated in Fe(phen)2(NCS)2 spin-crossover crystal. *Acc Chem Res* **2015**, *48* (3), 774-81.
17. Cammarata, M.; Bertoni, R.; Lorenc, M.; Cailleau, H.; Di Matteo, S.; Mauriac, C.; Matar, S. F.; Lemke, H.; Chollet, M.; Ravy, S.; Lahlou, C.; Létard, J. F.; Collet, E., Sequential Activation of Molecular Breathing and Bending during Spin-Crossover Photoswitching Revealed by Femtosecond Optical and X-Ray Absorption Spectroscopy. *Physical Review Letters* **2014**, *113* (22), 227402.
18. Zerdane, S.; Cammarata, M.; Iasco, O.; Boillot, M. L.; Collet, E., Photoselective MLCT to d-d pathways for light-induced excited spin state trapping. *The Journal of chemical physics* **2019**, *151* (17), 171101.
19. Lemke, H. T.; Kjær, K. S.; Hartsock, R.; Brandt van Driel, T.; Chollet, M.; Glowina, J. M.; Song, S.; Zhu, D.; Pace, E.; Matar, S. F.; Nielsen, M. N.; Benfatto, M.; Gaffney, K. J.; Collet, E.; Cammarata, M., Coherent structural trapping through wave packet dispersion during photoinduced spin state switching. *Nat. Commun.* **2017**, *8*, 15342.
20. Zerdane, S.; Wilbraham, L.; Cammarata, M.; Iasco, O.; Rivière, E.; Boillot, M. L.; Ciofini, I.; Collet, E., Comparison of structural dynamics and coherence of d-d and MLCT light-induced spin state trapping. *Chem. Sci.* **2017**, *8*, 4978-4986.
21. Marino, A.; Cammarata, M.; Matar, S. F.; Létard, J. F.; Chastanet, G.; Chollet, M.; Glowina, J. M.; Lemke, H. T.; Collet, E., Activation of coherent lattice phonon following ultrafast molecular spin-state photo-switching: A molecule-to-lattice energy transfer. *Struct Dyn* **2016**, *3* (2), 023605.
22. Aubock, G.; Chergui, M., Sub-50-fs photoinduced spin crossover in [Fe(bpy)(3)](2+). *Nature Chemistry* **2015**, *7* (8), 629-633.
23. Huse, N.; Cho, H.; Hong, K.; Jamula, L.; de Groot, F. M. F.; Kim, T. K.; McCusker, J. K.; Schoenlein, R. W., Femtosecond Soft X-ray Spectroscopy of Solvated Transition-Metal Complexes: Deciphering the Interplay of Electronic and Structural Dynamics. *Journal of Physical Chemistry Letters* **2011**, *2* (8), 880-884.

24. Kjær, K. S.; Van Driel, T. B.; Harlang, T. C. B.; Kunnus, K.; Biasin, E.; Ledbetter, K.; Hartsock, R. W.; Reinhard, M. E.; Koroidov, S.; Li, L.; Laursen, M. G.; Hansen, F. B.; Vester, P.; Christensen, M.; Haldrup, K.; Nielsen, M. M.; Dohn, A. O.; Pápai, M. I.; Møller, K. B.; Chabera, P.; Liu, Y.; Tatsuno, H.; Timm, C.; Jarenmark, M.; Uhlig, J.; Sundstöm, V.; Wärnmark, K.; Persson, P.; Németh, Z.; Szemes, D. S.; Bajnóczi, É.; Vankó, G.; Alonso-Mori, R.; Glowina, J. M.; Nelson, S.; Sikorski, M.; Sokaras, D.; Canton, S. E.; Lemke, H. T.; Gaffney, K. J., Finding intersections between electronic excited state potential energy surfaces with simultaneous ultrafast X-ray scattering and spectroscopy. *Chem Sci* **2019**, *10* (22), 5749-5760.
25. Zhang, W. K.; Alonso-Mori, R.; Bergmann, U.; Bressler, C.; Chollet, M.; Galler, A.; Gawelda, W.; Hadt, R. G.; Hartsock, R. W.; Kroll, T.; Kjaer, K. S.; Kubicek, K.; Lemke, H. T.; Liang, H. Y. W.; Meyer, D. A.; Nielsen, M. M.; Purser, C.; Robinson, J. S.; Solomon, E. I.; Sun, Z.; Sokaras, D.; van Driel, T. B.; Vanko, G.; Weng, T. C.; Zhu, D. L.; Gaffney, K. J., Tracking excited-state charge and spin dynamics in iron coordination complexes. *Nature* **2014**, *509* (7500), 345-348.
26. Chergui, M.; Collet, E., Photoinduced structural dynamics of molecular systems mapped by time-resolved x-ray methods. *Chemical Reviews* **2017**, *117* (16), 11025–11065.
