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Non-First-Order Kinetics of the High Spin−Low Spin Relaxation in $[Fe(bpp)_2](BF_4)_2$ after LIESST and Thermal Spin Trapping

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The iron(II) spin crossover complex $[Fe(bpp)_2](BF_4)_2$ (bpp = 2,6-bis(pyrazol-3-yl)pyridine) shows a complete high spin (HS, $^5T_2$) $\rightleftharpoons$ low spin (LS, $^1A_1$) transition in the temperature region 160−185 K with a hysteresis of 10 K. It also shows the well-known LIESST and reverse LIESST effects at low temperatures. Trapping of the metastable HS state is also possible by rapid cooling of the sample. The HS → LS relaxation was monitored at temperatures between 92.5 and 100 K using Mössbauer spectroscopy and shows strong deviations from first-order kinetics, regardless of the origin of the metastable HS states. $[Fe(bpp)_2](BF_4)_2$ is the first spin crossover complex in which long-lived metastable HS states could be generated by LIESST at temperatures as high as 80 K.

1. Introduction

The thermal high spin (HS) $\rightleftharpoons$ low spin (LS) transition in iron(II) complexes, denoted as $^5T_{2g} \rightleftharpoons {}^1A_{1g}$ in the approximation of O_h symmetry, is a well-known and extensively studied phenomenon[1,2] Over the last decade, the dynamics of the spin transition have received considerable attention.[3,4] Kinetic studies have been performed for solutions by perturbation of the equilibrium by various techniques, e.g. application of light or ultrasound, and detection of the relaxation back to equilibrium.

In the solid state, line shape analysis of Mössbauer relaxation spectra has proved to be a useful method to obtain information about the dynamics of the spin transition.[5] This method, however, is only suitable within a narrow range of rates determined by the lifetime of the nuclear excited state. A more common way to yield kinetic data is, as in solution, the detection of metastable spin states and the monitoring of their subsequent relaxation.

Metastable spin states can be generated by making use of the LIESST effect (light-induced excited spin state trapping).[6,7] The metastable HS state is formed by irradiating the sample into the $^1A_1{-}^1T_{1,2}$ ligand field or MLCT absorption bands at temperatures well below the thermal spin transition temperature. The mechanism involves double intersystem crossing from the excited $^1T_{1,2}$ states to the $^5T_2$ HS state via the low-lying triplet states. The thermal relaxation of the trapped HS state can then be observed at some higher temperatures. The lifetime of the LIESST state varies from weeks at ~10 K down to minutes or seconds at temperatures between 60 and 70 K.

According to Hauser,[4] the relaxation mechanism of these radiationless transitions can be understood in a nonclassical way, with the relaxation rates well correlated with the difference ΔE_{HL} between the lowest vibronic levels of the HS and LS states ("inverse energy gap law"). The trapped HS state can also be pumped back to the LS state by irradiating with light into the ligand field absorption band of the HS state (reverse LIESST),[8] which usually corresponds to red light for the $^5T_2 \rightarrow {}^5E$ transition. In this case, again the mechanism involves double intersystem crossing from the excited ^5E state to the $^1A_1$ ground state. The mechanism for LIESST and Reverse LIESST has been fully elucidated.[4]

Another means of obtaining metastable HS states in some solid spin crossover systems of iron(II) is by rapid cooling of the sample.[9,10] In these cases the derived activation energies of the HS−LS relaxation have been found to be larger by a factor of 2−3 than values found for systems which were studied by line shape analysis of Mössbauer spectra or by LIESST studies.[2] Moreover, first-order kinetics were reported for these cases. This is in contrast with relaxation studies on the spincrossover system $[Fe_xZn_{1-x}(ptz)_6](BF_4)_2$,[11] where strong deviations from first-order kinetics has been observed in the nondiluted crystal, which could be ascribed to cooperative interactions accompanying the spin transition. First-order kinetics were seen only in the highly metal-diluted crystals ($x \rightarrow 0$), where such cooperative interactions disappear.

We have decided to reinvestigate the spin state dynamics in the system $[Fe(bpp)_2](BF_4)_2$ (bpp = 2,6 bis (pyrazol-3-yl)-pyridine) since this sytem should allow a direct comparison of the decay of both thermally and light-induced metastable HS states. In the process we have observed the first complex where the LIESST effect yields long-lived metastable HS states in the liquid nitrogen temperature regime.

