that the nitrogen heteroatom of ACR plays an important role in the destabilization of the complex by the alcohol since polynuclear aromatic counterparts of ACR behave much differently in both the magnitude of their formation constants and interaction with the alcohols.

Finally, the cooperative effects of two quenching mechanisms appear to be in operation. Upon addition of the alcohol, the static interaction of ACR with β-CD is reduced and an increase in the contribution from the free ACR species is observed. This suggests a partial disruption of the complex, since NMR data provide evidence for the existence of some remaining ternary associations. Additionally, the increase in the collisional quenching, as determined from dynamic quenching constants, supports the weaker nature of the existing ternary associations.

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Subpicosecond ^{1}MLCT → $^5T_2$ Intersystem Crossing of Low-Spin Polypyridyl Ferrous Complexes

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Abstract: Two different $\Delta S = 2$ intersystem crossing processes, the $^1\mathrm{MLCT} \rightarrow {}^5\mathrm{T}_2$ and $^5\mathrm{T}_2 \rightarrow {}^1\mathrm{A}_1$ conversions which follow the photoexcitation of low-spin $\mathrm{Fe^{II}}$ complexes, are examined on the nanosecond, picosecond, and subpicosecond time scales. Aqueous solutions of the complexes $[\mathrm{Fe(tpen)}](\mathrm{ClO_4})_2$, $[\mathrm{Fe(tptn)}](\mathrm{ClO_4})_2$, $[\mathrm{Fe(t\text{-}tpchxn)}](\mathrm{ClO_4})_2$, $[\mathrm{Fe(bpy)_3}](\mathrm{ClO_4})_2$, $[\mathrm{Fe(phen)_3}](\mathrm{ClO_4})_2$, and $[\mathrm{Fe(terpy)_2}](\mathrm{ClO_4})_2$ are studied, where in the first three complexes the hexadentate ligands are tetrakis(2-pyridylmethyl)ethylenediamine (tpen), tetrakis(2-pyridylmethyl)-1,3-propylenediamine (tptn), and tetrakis(2-pyridylmethyl)-*trans*-cyclohexane-1,2-diamine (t-tpchxn). The $[\mathrm{Fe(tpen)}]^{2+}$ complex is a spin-crossover complex with a $^1\mathrm{A}_1$ ground state and a thermally accessible $^5\mathrm{T}_2$ excited state. In H_2O this complex exhibits an isosbestic point in its electronic absorption spectrum at 302 ± 2 nm. Picosecond laser-flash instrumentation is used with probe wavelengths from 266 to 460 nm to determine the nature of the (18 ± 2)-ns relaxation seen for $[\mathrm{Fe(tpen)}]^{2+}$. In the transient difference spectrum, there is a change from bleach to absorption response at ~300 nm. This definitively establishes the (18 ± 2)-ns relaxation as being associated with the $^5\mathrm{T}_2 \rightarrow {}^1\mathrm{A}_1$ conversion. The related complex $[\mathrm{Fe(tptn)}]^{2+}$, which is all low-spin in solution throughout the temperature range examined, also shows a transient difference spectrum with an isosbestic at ~300 nm, suggesting that formation of $^5\mathrm{T}_2$ is a general feature. Laser instrumentation with a ~500-fs pulse ($\lambda_{\mathrm{pump}} = 314$ nm) is used to measure the rate of formation of the $^5\mathrm{T}_2$ state following $^1\mathrm{MLCT} \leftarrow {}^1\mathrm{A}_1$ excitation of low-spin $\mathrm{Fe^{II}}$ complexes. All of the above complexes were examined, and the observed kinetics were found to be independent of probe wavelength in the 385–510-nm range. A plot for each complex of ΔOD versus time of data collected in increments of 167 fs over the first 10–15 ps following $^1\mathrm{MLCT} \leftarrow {}^1\mathrm{A}_1$ excitation clearly shows that the $^5\mathrm{T}_2$ state of these $\mathrm{Fe^{II}}$ complexes is formed within ~700 fs. Intersystem crossing is at least as fast as internal conversion and vibrational cooling in these complexes. Transient absorption spectra (333-fs increments) suggest, furthermore, that vibrational cooling in the $^5\mathrm{T}_2$ excited state is complete within ~2–3 ps. The reasons for the surprisingly fast (<~700 fs) MLCT → $^5\mathrm{T}_2$ intersystem crossing where $\Delta S = 2$ are discussed.

