

Thermal and light-induced spincrossover in iron(II) complexes—new perspectives in optical storage

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Abstract - Recently, we have discovered a fascinating photophysical effect in spincrossover complexes of iron(II): Light-Induced Excited Spin State Trapping (LIESST). At sufficiently low temperatures, the low spin state ($^1A_{1g}$) can be (quantitatively) converted to the high spin state ($^5T_{2g}$) by irradiating the sample into the $^1A_1 \rightarrow ^1T_1$ d-d absorption band (~ 540 nm). The metastable HS state has a practically infinite lifetime. It relaxes back to the LS state upon heating the sample. It can also be converted back to the LS state by irradiating into the $^5T_2 \rightarrow ^5E$ band (~ 850 nm). The system behaves like an optical switch. Kinetic studies on metal-diluted crystals show that the thermal relaxation is cooperative in nature in the solid state. The relative positioning - horizontally and vertically - of the two spin state potential wells is crucial for the lifetime of the metastable HS state.

1 INTRODUCTION

Temperature dependent spin transition (spincrossover) is a well-established phenomenon in the coordination chemistry of first-row transition elements. Many examples are known, e.g. for iron(II) compounds, for which the low spin $^1A_{1g}(O_h)$, "LS" \rightleftharpoons high spin ($^5T_{2g}(O_h)$, "HS") transition has been extensively studied employing various physical techniques (refs. 1-3).

In the course of our investigations of thermally driven spin transitions in solid state ferrous systems we have, recently and quite accidentally, observed a fascinating photophysical effect: If the sample is irradiated at sufficiently low temperatures with green light into the $^1A_1 \rightarrow ^1T_1$ ligand field absorption band, the thermodynamically stable LS state (1A_1) can be converted quantitatively to the metastable HS state (5T_2), where the system remains trapped with a practically infinite lifetime. We have called this phenomenon "Light-Induced Excited Spin State Trapping (LIESST)" (refs. 4,5).

The metastable HS state formed by LIESST in a solid can relax thermally to the stable LS state. It has also been demonstrated that a light-induced HS \rightarrow LS reversion can be effected by irradiating the sample with red light ($\lambda \approx 850$ nm) into the $^5T_2 \rightarrow ^5E$ band (ref. 6).

2 LIESST IN $[Fe(Rtz)_6]X_2$ ($X=BF_4, ClO_4$) CRYSTALS

The first example where we have observed the LIESST effect is $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole) (ref. 4). This complex compound is known to exhibit a thermally driven LS \rightarrow HS transition with a hysteresis of ca. 7 K near 130 K (refs. 7,8). The spin transition is accompanied by a dramatic colour change from white (HS) to purple (LS). At 273 K, there is only one absorption band at around 12.250 cm^{-1} arising from the spin-allowed $^5T_2 \rightarrow ^5E$ transition in the HS molecules (s. Fig. 1). At 8 K, this absorption band has completely vanished and is

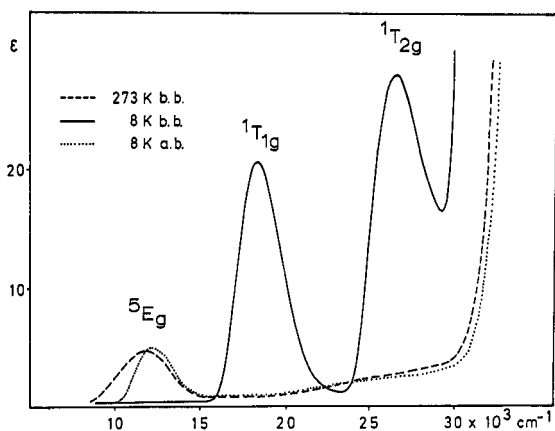


Fig. 1. Single-crystal absorption spectra (unpolarized light propagating //c) of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ before bleaching (b.b.) at 273 K and 8 K, and after bleaching (a.b.) for 2 min with white light (Xe arc lamp) at 8 K (from ref. 5).

replaced by the two spin-allowed transitions ${}^1A_1 \rightarrow {}^1T_1$ (18.400 cm^{-1}) and ${}^1A_1 \rightarrow {}^1T_2$ (26.650 cm^{-1}) in the LS molecules (ref. 5). After bleaching the crystal with white light (Xe arc lamp, 150 W, ~ 2 min) at 8 K, the typical HS spectrum is again obtained. At around 10 K, the trapped metastable HS state does not decay noticeably within 24 hours. Relaxation back to the thermodynamically stable LS state occurs only if the temperature is raised to above 50 K. We have also followed LIESST in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ by magnetic susceptibility measurements (ref. 5). If the sample is irradiated at $T < 50 \text{ K}$, values for μ_{eff} typical for HS-Fe(II) are obtained.

