

## New Examples of Light-induced Excited Spin State Trapping (LIESST) in Iron(II) Spin-crossover Systemst

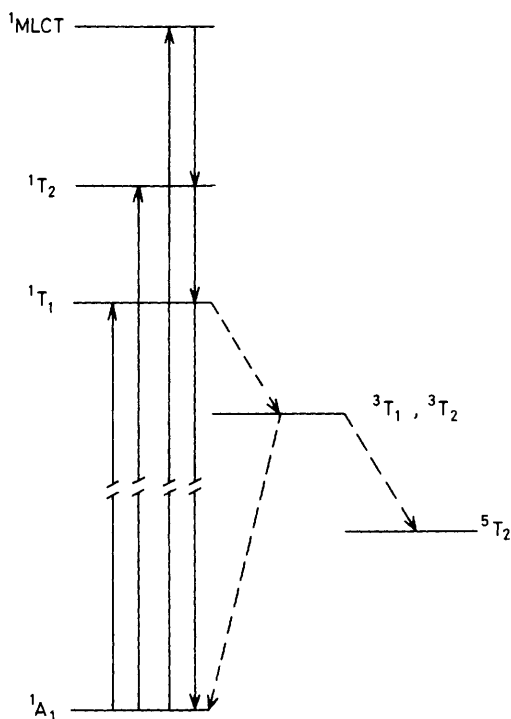
S. Decurtins, P. Gülich,\* C. P. Köhler, and H. Spiering

*Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany*

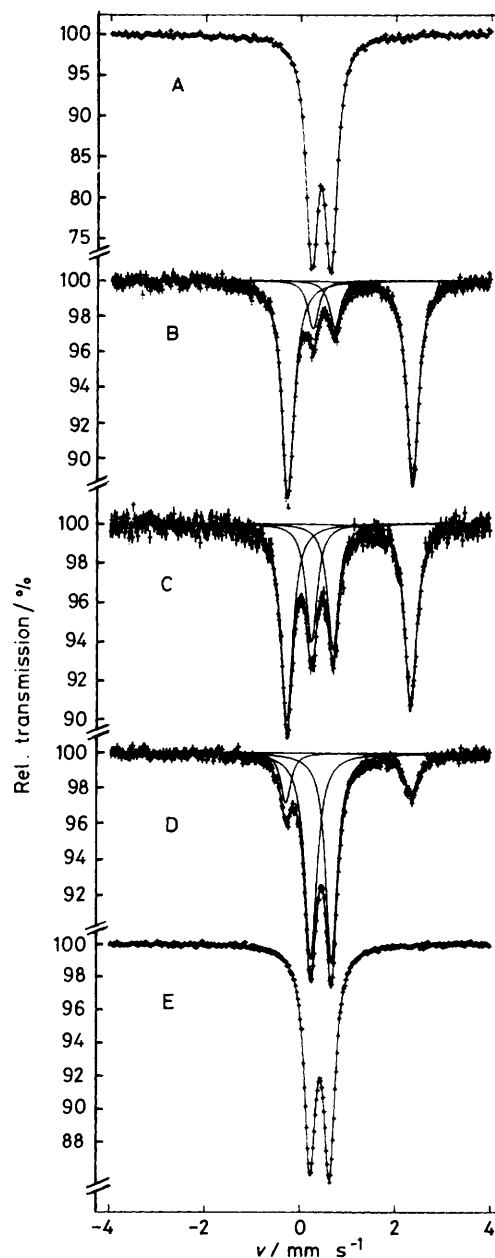
Two new examples are reported of (quantitative) light-induced excited spin state trapping (LIESST) in coloured polycrystalline iron(II) spin-crossover compounds, with practically infinite lifetimes of the high spin state below a critical temperature (25 and 55 K, respectively); LIESST now appears to be a common effect for iron(II) spin-crossover systems.

A variety of iron(II) complexes are known to show a temperature- or pressure-induced high-spin ( $S = 2$ )  $\rightleftharpoons$  low-spin ( $S = 0$ ) transition.<sup>2</sup> We recently discovered the effect of a light-induced low-spin (L.S.)  $\rightarrow$  high-spin (H.S.) transition in case of the  $[\text{Fe}(\text{ptz})_6][\text{BF}_4]_2$  (ptz = 1-propyltetrazole) spin-crossover complex.<sup>3</sup> We called this phenomenon light-induced excited spin state trapping (LIESST). Here we report our results for LIESST experiments with two other spin-crossover complexes, namely  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (phen = 1,10-phenanthroline) and  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$  (2-pic = 2-aminomethylpyridine). With these highly coloured compounds Mössbauer spectroscopy proves to be an elegant tool for identifying the pure light-induced H.S. states. With these new examples it is now well established that LIESST is a general phenomenon in iron(II) spin-crossover compounds.