2. Experimental Section

2.1. Preparation. The ligand 2,6-bis(pyrazol-3-yl)pyridine (bpp) was prepared by the method of Lin and Lang.[12] $[Fe(bpp)_2](BF_4)_2{\cdot}3H_2O$ was obtained by reaction of the ligand with $[Fe(H_2O)_6](BF_4)_2$ in hot

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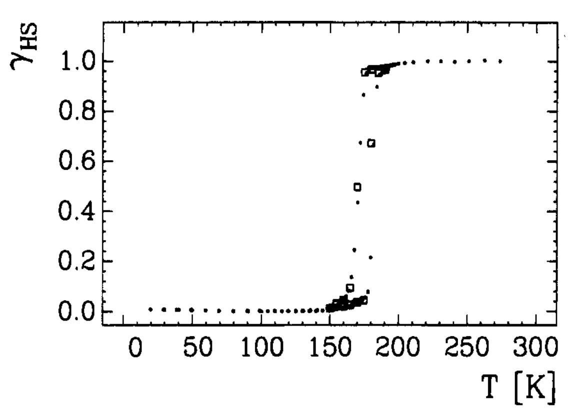

Figure 1. Molar fraction γ_{HS} of the $^5T_2$ (HS) state in $[Fe(bpp)_2](BF_4)_2$ as a function of temperature derived from magnetic susceptibility (O) and Mössbauer measurements (□). There is no indication for different Debye–Waller factors for HS and LS states, respectively, in this system.

ethanolic solution.[13] The anhydrous form was obtained by heating the compound at 110 °C in an N_2 atmosphere. The samples used in the present study were enriched to 30% in ^{57}Fe.

2.2. Susceptibility Measurements. The magnetic susceptibilities $\chi(T)$ were measured between 20 and 300 K with a Foner type magnetometer equipped with a helium flow cryostat. The applied external field was 1 T. The HS fraction $\gamma_{HS}(T)$ was calculated from the measured susceptibilities with the assumptions that (i) the iron complex in the HS state shows a Curie law behavior and (ii) the LS state shows a temperature independent paramagnetism. The diamagnetic correction for the ferrous complex was determined from Pascal constants.

2.3. Mössbauer Measurements. Mössbauer spectra were recorded between 10 and 300 K in the transmission geometry. The source was ^{57}Co/Rh kept at room temperature. The samples were sealed in polished plexiglass containers and mounted in a He-flow cryostat (CF506, Oxford Instruments), which was equipped with windows of transparent mylar foil to allow irradiation of the sample with light. LIESST experiments with green light yielding light-induced HS states were performed using a Xe-arc lamp and appropriate filters or with the 514.5 nm line of a Ar^+ laser (Coherent, Innova70); irradiation was done at ≤80 K. Thermal trapping of the HS state was achieved by immersing the sample in liquid nitrogen followed by rapid transfer to the cryostat.

Mössbauer spectra were fitted by use of the transmission integral with the program MOSFUN.[14] For kinetic measurements the relaxation was followed by monitoring the HS fraction in the temperature interval 92.5–100 K using Mössbauer spectroscopy. Spectra were recorded every 10 min.

3. Results

3.1. Thermal Spin Crossover. The essential characteristics of the thermal spin crossover have been published earlier.[10,13] However, since the spin transition temperature $T_{1/2}$ ($\gamma_{HS} = 0.5$) varied by up to 10 K for samples from different preparations, we have reinvestigated the spincrossover behavior of the enriched sample. The spin transition curves, derived from the magnetic and Mössbauer measurements are shown in Figure 1.

The transition is accompanied by a hysteresis of 10 K and is almost complete within 175-161 and 175–185 K, respectively. The transition temperatures $T_{1/2}$ are for decreasing temperature $T_{1/2}\downarrow = 170$ K and for increasing temperature $T_{1/2}\uparrow = 180$ K. The measurements show good agreement between the data from magnetic measurements and Mössbauer spectroscopy (cf. Figure 1); there is no indication of different Debye–Waller factors for HS and LS states in this complex. Therefore, we have taken the Debye–Waller factors to be equal for the two spin states.