As the lifetime of the metastable HS state is extremely long, the sequence of ${}^{57}\text{Fe}$ Mössbauer spectra reproduced in Fig. 2 could easily be recorded. The Mössbauer spectra demonstrate again the light-induced LS \rightarrow HS conversion at 15 K (a \rightarrow b), the thermal back relaxation HS \rightarrow LS at ca. 55 K (c, d), and the well-established thermal LS \rightleftharpoons HS transition at around 130 K (e, f).

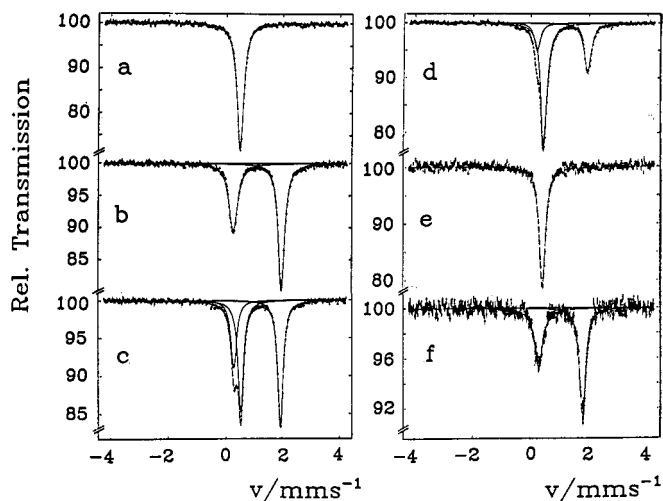


Fig. 2. Mössbauer spectra of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (from ref. 4) (a) Before bleaching (measuring temperature $T_M = 15 \text{ K}$); (b) after bleaching at 15 K ($T_M = 15 \text{ K}$); (c) after heating to ca. 55 K for a few minutes and subsequent cooling to $T_M = 15 \text{ K}$; (d) after repeating cycle (c); (e) after heating to 97 K ($T_M = 97 \text{ K}$); (f) after heating to 148 K ($T_M = 148 \text{ K}$).

The mechanism of LIESST can be explained on the basis of Fig. 3: Irradiating the cold sample induces spin-allowed transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (s. Fig. 1). The excited spin-singlet states are short-lived and can decay back to the ${}^1A_{1g}$ ground state within nanoseconds. There is, however, an alternative decay path, made possible by spin-orbit coupling, which leads to a population of the spin triplet states ${}^3T_{1g}$ and ${}^3T_{2g}$ (intersystem crossing). These

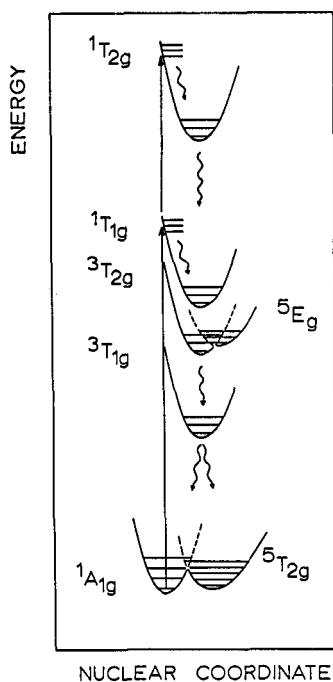


Fig. 3. Potential surface diagram according to experimental and calculated energies of the ligand field states of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (from ref. 5)

again decay via intersystem crossing, either to the $^1A_{1g}$ ground state or to the metastable $^5T_{2g}$ state. There is no radiative decay path from the $^5T_{2g}$ to the $^1A_{1g}$ state, and the $^5T_{2g}(\text{HS})$ state remains trapped with practically infinite lifetime as long as the temperature is sufficiently low so that the energy barrier between the $^5T_{2g}$ and the $^1A_{1g}$ potential surfaces, which are well separated by the large difference in the metal-ligand bond length of ca. 0.2 \AA (ref. 9), is not thermally overcome. The trapped HS state can be pumped back to the LS state by irradiating with red light (of ca. 850 nm) into the $^5T_{2g} \rightarrow ^5E_g$ absorption band (ref. 6).

