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Intersystem Crossing in Fe(II) Coordination Compounds

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Abstract

Due to the fact that for d^6-systems there are a number of low-lying ligand field (LF) states the relaxation from excited states of Fe(II) coordination compounds is, in general, a very fast and radiationless process. In Fe(II) spin-crossover systems, however, the zero point energy difference between the two lowest states, namely the low-spin (LS) $^1A_1$ and the high-spin (HS) $^5T_2$ state, is of the order of k_BT, and some systems can be converted quantitatively to the HS state well below the thermal transition temperature by irradiating either into MLCT or LF absorption bands of the LS species, with HS→LS relaxation rates as small as 10^{-6} s^{-1} at ~10 K. It is also possible to achieve a light-induced transient population of a HS state in Fe(II) LS compounds, but in this case the HS→LS relaxation rates can be larger than 10^6 s^{-1} even at low temperatures. The HS→LS relaxation rates show strong deviations from Arrhenius kinetics with nearly temperature independent tunnelling below ~70 K and a thermally activated behaviour above ~100 K. The range of 12 orders of magnitude in the low temperature tunnelling rate can be understood in terms of nonadiabatic multiphonon relaxation, where in the strong coupling limit, with the Huang-Rhys parameter S much larger than the reduced energy gap p, an inverse energy gap law holds.

1. INTRODUCTION

Compared to the coordination compounds of most other transition metal ions the photophysical and photochemical properties of Fe(II) coordination compounds have received very little attention. In fact one of the standard works of inorganic photochemistry "Concepts in Inorganic Photochemistry" devotes two sections to systems with 6 d-electrons without even mentioning Fe(II) compounds [1]. This is basically due to the fact that Fe(II) coordination compounds, in general, do not show any luminescence, because of a number of low-lying ligand field (LF) states which provide a very efficient nonradiative decay path back to the ground state on the subnanosecond timescale. Thus the important experimental method of time resolved luminescence spectroscopy, with which quantum efficiencies for intersystem crossing (ISC) and internal conversion (IC) processes in coordination compounds of most other transition metal ions have been determined, cannot be applied to Fe(II) compounds.

That despite this efficient nonradiative relaxation Fe(II) coordination compounds might possess some unique photophysical properties emerged some years ago, when Decurtins *et al.* [2,3] showed that in a number of Fe(II) spin-crossover compounds a quantitative light-induced $^1A_1$ (LS)→$^5T_2$ (HS) conversion could be achieved at temperatures well below the thermal transition temperature, by irradiating the sample in the visible either into the spin allowed d-d or MLCT absorption bands of the LS species. In the spin-crossover system $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-n-propyltetrazole), for instance, the HS→LS relaxation rate is less than 10^{-6} s^{-1} at 10 K, and thus the light-induced metastable state could unambiguously be identified as the $^5T_2$ state. The mechanism for the light-induced LS→HS conversion, subsequently called "Light-Induced Excited Spin State Trapping (LIESST)", proposed by Decurtins *et al.* [3], involving two ISC steps with $\Delta S = 1$, has recently been proved to be correct [4].

Since the discovery of LIESST long-lived metastable HS states have been found for an increasing number of Fe(II) spin-crossover systems. However, not for all compounds does the light-induced metastable state have such an astonishingly long lifetime at low temperatures. Xie and Hendrickson [5] investigated the HS→LS relaxation as a function of temperature of the spin-crossover compound $[Fe(mepy)_2(py)(tren)](PF_6)_2$ embedded in poly-styrene sulfonate. They found a thermally activated process for T > 100 K, but below ~70 K they observed a strong deviation from Arrhenius kinetics with a more or less temperature independent tunnelling rate of $\sim 10^4$ s^{-1}. For the $[Fe(pic)_3]Cl_2 \cdot MeOH$ (pic = 2-picolylamine) spin-crossover system a similar behaviour is observed, but in this case with a low T tunnelling rate of $\sim 10^{-1}$ s^{-1} [3, 6].

It is also possible to create a light-induced metastable HS state in LS systems such as $[Fe(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridine) , but in these systems the HS→LS relaxation is considerably faster even at low temperatures [7].

The crucial parameters governing the lifetime of the metastable HS state are the horizontal and vertical displacements of the LS and HS potential wells relative to each other. The theory of nonadiabatic multiphonon relaxation [8], as first applied to HS→LS ISC processes by Buhks *et al.* [9], can be used to explain the observed variation of the low T tunnelling rates over 12 orders of magnitude.

The discussion of the mechanism of LIESST and of the HS→LS relaxation constiute the two central themes of this paper.

2. LIGAND FIELD THEORETICAL CONSIDERATIONS

According to the Tanabe-Sugano diagram [10] for a transition metal ion with 6 d-electrons (Fig. 1) octahedral Fe(II) complexes can either have a $^5T_2$ (HS) ground state for ligands exerting but a weak LF such as H_2O, or a $^1A_1$ (LS) ground state for ligands exerting a strong LF such as CN^-. If for a given ligand the LF strength happens to be in the vicinity of the crossover point Δ_{crit}, a thermal spin transition may occur. In order to actually understand this, it is not sufficient to just look at the Tanabe-Sugano diagram. Such a diagram only depicts the *electronic* energies of the excited states relative to the respective ground state as a function of the LF strength 10Dq. The LF strength is not only determined by the properties of the ligand but it is also a function of the metal-ligand distance r. For neutral ligands $10Dq(r) \sim 1/r^6$ [11]. Thus if for a given ligand the LF strength at the equilibrium distance of say the LS state $10Dq^{LS} = 10Dq(r_{LS})$ is known from experiment, 10Dq(r) for an arbitrary value of r can be estimated for this ligand, and assuming an appropriate potential surface for the LS state along the totally symmetric normal coordinate, the energies of all the other LF states along this coordinate can then be calculated. For the HS state, for instance, the resulting potential surface will always be displaced towards a substantially larger metal-ligand distance irrespective of the ligand (Fig. 2). This is not surprising, since in the $^1A_1$ state the 6 d-electrons occupy the basically nonbonding t_2-orbitals, whereas in the $^5T_2$ state two of those electrons get promoted to the antibonding e-orbitals. The vertical displacement of the HS surface, on the other hand, depends strongly upon the ligand. In a HS system it will of course be

