Intersystem crossing in the [Fe(ptz)$_6$](BF$_4$)$_2$ spin crossover system (ptz = 1-propyltetrazole)

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[Fe(ptz)$_6$](BF$_4$)$_2$ (ptz = 1-propyltetrazole) is an Fe(II) spin crossover system, which shows a light-induced low-spin ($^1$A$_1$) $\rightarrow$ high-spin ($^5$T$_2$) conversion below $\sim 50$ K by irradiating into the spin allowed $^1$A$_1$ $\rightarrow$ $^5$T$_1$ d-d absorption band. This phenomenon, known as light-induced excited spin state trapping (LIESST), is reversible, and a subsequent irradiation into the $^3$T$_2$ $\rightarrow$ $^5$E band results in a light-induced $^5$T$_2$ $\rightarrow$ $^1$A$_1$ conversion (reverse LIESST). Single crystal absorption spectra of the title compound in the region of d-d transitions are reported. In addition to the well-established spin allowed $^1$A$_1$ $\rightarrow$ $^1$T$_1$ and $^1$A$_1$ $\rightarrow$ $^3$T$_2$ transitions of the low-spin species and the $^3$T$_2$ $\rightarrow$ $^3$E transition of the high-spin species two weak bands in the NIR are assigned to the spin forbidden $^1$A$_1$ $\rightarrow$ $^3$T$_1$ and $^1$A$_1$ $\rightarrow$ $^3$T$_2$ transitions. Direct irradiation into the $^1$A$_1$ $\rightarrow$ $^3$T$_1$ absorption band at 20 K results in a quantitative $^1$A$_1$ $\rightarrow$ $^5$T$_2$ conversion, proving that this low lying triplet state plays an important role in the mechanism of LIESST. A full kinetic scheme for LIESST and reverse-LIESST with the $^3$T$_1$ state as intermediate state is developed, and the quantum efficiencies for the various intersystem crossing steps involved are given: they are of the order of unity for the first step from the initially excited $^1$T$_1$ and $^3$E states to the intermediate $^3$T$_1$ state, respectively. The branching ratio from the $^3$T$_1$ state to the $^1$A$_1$ and the $^3$T$_2$ states is 1:4.

I. INTRODUCTION

Thermal spin crossover is a well-known phenomenon in coordination compounds of first row transition elements. The spin transition from low-spin (LS) at low temperatures to high-spin (HS) at some elevated temperature has been most widely studied for Fe(II) compounds, using a variety of experimental techniques.$^{1,2}$

Some years ago Decurtins et al.$^{3,4}$ showed that in a number of Fe(II) coordination compounds, exhibiting a thermal spin transition, a quantitative light-induced LS ($^1$A$_1$) $\rightarrow$ HS ($^5$T$_2$) conversion could be observed below $\sim 50$ K, i.e., at temperatures well below the thermal transition temperature, by irradiating the sample in the visible either into a spin allowed d-d or a MLCT absorption band. Prior to the discovery of Decurtins et al., McGarvey and Lawthers$^5$ found a rapid depopulation of the LS state upon pulsed laser excitation of some Fe(II) spin crossover complexes in solution at ambient temperatures. In their case the relaxation rates from the light-induced metastable state back to the $^1$A$_1$ ground state were of the order of 10$^7$ s$^{-1}$. In the case of Decurtins et al., i.e., in the solid state and at low temperatures, the relaxation rates were less than 10$^{-3}$ s$^{-1}$, and the light-induced state could unambiguously be identified as the $^3$T$_2$ state.

