Intersystem crossing dynamics in Fe(II) coordination compounds

Andreas Hauser, Andreas Vef, and Peter Adler

Institut für Anorganische Chemie, Johanniter Gutenberg Universität, Staudingerweg 9, 6500 Mainz, Germany

(Received 21 March 1991; accepted 6 September 1991)

The $^5T_2$ (HS) $\rightarrow ^1A_1$ (LS) intersystem crossing rates have been determined for a number of Fe(II) coordination compounds between 10 and 270 K using time-dependent optical spectroscopy. Strong deviations from Arrhenius kinetics with nearly temperature independent tunneling at low temperatures and a thermally activated behavior at elevated temperatures with apparent activation energies smaller than the classical energy barrier were found. The tunneling rates range from $\sim 10^{-6}$ s$^{-1}$ for the doped spin crossover system $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6]$ (BF$_4$)$_2$ to $\sim 10^6$ s$^{-1}$ for the doped low-spin (LS) system $[\text{Zn}_{1-x}\text{Fe}_x(\text{bipy})_3]$ (PF$_6$)$_2$. The large range of 12 orders of magnitude in the low temperature tunneling rates as well as the activated region can be understood in terms of nonadiabatic multiphonon relaxation. Values for the Huang–Rhys parameter $S$ of 40–50 and for the reduced energy gap $\rho$ of 1–12 are estimated for the present series of compounds. The validity of an inverse energy gap law in the strong vibronic coupling limit with $S \gg \rho$ is borne out by experiment.

I. INTRODUCTION

Thermal spin transitions from a $^1A_1$ low-spin (LS) state at low temperature to a $^5T_2$ high-spin (HS) state at some elevated temperature for Fe(II) coordination compounds both in the solid state and in solution have been the subject of many studies over the last two decades, and several reports reviewing the matter have been compiled. The spin transition is accompanied by a large change in metal–ligand bond length. Figure 1 shows the potential wells for the two states along the totally symmetric normal coordinate. The condition for a thermal entropy driven spin transition to occur is that the zero point energy difference $\Delta E^0_{HL}$ is positive and of the order of $k_B T$: The transition temperature $T_{1/2}$, defined as the temperature at which both spin states are present in equal amounts is an approximate measure for $\Delta E^0_{HL}$.

Work on the LS $\rightarrow$ HS intersystem crossing dynamics in Fe(II) spin crossover compounds has been performed mostly in solution at ambient temperatures and the results have been discussed in terms of absolute rate theory. An extensive review has recently been presented by Beattie. McGarvey and Lawthers were the first to find a rapid conversion of the $^1A_1$ state to some short-lived metastable state, to which they assigned the $^5T_2$ state, upon pulsed laser excitation of some Fe(II) spin crossover complexes in solution. Laser flash photolysis has since become the most common technique for determining HS $\rightarrow$ LS relaxation rates. In solution, only a limited temperature range is available and $\ln[k_{HL}]$ vs $1/T$ plots (Arrhenius plots) usually result in straight lines. Experimental activation energies $E^a$ for the HS $\rightarrow$ LS relaxation for most of the Fe(II) spin crossover complexes studied were found to be $\sim 1000$–$1500$ cm$^{-1}$ with preexponential factors $A$ of $\sim 10^{-7}$–$10^6$ s$^{-1}$, i.e., HS $\rightarrow$ LS relaxation rates in solution at ambient temperatures are of the order of $10^6$ to $10^8$ s$^{-1}$.  

I.$^a$

$^a$ Present address: MPI für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Germany.

Similar HS $\rightarrow$ LS relaxation rates and activation parameters around room temperature as in solution were obtained for some Fe(II) spin crossover complexes in the solid state by line shape analysis of Mössbauer spectra. The technique is restricted to the small range of rate constants of $10^6<k_{HL}<10^9$ s$^{-1}$. Somewhat greater activation energies were found for the relaxation of thermally trapped HS states.