The physics of the LIESST effect looks remarkably straightforward and is illustrated in the simplified Jablonski-type diagram of Figure 1. Illuminating the sample with white light



**Figure 1.** Simplified Jablonski-type energy-level diagram to explain the observed LIESST phenomenon in iron(II) spin crossover complexes.



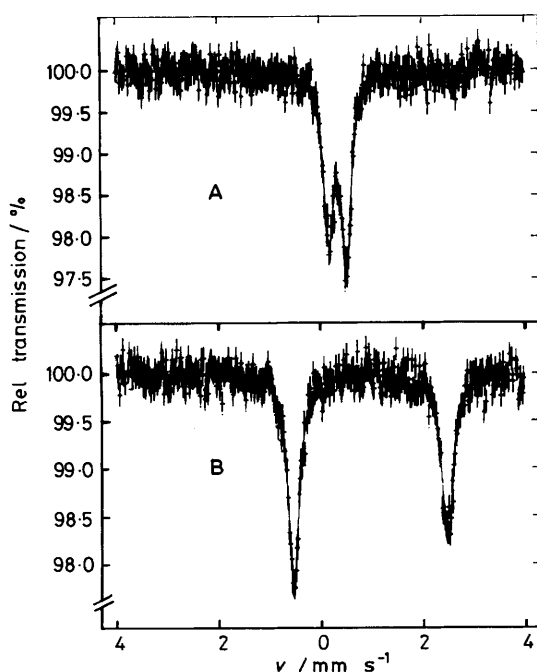
**Figure 2.** Mössbauer spectra of  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$  recorded at  $T_M = 4.2$  K (A) before bleaching, (B) after bleaching with white light for 1 h, and (C, D, and E) warming up to 30–32 K for a short time and cooling back to 4.2 K in three cycles.

† In partial fulfilment for the Ph.D. thesis of C.P.K.

**Table 1.** Isomer shift ( $\delta$ ), quadrupole splitting ( $\Delta E_Q$ ), line width ( $\Gamma$ ), and area function ( $A$ ) for the high-spin and low-spin Mössbauer resonances of  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$  (spectra 2A—E) and of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (spectra 3A, B) measured at  $T_M$ .

Sample treatment	Spectrum	$T_M/\text{K}$	$\delta/\text{mm s}^{-1}$		$\Delta E_Q/\text{mm s}^{-1}$		$\Gamma/\text{mm s}^{-1}$		$A(\%)$	
			H.S.	L.S.	H.S.	L.S.	H.S.	L.S.	H.S.	L.S.
Before bleaching	2(A)	4.2	—	0.407(5)	—	0.412(1)	—	0.269(4) <sup>a</sup> 0.279(4) <sup>b</sup>	0	100
After bleaching for 1 h at 4.2 K	2(B)	4.2	1.035(5)	0.48(1)	2.627(4)	0.46(2)	0.30(1) <sup>a</sup> 0.29(1) <sup>b</sup>	0.26(5) <sup>a</sup> 0.27(4) <sup>b</sup>	83(1)	17(1)
First warming to 30—32 K	2(C)	4.2	1.031(5)	0.472(6)	2.617(7)	0.453(9)	0.29(1) <sup>a</sup> 0.29(1) <sup>b</sup>	0.28(3) <sup>a</sup> 0.27(2) <sup>b</sup>	62(1)	38(1)
Second warming to 30—32 K	2(D)	4.2	1.024(9)	0.454(5)	2.64(2)	0.439(3)	0.24(3) <sup>a</sup> 0.36(4) <sup>b</sup>	0.30(1) <sup>a</sup> 0.28(1) <sup>b</sup>	18(1)	82(1)
Third warming to 30—32 K	2(E)	4.2	—	0.429(5)	—	0.412(1)	—	0.271(4) <sup>a</sup> 0.280(4) <sup>b</sup>	0	100
Before bleaching	3(A)	6	—	0.351(6)	—	0.34(1)	—	0.25(4) <sup>a</sup> 0.22(3) <sup>b</sup>	0	100
After bleaching for 1 h at 6 K	3(B)	6	0.971(7)	—	3.01(1)	—	0.27(3) <sup>a</sup> 0.26(3) <sup>b</sup>	—	100	0

<sup>a</sup> Low velocity component. <sup>b</sup> High-velocity component.