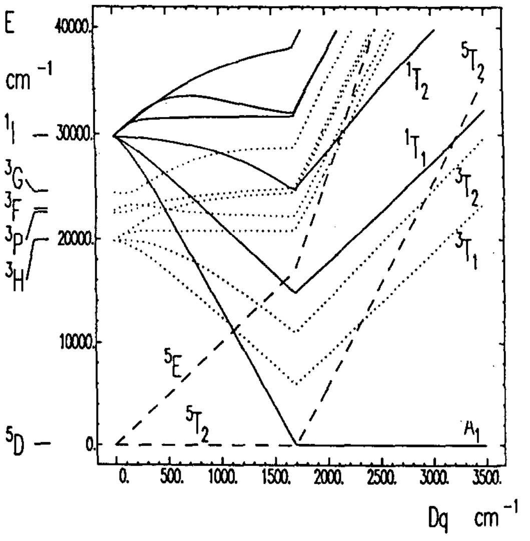

Fig. 1 : Tanabe-Sugano diagram for a d^6-system.

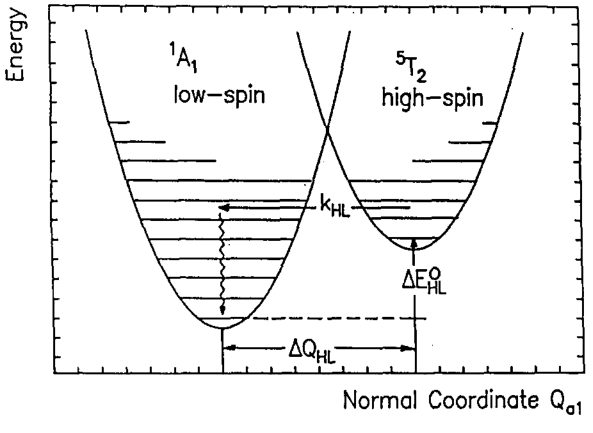

Fig. 2 : Potential wells for the HS and the LS state of Fe(II) in octahedral coordination along the totally symmetric normal coordinate.

displaced towards lower energy, in a LS system towards higher energy. In order for a thermal spin transition to occur, the zero point energy difference ΔE^0_{HL} has to be positive and of the order of k_BT (Fig. 2), in which case only the LS state will be populated at low temperatures, but at higher temperatures an almost quantitative entropy driven population of the HS state will take place, because of the 15-fold electronic degeneracy of the HS state and its higher density of vibrational states.

The crossover point in the Tanabe-Sugano diagram now simply means, that for a given ligand there is a nuclear configuration for which the HS and the LS state are accidentally degenerate, but it is clear that this nuclear configuration can never correspond to the equilibrium configuration of the ground state.

Fe-L bondlengths in the LS state r_{LS} are characteristically ~1.96 - 2.00 Å and the bondlength difference between the HS and the LS state $\Delta r_{HL} = r_{HS} - r_{LS}$ in Fe(II) spin-crossover compounds is in the range ~0.16 - 0.21 Å [12]. Thus from the proportionality $(10Dq^{LS}/10Dq^{HS}) = (r_{HS}/r_{LS})^6$, the LF strength is expected to increase by almost a factor of 2 on going from the HS to the LS state. So in fact for a Fe(II) spin-crossover compound $10Dq^{HS}$ will be well to the left and $10Dq^{LS}$ well to the right of the crossover point in the Tanabe-Sugano diagram.

3. LIGHT-INDUCED EXCITED SPIN STATE TRAPPING (LIESST)

3.1 The $[Fe(ptz)_6](BF_4)_2$ spin-crossover system

The $[Fe(ptz)_6](BF_4)_2$ spin-crossover system plays a very important role in the discussion of LIESST. Not only was the phenomenon of the light-induced LS→HS conversion discovered during an investigation of the optical properties of $[Fe(ptz)_6](BF_4)_2$, but it is with this compound that it has eventually been possible to prove the mechanism and establish a full scheme for LIESST. This well justifies devoting a whole section to just this one system.

The thermal spin transition in $[Fe(ptz)_6](BF_4)_2$ has been discussed before [3, 13]. It manifests itself with a dramatic change in colour from colourless at 293 K to deep purple at low temperature. In Figs. 3a and b the corresponding single crystal absorption spectra are shown. Referring once again to the Tanabe-Sugano diagram (Fig. 1), the assignment of the band in the NIR of the 293 K spectrum to the spin allowed $^5T_2 \rightarrow {}^5E$ transition characteristic of the HS species with $10Dq^{HS} = E(^5E) - E(^5T_2) = 11760\ cm^{-1}$ is straightforward. By the same token the two bands in the visible of the 20 K spectrum can be assigned to the spin allowed transitions of the LS species $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$, with $10Dq^{LS} \approx E(^1T_1) - E(^1A_1) + \left(E(^1T_2) - E(^1T_1)\right)/4 = 20200\ cm^{-1}$ [14]. Thus the predicted increase of almost a factor of 2 on going from the HS to the LS state is confirmed experimentally.