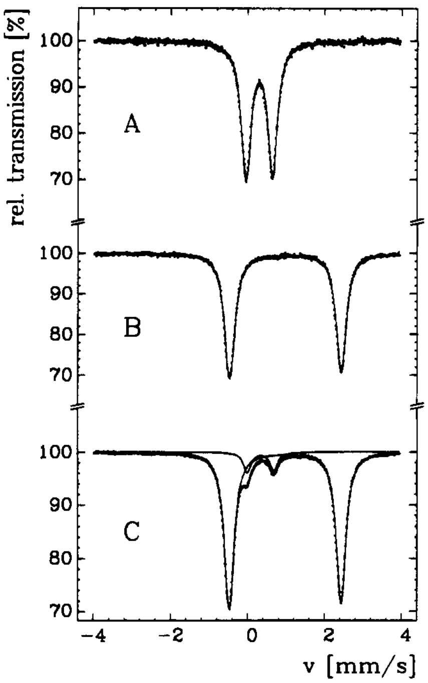

Figure 2. ^{57}Fe Mössbauer spectra recorded at 30 K before (A) and after (B) irradiation of a polycrystalline sample of $[Fe(bpp)_2](BF_4)_2$ with green light. Irradiation of the sample of spectrum B with red light causes partial back-conversion to the stable LS state (spectrum C).

3.2. LIESST Experiments. The results of irradiation experiments at a temperature of 30 K are shown in Figure 2. It is obvious that the compound shows both LIESST and reverse LIESST effects. The $^1A_1$ (LS) state is converted quantitatively to the $^5T_2$ (HS) state by irradiation with green light (parts A and B of Figure 2). Partial back conversion from the $^5T_2$ to the $^1A_1$ state is observed upon irradiation with red light (Figure 2C). The incomplete $^5T_2$ (HS) → $^1A_1$ (LS) conversion has been suggested to be due to the broad band excitation, which is discussed in detail in ref 15.

It was found that the metastable $^5T_2$ (HS) state generated by LIESST in $[Fe(bpp)_2](BF_4)_2$ has a lifetime on the order of several days at 30 K. Thermal decay of the metastable HS states sets in by subsequent heating of the sample. We have observed that a small fraction (ca. 5%) of the metastable HS state relaxes rapidly (within minutes) between 60 and 70 K, but no further decay was observed in this temperature region even after 2 days. Complete HS → LS relaxation occurs between 90 and 100 K within hours (see Figure 3A). Each data point of Figure 3A representing the molar fraction of the HS state was extracted from a Mössbauer spectrum (normalized area fraction of the quadrupole doublet of the HS state) recorded for 10 min. As can be seen from Figure 3A, the relaxation curves show strong deviations from single exponential decay, which establishes that the thermal decay of the LIESST state does not follow first-order kinetics.

LIESST experiments yielding long-lived HS states are possible even at 80 K. However, one finds significant differences as compared to LIESST experiments carried out at lower temperatures (e.g. 30 K). The Mössbauer spectra depicted in Figure 5 clearly demonstrate that the maximum percentage of HS molecules formed by irradiation of the sample depends on the intensity of the laser light.

3.3. Thermal Trapping of the HS State. In the spin crossover system under study the $^5T_2$ (HS) state can be thermally

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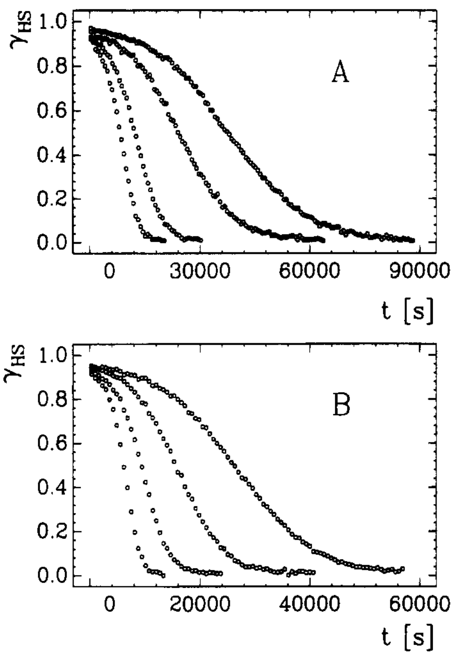

Figure 3. HS–LS relaxation curves after LIESST (A) and rapid cooling (B) of the sample at 92.5, 95, 97.5, and 100 K. Each data point represents the HS fraction derived from a single Mössbauer spectrum. Obviously the curves show strong deviations from first-order kinetics.