Figure 1 shows the potential energy surfaces of the low-lying ligand field (LF) states for a d$^5$ ion$^6$ such as Fe(II) with a LF strength appropriate for a spin crossover system. A mechanism for the light-induced $^1$A$_1$ $\rightarrow$ $^3$T$_2$ conversion, subsequently called “Light-Induced Excited Spin State Trapping (LIESST),” was proposed by Decurtins et al.$^4$ involving a first intersystem crossing (isc) step with $\Delta S = 1$ from either the initially excited $^1$T$_1$ LS state as in the title compound [Fe(ptz)$_6$](BF$_4$)$_2$ (ptz = 1-propyltetrazole) or the MLCT as in [Fe(pic)$_3$]Cl$_2$·EtOH (pic = 2-picolylamine) to the low-lying $^3$T$_1$ LF state. In a second isc step with $\Delta S = 1$ the system can drop into the $^3$T$_2$ state, where at sufficiently low temperatures it remains trapped. The large difference of 0.15–0.2 Å in metal–ligand bondlength between the two states$^7$ effectively separates the two oscillator potentials.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Potential wells of the $^1$A$_1$ ground state and the thermally accessible $^3$T$_2$ state as well as the higher excited ligand field states for a d$^5$ spin crossover system. Arrows indicate the mechanism of LIESST and reverse-LIESST.}
\end{figure}
Since the discovery of LIESST in \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) long-lived metastable \(5^T_2\) states have been found for an increasing number of Fe(II) spin crossover systems, not only for neat compounds,\textsuperscript{4-10} but also for dilute mixed crystals, notably for \([\text{Zn} \rightarrow \text{Fe} (\text{ptz})_6] (\text{BF}_4)_2\) (\(x \approx 0.1\)),\textsuperscript{11} and for spin crossover complexes embedded in polymer matrices.\textsuperscript{12} LIESST is therefore quite a common phenomenon in spin crossover compounds and, more importantly, it is basically a property of a single complex.

In \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) the trapped \(5^T_2\) state relaxes thermally back to the \(1^A_1\) ground state at temperatures above \(\sim 50\, \text{K}\), but the system can also be optically pumped back to the \(1^A_1\) state by irradiating into the spin allowed \(5^T_2 \rightarrow 5^E\) absorption in the NIR,\textsuperscript{11} i.e., LIESST is reversible. This fits in nicely with the isc mechanism involving the low-lying \(3^T_1\) state as an intermediate state. However, it is not a proof of the mechanism proposed by Decurtins \textit{et al.}\textsuperscript{4}

In this paper the \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) system and its single crystal absorption spectra in the region of \(d-d\) transitions are revisited, and a ligand field analysis of the observed spin allowed and spin forbidden transitions is presented. Irradiation experiments with wavelengths across the visible and into the NIR help to establish a full kinetic scheme for LIESST and reverse-LIESST, and the quantum efficiencies for the various isc steps are given.

II. EXPERIMENT

\([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) (ptz = 1-propyltetrazole) was prepared according to a procedure previously described.\textsuperscript{13} Single crystals in the form of colorless hexagonal plates up to several millimeters in diameter and up to 1 mm thick were grown from nitromethane by slow evaporation in a dry nitrogen flow at 293 K. The space group at 293 is \(R \bar{3}\),\textsuperscript{14} but the trigonal distortion from octahedral symmetry of the individual complex is very small. The calculated density \(\rho\) at 293 K is 1.31 g/cm\(^3\) (Ref. 15) and the concentration \(c_0\) of complexes is 1.45 \(\text{mol/cm}^3\). The thickness \(d\) of the crystal used in the experiment was determined with sliding calipers to be 595 \(\mu\text{m}\).

Single crystals absorption spectra were recorded with a UV/VIS/NIR spectrophotometer (Omega-10, Bruins Instruments). Sample temperatures down to 10 K were achieved with the cold helium gas flow-tube technique.

Irradiation experiments were performed with an AR + laser (Spectra Physics 2020, \(\lambda = 514.5\, \text{nm}\)), a Kr + laser (Spectra Physics 164, \(\lambda = 646.5, 676.6, 752.5\, \text{nm}\)), and a Ti–Sapphire laser (Spectra Physics 3900, tunable from 680 to 980 nm). Laser powers used were of the order of a few tens of mW with irradiation times of a few minutes.