Introduction

Molecules which exhibit the phenomenon of thermal spin-crossover have been of interest since 1932, when Cambi first noted anomalous magnetic behavior in certain ferric dithiocarbamates.[1] Since the first full review of the subject by Martin and White in 1968, a considerable amount of effort has been put forth to understand these types of complexes.[2] Aside from providing fundamental information about spin-state interconversions, the spin-crossover transformation, as it occurs in complexes of $\mathrm{Fe^{II}}$ in particular, is intimately related to oxygenation and carbonylation of myoglobin and hemoglobin and as well of the electron-transport chains associated with heme proteins such as P450.[3] Thus, the most widely studied of spin-crossover complexes are those containing iron. Most of the research on spin-crossover systems has concentrated on studies in the solid state. However, the benchmark paper by Sorai and Seki[4] establishing that cooperativity can have an overriding influence on the nature and mechanism of spin-crossover transformations serves to illustrate that understanding the intramolecular phenomenon of spin-crossover in the solid state is a complex problem.[5]

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(1) (a) Cambi, L.; Cagnasso, A. *Atti. Accad. Naz. Lincei* **1931**, *13*, 809. (b) Cambi, L.; Szego, L. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2591.

(2) (a) Martin, R. L.; White, A. H. *Transition Met. Chem.* **1968**, *4*, 113. (b) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527–622. (c) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83. (d) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293. (e) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543. (f) König, E.; Ritter, G.; Kulshreshtha, S. K. *Chem. Rev.* **1985**, *85*, 219. (g) Bacci, M. *Coord. Chem. Rev.* **1988**, *86*, 245. (h) Gütlich, P. In *Chemical Mössbauer Spectroscopy*; Herber, R. H., Ed.; Plenum Press: New York, 1984. (i) Maeda, Y.; Takashima, Y. *Comments Inorg. Chem.* **1988**, 7, 41. (j) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1–22. (k) Toftlund, H. *Coord. Chem. Rev.* **1989**, *94*, 67–108.

(3) (a) Maltempo, M. M.; Moss, T. H. *Q. Rev. Biophys.* **1976**, *9*, 91. (b) Emptage, M. H.; Zimmerman, R.; Que, L., Jr.; Münck, E.; Hamilton, W. D.; Orme-Johnson, W. H. *Biochim. Biophys. Acta* **1977**, *495*, 12. (c) Messana, C.; Cerdonio, M.; Shenkin, P.; Noble, R. W.; Fermi, G.; Perutz, R. N.; Perutz, M. F. *Biochemistry* **1978**, *17*, 3653. (d) Champion, P. M.; Münck, E.; Debrunner, P. G.; Hollenberg, P. F.; Hager, L. P. *Biochemistry* **1973**, *12*, 426. (e) Dyson, H. J.; Beattie, J. K. *J. Biol. Chem.* **1982**, *257*, 2267. (f) Fisher, M. T.; Sligar, S. G. *Biochemistry* **1987**, *26*, 4797–4803. (g) Backes, W. L.; Sligar, S. G.; Schenkman, J. B. *Biochemistry* **1982**, *21*, 1324–1330. (h) Tamburini, P. P.; Gibson, G. G.; Backes, W. L.; Sligar, S. G.; Schenkman, J. B. *Biochemistry* **1984**, *23*, 4526–4533.

(4) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555.

0002-7863/93/1515-298$04.00/0

Solution studies of the ${}^1A_1 \leftrightarrow {}^5T_2$ spin-state interconversion for Fe^{II} spin-crossover complexes make it possible to minimize intermolecular interactions and to concentrate on the intramolecular dynamics of the system. There have been only a limited number of these types of studies, most of which have been reviewed by Beattie.[6] The solution dynamics of spin-state interconversion have been studied using laser Raman temperature-jump,[7] ultrasonic relaxation,[8] and photoperturbation (i.e., laser-flash photolysis) techniques.[9] A few complexes have been examined by multiple methods; it is gratifying that the same relaxation rates were measured by the different techniques.