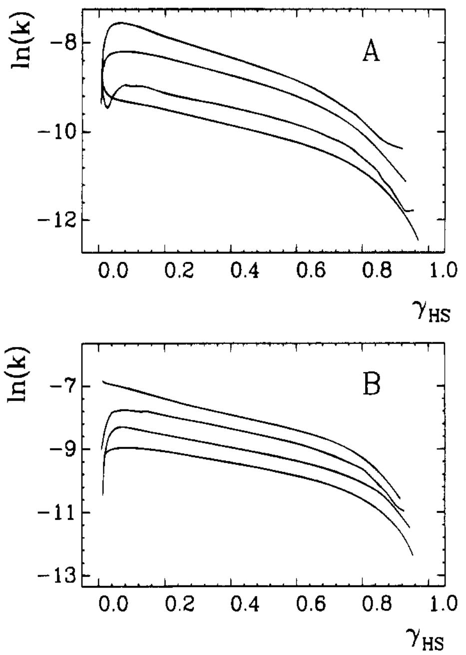

Figure 4. γ_{HS} dependence of the relaxation rates after LIESST (A) and rapid cooling (B) at 92.5, 95, 97.5, and 100 K. For γ_{HS} values greater than 0.7 a significant slowing down of the relaxation process is observed.

trapped by rapid cooling of the sample to 78 K. The fraction of the metastable HS state derived from the area fraction of the quadrupole doublet of the Mössbauer spectra was in all runs more than 90%. Noticeable thermal relaxation of the metastable HS state began at ≥90 K. For a quantitative examination of the relaxation kinetics, Mössbauer spectra were recorded every 10 min at 92.5, 95, 97.5, and 100 K. The relaxation curves are plotted in Figure 3B, again with each data point representing the HS fraction derived from a single ^{57}Fe Mössbauer spectrum as a function of time. The curves deviate strongly from first-order kinetics. This contrasts with earlier results reported by Goodwin et al.,[10] who have found first-order kinetics after rapid cooling of the sample. The reason is that these authors, in their experiments, reached only ca. 50–60% of the trapped HS state after rapid cooling. Therefore, the sigmoidal behavior of the relaxation curves could no longer be followed in the logarithmic plot ln γ_{HS} vs time.

4. Discussion

The dynamics of the HS–LS relaxation have been studied by Hauser in various iron(II) compounds of different ligand field strengths.[4] He also studied the kinetics of metal-diluted systems, for which the relaxation rates showed strong deviations from Arrhenius kinetics with nearly temperature independent tunneling below ~70 K and a thermally activated behavior above ca. 100 K. Moreover, for temperatures above 140 K, fast rates on the order of 10^2–10^8 s^{-1} were predicted, which could be confirmed on metal-diluted spin crossover compounds. In concentrated materials changes of the rate constants are expected, but they are estimated not to exceed by more than 1 order of magnitude those obtained for diluted samples.

In view of this it is remarkable that the HS state can be trapped thermally in [Fe(bpp)$_2$](BF$_4$)$_2$ by rapid cooling from room temperature down to 80 K. We consider this observation indicative of the occurrence of a crystallographic phase transition in accordance with the suggestion of Goodwin et al.[10] based on the hysteresis seen in the $\mu_{eff}(T)$ curve. As the rate of the spin transition k_{HL} is very fast at temperatures above 140 K, it seems to be clear that the formation of the meatastable HS states by rapid cooling is caused by freezing in the high temperature crystal structure. The structural relaxation is reflected by the spin state conversion from HS to LS and takes place on a time scale of days to hours between 90 and 100 K. Thus, the HS → LS relaxation is determined by the rate k_{ph} of the structural phase change.

We have attempted to describe quantitatively the relaxation of parts A and B of Figure 3 employing a model, which was proposed by Hauser[11] for the radiationless HS → LS relaxation after LIESST in [Fe$_x$Zn$_{1-x}$(ptz)$_6$](BF$_4$)$_2$. He also observed strong deviations from first-order kinetics in concentrated crystals, whereas in highly metal-diluted mixed crystals the HS → LS relaxation showed first-order kinetics. In that case, Hauser[11] was able to explain quite well that the sigmoidal shape of the relaxation curves originates from cooperative interactions between the spin state changing complex molecules.[16–18] Hauser was able to reproduce the HS → LS relaxation curves in [Fe$_x$Zn$_{1-x}$(ptz)$_6$[(BF$_4$)$_2$ by assuming the activation energy to be a linear function of the HS fraction; then plots of ln k versus γ_{HS} yielded straight lines. Applying Hauser's model to the system under study gave straight lines only for γ_{HS} values lower than ca. 0.7; for γ_{HS} values greater than 0.7 the relaxation process slows down significantly (cf. Figure 4) The different γ_{HS} dependence of the relaxation rate in the present case as compared to Hausers's LIESST relaxation studies in [Fe$_x$Zn$_{1-x}$(ptz)$_6$](BF$_4$)$_2$ is not surprising. It was found that the high temperature structure in [Fe(ptz)$_6$](BF$_4$)$_2$ can be preserved by rapidly cooling the crystal, but depite this, the spin transition proceeds to completion in this instance. Thus the HS → LS relaxation in Hauser's case is determined by k_{HL} and not influenced by additional phase changes.