III. RESULTS AND DISCUSSION

A. Spin allowed \(d-d\) transitions in \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\)

The thermal spin transition in \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) has been discussed in detail before.\textsuperscript{4,13} It manifests itself with a dramatic change in color from colorless at 293 K to deep purple at low temperature. The spin transition is accompanied by a crystallographic phase transition with a hysteresis of 7 K (\(T^*_2 = 128\, \text{K}, T^*_1 = 135\, \text{K}\)).

According to the Tanabe–Sugano diagram for an ion with a \(d^6\) electronic configuration in an octahedral LF,\textsuperscript{6} one expects quite different absorption spectra for HS and LS species.

In Figs. 2(a) and 2(b) the well-known unpolarized single crystal absorption spectra with the light propagating along the crystal c axis at 293 K and 20 K are shown. At 293 K there is just the one band in the NIR, corresponding to the spin allowed \(5^T_2 \rightarrow 5^E\) transition of the HS species. The maximum is \(\lambda = 11\, 760\, \text{cm}^{-1}\) (\(\lambda = 850\, \text{nm}, e_{\text{BS}}^{\text{HS}} = 0.42\, \text{l/mol/cm}, \text{OD: optical density}\)). At 20 K the NIR band has gone, instead there are two new absorption bands in the visible: one with its maximum at 18, 210 cm\(^{-1}\) (\(\lambda = 549\, \text{nm}, e_{\text{BS}}^{\text{LS}} = 27.5\, \text{l/mol/cm}\) the other one at 26, 400 cm\(^{-1}\) (\(\lambda = 379\, \text{nm}, e_{\text{BS}}^{\text{LS}} = 42.5\, \text{l/mol/cm}\)), to which we assign the spin allowed \(1^A_1 \rightarrow 1^T_1\) and \(1^A_1 \rightarrow 1^T_2\) transition, respectively. The experimental data are collected in Table I.

The extinction coefficients differ somewhat from those reported by Decurtins \textit{et al.},\textsuperscript{4} the reason being that the experimental density reported by Franke \textit{et al.}\textsuperscript{13} and used by Decurtins \textit{et al.} is wrong. They also differ from those given by Ref. 11, but Ref. 11 (myself that is) got them totally wrong not only because the same density as Decurtins \textit{et al.} was used, but also because of an error of a factor of 2 in determining the crystal thickness.

B. Spin forbidden \(d-d\) transitions in \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\)

According to the Tanabe–Sugano diagram for a \(d^6\) system\textsuperscript{6} there are a large number of excited triplet states in addition to the quintet and singlet states. Since the electronic configurations of the triplet states differ from the \(t^2\) configuration of the \(1^A_1\) ground state, spin forbidden singlet \(\rightarrow\) triplet transitions will be both weak and broad and therefore very difficult to detect.

Figure 3(a) shows a blow up of the low energy part of the absorption spectrum of the LS species at 20 K. And indeed two very weak and broad bands can just be made out: one at 10, 280 cm\(^{-1}\) (\(\lambda = 980\, \text{nm}, e_{\text{BS}}^{\text{LS}} = 0.21\, \text{l/mol/cm}\) and the other one at 14, 300 cm\(^{-1}\) (\(\lambda = 670\, \text{nm}, e_{\text{BS}}^{\text{LS}} \approx 0.4\, \text{l/mol/cm}\)) on the rising slope of the \(1^A_1 \rightarrow 1^T_1\) band, to which we can tentatively assign the spin forbidden transitions \(1^A_1 \rightarrow 3^T_1\) and \(1^A_1 \rightarrow 3^T_2\). That these weak bands are intrinsic to \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) and are not an artifact of the spectrometer is borne out by the comparison with the spectrum of the isomorphous \([\text{Zn(ptz)}_6] (\text{BF}_4)_2\). In this spectrum the comparatively sharp lines corresponding to vibrational overtones of the ligand vibrations are identical to those in the \([\text{Fe(ptz)}_6] (\text{BF}_4)_2\) system, but the two broad bands are missing.