Some years ago, Decurtins et al. showed that in the [Fe(ptz)$_6$] (BF$_4$)$_2$ spin crossover system (ptz = 1-propyltetrazole), a quantitative light-induced $^1A_1$ (LS) $\rightarrow$ $^5T_2$ (HS) conversion could be observed below $\sim 50$ K, well below the thermal transition temperature, by irradiating the sample into the spin allowed $^1A_1 \rightarrow ^5T_2$ d–d absorption band in the visible. In the case of [Fe(ptz)$_6$] (BF$_4$)$_2$, in the solid state and at low temperatures, the HS $\rightarrow$ LS relaxation rate was less than $10^{-6}$ s$^{-1}$ and the light-induced state could be iden-

---

FIG. 1. Potential wells for the high-spin and the low-spin states of Fe(II) in octahedral coordination along the totally symmetric normal coordinate $Q_{o1}$. In the simple SCC model, the force constants in the two states are taken to be equal.
The metastable low-spin (LS) state can also be reached by irradiating the light-induced metastable (LIESST) state in Fe(II).

The mechanism (Fig. 2) proposed by Decurtins et al. involves two intersystem crossing steps with an activated process in the form of an inverse energy gap law in the strong vibronic coupling limit. The theory of nonadiabatic multiphonon relaxation, a fully quantum mechanical approach based on Fermi's golden rule, is used to explain the observed variation of the low temperature tunneling rates in the form of an inverse energy gap law in the strong vibronic coupling limit.

II. EXPERIMENTAL SECTION

A. Preparation of samples

[Fe(ptz)_3]Cl_2 · MeOH (pic = 2-picolyamine) was prepared as described by Sorai et al. [Mn(pic)_3]Cl_2 · MeOH was prepared following the same procedure, but starting from water-free MnCl_2. Dilute single crystals of [Mn(pic)_3]Cl_2 · MeOH with x≈0.0005 up to several millimeters edge were grown by slow evaporation from a water-free methanolic solution.

For Fe(bipy)_3] (PF_6)_2 and [Zn(bipy)_3] (PF_6)_2 (bipy = 2,2'-bipyridine) doped into [Mn(bipy)_3] (PF_6)_2, low temperature relaxation rates of ~10^6 s^-1 have been determined. The question now is, what are the parameters which govern the excited state lifetime, leading to a low temperature tunneling rate of less than 10^{-8} s^-1 in one case and 10^6 s^-1 in another?

In this paper, we present a systematic study of the HS→LS relaxation rates k_{HL}(T) for a number of Fe(II) coordination compounds in the temperature range 10-270 K. Various methods of optical spectroscopy enable us to cover 14 orders of magnitude in determining rate constants from ~10^{-6} to 10^{8} s^{-1}. In order to eliminate the complications of cooperative effects in neat materials and of inhomogeneities in polymer matrices, we restrict ourselves to dilute mixed crystals where the HS→LS relaxation is expected to be single exponential. In particular, the relaxation rates k_{HL}(T) for a number of Fe(II) coordination compounds, not only for neat compounds, but also for dilute mixed crystals, notably for [Zn_{1-x}Fe_x(ptz)_3] (BF_4)_2 (x≈0.1), [Mn_{1-x}Fe_x(pic)_3] Cl_2 · MeOH (x≈0.0005), [Zn_{1-x}Fe_x(mepy)_3(tren)] (PF_6)_2, and [Zn_{1-x}Fe_x(py)_3(tren)] (PF_6)_2 (x≈0.0005) are reported and discussed together with the results for the low-spin system [Zn_{1-x}Fe_x(bipy)_3] (PF_6)_2 (x≈0.0001) from Ref. 14.

The theory of nonadiabatic multiphonon relaxation, a fully quantum mechanical approach based on Fermi's golden rule, as first applied to HS→LS intersystem crossing processes by Buolks et al., is used to explain the observed variation of the low temperature tunneling rates in the form of an inverse energy gap law in the strong vibronic coupling limit.
grown by slow evaporation from acetonitrile/acetone. [Fe(bipy)3] (PF6)2 and [Zn(bipy)3] (PF6)2 (bipy = 2,2'-bipyridine) were prepared by standard methods.20 Dilute single crystals of [Zn1−xFex(bipy)3] (PF6)2 with x≈0.0001 in the form of light red hexagonal needles were grown from an ethanol/acetonitrile solution.