Both the Raman temperature-jump and ultrasonic relaxation techniques rely on the presence of an equilibrium between the high- and low-spin forms of a complex. The photoperturbation technique does not suffer from this restriction and can be used to examine a wider variety of complexes. In addition, the use of picosecond and subpicosecond lasers extends the accessible dynamic range by several orders of magnitude as compared to other relaxation techniques. Although laser photolysis was used on other low-spin ferrous complexes as early as 1976 (vide infra), McGarvey and Lawthers[9c] were the first to apply photoperturbation to spin-crossover complexes. ${}^1MLCT \leftarrow {}^1A_1$ excitation of a predominantly low-spin Fe^{II} complex in solution resulted in a bleaching of the ground-state absorption spectrum, and this bleaching was attributed to photoinduced formation of the excited ${}^5T_2$ state.

Laser photolysis has been applied to a variety of non-spin-crossover complexes.[9] The main drawback with laser photolysis is the ambiguity in assigning excited states on the basis of transient absorption spectra alone. Fink and Ohnesorge,[10] while studying the temperature dependence of d^6 metal–imine chelates of Ru^{II} and Ir^{III}, suggested that the lack of emission from Fe^{II} complexes might result from complete crossover to the high-spin ${}^5T_2$ state upon photoexcitation, but they could offer no good argument against involvement of the ${}^3T_1$ and/or ${}^3T_2$ states. An early photophysical study of $[Fe(bpy)_3]^{2+}$ by Kirk et al.[11] revealed a ground-state bleaching recovery of 0.83 ± 0.07 ns. The authors proposed as possible excited states ${}^3MLCT$, ${}^1T_{1g}$, and ${}^3T_{1g}$. Soon thereafter, Street et al.[12] performed analogous experiments on $[Fe(phen)_3]^{2+}$ in aqueous solution and observed an excited state with a (710 ± 70)-ps lifetime. This state was assigned as ${}^3T_1$, although ${}^1T_1$, ${}^3T_2$, and ${}^1T_2$ were indicated as possibilities. Creutz et al.[13] examined transient spectra of $[Fe(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, and $[Os(bpy)_3]^{2+}$ in the 300–500-nm region and argued that the lack of any intense excited-state absorption features for $[Fe(bpy)_3]^{2+}$, particularly in the region about 400 nm where the $bpy^{\bullet-}$ species is expected to absorb, is strong evidence that the excited state is not charge-transfer but rather ligand-field in nature. Assignments for both the (0.81 ± 0.07)-ns state of $[Fe(bpy)_3]^{2+}$ and the (0.80 ± 0.07)-ns state of $[Fe(phen)_3]^{2+}$ were left as either ${}^3T_1$ or ${}^5T_2$. A year later, Bergkamp and co-workers,[14] from the same group, examined the temperature dependence of the ligand-field relaxation of $[Fe(phen)_3]^{2+}$ in a 4:1 (v/v) EtOH/MeOH mixture. They reaffirmed their conclusion regarding the ligand-field nature of the photoinduced excited state and showed that the initially formed MLCT state is depopulated in ≤10 ps following photoexcitation. They found biphasic kinetics at temperatures below the glass transition of the solvent and attributed the fast and slow processes to decay from the ${}^3LF$ and ${}^5LF$ states, respectively. This picture remained essentially unchanged[15] for several years, save for a quantum yield study by Bergkamp et al.[16] indicating nearly 100% efficiency for the formation of the excited LF state. Very recently, Hauser[17] reexamined the temperature dependence of the relaxation of $[Fe(phen)_3]^{2+}$ doped into different matrices. Hauser found only a single exponential decay from room temperature down to 13 K and concluded that the biphasic kinetics observed by Bergkamp et al.[14] was an artifact due to local heating effects of the laser pulse and poor thermal transfer characteristics of glasses.

We present here what we believe to be the most conclusive spectroscopic evidence to date indicating that the excited state formed upon photoexcitation of Fe^{II} polypyridyl complexes is, in fact, the ${}^5T_2$ state. In addition, our subpicosecond transient absorption experiments reveal that formation of this excited state occurs in less than ~700 fs following ${}^1MLCT \leftarrow {}^1A_1$ excitation. The mechanistic implications of these results as they apply to intersystem crossing, internal conversion, and vibrational relaxation following photoexcitation of low-spin Fe^{II} complexes are discussed in detail.