27. Marino, A.; Chakraborty, P.; Servol, M.; Lorenc, M.; Collet, E.; Hauser, A., The Role of Ligand- Field States in the Ultrafast Photophysical Cycle of the Prototypical Iron(II) Spin- Crossover Compound [Fe(ptz)₆](BF₄)₂. *Angewandte Chemie-International Edition* **2014**, *53* (15), 3863-3867.
28. Bertoni, R.; Collet, E.; Cailleau, H.; Boillot, M. L.; Tissot, A.; Laisney, J.; Enachescu, C.; Lorenc, M., Temperature dependence of the cooperative out-of-equilibrium elastic switching in a spin-crossover material. *Phys Chem Chem Phys* **2019**, *21* (12), 6606-6612.
29. Ridier, K.; Bas, A.-C.; Shalabaeva, V.; Nicolazzi, W.; Salmon, L.; Molnár, G.; Bousseksou, A.; Lorenc, M.; Bertoni, R.; Collet, E.; Cailleau, H., Finite Size Effects on the Switching Dynamics of Spin-Crossover Thin Films Photoexcited by a Femtosecond Laser Pulse. *Adv Mater* **2019**, *31* (25), 1901361.
30. Bertoni, R.; Lorenc, M.; Cailleau, H.; Tissot, A.; Laisney, J.; Boillot, M. L.; Stoleriu, L.; Stancu, A.; Enachescu, C.; Collet, E., Elastically driven cooperative response of a molecular material impacted by a laser pulse. *Nat Mater* **2016**, *15* (6), 606-10.
31. Bertoni, R.; Lorenc, M.; Graber, T.; Henning, R.; Moffat, K.; Létard, J. F.; Collet, E., Cooperative elastic switching vs. laser heating in [Fe(phen)₂(NCS)₂] spin-crossover crystals excited by a laser pulse. *Crystengcomm* **2016**, *18* (38), 7269-7275.
32. Collet, E.; Lorenc, M.; Cammarata, M.; Guerin, L.; Servol, M.; Tissot, A.; Boillot, M. L.; Cailleau, H.; Buron-Le Cointe, M., 100 Picosecond Diffraction Catches Structural Transients of Laser-Pulse Triggered Switching in a Spin-Crossover Crystal. *Chemistry-a European Journal* **2012**, *18* (7), 2051-2055.
33. Collet, E.; Moisan, N.; Balde, C.; Bertoni, R.; Trzop, E.; Lailhe, C.; Lorenc, M.; Servol, M.; Cailleau, H.; Tissot, A.; Boillot, M. L.; Graber, T.; Henning, R.; Coppens, P.; Buron-Le Cointe, M., Ultrafast spin-state photoswitching in a crystal and slower consecutive processes investigated by femtosecond optical spectroscopy and picosecond X-ray diffraction. *Physical Chemistry Chemical Physics* **2012**, *14* (18), 6192-6199.
34. Lorenc, M.; Hebert, J.; Moisan, N.; Trzop, E.; Servol, M.; Buron-Le Cointe, M.; Cailleau, H.; Boillot, M. L.; Pontecorvo, E.; Wulff, M.; Koshihara, S.; Collet, E., Successive Dynamical Steps of Photoinduced Switching of a Molecular Fe(III) Spin-Crossover Material by Time-Resolved X-Ray Diffraction. *Physical Review Letters* **2009**, *103* (2), 028301
35. Chastanet, G.; Desplanches, C.; Baldé, C.; Rosa, P.; Marchivie, M.; Guionneau, P., A critical review of the T(LIESST) temperature in spin crossover materials – What it is and what it is not. *Chemistry Squared* **2018**, *2*, 2.
36. Chastanet, G.; Lorenc, M.; Bertoni, R.; Desplanches, C., Light-induced spin crossover—Solution and solid-state processes. *Cr Chim* **2018**, *21* (12), 1075-1094.
37. Létard, J.-F.; Capes, L.; Chastanet, G.; Moliner, N.; Létard, S.; Real, J.-A.; Kahn, O., Critical temperature of the LIESST effect in iron(II) spin crossover compounds. *Chemical Physics Letters* **1999**, *313* (1), 115-120.
38. Collet, E.; Azzolina, G.; Ichii, T.; Guerin, L.; Bertoni, R.; Moréac, A.; Cammarata, M.; Daro, N.; Chastanet, G.; Kubicki, J.; Tanaka, K.; Matar, S. F., Lattice phonon modes of the spin crossover crystal [Fe(phen)₂(NCS)₂] studied by THz, IR, Raman spectroscopies and DFT calculations. *The European Physical Journal B* **2019**, *92* (1).
39. Marchivie, M.; Guionneau, P.; Howard, J. A. K.; Chastanet, G.; Letard, J. F.; Goeta, A. E.; Chasseau, D., Structural characterization of a photoinduced molecular switch. *Journal of the American Chemical Society* **2002**, *124* (2), 194-195.
40. Balde, C.; Desplanches, C.; Wattiaux, A.; Guionneau, P.; Gutlich, P.; Letard, J. F., Effect of metal dilution on the light-induced spin transition in [Fe(x)Zn(1-x)(phen)₂(NCS)₂] (phen = 1,10-phenanthroline). *Dalton Trans* **2008**, (20), 2702-7.