B. Optical spectroscopy and lifetime measurements

Polarized temperature-dependent single crystal absorption spectra were recorded with a UV/VIS/NIR spectrophotometer (Bruins Instruments Omega 10) equipped with a pair of Glan–Taylor polarizers. Sample temperatures between 10 and 340 K were achieved with a cold He-gas flow technique.

Since all processes leading from the initial excitation to the metastable HS state as well as the HS → LS relaxation are radiationless, excited state decay curves have to be recorded in transient absorption. Three different methods were employed to cover the range from 10−5 to 105 s−1 for the relaxation rate kHSL:

(i) 10−4 < kHSL < 10−2 s−1. In this range, an initial population of the light-induced metastable state of 100% could be achieved by irradiating the whole crystal for several minutes with either the 514.5 or the 488.0 nm line of a cw Ar+ laser (SpectraPhysics Model 2020) with laser powers of up to 100 mW. The crystal was kept at the temperature at which the relaxation curve was to be recorded throughout the irradiation. After switching off the laser, the decay of the metastable state was monitored by recording full absorption spectra at appropriate time intervals. Temperature stability over a maximum period of six hours was ±0.5 K. Sample heating due to the irradiation was not critical because the laser powers used were comparatively small and the cold He-gas flow around the sample was kept high.

(ii) 10−2 < kHSL < 10−1 s−1. For relaxation rates in this range, one has to use pulsed excitation and usually people use pulsed Nd:YAG lasers and the like.3,12 However, with the pulse energies needed in order to achieve a sufficient initial population of the metastable state, there are severe heating problems especially at low temperatures and for samples with low heat conductivities. We therefore devised the apparatus shown in Fig. 3. The Ar+ laser was operated in the multiline mode and the lines were separated with an Amici prism. One of the strong lines (514.5 or 488.0 nm) was used for excitation, one of the weaker lines was further attenuated and served as probe beam. The excitation beam was passed through a mechanical chopper or electronic shutter, reunited with the probe beam, and together they were weakly focused onto the sample. The light intensity within the irradiated volume was thus quite high. With laser powers of typically 100 mW for the excitation beam and irradiating into a MLCT band a sufficient population of the metastable state for relaxation rates of up to 105 s−1 could be obtained. The collinear probe beam ensured that exactly the irradiated volume was interrogated. Behind the sample, the probe beam was separated from the excitation beam in a 1/4 m double monochromator (Spex 1680) and passed onto a photomultiplier (Hamamatsu R928). The signal from the photomultiplier was amplified in a preamplifier (Analog Devices Model 341) and transients were recorded with a digital scope (Tektronix 2430A) making full use of its averaging capabilities. Sample temperatures between 10 and 250 K were achieved in a cryostat (Cryovac) operated in the continuous flow mode.

(iii) 10−1 < kHSL < 100 s−1. For high relaxation rates, the previously described system14 with a frequency doubled Nd:YAG laser was used. This system was used mainly at temperatures above 150 K and in this case heating problems are not quite as severe as at low temperatures.