Experimental Section

Compound Preparations. All reagents were of reagent grade and used as received unless otherwise indicated. All syntheses involving Fe^{II} complexes were performed under a nitrogen atmosphere in deoxygenated solvents using standard Schlenk techniques. The ferrous compounds are stable indefinitely in air as solids. All solvents used for photophysical measurements were of spectrophotometric grade (Fisher). Aqueous solutions of the ferrous complexes could be prepared in air and showed only slight degradation (<10%) after sitting for several days.

$FeCl_2{\cdot}2H_2O$. $FeCl_2{\cdot}2H_2O$ was freshly prepared by dissolving 25 g of $FeCl_2{\cdot}4H_2O$ (Fisher), 1 g of Fe powder (Baker), and 1 mL of concentrated HCl in 100 mL of deoxygenated H_2O. The mixture was refluxed under N_2 for approximately 1 h, during which time the solution became pale green. The solution was filtered and concentrated to dryness under reduced pressure. The pale green solid was then placed under a hard vacuum and heated at 80 °C in an oil bath for 2 h. The resulting white solid was transferred to a vessel and stored under N_2.

(Tetrakis(2-pyridylmethyl)-1,3-propylenediamine)iron(II) Perchlorate, $[Fe(tptn)](ClO_4)_2$. This molecule was prepared by modification of a previously reported procedure.[18] 1,3-Propylenediamine (2.1 mL, 25 mmol, Aldrich) was combined with 2-pyridinecarboxaldehyde (4.8 mL, 50 mmol, Aldrich) in MeOH and gently heated just below reflux for 1 h. To the resulting yellow solution was added $NaBH_4$ (2.5 g) in small portions until gas evolution ceased. The mixture was allowed to stir overnight and then heated to reflux for ca. 30 min. Concentrated HCl was then added to the solution dropwise until gas evolution ceased. The solution was made slightly basic with an aqueous NaOH solution, and the resulting mixture was extracted with four 50-mL portions of $CHCl_3$. The extract was dried overnight with $MgSO_4$ and concentrated to near dryness. The residue was dissolved in EtOH (20 mL) and added to an aqueous solution of 2-picolyl chloride hydrochloride, which had been made slightly basic with an aqueous NaOH solution. This reaction mixture was allowed to stir at room temperature for 4 days, during which time the pH was maintained between 7 and 9 by occasional dropwise addition of an aqueous NaOH solution (5 M). The deep red reaction mixture was filtered on a medium-porosity frit to yield free tptn. The yield for the reaction was not recorded, but it is estimated to be <10%.

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(5) (a) Rao, C. N. R. *Int. Rev. Phys. Chem.* **1985**, *4*, 19. (b) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 1468–1470. (c) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 131–139. (d) Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1984**, *23*, 3870–3877.

(6) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 1–53.

(7) (a) Dwey, T. G.; Turner, D. H. *Adv. Mol. Relax. Interact. Process* **1978**, *13*, 331. (b) Beattie, J. K.; Sutin, N.; Turnder, D. H.; Flynn, G. W. *J. Am. Chem. Soc.* **1973**, *95*, 2052. (c) Hoselton, M. A.; Drago, R. S.; Wilson, L. J.; Sutin, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 6979. (d) Reeder, K. A.; Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 1071.

(8) (a) Beattie, J. K.; Binstead, R. A.; West, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3044. (b) Binstead, R. A.; Beattie, J. K.; Dose, E. V.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 5609. (c) Beattie, J. K.; McMahon, K. J. *Aust. J. Chem.* **1988**, *41* (9), 1315.

(9) (a) Lawthers, I.; McGarvey, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4280. (b) McGarvey, J. J.; Lawthers, I.; Toftlund, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1576. (c) McGarvey, J. J.; Lawthers, I. *Ibid.* **1982**, 906. (d) Xie, C.-L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6981–6988. (e) Conti, A. J.; Xie, C.-L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 1171–1180.

(10) Fink, D. W.; Ohnesorge, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 4995.

(11) Kirk, A. D.; Hoggard, P. E.; Porter, G. B.; Rockley, M. G.; Windsor, M. W. *Chem. Phys. Lett.* **1976**, *37*, 199.