The thermal $^5T_2 \rightarrow ^1A_1$ relaxation kinetics were examined with neat $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ crystals as well as with mixed crystals $[\text{Fe}_x\text{Zn}_{1-x}(\text{ptz})_6](\text{BF}_4)_2$ using optical spectroscopy (ref. 10). It was found that (a) for diluted systems ($x < 0.1$) a single-ion treatment of both the spin state equilibrium (with $\Delta H_{\text{HL}} = H_{\text{HS}} - H_{\text{LS}} = 510(12) \text{ cm}^{-1}$, $\Delta S_{\text{HL}} = S_{\text{HS}} - S_{\text{LS}} = 5.1(2) \text{ cm}^{-1}/\text{K}$ at $T = 100 \text{ K}$) and the $^5T_2 \rightarrow ^1A_1$ relaxation of the light-induced HS state (with Arrhenius activation energy $E_a^0 = 810(30) \text{ cm}^{-1}$ and frequency factor $A \sim 10^5 \text{ s}^{-1}$ is appropriate, and (b) for concentrated systems ($0.1 < x < 1$) cooperative effects become more and more important for both the $\text{LS} \rightleftharpoons \text{HS}$ equilibrium and the thermal relaxation of the metastable HS state. Figures 4 and 5 elucidate the importance of cooperative effects. These are of elastic rather than of electronic origin.

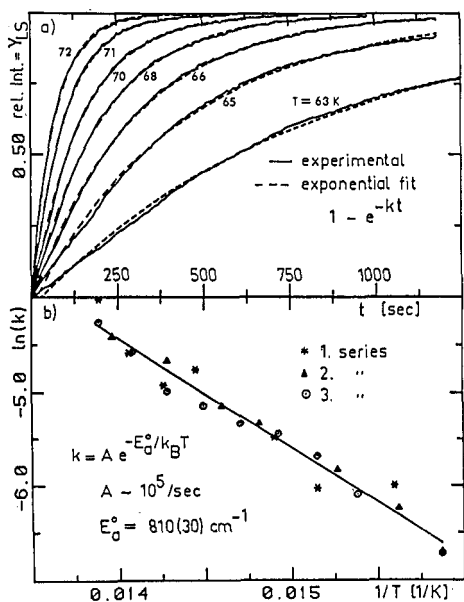


Fig. 4. (a) Normalized $^5T_2 \rightarrow ^1A_1$ relaxation curves for mixed crystals of $[\text{Fe}_x\text{Zn}_{1-x}(\text{ptz})_6](\text{BF}_4)_2$ ($x \approx 0.1$) at various temperatures.

(b) Arrhenius plot $\ln(k)$ vs. $1/T$. An exponential fit $y_{\text{LS}}(t) = 1 - \exp(-kt)$ describes well the relaxation curves in the dilute material ($x \approx 0.1$) with constant activation energy $E_a^0 = 810(30) \text{ cm}^{-1}$ and frequency factor $A \sim 10^5 \text{ s}^{-1}$ (from ref. 10)

The "lattice expansion model" (ref. 11) based on long-range elastic interactions arising from the drastic volume change $\Delta V = V_{\text{HS}} - V_{\text{LS}}$ (ref. 9) is well suited to explain the experimental