III. RESULTS

A. Temperature-dependent absorption spectra

The temperature-dependent absorption spectra of [Zn1−xFex(ptz)6] (BF4)2 (x≈0.1) with the characteristic spin-allowed 1A1 → 1T1, 1T2 and 3T2 → 3E d–d transitions for the system in the LS and the HS states, respectively, have been reported previously.15 From the relative optical density (OD) at the maximum of the 1A1 → 1T1 absorption band as a function of temperature, the HS fraction γHIS(T) shown in Fig. 4 can be extracted. In contrast to the neat material,
where cooperative effects lead to a first-order crystallographic phase transition, the thermal spin transition in the dilute complex is gradual with a transition temperature $T_{1/2} = 95 \pm 2$ K. The absorption spectra of the other four compounds of our series are dominated by low-energy MLCT bands with much higher extinction coefficients. Figure 5(a) shows the temperature dependence for $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_3(\text{tren})\right](\text{PF}_6)_2$ (x≈0.0005). Because of the much shorter metal–ligand bond length in the LS state and thus the larger overlap of metal and ligand orbitals in the LS state, the MLCT bands are much more intense in this state, but the MLCT intensity of the HS state is not zero. This makes extracting $\gamma_{\text{HS}}(T)$ a little bit more complicated. The optical density at the band maximum $OD_{580}(T) = c_0d\left[e_{580,\text{LS}}^\text{e}T_{1/2}(T) + e_{585,\text{HS}}^\text{HS}T_{1/2}(T)\right]$, with $c_0$ the molar concentration of the spin crossover complex, $e_{580,\text{LS}}^\text{e}$ and $e_{585,\text{HS}}^\text{HS}$ the extinction coefficients of the LS and the HS species at 580 nm, respectively, and $d$ the thickness of the crystal. Setting $c_0d e_{580}^\text{e} = OD_{580}(15 \text{ K})$ and $c_0d e_{585}^\text{HS} = OD_{580}(325 \text{ K})$ by assuming that at 15 K $\gamma_{\text{LS}} \approx 1$ and at 325 K $\gamma_{\text{HS}} \approx 1$, the transition curve $\gamma_{\text{HS}}(T)$ in Fig. 4 with $T_{1/2} = 210 \pm 4$ K is obtained.

The spectra of $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{py})_3(\text{tren})\right](\text{PF}_6)_2$ are much the same as those of the methyl substituted complex, except that they are almost temperature independent up to 300 K. Although potentially a spin crossover compound, its $T_{1/2}$ is above 350 K. The spectra of $\left[\text{Mn}_{1-x}\text{Fe}_x(\text{pic})_3\right]\text{Cl}_2\cdot\text{MeOH}$ are quite similar. The main MLCT band is slightly blue shifted and with only one maximum at ~480 nm. From the transition curve $\gamma_{\text{HS}}(T)$ included in Fig. 4, we find $T_{1/2} = 118 \pm 4$ K.

The polarized absorption spectra of $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{bipy})_3\right](\text{PF}_6)_2$ have been discussed in detail by Ferguson and Herren. Suffice to say that $\text{Fe(bipy)}_3^{2+}$ is a typical low-spin complex and that there is no marked temperature dependence of the intensity of the MLCT band at ~500 nm.

### B. Relaxation measurements

Of the five compounds of our series, only $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6\right](\text{BF}_4)_2$ is almost identical to the room temperature spectrum. At 10 K, the HS→LS relaxation rate $k_{\text{HL}}(T)$ is less than $10^{-6}$ s$^{-1}$, only at temperatures above ~50 K does a noticeable relaxation set in. Relaxation curves over the limited temperature interval of 60–72 K have been reported previously and were found to be single exponential. In this work, the temperature interval has been extended from 40–130 K. In the region of the thermal spin transition, $k_{\text{HL}}(T)$ can be calculated from the observed relaxation rate $k_{\text{obs}}$ according to

$$k_{\text{HL}}(T) = k_{\text{obs}}(T)\left[1 - \gamma_{\text{HS}}(T)\right].$$

Figure 6 shows the resulting rate constants plotted as $\ln[k_{\text{HL}}(T)]$ vs $1/T$ (Arrhenius plot). At high temperatures, an approximately straight line is obtained, but towards low temperatures, there is a strong deviation from this. From the linear part, a high temperature activation energy of ~1100 cm$^{-1}$ with a preexponential factor $A \approx 5 \times 10^7$ s$^{-1}$ can be estimated. These values are in the range generally observed for HS→LS relaxation at ambient temperatures. The values reported in Ref. 15 are considerably smaller because they were estimated from a temperature interval where the deviation from the linear behavior is already pronounced.