(12) Street, A. J.; Goodall, D. M.; Greenhow, R. C. *Chem. Phys. Lett.* **1978**, *56*, 326.

(13) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(14) Bergkamp, M. A.; Brunschwig, B. S.; Gütlich, P.; Netzel, T. L.; Sutin, N. *Chem. Phys. Lett.* **1981**, *81*, 147.

(15) For a recent review of ultrafast spectroscopy on transition-metal systems, see: Serpone, N.; Jamieson, M. A. *Coord. Chem. Rev.* **1989**, *93*, 87.

(16) Bergkamp, M. A.; Chang, C.-K.; Netzel, T. L. *J. Phys. Chem.* **1983**, *87*, 4441.

(17) Hauser, A. *Chem. Phys. Lett.* **1990**, *173*, 507.

(18) Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand.* **1981**, A35, 575.

[Fe(tptn)](ClO$_4$)$_2$ was prepared by dissolving tptn in deoxygenated 1:1 MeOH/H$_2$O (0.23 g in 5 mL). An aqueous solution of FeCl$_2$·2H$_2$O was then added to the stirring tptn solution, resulting in the immediate formation of a clear, deep red solution. The reaction mixture was heated to near reflux for ca. 2 h and then allowed to cool. An aqueous solution of NaClO$_4$ (0.3 g in 8 mL) was added dropwise to the stirring reaction mixture, resulting in the formation of a precipitate. The reaction mixture was immersed in ice to induce further precipitation, and the product was filtered off and dried under a stream of N$_2$ and then stored in air. Anal. Calcd for FeC$_{27}$H$_{31}$N$_6$Cl$_2$O$_8$: C, 46.18; H, 4.30; N, 11.97; Fe, 7.96. Found: C, 45.92; H, 4.07; N, 12.03; Fe, 8.00.

[Fe(tpen)](ClO$_4$)$_2$ was prepared as previously described.[19] **[Fe(bpy)$_3$](ClO$_4$)$_2$** and **[Fe(phen)$_3$](ClO$_4$)$_2$** were both prepared by dissolving the free ligand (Aldrich) in MeOH (6.0 mmol in 20 mL, typical) and deoxygenating the solvent. An aqueous solution of FeCl$_2$·2H$_2$O (2.0 mmol of 5 mL) was then added to the stirred ligand solution, producing a blood-red solution which was then heated for 1 h at 50 °C. Once the solution cooled to room temperature, dropwise addition of an aqueous NaClO$_4$ solution resulted in the immediate formation of a microcrystalline solid, which was filtered and dried under N$_2$ and then stored in air. Elemental analyses and optical characteristics of the compounds were consistent with those reported in the literature.

Physical Measurements. Optical spectra were collected using a Hewlett-Packard 8452A diode array spectrophotometer. Each spectrum was obtained as a signal average of 250 spectra collected at intervals of 0.1 s. Variable-temperature spectra were obtained using a Hewlett-Packard Model 89054A thermostated cell holder connected to a Fisher Model 800 Isotemp circulating temperature bath. Temperature stability was better than ±0.5 K; the absolute accuracy is estimated to be ±2 K. Variable-temperature spectra were collected after the sample had been allowed to thermally equilibrate at each temperature for 15 min. Spectral changes were found to be reversible, as complete thermal cycling resulted in better than 95% recovery of the starting spectrum. Optical spectra were also collected on all samples both before and after each laser experiment. In no case was there any evidence that laser photolysis induced significant (>5%) irreversible changes in the optical properties of the sample.

Nanosecond Experiments. Transient kinetics on the nanosecond and microsecond time scales were obtained using a XeCl excimer-pumped dye laser in conjunction with a Xe flashlamp, monochromator, photomultiplier, and a transient digitizer. The instrument-limited response time of the system following deconvolution is approximately 10 ns. Details of this facility will be described in a forthcoming paper.[20]

Picosecond Experiments. Picosecond experiments (FWHM ≈ 80 ps for excitation pulse) were performed using a mode-locked, Q-switched, cavity-dumped Nd:YAG laser and a synchronously-pumped dye laser which has been described previously.[21]

Subpicosecond Experiments. Subpicosecond experiments were performed using a colliding-pulse, mode-locked ring dye laser amplified at 10 Hz through a 4-stage amplifier using a Q-switched, frequency-doubled Nd:YAG laser as previously described.[22] The system was modified by the introduction of two prisms to partially compensate for pulse dispersion which occurs through the amplifier chain. The FWHM pulse width of the frequency-doubled excitation pulse (λ = 314 nm) is approximately 500 fs.