Despite the fact, that there are triplet states originating from the same configuration as the \(3^T_2\) state, no absorption bands corresponding to quintet \(\rightarrow\) triplet transitions could be observed.

C. Ligand field analysis

The LF strength for the HS species at 293 K can be taken directly from the absorption spectrum:
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![Graph showing absorption spectra](image)

**FIG. 2.** Single crystal absorption spectra of $[\text{Fe(ptz)}_6](\text{BF}_4)_2$: (a) at 293 K, (b) at 20 K, (c) after irradiation at 514.5 nm (20 K), (d) after irradiation at 820 nm (20 K), for comparison the normal 20 K spectrum is included (---), (e) after irradiation at 980 nm (20 K).

**TABLE I.** Positions ($\lambda_{\text{max}}, \bar{\nu}_{\text{max}}$), extinction coefficients ($\varepsilon$) and half-widths ($\Delta \bar{\nu}_{1/2}$) of the $d$-$d$ absorption bands of $[\text{Fe(ptz)}_6](\text{BF}_4)_2$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$T$ [K]</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\bar{\nu}$ [cm$^{-1}$]</th>
<th>$\Delta \bar{\nu}_{1/2}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1 \rightarrow ^1T_2$</td>
<td>20</td>
<td>549</td>
<td>18 200</td>
<td>2 780</td>
</tr>
<tr>
<td>$^3T_1$</td>
<td>20</td>
<td>379</td>
<td>26 400</td>
<td>3 500</td>
</tr>
<tr>
<td>$^3T_2$</td>
<td>20</td>
<td>980</td>
<td>10 280</td>
<td>3 510</td>
</tr>
<tr>
<td>$^3T_2 \rightarrow ^3E$</td>
<td>20</td>
<td>850</td>
<td>11 760</td>
<td>3 890</td>
</tr>
</tbody>
</table>

10$Dq^{HS} = E(^3E) - E(^3T_2) = 11 760$ cm$^{-1}$. In a first approximation the LF strength for the LS state can be estimated using the expression $10Dq^{LS} = E(^1T_1) - E(^1A_1) + (E(^1T_2) - E(^1T_1))/4$, and we get $10Dq^{LS} \approx 20 200$ cm$^{-1}$. $10Dq$ changes dramatically on going from HS to LS. For a neutral ligand, such as our ptz, $10Dq$ is expected to vary as $\sim 1/r^6$, where $r$ is the metal–ligand distance. Therefore the proportionality $10Dq^{LS}/10Dq^{HS} = (r_{HS}/r_{LS})^6$ should hold, with $r_{HS}$ and $r_{LS}$ being the Fe–N bondlengths in the HS and the LS state, respectively. We know $r_{HS}$ at 293 K for $[\text{Fe(ptz)}_6](\text{BF}_4)_2$ to be 2.176 Å. There are as yet no...
low temperature data for $r_{LS}$ in [Fe(ptz)$_6$](BF$_4$)$_2$ available, but a typical value for it would be in the range 1.96–2.00 Å.\(^3\)

\[
\begin{align*}
\Delta r_{HL} &= r_{HS} - r_{LS} \approx 0.18 \text{ Å} \\
\frac{10Dq^{LS}}{10Dq^{HS}} &= 1.72, \left(\frac{r_{HS}}{r_{LS}}\right)^6 = 1.74.
\end{align*}
\]

We should not overrate this apparently perfect agreement. It gives us confidence, however, that ligand field theory can be used in a first step for describing the absorption spectra, and therefore the electronic structure, of [Fe(ptz)$_6$](BF$_4$)$_2$.