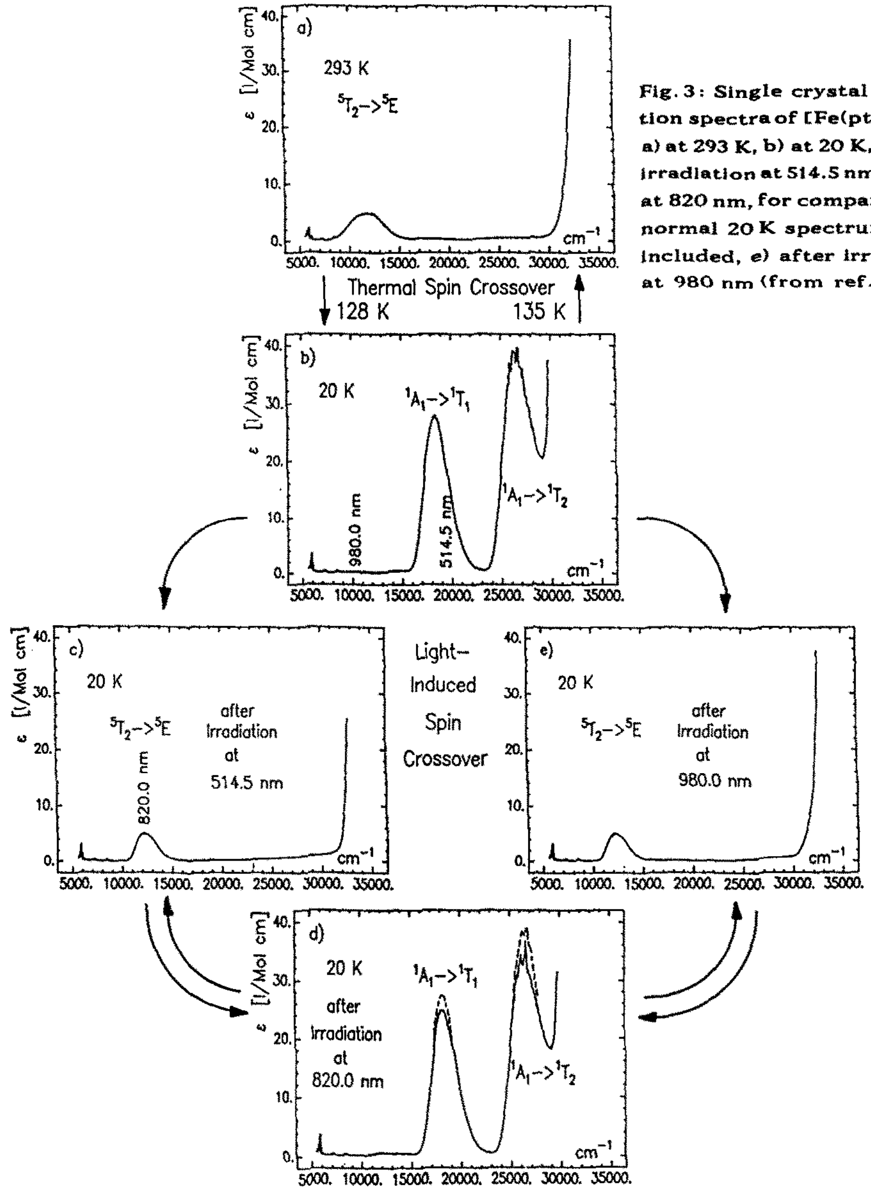

Fig. 3: Single crystal absorption spectra of [Fe(ptz)$_6$](BF$_4$)$_2$ a) at 293 K, b) at 20 K, c) after irradiation at 514.5 nm, d) after at 820 nm, for comparison the normal 20 K spectrum (--) is included, e) after irradiation at 980 nm (from ref. [4]).

In Fig. 4 the transition curve for the thermal spin transition of [Fe(ptz)$_6$](BF$_4$)$_2$ as derived from the temperature dependence of the $^1A_1 \rightarrow ^1T_1$ band is shown. Due to cooperative effects the spin transition in the neat material is accompanied by a crystallographic phase transition with a hysteresis of 7 K ($T_c^{\downarrow}$ = 128 K, $T_c^{\uparrow}$ = 135 K).

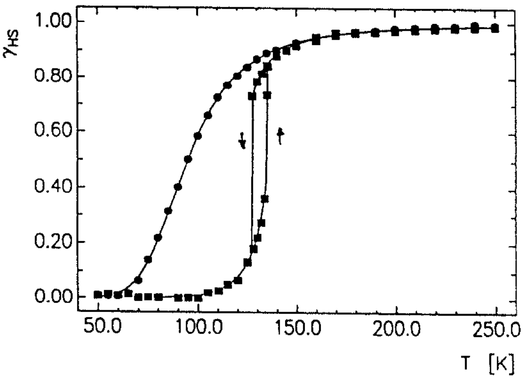

Fig. 4 : The HS fraction γ_{HS} as function of the thermal spin transition in $[Fe(ptz)_6](BF_4)_2$ (■) and $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ (x ≈ 0.1) (●).

The transition curve for the dilute mixed crystal $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ (x ≈ 0.1), included in Fig. 4, is more gradual, as is expected for a simple spin equilibrium. The transition temperature $T_{1/2}$, defined as the temperature at which the HS fraction γ_{HS} = 0.5, for the dilute system is ~95 K.

Irradiating the crystal at 20 K with the 514.5 nm line of an Ar^+ laser, i. e., into the $^1A_1 \rightarrow {}^1T_1$ band, quickly leads to a complete $^1A_1 \rightarrow {}^5T_2$ conversion (LIESST). The absorption spectrum after the irradiation, with the typical $^5T_2 \rightarrow {}^5E$ band in the NIR, is shown in Fig. 3c. At 20 K the light-induced HS state is metastable with a practically infinite lifetime. Only at temperatures above ~50K does a noticeable thermal HS→LS relaxation set in [3, 15].