41. Lee, J. J.; Sheu, H. S.; Lee, C. R.; Chen, J. M.; Lee, J. F.; Wang, C. C.; Huang, C. H.; Wang, Y., X-ray absorption spectroscopic studies on light-induced excited spin state trapping of an Fe(II) complex. *Journal of the American Chemical Society* **2000**, *122* (24), 5742-5747.
42. Letard, J. F.; Guionneau, P.; Rabardel, L.; Howard, J. A. K.; Goeta, A. E.; Chasseau, D.; Kahn, O., Structural, magnetic, and photomagnetic studies of a mononuclear iron(II) derivative exhibiting an exceptionally abrupt spin transition. Light-induced thermal hysteresis phenomenon. *Inorganic Chemistry* **1998**, *37* (17), 4432-4441.

43. Real, J. A.; Gallois, B.; Granier, T.; Suez-Panama, F.; Zarembowitch, J., Comparative investigation of the spin-crossover compounds Fe(btz)₂(NCS)₂ and Fe(phen)₂(NCS)₂ (where btz = 2,2'-bi-4,5-dihydrothiazine and phen = 1,10-phenanthroline). Magnetic properties and thermal dilatation behavior and crystal structure of Fe(btz)₂(NCS)₂ at 293 and 130 K. *Inorganic Chemistry* **1992**, *31* (24), 4972-4979.
44. Herber, R. H., VTFTIR and light-induced excited spin state trapping in bis(2,2'-bipyridine)bis(thiocyanato)iron and related spin-crossover compounds. *Inorganic Chemistry* **1987**, *26* (1), 173-178.
45. Briois, V.; Moulin, C. C. D.; Sainctavit, P.; Brouder, C.; Flank, A. M., Full Multiple-Scattering and Crystal-Field Multiplet Calculations Performed on the Spin Transition Fe-li(Phen)₂(Ncs)₂ Complex at the Iron K(2,3) and L(2,3) X-Ray-Absorption Edges. *Journal of the American Chemical Society* **1995**, *117* (3), 1019-1026.
46. Collet, E.; Guionneau, P., Structural analysis of spin-crossover materials: From molecules to materials. *Cr Chim* **2018**, *21* (12), 1133-1151.
47. Baranovic, G.; Babic, D., Vibrational study of the Fe(phen)₂(NCS)₂ spin-crossover complex by density-functional calculations. *Spectrochim Acta A* **2004**, *60* (5), 1013-1025.
48. Reiher, M., Theoretical Study of the Fe(phen)₂(NCS)₂ Spin-Crossover Complex with Reparametrized Density Functionals. *Inorganic Chemistry* **2002**, *41* (25), 6928-6935.
49. Moussa, N. O.; Trzop, E.; Mouri, S.; Zein, S.; Molnár, G.; Gaspar, A. B.; Collet, E.; Buron-Le Cointe, M.; Real, J. A.; Borshch, S.; Tanaka, K.; Cailleau, H.; Bousseksou, A., Wavelength selective light-induced magnetic effects in the binuclear spin crossover compound $\text{Fe}(\text{btz})_2(\text{NCS})_2(\text{bpym})$. *Physical Review B* **2007**, *75* (5), 054101.
50. Bonhommeau, S.; Molnar, G.; Galet, A.; Zwick, A.; Real, J. A.; McGarvey, J. J.; Bousseksou, A., One shot laser pulse induced reversible spin transition in the spin-crossover complex [Fe(C₄H₄N₂)₂{Pt(CN)₄}] at room temperature. *Angew Chem Int Ed Engl* **2005**, *44* (26), 4069-73.
51. König, E.; Watson, K. J., *Chemical Physics Letters* **1970**, *6* (5), 457-459.
52. Kato, K.; Takata, M.; Moritomo, Y.; Nakamoto, A.; Kojima, N., On-off optical switching of the magnetic and structural properties in a spin-crossover complex. *Applied Physics Letters* **2007**, *90* (20), 201902.
53. Desaix, A.; Roubeau, O.; Jeftic, J.; Haasnoot, J. G.; Boukheddaden, K.; Codjovi, E.; Linarès, J.; Noguès, M.; Varret, F., Light-induced bistability in spin transition solids leading to thermal and optical hysteresis. *Eur. Phys. J. B* **1998**, *6* (2), 183-193.
54. Balde, C.; Desplanches, C.; Nguyen, O.; Létard, J.-F.; Freysz, E., Complete temperature study of the relaxation from HS to LS state in the mixed [FexZn1-x(Phen)₂(NCS)₂] systems (with x = 1, 0.73, 0.5, 0.32, 0.19 and 0.04). *Journal of Physics: Conference Series* **2009**, *148*, 012026.
55. Hauser, A., Light-induced spin crossover and the high-spin -> low-spin relaxation. *Top Curr Chem* **2004**, *234*, 155-198.