Using the strong field matrices of Tanabe and Sugano,\(^6\) the term energies can be calculated. In a first calculation the electronic repulsion parameters $B$ and $C$ for the complex are set to be equal to those of the free ion $B_0$ and $C_0$ reduced by some reduction factor $\beta$. With $B_0 = 917$ cm$^{-1}$ and $C_0 = 4040$ cm$^{-1}$, a best fit to the experimental energies is obtained with $\beta = 0.82$ and $10Dq = 19 410$ cm$^{-1}$. The overall agreement between experimental and calculated energies is fair (see Table II). But as Ferguson pointed out,\(^18\) there is no reason for $B$ and $C$ to be reduced by the same amount, since they are linear combinations of radial integrals containing different powers of $r$. Thus a better fit to the experimental energies can be obtained with $B = 638$ cm$^{-1}$, $C = 3742$ cm$^{-1}$, and $10Dq = 20 550$ cm$^{-1}$.

D. LIEST and reverse-LIEST in [Fe(ptz)$_6$](BF$_4$)$_2$

Irradiating the crystal at 20 K with the 514.5 nm line of an Ar$^+$ laser, i.e., into the $^1A_1 \rightarrow T_1$ band, quickly led to a complete $^1A_1 \rightarrow ^5T_2$ conversion (LIEST). The absorption spectrum after the irradiation, with the typical $^5T_2 \rightarrow ^5E$ band in the NIR is shown in Fig. 2(c). The band maximum is now at 12 200 cm$^{-1}$ ($\lambda = 820$ nm, $e_{LS}^{10Dq} = 4.8$ l/mol cm), slightly blue shifted from the 293 K value, as is to be expected for a $d$-$d$ transition. Correspondingly $10Dq^{HS} = 12 200$ cm$^{-1}$ at 20 K. At this temperature the light-induced HS state is metastable with a practically infinite lifetime. Only at temperatures above $\sim 50$ K does a noticeable HS $\rightarrow$ LS relaxation set in.\(^4,21\)

Figure 2(d) shows the absorption spectrum after a subsequent irradiation using the Ti Sapphire laser at 820 nm, i.e., into the $^5T_2 \rightarrow ^5E$ band, the temperature being kept at 20 K all through the cycle. We again observe the typical LS absorption spectrum. However, the light-induced $^5T_2 \rightarrow ^1A_1$ conversion (reverse-LIEST) is not quite complete. After repeatedly irradiating at 820 nm a “saturation” value for the LS fraction of $\gamma_{LS} = 0.9$ 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. And indeed the $^1A_1 \rightarrow ^5T_2$ and $^1A_1 \rightarrow ^3T_2$ bands overlap with the $^5T_2 \rightarrow ^5E$ band [see Figs. 3(a) and 3(b)]. Although the minimum between the two broad spin forbidden bands is at $\sim 820$ nm, the absorption at that wavelength is not zero.

We notice that the maximum of the $^1A_1 \rightarrow ^3T_1$ band at 10 280 cm$^{-1}$ (977 nm) is just to the low energy side of the $^5T_2 \rightarrow ^5E$ band. Starting again from a LS fraction $\gamma_{LS} = 1$ [Fig. 2(b)] at 20 K, irradiating the crystal at 980 nm using the Ti Sapphire laser again results in a complete light-in-
duced $^1A_1 \rightarrow ^3T_2$ conversion [Fig. 2(e)]. That means, a direct excitation of the $^1A_1 \rightarrow ^3T_1$ transition results in LIEST as well. This experiment proves two things: The two weak bands are not due to impurities and therefore the assignment as spin forbidden bands is justified and, more importantly, it shows that the mechanism for LIEST with the $^3T_1$ state as intermediate state is correct.