The mechanism proposed by Decurtins *et al.* [3] for LIESST is depicted in Fig. 5. A first ISC step with $\Delta S = 1$ leads the system from the initially excited $^1T_1$ state to the $^3T_1$ state. In a second ISC step, again with $\Delta S = 1$, the system can drop into the $^5T_2$ state, where at sufficiently low temperature it remains trapped, because of the energy barrier between LS and HS state due to the difference of ~0.18 Å in metal-ligand bondlength. Even if the quantum efficiencies of the various steps are not unity, continuous excitation will eventually convert the whole crystal to the HS state.

The fact that LF theory puts the low-lying $^3T_1$ state to just below the ^5E state suggests, that LIESST should be reversible. And indeed the system can also be optically pumped back to the LS state (reverse-LIESST). Fig 3d shows the absorption spectrum after a subsequent irradiation at 820 nm, i. e., into the $^5T_2 \rightarrow {}^5E$ band, the temperature being kept at 20 K all through the cycle. Again the typical LS spectrum is observed. However, the light-induced $^5T_2 \rightarrow {}^1A_1$ conversion is not complete. After repeated irradiation at 820 nm a "saturation" value for the LS fraction γ_{LS} = 0.9 is reached. The most straightforward reason for this would be, that the LS species has a weak absorption band overlapping with the $^5T_2 \rightarrow {}^5E$ band in such a way, that this absorption in turn results in a light-induced $^1A_1 \rightarrow {}^5T_2$ conversion.

Indeed there are two very weak bands on the low energy side of the $^1A_1 \rightarrow {}^1T_1$ band, to which the spin forbidden transitions $^1A_1 \rightarrow {}^3T_1$ and $^1A_1 \rightarrow {}^3T_2$ can be assigned (Fig. 6). That these weak bands are intrinsic to $[Fe(ptz)_6](BF_4)_2$ is borne out by the comparison with the spectrum of $[Zn(ptz)_6](BF_4)_2$. In this spectrum the comparatively sharp lines corresponding to vibrational overtones of the ligand vibrations are identical to those in $[Fe(ptz)_6](BF_4)_2$, but the two broad bands are missing. Since the two triplet states originate from the same configuration as the two excited singlet states, namely the the (t_2^5e) configuration, the absorption bands of the spin forbidden transitions are just as broad as those of the spin allowed ones.

The maximum of the $^1A_1 \rightarrow {}^3T_1$ band at 10280 cm^{-1} (~980 nm) is just to the low energy side of the $^5T_2 \rightarrow {}^5E$ band. Starting from a LS fraction γ_{LS} of 1 at 20 K, and irradiating the crystal at 980 nm again results in a complete light-induced $^1A_1 \rightarrow {}^5T_2$ conversion (Fig 3e). A direct irradiation into the $^1A_1 \rightarrow {}^3T_1$ band therefore results in LIESST too, proving two things : The two weak bands are not due to impurities and therefore the assignment to spin forbidden transitions is justified and, more importantly, it shows that the mechanism for LIESST with the $^3T_1$ state as intermediate state is correct.

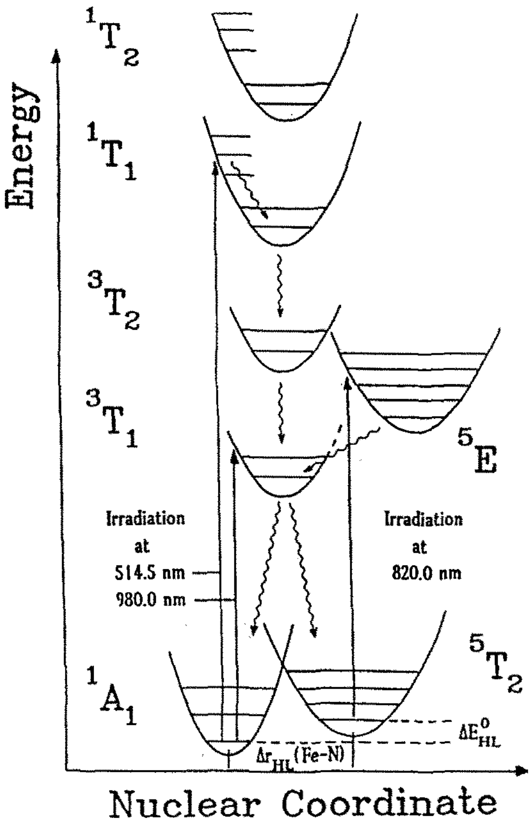

Fig. 5 : Potential wells for the ^1A ground state and the thermally accessible $^5T_2$ stated as well the higher excited LF states of a d^6 spin-crossover system. Arrows indicate the mechanism of LIESST.

In view of this the "saturation" value of γ_{LS} = 0.9 reached after long irradiation at 820 nm had better be called steady state value, since for this value of γ_{LS} the rates for LIESST and reverse-LIESST are equal but not zero. The value of 0.9 reached by irradiating at 820 nm is the maximum steady state value for γ_{LS}, since this wavelength corresponds to the maximum of the $^5T_2 \rightarrow {}^5E$ absorption band, whereas the absorption of the LS species, although not zero, is minimal at this wavelength.

The depletion and the buildup of the LS state in LIESST and reverse-LIESST can be followed quantitatively. The quantum efficiencies of the first ISC step either from the $^1A_1$ state for LIESST or the ^5E state for reverse-LIESST are ~1 and ~0.75. respectively. The branching ratio from the $^3T_1$ state either to the $^1A_1$ ground state or the metastable $^5T_2$ state is 1:4 [4]. The actual rate constants for the various ISC processes, except of course the $^5T_2 \rightarrow ^1A_1$ relaxation, are $\geq 10^{10}$ s^{-1}.