![FIG. 6. The Arrhenius plot of the experimental relaxation rate constants $k_{\text{HL}}(T)$ for (○) $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6\right](\text{BF}_4)_2$; (▲) $\left[\text{Mn}_{1-x}\text{Fe}_x(\text{pic})_3\right]\text{Cl}_2\cdot\text{MeOH};$ (▼) $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{py})_3(\text{tren})\right](\text{PF}_6)_2; and (■) $\left[\text{Zn}_{1-x}\text{Fe}_x(\text{bipy})_3\right](\text{PF}_6)_2$.](image)
TABLE I. Transition temperature \( T_{1/2} \), high temperature activation energy \( E^* \), preexponential factor \( A \), and low temperature tunneling rate \( k_{\text{HL}}(T \to 0) \) for several Fe(II) coordination compounds. Included are the estimated reduced energy gaps \( \rho \) according to the inverse energy gap law.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_{1/2} ) (K)</th>
<th>( E^* ) (cm(^{-1}))</th>
<th>( A ) ( (s^{-1}) )</th>
<th>( \rho )</th>
<th>( k_{\text{HL}}(T \to 0) ) ( (s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn}_{1-x}\text{Fe}_x(\text{bipy})_3(\text{PF}_6)_2 )</td>
<td>95</td>
<td>1100</td>
<td>5 \times 10^7</td>
<td>&lt;1</td>
<td>~5 \times 10^{-7}</td>
</tr>
<tr>
<td>( \text{Mn}_{1-x}\text{Fe}_x(\text{pic})_3\text{Cl}_2 \cdot \text{MeOH} )</td>
<td>118</td>
<td>907</td>
<td>2 \times 10^8</td>
<td>~1-2</td>
<td>2.5 \times 10^{-1}</td>
</tr>
<tr>
<td>( \text{Zn}_{1-x}\text{Fe}_x(\text{mepy})(\text{tren})\text{Cl}_2 \cdot \text{MeOH} )</td>
<td>210</td>
<td>837</td>
<td>5 \times 10^8</td>
<td>~3-4</td>
<td>1.4 \times 10^{-1}</td>
</tr>
<tr>
<td>( \text{Zn}_{1-x}\text{Fe}_x(\text{py})(\text{tren})\text{Cl}_2 \cdot \text{MeOH} )</td>
<td>&gt;350</td>
<td>640</td>
<td>1 \times 10^9</td>
<td>~7-8</td>
<td>4 \times 10^3</td>
</tr>
<tr>
<td>( \text{Zn}_{1-x}\text{Fe}_x(\text{bipy})(\text{mepy})(\text{PF}_6)_2 )</td>
<td>Low spin</td>
<td>364</td>
<td>2 \times 10^9</td>
<td>~11-13</td>
<td>6 \times 10^3</td>
</tr>
</tbody>
</table>

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.194.8.73 On: Fri, 13 Dec 2013 09:23:26
Buhks et al. described the "HS→LS relaxation in terms of a radiationless nonadiabatic multiphonon process occurring between two distinct zero-order spin states characterized by different nuclear configurations."16 The most simple model for treating this problem is in the SCC space, where the potentials are taken to be displaced by $\Delta Q_{HL}$ along only one internal vibration, namely the totally symmetric vibration. For Fe(II) with $\Delta S = 2$, only higher-order spin–orbit coupling can mix the two states via the low-lying $^2T_i$ state. Starting from Fermi's golden rule and using the Condon approximation, the probability for a radiationless transition from the $n$th vibrational level of the HS state to the $m$th level of the LS state is given by $^{16,23}$

$$w_{nm} = \frac{2\pi}{\hbar} \beta_{HL}^2 \left| \langle \chi_n | \chi_m \rangle \right|^2 \rho(E_n),$$

where the density of final states $\rho(E_n)$ has to be evaluated at $E_n = E_m$ to ensure energy conservation. The electronic matrix element $\beta_{HL} = \langle \Phi_{LS} | \hat{H}_{m} | \Phi_{HS} \rangle \approx 150$ cm$^{-1}$ for ligand field strengths in the vicinity of the spin crossover point.16 If in addition the potentials are taken to be harmonic with equal force constants $f$ and vibrational frequencies $\omega$, the electronic degeneracy of the final state becomes

$$w_{nm} = \frac{2\pi}{\hbar \omega} \beta_{HL}^2 \left| \langle \chi_n | \chi_m \rangle \right|^2.$$