In view of this the “saturation” value of $\gamma_{LS} = 0.9$ reached after long irradiation at 820 nm had better be called steady state value, since for this value of $\gamma_{LS}$ the rates for LIEST and reverse-LIEST are equal to each other and not zero. Naturally this steady state value depends upon the quantum efficiencies of the various isc steps involved and upon the relative extinction coefficients of the LS state and the HS and the LS absorption. The steady state value of $\gamma_{LS}$ therefore depends upon irradiation wavelength. Figure 4 shows the absorption spectra obtained after irradiation at different wavelengths across the region of spectral overlap of the $^5T_2 \rightarrow ^5E$ and $^1A_1 \rightarrow ^3T_1, ^3T_2$ transitions. In Fig. 3(c) the steady state LS fraction $\gamma_{LS}$ as a function of irradiation wavelength extracted from these spectra is shown. As is to be expected from the mechanism for LIEST for wavelengths outside the $^5T_2 \rightarrow ^5E$ band, i.e., $\lambda = 980$ nm (10 200 cm$^{-1}$) and $\lambda = 680$ nm (14 700 cm$^{-1}$), $\gamma_{LS}$ after irradiation is zero. Irradiation at the maximum of the $^5T_2 \rightarrow ^5E$ band, i.e., $\lambda = 820$ nm (12 200 cm$^{-1}$), results in a maximum steady state value for $\gamma_{LS}$ of 0.9.

LIEST and reverse-LIEST can be followed quantitatively. Figure 5(a) shows the depletion of the LS state as a function of the irradiated energy $E$ at 514.5 nm (LIEST) at 20 K, Fig. 5(b) the subsequent buildup of the LS state as a function of irradiated energy $E$ at 752.5 nm (reverse-LIEST) as reported by Hauser (for more experimental details see Ref. 11). For thin crystals with OD$_4$, at the irradiation wavelength $\ll 1$, depletion and buildup are expected to be exponential:

$$\gamma_{LS}(E) = \gamma_{LS}(E=0) \cdot e^{-k_{aEff}E}$$

for LIEST at 514.5 nm

$$\gamma_{LS}(E) = \gamma_{LS}(E \rightarrow \infty) \cdot \left(1 - e^{-k_{bEff}E}\right)$$

for reverse-LIEST at 752.5 nm.

Exponential fits with a least-squares routine give $k_{aEff} = 1.40(4) \times 10^{-8}$ cm$^2$/erg and $\gamma_{LS}(E=0) = 1$ for LIEST, and $k_{bEff} = 1.04(5) \times 10^{-9}$ cm$^2$/erg and $\gamma_{LS}(E \rightarrow \infty) = 0.85(3)$ for reverse-LIEST.

With this wealth of information we are now in a position to develop a full scheme for LIEST and reverse-LIEST and to determine the quantum efficiencies of the various isc steps involved.

IV. A KINETIC MODEL FOR LIEST AND REVERSE-LIEST

In the Jablonski diagram for a $d^6$ system (Fig. 6) the relevant intersystem crossing (isc) and internal conversion (ic) steps in the mechanism of LIEST are shown. Since to this date no luminescence from any Fe(II) spin crossover compound has been observed, we only have to consider radiationless processes. The radiationless relaxation from the higher excited states $^1T_1, ^5E$, and $^3T_2$ to either the $^1A_1$ or the $^3T_2$ state is on the subnanosecond timescale. At 20 K the $^5T_2 \rightarrow ^1A_1$ relaxation on the other hand is negligible.

For the irradiation at 514.5 nm the only excitation is...
from the $^1A_1$ to the $^1T_1$ state, i.e., the excitation rate constants $k_2$ and $k_3$ are zero. The following set of differential equations for the concentrations of the states involved hold:

$$
\frac{d[^1A_1]}{dt} = -k_1[^1A_1] + k_{-1}[^1T_1] + k_2[^3T_1],
$$

$$
\frac{d[^1T_1]}{dt} = k_1[^1A_1] - (k_{-1} + k_c)[^1T_1],
$$

$$
\frac{d[^3T_1]}{dt} = k_c[^1T_1] - (k_a + k_b)[^3T_1],
$$

$$
\frac{d[^3T_2]}{dt} = k_b[^3T_1].
$$

(3)