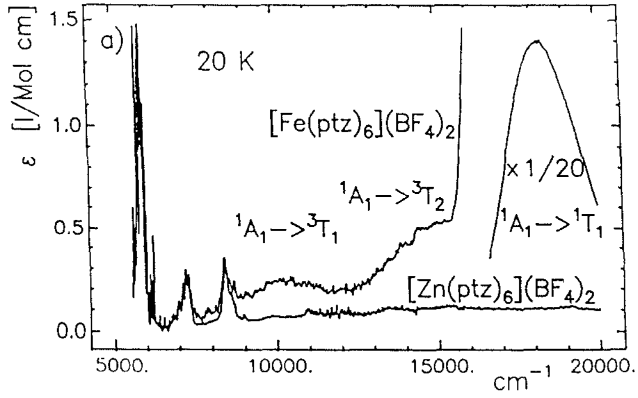

Fig. 6 : Blow up of the low energy part of the LS spectrum of $[Fe(ptz)_6](BF_4)_2$ at 20 K with the spin forbidden d-d transitions (from ref. [4]).

3.2 LIESST in other systems

LIESST is quite a common phenomenon for Fe(II) spin-crossover compounds and it is basically a property of the single complex molecule. Long-lived metastable HS-states have been found for an increasing number of Fe(II) spin-crossover systems, not only for neat compounds [16], but also for dilute mixed crystals [15, 17], and for spin-crossover complexes embedded in polymer matrices [18].

In most systems, however, the d-d bands of the LS species are obscured by low-lying MLCT bands. But because of the shorter Fe-L bondlength in the LS state and the resulting larger orbital overlap the MLCT bands are more intense in the LS state, and irradiation into the MLCT band at 10 K produces long-lived HS states too [3, 17].

In a certain sense LIESST is even more general than that. Prior to the discovery of Decurtins *et al.* [2, 3] McGarvey and Lawthers [19] noticed a rapid depopulation of the $^1A_1$ state upon pulsed laser irradiation for some Fe(II) spin-crossover compounds, but with relaxation rates of the order of 10^7 s^{-1} in solution and at ambient temperatures the light-induced states were comparatively short-lived. Even for the LS systems $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ at 293 K in solution a transient state with a lifetime of 0.83 ns [20] and 0.71 ns [21], respectively was found. Kirk *et al.* [20] list as possibilities for this state either a ^{3}MLCT state or the low-lying LF states $^1T_1$ or $^3T_1$. Street *et al.* [21a] tentatively identify it with the $^3T_1$ state and Creutz *et al.* [21b], although basically agreeing with this assignment, point out that it could also be the $^5T_2$ state. With hindsight of course this last suggestion is the most probable one. It is furthermore supported by the time-differential Mössbauer emission study of

Grimm *et al.* [22], who observed anomalous HS states as an after effect of the nuclear decay in [^{57}Co/Co(phen)$_3$](ClO$_4$)$_2$·2H$_2$O. In Fig. 7 the corresponding integral Mössbauer emission spectra at 40 and 172 K are reproduced. The 172 K spectrum consists of just the same LS doublet as is observed in a Mössbauer absorption spectrum of [Fe(phen)$_3$](ClO$_4$)$_2$, but at 40 K additional quadrupol doublets characteristic for HS states appear, indicating that after the ^{57}Co(EC)^{57}Fe process at least some of the Fe(II) complexes end up in a HS state with a lifetime on the Mössbauer timescale of 10^{-7} s. Grimm *et al.* [22] determined a lifetime of 205 ns at 47 K for the HS state marked with HS1 in Fig 7b. This compares well with the 188 ns at ~50 K found for the light-induced transient state for [Fe(phen)$_3$]$^{2+}$ embedded in a Nafion polymer foil [17].

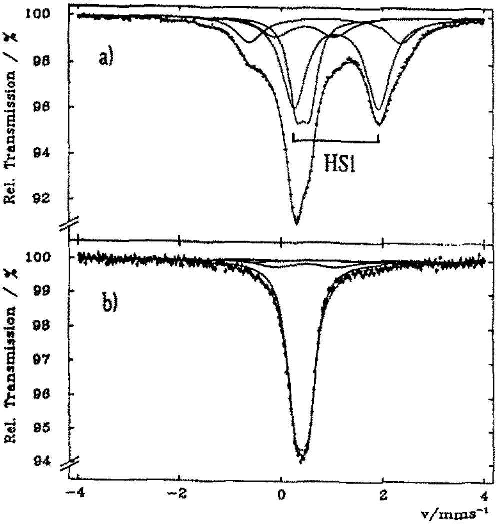

Fig. 7 : Integral ^{57}Co Mössbauer emission spectra of [^{57}Co/Co(phen)$_3$](ClO$_4$)$_2$·2H$_2$O at a) 40 K and b) 172 K (from ref. [23]).

The quantum efficiency for the light-induced population of the metastable HS state in the LS system [Zn$_{1-x}$Fe$_x$(bipy)$_3$](PF$_6$)$_2$ ($x \approx 0.0001$) is with ~0.6 [12] of the same order of magnitude as the one determined for the [Fe(ptz)$_6$](BF$_4$)$_2$ spin-crossover system. So, except for the lifetime of the ligh-induced HS state, there is no big difference in the photophysical behaviour of Fe(II) LS and spin-crossover compounds.