The condition for energy conservation is now given by $n = m + p$, where $p = \Delta E_{HL}^0 / \hbar \omega$ is the reduced energy gap, a measure for the vertical displacement of the two potential wells relative to each other. The Franck-Condon factor $\left| \langle \chi_n | \chi_m \rangle \right|^2$ can be evaluated using the recursion method of Struck and Fonger.24 The HS→LS relaxation rate constant $k_{HL}(T)$ can now be calculated by taking a thermal average of $w_{nm}$ over the vibrational levels $m$ of the initial state

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

where the thermally averaged Franck-Condon factor $F_p(T)$ is given by $^{23}$

$$F_p(T) = \frac{\sum_m \left| \langle \chi_n + p | \chi_m \rangle \right|^2 e^{-m \hbar \omega/kT}}{\sum_m e^{-m \hbar \omega/kT}}.$$

For $T \to 0$, $F_p(T)$ simplifies to

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

where $S = \frac{1}{2}f\Delta Q_{HL}^2 / \hbar \omega = \mu \omega \Delta Q_{HL}^2 / \hbar$ is the Huang–Rhys factor, a measure for the horizontal displacements of the two potential wells relative to each other. With $\Delta Q_{HL} = \sqrt{\Delta \Omega_{HL} \approx 0.5 \AA}$, a mean force constant $f \approx 2 \times 10^5$ dyn/cm, and a typical vibrational frequency $\hbar \omega$ in the range from 200 to 300 cm$^{-1}$, a value for $S$ of $\sim 40$–50 is estimated. This value for $S$ is substantially larger than the value of $\sim 20$ originally suggested by Buhks et al.,16 who used values for the vibrational frequency and $\Delta Q_{HL}$ comparable to ours, but instead of making an educated guess regarding the force constant, they assumed a reduced mass $\mu_{14}$, i.e., just the mass of the coordinating atom, which in turn leads to an unrealistically small force constant of $\sim 0.5 \times 10^5$ dyn/cm. For our rather complicated ligands, it is very difficult to know what the reduced mass is. For the totally symmetric stretch vibration, it is certainly considerably larger than just the mass of the coordinating atom, but of course a lot less than the mass of the ligand as a whole.

It is fair to assume that $\Delta r_{HL}$, $f$, and $\hbar \omega$ and therefore $S$ will not vary to any great extent within our series of compounds, where for all of them the central ion is coordinated by six nitrogen atoms. What will vary though is the opposite to the normal energy gap law with $\Delta E_{HL}^0$ and thus the reduced energy gap $p$. In Fig. 8(a), $\ln [k_{HL}(T \to 0)]$ calculated with $S = 45$ and $\hbar \omega = 250$ cm$^{-1}$ and for various values of the parameter $p$ is plotted against $1/T$. The characteristic features of the resulting curves are a temperature-independent tunneling rate at low temperatures and a thermally activated process at higher temperatures with an apparent activation energy which is lower than the classical energy barrier $E^c = S \hbar \omega/4$ for $p = 0$ and which decreases with increasing reduced energy gap $p$. The low temperature tunneling rate $k_{HL}(T \to 0)$ on the other hand increases almost exponentially with increasing $p$ [Fig. 8(b)]. This is opposite to the normal energy gap law with $S < p$, i.e., in the so-called weak vibronic coupling limit.23