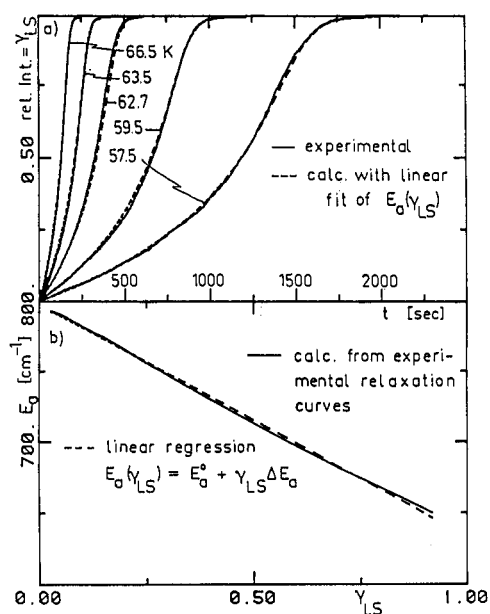


Fig. 5. (a) Normalized ${}^5T_2 \rightarrow {}^1A_1$ relaxation curves for neat crystals of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at various temperatures. The sigmoidal (rather than exponential) form of the decay curves is due to cooperative effects. The activation energy E_a is now a function of γ_{LS} (molar fraction of LS molecules) as shown in (b). The solid line in (b) was obtained from a simultaneous fit of the five measured decay curves of Fig. 5a. The broken line results from a linear regression (slope $E_a = 164 \text{ cm}^{-1}$; intercept $E_a^0 = 797 \text{ cm}^{-1}$) (from ref. 10)

findings. In particular, the model predicts the activation energy $E_a(\gamma_{\text{LS}})$ to be a linear function of the fraction of LS molecules.

Current investigations on the ligand-substituted system $[\text{Fe}^{\text{II}}(\text{mtz})_6](\text{BF}_4)_2$ ($m = \text{methyl}$), in which the iron complex molecules occupy two different crystallographic sites (ref. 12), have revealed some surprising results. (i) Only one of the two iron sites (A) undergoes thermal spin transition; the transition temperature ($T_c \approx 65 \text{ K}$) is considerably lower than in the ptz system. The other iron site (B) remains in the HS state down to 4 K. (ii) Both lattice sites A and B can be pumped back and forth between the LS and the HS states using light of appropriate wavelengths. Site A molecules, with the LS state as ground state at $T < T_c \approx 65 \text{ K}$, undergo LIESST and "Reversed LIESST" in much the same way as the ptz system. Site B molecules, with the HS state as ground state at all temperatures, are converted to the now metastable LS state upon irradiation with red light ($\sim 850 \text{ nm}$); this trapped LS state has again practically infinite lifetime at ca. 20 K (ref. 12).

Preliminary results from current studies of the mixed crystal system $[\text{Fe}_x\text{Ni}_{1-x}(\text{mtz})_6](\text{ClO}_4)_2$ indicate the possibility of keeping the metastable states formed by LIESST trapped up to temperatures above 100 K (ref. 12).

3 LIESST IN OTHER IRON(II) SPINCROSSOVER COMPOUNDS

LIESST is not unique to $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ and related systems, nor is it restricted to crystalline materials. Since the discovery of LIESST in 1984, long-lived metastable HS states have been observed in a number of iron(II) spincrossover compounds: $[\text{Fe}(\text{pic})_3]X_2$ sol ($X: \text{Cl}, \text{Br}$; sol: MeOH, EtOH) (ref. 5), $[\text{Fe}(\text{phen})_2(\text{SCN})_2]$ (ref. 13), $[\text{Fe}(\text{bipy})_2(\text{SCN})_2]$ (ref. 14), $[\text{Fe}(\text{2-mephen})_3](\text{ClO}_4)_2$ (ref. 15), all in the solid state, and $[\text{Fe}(\text{2-mephen})_3]^{2+}$ doped into poly-vinyl-acetate and Nafion foils (ref. 16). In all of these compounds the relaxation rate of the metastable HS state is smaller than 10^{-4} s^{-1} at 10 K. However, the phenomenon of LIESST is even more general, albeit the rates for (thermal) $\text{HS} \rightarrow \text{LS}$ relaxation are often quite considerably larger. McCarvey and Lawthers (ref. 17) were the first to notice a rapid depopulation of the LS state upon pulsed laser photolysis of an iron(II) spincrossover compound in solution. They obtained relaxation rates of the order of 10^7 s^{-1} at room temperature. Recently,