Since we are working with the comparatively low laser powers of cw lasers the excitation rate constant $k_1$ is much smaller than the sum of ic and isc rate constants ($k_{-1} + k_c$), and the differential equation for $[^1A_1]$ takes the simple form:

$$
\frac{dY_{LS}}{dt} = -k_1\eta_a\eta_bY_{LS}
$$

(4)

with the LS fraction $\gamma_{LS} = [^1A_1]/c_0$ and the quantum efficiencies $\eta$ for the two isoelectronic steps $\eta_a = k_c/(k_{-1} + k_c)$ and $\eta_b = k_b/(k_a + k_b)$.

$$
\gamma_{LS}(t) = \gamma_{LS}(0) \cdot e^{-k_1\eta_a\eta_b t},
$$

$$
\gamma_{HS}(t) = 1 - \gamma_{LS}(t).
$$

(5)

For irradiation at 752.5 nm we get simultaneous excitation from the $^3T_2$ to the $^3E$ state and from the $^1A_1$ to the $^3T_1$ state, but $k_1$ is now equal to zero, and the following set of differential equations results:

$$
\frac{d[^3T_1]}{dt} = k_d[^3E] + k_3[^1A_1] - (k_a + k_b)[^3T_1],
$$

$$
\frac{d[^3T_2]}{dt} = -k_1[^1A_1] + k_3[^3T_1].
$$

(6)

With $k_d \ll (k_{-3} + k_d)$ and $k_3 \ll (k_a + k_b)$ these equations simplify to:

$$
\frac{d\gamma_{LS}}{dt} = - (k_3\eta_b + k_b\eta_a)\gamma_{LS} + k_b\eta_a,
$$

(7)

where $\eta_a = k_a/(k_a + k_b) = 1 - \eta_b$.

$$
\gamma_{LS}(t) = \gamma_{LS}(\infty) \cdot e^{-(k_3\eta_b + k_b\eta_a)t},
$$

(8)

with $\gamma_{LS}(\infty) = \frac{k_3\eta_b\eta_a}{k_3\eta_b + k_b\eta_a}$,

(9a)

and $\gamma_{HS}(\infty) = \frac{k_3\eta_b\eta_a}{k_3\eta_b}.

(9b)

The excitation rate constants $k_1, k_2, k_3$ are functions of the absorption cross-section $\sigma_\lambda$ at the excitation wavelength $\lambda$ of the corresponding absorption process and the photon flux $\Phi_\lambda$.

$$
\sigma_\lambda = \ln(10) \cdot \frac{1000}{N_A} \cdot \epsilon_\lambda = 3.81 \times 10^{-21} \cdot \epsilon_\lambda.
$$

(11)

The photon flux is given by

$$
\Phi_\lambda = I_\lambda/(hv) = \frac{\lambda}{hc} I_\lambda,
$$

(12)

where $N_A$ is Avogadro’s number, $c$ the speed of light, $h$ Planck’s constant, and $I_\lambda$ the irradiation intensity:

$$
k_1 = \tilde{k}_1 \cdot I_\lambda, \quad \text{with} \quad \tilde{k}_1 = 3.81 \times 10^{-21} \cdot \frac{\lambda}{hc} \cdot \epsilon_\lambda.
$$

(13)

Inserting Eq. (13) into Eq. (8) and setting $I_\lambda \cdot t = \varepsilon_\lambda$ and $\varepsilon_\lambda = \Phi_\lambda$ for the irradiated energy, we get

$$
\gamma_{LS}(\varepsilon_\lambda) = \gamma_{LS}(0) \cdot e^{-k_1\eta_a\eta_b\varepsilon_\lambda},
$$

(14a)

and

$$
\gamma_{LS}(\varepsilon_\lambda) = \gamma_{LS}(\infty) \cdot \left\{e^{-k_1\eta_a\eta_b\varepsilon_\lambda} - \gamma_{LS}(0)\right\},
$$

(14b)