Clearly the calculated curves show the same general behavior as the experimental ones. Moreover, $k_{HL}(T \to 0)$ increases dramatically from $\sim 5 \times 10^{-7}$ s$^{-1}$ for...
[Zn$_{1-x}$Fe$_x$(ptz)$_6$] (BF$_4$)$_2$ with $T_{1/2} = 95$ K to $6 \times 10^9$ s$^{-1}$ for [Zn$_{1-x}$Fe$_x$(bipy)$_3$] (PF$_6$)$_2$ which is a low-spin compound with $T_{1/2}$ much larger than room temperature. Although $T_{1/2}$ is but a crude measure of the energy gap $\Delta E_{HL}$, the observed low temperature tunneling rates for our series of compounds do indeed increase with increasing $T_{1/2}$. Unfortunately, $\Delta E_{HL}$ and therefore $\rho$ are very difficult to determine experimentally. It is customary to assume the thermodynamic parameters for the spin transitions $\Delta H_{HL}$ and $\Delta S_{HL}$ to be temperature independent and to determine them from $k_B T \ln (K)$ vs $T$ plots. If $\Delta H_{HL}$ and $\Delta S_{HL}$ were really temperature independent, then $\Delta E_{HL}$ could be identified as $\Delta H_{HL}$, but they are not at all temperature independent, and in fact, $k_B T \ln (K)$ vs $T$ plots usually have quite pronounced curvatures towards low temperatures. $\Delta E_{HL}$ should be set equal to $\Delta H_{HL}$. For the spin crossover system [Zn$_{1-x}$Fe$_x$(pic-ND$_2$)$_3$] Cl$_2$·EtOD, for instance, with $T_{1/2} = 100$ K, a value for $\Delta H_{HL}$ of $\sim 350$ cm$^{-1}$ is estimated from the linear part of the $k_B T \ln (K)$ vs $T$ plot, but extrapolating to $T = 0$ gives $\Delta H_{HL}$ ($T = 0$) $\approx 150$ cm$^{-1}$, i.e., $\Delta E_{HL}$ is substantially smaller than $\Delta H_{HL}$ from the linear part of the plot. $\Delta H_{HL}$ ($T = 0$) can only be determined successfully for systems with $T_{1/2} < 120$ K, because $K$ has to be evaluated with great accuracy at low temperatures. Certainly a value for $\rho$ of $< 1$ can be assigned to the [Zn$_{1-x}$Fe$_x$(ptz)$_6$] (BF$_4$)$_2$ system and one of between 1 and 2 is appropriate for [Mn$_{1-x}$Fe$_x$(pic)$_3$] Cl$_2$·MeOH. The observed extremely small low temperature tunneling rates $k_{HL}$ ($T < 200$ K) for the two systems lie within the predicted range, based on our estimate of $\rho$. For the low-spin system [Zn$_{1-x}$Fe$_x$(bipy)$_3$] (PF$_6$)$_2$, albeit not too far away from the spin crossover point, it is safe to assume $\rho$ to be $> 10$, and from Fig. 8(b), we would indeed expect $k_{HL}$ ($T = 0$) to be more than ten orders of magnitude larger than in the [Zn$_{1-x}$Fe$_x$(ptz)$_6$] (BF$_4$)$_2$ system. This gives us confidence that our estimate for the range of $\rho$ is realistic and we can now tentatively assign the values of $\rho$ listed in Table I to the compounds of our series.

To expect a more quantitative agreement of the experimental $ln[k_{HL}(T)]$ vs $1/T$ curves with the curves calculated on the basis of the SCC model with harmonic potentials and equal force constants, and to actually attempt a numerical fit of some sort would, however, be presumptuous in view of the approximations made. Although the simple SCC model predicts apparent activation energies at high temperatures which are smaller than the classical energy barrier and thus interprets the thermally activated relaxation process as a nonadiabatic tunneling process from excited vibrational states, they are still larger than the ones observed experimentally. Well, taking equal force constants and harmonic potentials is of course a drastic approximation, since we know that the force constants of the two states differ considerably, and for the extremely large differences of $\sim 0.2$ Å in metal-ligand bond lengths, anharmonic terms in the potentials are not really negligible. Both effects would influence the calculated rate constants in the high temperature regime. Furthermore, for most of our compounds, there is probably more than one active vibrational mode, because the point group is usually lower than $O_h$ and if not then the $^5T_2$ state would be susceptible to a Jahn–Teller effect. Especially for the [Mn$_{1-x}$Fe$_x$(pic)$_3$] Cl$_2$·MeOH and [Zn$_{1-x}$Fe$_x$(R-py)$_3$](tren) (PF$_6$)$_2$ systems, where half of the coordinating nitrogen atoms belong to NH$_2$ groups and the other half to a pyridyl ring, we would expect at least two quite different frequencies to be active. This is expected to result in a much more gradual transition from the thermally activated high temperature regime to the low temperature tunneling regime than calculated on the basis of the simple SCC model. This is indeed observed experimentally.