In analogy to reverse-LIESST it should in principle be possible to create metastable LS states in HS compounds with $\Delta E^0_{HL} < 0$ by irradiating into the $^5T_2 \rightarrow {}^5E$ absorption band. However, in order to have an nonvanishing quantum efficiency for the first ISC step, the ^5E state must be higher in energy than the $^3T_1$ state, and this is only the case for LF strengths fairly close to the spin-crossover systems. In the methyl substituted [Fe(mtz)$_6$](BF$_4$)$_2$ such a LS→HS conversion is indeed possible [24]. In this system the complex molecules sit on two different crystallographic sites. The ones on site A show a thermal spin transition with $T_{1/2} \approx 72$ K and behave pretty much the same way as the [Fe(ptz)$_6$](BF$_4$)$_2$ system. The ones on site B remain in the HS state at all temperatures, but can be converted to the LS state by irradiating in the NIR. At 10 K the lifetime of this now metastable LS state is again practically infinite, only above ~45 K does a noticeable LS→HS relaxation set in.

4. THE HS→LS RELAXATION

Work on the LS ⇌HS ISC dynamics in Fe(II) spin-crossover compounds has mostly been performed in solution at ambient temperatures [25]. Over the limited temperature interval available in solution ln[k_{HL}] vs. 1/T plots (Arrhenius plots) usually result in straight lines, and consequently the results have generally been discussed in terms of absolute rate theory. But as had already been pointed out by Buhks *et al.* [9] from theoretical considerations and was confirmed experimentally by Xie und Hendrickson [5] the HS→LS relaxation is a highly nonadiabatic process, for the description of which classical concepts are not really adequate.

Fig. 8 shows the Arrhenius plots of the HS→LS relaxation rate constants for a number of Fe(II) coordination compounds determined in transient absorption after pulsed laser excitation. For the dilute mixed crystals studied the determination of the rate constants from the relaxation curves is straight forward as the relaxation is single exponential [17]. All five systems show strong deviations from simple Arrhenius behaviour. At elevated temperatures the relaxation process is thermally-activated, but at low temperatures the relaxation rates are much less temperature dependent, going towards a temperature independent tunnelling rate for T → 0. In table I the low temperature tunnelling rate constants $k_{HL}(T\rightarrow 0)$ and the activation parameters E^a and A for the high temperature region T ≥ 100 K are listed. In addition the low T tunneling rate constants for some other systems are included in table I. The low T tunnelling rates are spread over more than twelve orders of magnitude from $< 10^{-6}$ s^{-1} for the spin-crossover system $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ ($x \approx 0.1$) to [1] $> 10^6$ s^{-1} for the LS system $[Fe(phen)_3]^{2+}$ embedded in Nafion.

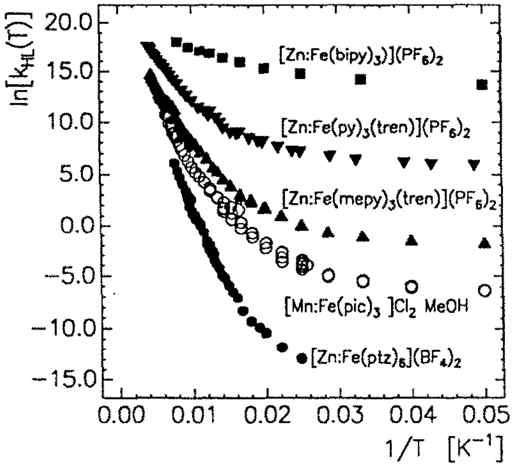

Fig. 8 : Arrhenius plot of the experimental rate constants $k_{HL}(T)$ for some dilute Fe(II) mixed crystal systems (from ref. [17]).

In the theory of nonadiabatic multiphonon relaxation the HS→LS ISC is described as a process occurring between two distinct zero order spin states characterised by different nuclear configurations, during which the electronic energy of the initial state is transformed into vibrational energy of the final state in a nonadiabatic step. The most simple model treats this problem in single configurational coordinate (SCC) space, with the potentials displaced by ΔQ_{HL} along one, namely the totally symmetric,

Table I : Transition temperature $T_{1/2}$, activation energy E^a and frequency factor A for the high temperature region, and low T tunnelling rate constant $k_{HL}(T \rightarrow 0)$ for some Fe(II) coordination compounds. The reduced energy gap p has been estimated according to the "inverse energy gap law".

	$T_{1/2}$ [K]	E^a [cm^{-1}]	A [s^{-1}]	p	$k_{HL}(T \rightarrow 0)$ [s^{-1}]
$[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$	95	1100	5×10^7	< 1	$\sim 5 \times 10^{-7}$
$[Mn_{1-x}Fe_x(pic)_3]Cl_2 \cdot EtOH$ a)	76				6×10^{-6}
$[Zn_{1-x}Fe_x(pic)_3]Cl_2 \cdot EtOH$ a)	95				2.5×10^{-5}
$[Mn_{1-x}Fe_x(pic)_3]Cl_2 \cdot MeOH$	118	907	2×10^8	$\sim 1-2$	2.5×10^{-3}
$[Zn_{1-x}Fe_x(pic)_3]Cl_2 \cdot MeOH$ a)	140				9×10^{-3}
$[Zn_{1-x}Fe_x(mepy)_3(tren)](PF_6)_2$	210	837	5×10^8	$\sim 3-4$	1.4×10^{-1}
$[Fe(mepy)_2(py)(tren)]^{2+}$ in PMMA b)	270				$\sim 5 \times 10^1$
$[Fe(mepy)(py)_2(tren)]^{2+}$ in PMMA b)	370				$\sim 2 \times 10^2$
$[Zn_{1-x}Fe_x(py)_3(tren)](PF_6)_2$	> 400	640	1×10^9	$\sim 7-8$	4×10^2
$[Zn_{1-x}Fe_x(bipy)_3](PF_6)_2$	low-spin	364	2×10^9	$\sim 11-13$	6×10^5
$[Fe(phen)_3]^{2+}$ in Nafion b)	low-spin				$\sim 5 \times 10^6$