Comparing Eqs. (14a) and (14b) with Eqs. (2a) and (2b) it follows that:

$$
k_{d\varepsilon} = 1.40(5) \times 10^{-8} \text{ cm}^2/\text{erg} = \tilde{k}_1\eta_a\eta_b,
$$

(15a)

$$
k_{b\varepsilon} = 1.04(4) \times 10^{-6} \text{ cm}^2/\text{erg} = \tilde{k}_1\eta_b + \tilde{k}_2\eta_a.
$$

(15b)

Furthermore from Fig. 3(c) the steady state ratio at 752.5 nm can be derived, and inserting Eq. (13) into Eq. (9a) we get
The quantum efficiencies for the first isc step either from the \( ^1T_1 \) or the \( ^3E \) state to the intermediate \( ^3T_1 \) state are close to unity. The branching ratio from the \( ^3T_1 \) state to the \( ^1A_1 \) ground state and \( ^3T_2 \) state is \( \sim 1:4 \). The actual rate constants for the various isc processes except for the \( ^3T_2 \rightarrow ^1A_1 \) relaxation are \( \geq 10^{10} \text{s}^{-1} \). In their pulsed laser experiments neither McGarvey and Lawthers,\(^5\) nor Creutz \textit{et al.},\(^10\) nor Xie and Hendrickson\(^20\) found any evidence for a transient population of an intermediate state on the nanosecond timescale.

The question now is: do the quantum efficiencies depend upon the irradiation wavelength or not, or in other words, is the thermalization within the \( ^1T_1 \), the \( ^3E \), and the \( ^3T_1 \) state faster than the isc processes. If the quantum efficiencies are independent of the irradiation wavelength then the factor \( \eta_a \eta_1/\eta_b \) in Eq. (16) too is wavelength independent and with the above values becomes 0.21. In Fig. 3(c) \( \gamma_{18} (\infty) \) as a function of the irradiation wavelength calculated with this value and the experimental extinction coefficients for the \( ^3T_2 \rightarrow ^3E \) and the \( ^1A_1 \rightarrow ^3T_1 \), \( ^3T_2 \) transitions in the region of spectral overlap are shown. The agreement between the calculated curve and the experimental points is very good, and we may conclude that the quantum efficiencies for the isc processes are indeed independent of the irradiation wavelength, and that therefore at 20 K thermalization within the excited states is faster than the isc processes. This puts the isc rate constants at 20 K except for \( k_{111} \) into the range from \( 10^{10} \) to \( 10^{12} \text{s}^{-1} \).

In principle the isc rate constants could be calculated using the theory of radiationless multiphonon relaxation.\(^23,24\) Especially a calculation of the ratio \( k_a/k_b = \eta_a/\eta_b \) would be interesting. But in order to do this, we would need some good potential energy surfaces for the three states involved. The harmonic approximation most certainly is not good enough, because the differences in metal–ligand equilibrium distances are too large.

A further open question regards the temperature dependence of the various quantum efficiencies. Here we have only determined them at 20 K.

**V. CONCLUSIONS**

Due to the fact that generally there is no luminescence from any of the excited states in Fe(II) coordination compounds, there are only a comparatively small number of studies in the literature on their photophysical and photochemical properties.\(^5,19,20\) With the help of the extraordinarily long lifetime of the light-induced metastable HS states in Fe(II) spin crossover compounds this apparent disadvantage has been turned into an advantage, and in the case of [Fe(ptz)\(_6\)]\((BF_4)_2\) a fairly complete description of the excited LF states has been obtained, and a scheme of the isc processes has been firmly established both qualitatively and quantitatively. The same principles hold for other Fe(II) spin crossover systems too, and most probably they are also valid for other Fe(II) coordination compounds, except as we go away from the spin crossover region to say low-spin compounds with a higher LF strength the energy gap between the \( ^1A_1 \) ground state and the \( ^3T_2 \) state increases and consequently the lifetime of the light-induced metastable HS state decreases rapidly according to the energy gap law for radiationless transitions.\(^23,24\)

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