**Figure 3.** Mössbauer spectra of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  recorded at  $T_M = 6$  K (A) before bleaching and (B) after bleaching with white light for 1 h.

leads to a population of the  $^1T_1$ ,  $^1T_2$ , and  $^1\text{MLCT}$  (metal to ligand charge transfer) states. These states are very short-lived and can decay rapidly back to the  $^1A_1$  ground state *via* spin-allowed transitions. As the  $^3T_1$  and  $^3T_2$  ligand field states are somewhat lower in energy than the  $^1T_1$  and  $^1T_2$  states,<sup>4</sup> an alternative decay path, favoured by spin-orbit coupling, leads to a population of the spin triplet states (intersystem crossing). Spin-forbidden transitions also occur when the triplet states decay, initiated again by spin-orbit coupling, either to the  $^1A_1$

ground state or to the excited  $^5T_2$  ligand field state. There is no radiative relaxation path between the  $^5T_2$  and  $^1A_1$  states. Therefore, the excited H.S. ( $^5T_2$ ) state remains trapped for practically an infinite life-time provided the temperature is sufficiently low so that the energy barrier between the H.S. and the L.S. potential minima is not thermally overcome.

The critical temperature, above which the H.S. molecules produced by LIEST relax back to the normal L.S. ( $^1A_1$ ) state within minutes has been found to lie around 50 K in the case of  $[\text{Fe}(\text{ptz})_6][\text{BF}_4]_2$ .<sup>3</sup> In the new examples presented here it has been determined to be around 55 K for  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and around 25 K for  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ . Detailed kinetic measurements of the relaxation process in the case of  $[\text{Fe}(\text{ptz})_6][\text{BF}_4]_2$  will be published shortly.<sup>4</sup>

The Mössbauer spectra were measured in transmission geometry using a 50 mCi  $^{57}\text{Co}/\text{Rh}$  source kept at 293 K and a conventional spectrometer. The samples were sealed into optically transparent Plexiglass holders and placed in a liquid helium bath cryostat. For the light excitation, the samples were illuminated with an arc lamp. The spectra, consisting of two quadrupole doublets originating from the L.S. ( $^1A_1$ ) and H.S. ( $^5T_2$ ) states, respectively, were fitted as a superposition of four independent lines using the MOSFUN program of Müller.<sup>5</sup>

In order to achieve a quantitative light-induced spin transition the samples should be in a crystalline and transparent state. Therefore,  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  was prepared by removal of one phenanthroline group from  $[\text{Fe}(\text{phen})_3](\text{NCS})_2 \cdot \text{H}_2\text{O}$  in a Soxhlet apparatus using acetone during 2 weeks under nitrogen.<sup>6</sup> Small dark blue-violet crystals were obtained. The chemical purity was checked by Mössbauer spectroscopy. The compound  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$  was prepared by the procedure previously described.<sup>7</sup> The crude material was recrystallized from ethanol at 45 °C to provide yellow-brown crystals of up to 1 mm in length. Their purity was checked by Mössbauer spectroscopy and magnetic susceptibility measurements.

Spectrum (A) of Figure 2 shows the typical L.S. quadrupole doublet of  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$  at 4.2 K before bleaching. After bleaching with white light for 1 h the compound was

>80% converted from the L.S. into the H.S. state (Figure 2B). Quantitative L.S.  $\rightarrow$  H.S. conversion should be possible for a sufficiently thin absorber. Heating the sample to 30–32 K for a short time causes the compound to relax gradually back to the L.S. state (Figure 2C–E).

Analogous observations have been made with  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ . Figure 3 shows its Mössbauer spectra taken at 6 K (A) before bleaching with white light and (B) after bleaching for 1 h.

S.D. thanks the Alexander von Humboldt Foundation for a Fellowship. We are grateful for financial support from the Deutsche Forschungsgemeinschaft, the Stiftung Volkswagenwerk, and the Fonds der Chemischen Industrie.

Received, 24th September 1984; Com. 1356

## References

- 1 First presented in a Plenary Talk at the American Chemical Society Meeting in St. Louis, MO, April 8–13, 1984; the lecture will be published in '25 years of Chemical Mössbauer Spectroscopy,' ed. R. H. Herber, Plenum Press, New York.
- 2 P. Gülich, *Struct. Bonding (Berlin)*, 1981, **44**, 83.
- 3 S. Decurtins, P. Gülich, C. P. Köhler, H. Spiering, and A. Hauser, *Chem. Phys. Lett.*, 1984, **105**, 1.
- 4 S. Decurtins, P. Gülich, A. Hauser, K. M. Hasselbach, and H. Spiering, *Inorg. Chem.*, submitted for publication.
- 5 E. W. Müller, Laborbericht, Institut für Anorganische und Analytische Chemie, Universität Mainz, D-6500 Mainz; *Mössbauer Effect Ref. Data J.*, 1981, **4**, 89.
- 6 P. Ganguli, P. Gülich, E. W. Müller, and W. Irlner, *J. Chem. Soc., Dalton Trans.* 1981, 441.
- 7 M. Sorai, J. Enslin, and P. Gülich, *Chem. Phys.*, 1976, **18**, 199.