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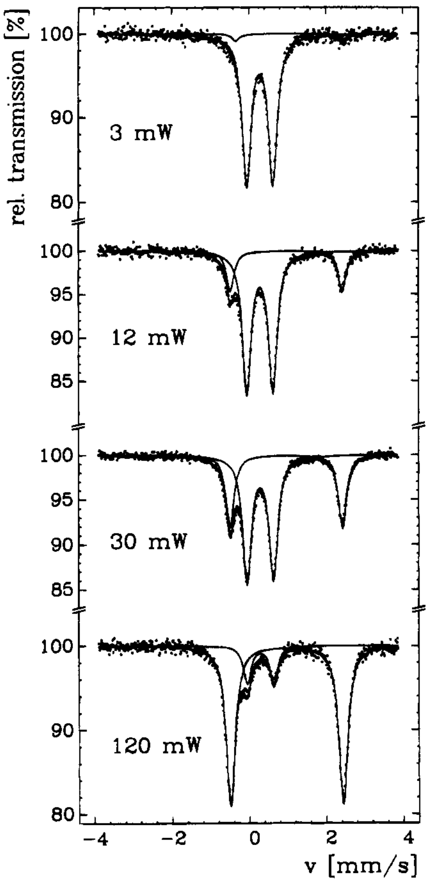

Figure 5. ^{57}Fe Mössbauer spectra recorded after irradiation of the sample at 80 K with different laser light intensities, where in each case the irradiation was carried out until no further changes in the HS/LS ratio were observed. The spectra clearly demonstrate that the saturation HS/LS ratio depends on the intensity of the laser light.

For a quantitative description of the HS → LS relaxation of the thermally trapped metastable HS state in [Fe(bpp)$_2$](BF$_4$)$_2$ one must find an expression for the rate of the structural phase transition. Tentatively we have applied different phenomenological expressions for phase transitions given in the literature, but without success; the observed relaxation behavior could not be reproduced satisfactorily. The reason may be that parameters which govern the kinetics of a phase transition such as nucleation rate and phase propagation appear to be complicated functions of γ_{HS}.

The relaxation of the metastable LIESST state occurs in two steps. When the sample is heated, a small fraction (5%) relaxes to the $^1A_1$ (LS) ground state within minutes between 60 and 70 K; no further change was observed within 2 days. We believe that this minor change of the HS/LS ratio initiates a phase transformation, and apparently the new phase stabilizes the HS state. Only after heating up to ca. 90 K does further relaxation (second step) set in, yielding the curves shown in Figure 3A. A comparison between parts A and B of Figure 3 shows that the relaxation behavior is essentially the same for the thermally and light-induced trapped HS states. This again is evidence for the suggestion that the observed HS → LS back conversion actually reflects the structural phase transformation, regardles of how the metastable state was generated. Further support comes from the very similar behavior in the ln k vs γ_{HS} plots (Figure 4) and, in addition, from the virtually identical values for the Mössbauer parameters for the metastable quintet states produced by the two different methods (δ = 0.978 mm/s, ΔE_Q = 2.903 mm/s at 90 K).

It is remarkable that for the present complex the LIESST effect is possible at temperatures near 80 K. Our experience from LIESST studies tells us that the lifetime of the LIESST state is on the order of seconds at most near 70 K. The observed dependence of the saturation concentration of the HS state (at 80 K) on the intensity of the laser light is also unusual. This can be understood in view of a structural phase transformation, because as soon as a minimum fraction of HS is generated by LIESST, a new phase will be induced, which stabilizes the HS state. This new structure phase also decays within days to hours between 90 and 100 K as reflected by the observed HS → LS conversion similar to the relaxation studies after LIESST at 30 K.

5. Conclusion

The thermal spin transition in [Fe(bpp)$_2$](BF$_4$)$_2$ is accompanied by a structural phase transition. The rate of this phase transition is comparatively slow; it allows the HS ($^5T_2$) state of iron(II) to be trapped by rapidly cooling the crystal and also determines the HS → LS relaxation kinetics. The same behavior is seen after light-induced formation of the HS state at low temperatures (after slow cooling of the crystal and complete conversion thermally to the LS state). It therefore appears that the relaxation kinetics for the LIESST generated state are governed by the structural phase change. It is apparently the structural phase change which enables LIESST experiments to be performed for this system at temperatures above ~80 K. This is the first time the LIESST effect has been observed at such a realtively high temperature.

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