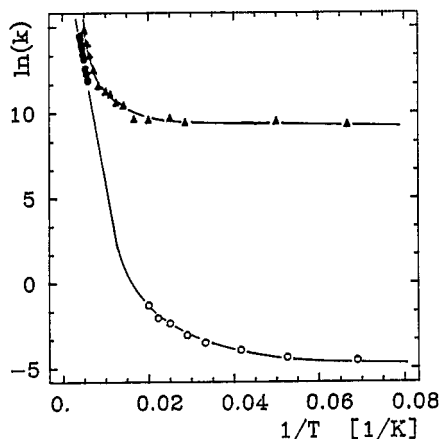


Fig. 6. HS \rightarrow LS relaxation rate as a function of temperature, $\ln(k)$ vs. $1/T$

- ▲ $[\text{Fe}(\text{mepy})_2(\text{py})(\text{tren})](\text{PF}_6)_2$ in PSS (from ref. 18)
- $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{MeOH}$ from lineshape analysis of Mössbauer spectra (from ref. 19)
- $[\text{Fe}_x\text{Zn}_{1-x}(\text{pic})_3]\text{Cl}_2 \cdot \text{MeOH}$ ($x \approx 0.03\%$) from optical spectra (from ref. 12)

Xie and Hendrickson (ref. 18) investigated the excited state lifetimes of $[\text{Fe}(\text{mepy})_2(\text{py})(\text{tren})](\text{PF}_6)_2$ doped into a poly-styrene sulfonate (PSS) matrix. They found temperature independent relaxation rates of $\sim 10^4 \text{ s}^{-1}$ below $\sim 80 \text{ K}$, evidence for nuclear tunnelling (s. Fig. 6). Above $\sim 100 \text{ K}$, an activated relaxation process became dominant. Recent work on $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{MeOH}$ (ref. 19) and $[\text{Fe}_x\text{Zn}_{1-x}(\text{pic})_3]\text{Cl}_2 \cdot \text{MeOH}$ ($x \approx 0.03\%$) (ref. 12) shows a similar high temperature region with an Arrhenius type relaxation behaviour and a more or less temperature independent relaxation rate of $\sim 10^{-2} \text{ s}^{-1}$ below $\sim 50 \text{ K}$ (s. Fig. 6).

4 DISCUSSION

The fact that LIESST is observed both in the dilute materials as well as in $[\text{Fe}(\text{2-mephen})_3]^{2+}$ doped into amorphous matrices shows that it is basically a single ion phenomenon. Our intermediate case of $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{MeOH}$ with a relaxation rate of $\sim 10^{-2} \text{ s}^{-1}$ at 10 K suggests that there is a smooth transition from the fast relaxation and tunnelling at low temperatures as observed by Xi and Hendrickson in $[\text{Fe}(\text{mepy})_2(\text{py})(\text{tren})](\text{PF}_6)_2$ and the extremely slow relaxation with no apparent tunnelling at low temperatures in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$. The question now is, what are the parameters responsible for the difference of more than eight orders of magnitude in the low temperature relaxation rates? The theory of HS \rightleftharpoons LS relaxation of Buhks et al. (ref. 20), although making a number of drastic assumptions, is a fully quantum mechanical approach based on non-adiabatic multiphonon relaxation. It predicts a temperature independent relaxation rate, i.e. a tunnelling process, at low temperatures and an activated process at higher temperatures. The important parameters in the theory are the energy gap ΔE_{HL} , the difference in metal-ligand bondlength Δr between the HS and the LS states, the force constant and the vibrational frequency along the reaction coordinate. A full discussion at all this would be beyond the scope at this paper. Suffice it to say that Xie and Hendrickson found a set of reasonable parameters to suit their case, and that for values of $\Delta E_{\text{HL}} = 400 \text{ cm}^{-1}$, $\Delta r = 0.2 \text{ \AA}$, $f_a = 1.8 \times 10^5 \text{ dyn/cm}$ and $\omega_a = 230 \text{ cm}^{-1}$ (values appropriate for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$) we estimate a low temperature relaxation rate according to Buhks et al. (ref. 20) of $\sim 10^{-4} \text{ s}^{-1}$. This is in the range needed to explain our extremely long-lived excited states at least semi-quantitatively.

The photophysical effects described above show that such spincrossover systems behave like an optical switch. They may therefore have the potential of future applications in optical information storage.

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