a) from ref. [26] b) $T_{eff} \approx 50$ K (see ref. [12])

normal coordinate only. With $\Delta S = 2$ only higher order spin-orbit coupling can mix the two states. Starting from Fermi's Golden Rule and using the Condon approximation the HS→LS relaxation rate constant is given by [8] :

$$k_{HL}(T) = \frac{2\pi}{\hbar^2 \omega} \beta_{HL}^2 \; F_p(T) \,, \qquad (4.1)$$

where the electronic matrixelement $\beta_{HL} = \langle \Phi_{LS} | H_{so} | \Phi_{HS} \rangle \approx 150 \text{ cm}^{-1}$ for LF strengths near the spin-crossover point [9]. For harmonic potentials with equal force constants f and vibrational frequencies ω, the thermally averaged Franck-Condon factor $F_p(T)$ is given by :

$$F_p(T) = \frac{\sum_m |\langle \chi_n | \chi_m \rangle|^2 \cdot e^{-m\hbar\omega/kT}}{\sum_m e^{-m\hbar\omega/kT}} \,, \qquad (4.2)$$

where te sum goes over all the vibrational levels m of the initial state, and $n = m + p$ (the reduced energy gap $p = \Delta E^0_{HL}/\hbar\omega$) in order to ensure energy conservation. For $T \to 0$ F_p simplifies to [8] :

$$F_p(T\to 0) = |\langle \chi_p|\chi_0\rangle|^2 = \frac{S^p e^{-S}}{p!}, \qquad (4.3)$$

where the Huang-Rhys factor $S = \frac{1}{2} f \, \Delta Q^2_{HL}/\hbar\omega$. With $\Delta Q_{HL} = \sqrt{6}\,\Delta r_{HL} \approx 0.5$ Å, a mean force constant $f \approx 2.0 \times 10^5$ dyn/cm (between the value of 1.5×10^5 dyn/cm for $[Fe(H_2O)_6]^{2+}$ [27a] and 2.7×10^5 dyn/cm for $[Fe(CN)_6]^{2+}$ [27b]) and a typical vibrational frequency $\hbar\omega$ in the range of 200 to 300 cm^{-1}, a value for S of 40 - 50 is estimated. Within the series of Fe(II) compounds with 6-fold N-coordination S will not vary to any great extent. What will vary though is the reduced energy gap p. In Fig. 9a $\ln[k_{HL}(T)]$ calculated with $S = 45$ and $\hbar\omega = 250$ cm^{-1} for is plotted against 1/T for various values of p. The characteristic features of the experimental curves, namely the low T tunnelling and the thermally activated region, are well reproduced. The low T tunnelling rate $k_{HL}(T\to 0)$ is predicted to increase exponentially with increasing p (Fig. 9b). Although $T_{1/2}$ is only a crude measure for ΔE^0_{HL}, the observed low T tunnelling rates do indeed increase with increasing $T_{1/2}$ (Fig. 10) from $\leq 10^{-6}$ s^{-1} for the spin-crossover system $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ ($x \approx 0.1$) with $T_{1/2} = 95$ K to $\geq 10^6$ s^{-1} for the LS systems with $T_{1/2}$ much larger than room temperature. This increase of more than 12 orders of magnitude is a consequence of the extremely large value of S and the resulting "inverse energy gap law" in the strong vibronic coupling limit.

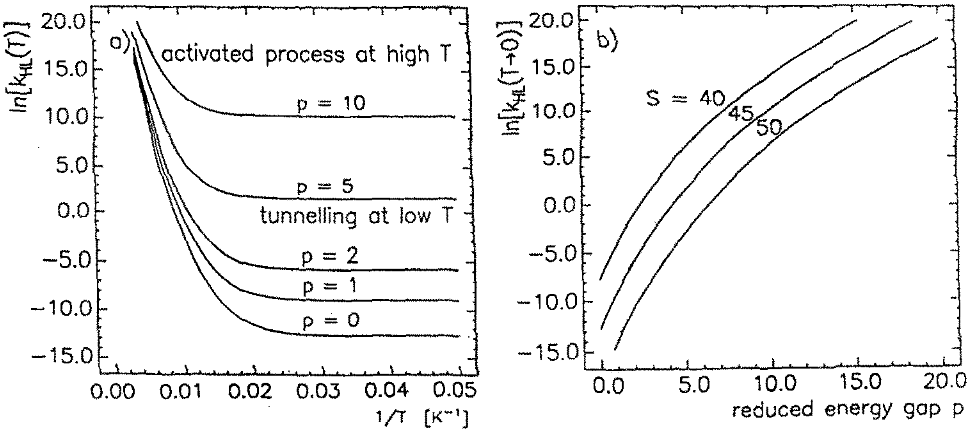

Fig. 9 : a) $\ln[k_{HL}(T)]$ vs. 1/T calculated with $S = 45$ and $\hbar\omega = 250$ cm^{-1} and the reduced energy p as parameter. b) Calculated low T tunneling rate constants $\ln[k_{HL}(T\to 0)$ vs. p with $\hbar\omega = 250$ cm^{-1} and S as parameter (from ref. [17]).