In the SCC model, coupled to low frequency phonons is basically neglected. The low frequency phonons just provide the heat bath for the energy dissipation and ensure implicitly that the conditions of energy conservation are met if there is an energy mismatch between the vibrational levels in the SCC. At high temperatures, where the low frequency phonons are thermalized, this is justified, but at low temperatures, the explicit coupling to the low frequency phonons should be taken into account. That this is important can be seen from the fact that the low temperature tunneling rates are not as temperature independent as the SCC model predicts.

What about other spin crossover systems, say of Fe(III) with a $^6A_1 \rightarrow ^3T_2$ or Co(II) with a $^2E \rightarrow ^2T_2$ spin transition? Well, at ambient temperatures, relaxation rates of $\sim 10^{-7}$–$10^9$ s$^{-1}$ for Fe(III) and Co(II) spin crossover complexes in solution have been determined and Lawthers and Mcgarvey have applied successfully the photoperturbation technique to Fe(III) systems. In principle, the same type of temperature dependence of the HS $\rightarrow$ LS relaxation rates as for the Fe(II) systems should be observed, but the low temperature tunneling rates for Fe(III) and Co(II) spin crossover compounds are expected to be several orders of magnitude larger than for Fe(II) spin crossover compounds, because $\Delta E_{HL}$ and therefore $S$ of the former are smaller. For Fe(III), a typical value for $\Delta E_{HL}$ is $\sim 0.1$ Å, giving a value for $S$ of $\sim 17$. Buhks et al. calculate the electronic matrix element for Fe(III) to be $\sim 50$ cm$^{-1}$ and from this a value for the low temperature tunneling rate $k_{HL}$ ($T = 0$) for small reduced energy gaps $\rho$ of $\sim 10^{-6}$–$10^{-7}$ s$^{-1}$ is estimated. For Co(II), the corresponding calculation is difficult to perform, because the $^2E$ state is susceptible to a strong Jahn–Teller effect and the SCC model becomes a very bad approximation.

V. CONCLUSIONS

Fe(II) coordination compounds, particularly those with ligand field strengths in the vicinity of spin crossover, constitute a model system for studying the dynamics of one of the most simple radiationless processes in chemistry, namely intersystem crossing. Because there are no luminescent processes competing with the intersystem crossing process, it has been possible to determine accurately the $^5T_2$ (HS) $\rightarrow ^1A_1$ (LS) relaxation rates over a large temperature interval and over 14 orders of magnitude. From our experimental results, it is now well established that the HS $\rightarrow$ LS relaxation in general is determined by a nearly temperature-independent tunneling rate at low temperatures.
and an activated behavior at elevated temperatures.

The theory of nonadiabatic multiphonon relaxation where the electronic energy of the initial HS state is transformed in a nonadiabatic process into vibrational energy of the LS state can explain the features of the HS→LS relaxation at least semiquantitatively. Above all, the spread of more than 12 orders of magnitude for the low temperature tunneling rate can be understood as a consequence of an inverse energy gap law for the strong coupling limit with $S \gg p$. The thermally activated relaxation process is still nonadiabatic and can be pictured as tunneling from excited vibrational states of the HS state.

The light-induced metastable states with lifetimes of several days at low temperatures are a unique feature of Fe(II) spin cross-over compounds. They involve the large value of $\Delta_0$ found for any coordination compound of a first row transition metal.

Future work should include an 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. On the experimental side, one should look at a system where just one parameter can be varied systematically, for instance, the vibrational frequencies in the two states, and anharmonicity accordingly.

**ACKNOWLEDGMENTS**

We thank D. Hinz for her skillful crystal growth, R. Jakobi, U. Manthe, and H. Spiering for helpful discussions, and P. Güttich for his generous support. This work was supported financially by the Bundesministerium für Forschung und Technologie and the University of Mainz. We thank H. U. Güdel and the University of Bern for the use of the pulsed Nd:YAG laser system. A. Hauser gratefully acknowledges a fellowship of the Schweizerische National Fonds.