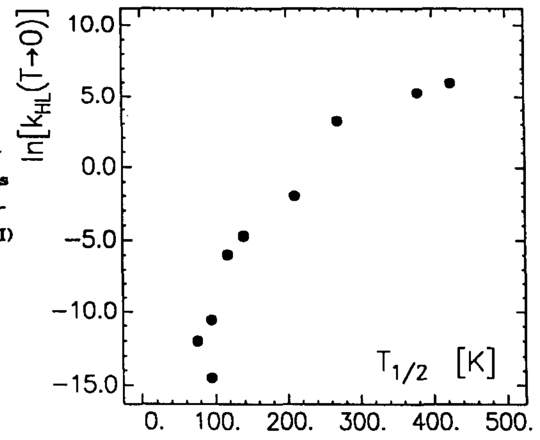

Fig. 10 : Experimental low temperature tunnelling rate constants $\ln[k_{HL}(T\rightarrow 0)]$ vs. the thermal transition temperature $T_{1/2}$ for the Fe(II) spin-crosssystems from table I.

What about other spin-crossover compounds, for instance of Fe(III) with a $^2T_2 \rightleftharpoons {}^6A_1$ or Co(II) with a $^2E \rightleftharpoons {}^4T_1$ spin transition? Well, Lawthers and McGarvey [28] have successfully applied pulsed laser excitation to Fe(III) systems in solution at room temperature. In principle the same type of temperature dependence of the HS→LS relaxation rates as for the Fe(II) systems should be observed. But because for Fe(III) systems Δr_{HL} is typically ~0.11 Å, and for the resulting value of S of ~ 17 is much smaller and low T tunnelling rates of 10^5 - 10^7 s^{-1} can be estimated for small reduced energy gaps p. For Co(III) systems predictions are more difficult, as the SCC model is most certainly a very bad approximation because of the strong Jahn-Teller effect in the ^2E state. But LIESST in the sense of the extremely long lived metastable states of the Fe(II) spin-crossover systems is not to be expected either.

5. PHOTOREFRACTIVE PROPERTIES OF FE(II) SPIN-CROSSOVER COMPOUNDS

Due to the large difference in the Fe-L bondlength between the LS and HS state the refractive index of an Fe(II) spin-crossover compound is expected to be substantially different in the two states. This effect can be used to create phase holograms. The most simple hologram is an excitation grating produced by the interference of two laser beams of the same wavelength on the sample. In a four wave mixing experiment a third beam can be diffracted at this excitation grating [29]. The intensity I of the diffracted beam is a measure of the modulation depth of the grating. For a phase grating the diffraction efficiency is given by [29] :

$$\eta = I/I_0 = (\pi \Delta n d/\lambda)^2 , \qquad (5.1)$$

where Δn is the modulation of the index of refraction, d the thickness of the grating and λ the wavelength of the probing beam.

If the grating decays after switching off the two exciting beams, the intensity in the diffracted beam falls off accordingly. Fig. 11 shows the relative intensity of the diffracted beam in so called degenerate four wave mixing geometry [29] with λ = 514.5 nm in a mixed crystal of $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ with $x \approx 0.05$ at 106 K. Since Δn is proportional to the population modulation ΔN and η is proportional to Δn^2, the grating lifetime τ_G is expected to be equal to half the lifetime of the excited state τ in the absence of energy tranfer processes. At 106 K with τ_G = 9.5 ms and τ = 22.2 ms from transient absorption this relation is confirmed within experimental error for the dilute mixed crystal.

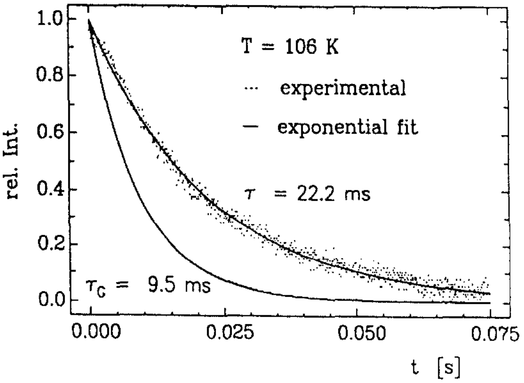

Fig. 11: Decay of the transient grating with τ_G = 9.5 ms and the light-induced HS state with τ = 22.2 ms determined in transient absorption at 106 K for $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ (x = 0.05).

From the diffraction efficiency η of 5×10^{-3} in the above experiment a value for $\Delta n/n$ of $\sim 5\times10^{-5}$ can be calculated at an estimated population modulation ΔN of $\sim 5\times10^{18}/cm^3$. This is a factor of 100 larger than for the ^2E state of Cr(III) in ruby [30] for the same value of ΔN. For Fe(II) spin-crossover compounds it should be possible to increase ΔN by an order of magnitude by using more concentrated crystals and to achieve diffraction efficiencies of some 10% (in a preliminary experiment 8% were achieved for $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ with $x \approx 0.1$ at 95 K), which in principle would make them attractive for application in real time holography.

6. CONCLUSIONS

The firmly established scheme for LIESST and reverse-LIESST in Fe(II) spin-crossover compounds with the large number of ISC processes between singlet, triplet and quintet states is in its complexity outstanding among coordination compounds.

Fe(II) coordination compounds constitute a model system for studying the dynamics of one of the most simple radiationless processes in chemistry, namely ISC. Because there are no luminescent processes competing with the HS→LS relaxation it has been possible to accurately determine the relaxation rate constants over a large temperature range and over more than 12 orders of magnitude. From the experimental results it is well established that the HS→LS relaxation is a highly nonadiabatic process.

The light-induced metastable states with lifetimes of several days at low T are a unique feature of Fe(II) spin-crossover compounds, due the value of S of ~ 40 - 50, which is by far the largest value found for th LF states of any coordination compound.

Future work should include the extension of the simple SCC model to allow for different force constants and vibrational frequencies in the two states, and anharmonicity should be taken into account too. The influence of more than one active vibration and the coupling to low frequency lattice (or solvent) vibrations should be investigated.

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