Results and Discussion

Establishing the Nature of the Excited State. The first goal of this study was to establish as definitively as possible the nature of the longest-lived excited state produced by photoexcitation of Fe^{II} polypyridyl complexes. The agreement found between laser photolysis studies, temperature-jump experiments, and ultrasonic relaxation results on certain spin-crossover complexes is compelling, insofar as with the latter techniques there is no question about the identity of the excited state; but could we find a way to generalize the result to other cases? There are two difficulties in making state assignments following laser photolysis of coordination compounds. First, there is no a priori way to predict the spectrum of any state, so nonspectral evidence must be invoked at some point. Second, spectral features are likely to be so broad and diffuse that it would be difficult to argue that a feature seen in one compound is the same as that observed in a second. Our strategy was to attempt a very careful study of a prototype, namely the spin-crossover complex [Fe(tpen)](ClO$_4$)$_2$, where there are independent means for identifying the excited state, and then to find a characteristic spectral feature adequate to support arguments that other compounds are or are not similar.

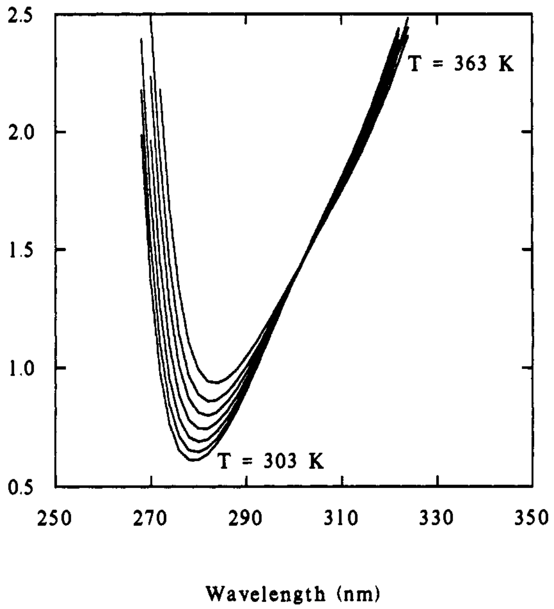
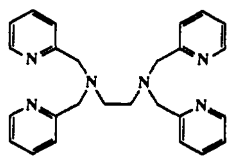


Figure 1. Variable-temperature optical spectra of [Fe(tpen)](ClO$_4$)$_2$ in aqueous solution (1.49 × 10^{-3} M) in the region near the isosbestic point. Inset numbers indicate temperature (K).



(tpen)

The detailed characterization of the spin-crossover complex [Fe(tpen)](ClO$_4$)$_2$ has already been reported.[19] The compound exhibits thermal spin-crossover in solution as well as in the solid state. The T_c for this compound, that is, the temperature at which the high-spin/low-spin ratio is 1, was determined to be ~360 K. Thus, at room temperature in aqueous solution this complex is predominantly low-spin. However, since the high-spin state is thermally accessible, it is clear that the $^5T_2$ state is the lowest-energy excited ligand-field state. Variable-temperature optical studies were performed to determine the optical properties of the $^5T_2$ state for comparison with the transient absorption experiments, see Figure 1. As expected, the intensity of the charge-transfer band decreases with increasing population of the $^5T_2$ state. (The high-temperature spectrum still contains a significant contribution from the low-spin form of the complex since K_{eq} = 1 at approximately 360 K.) The change is not symmetric over the whole band, as there is a proportionally larger drop in intensity in the low-energy part of the band. This is probably due to $^1T_1 \leftarrow {}^1A_1$ absorption, which appears as a low-energy shoulder on the MLCT band.

The most significant feature of the variable-temperature optical spectra is the presence of an isosbestic point at 302 ± 2 nm. The presence of an isosbestic point is a very strong indication that there are only two absorbing species in solution. There is clearly a simple, two-state thermal equilibrium in solution between the high-spin $^5T_2$ and low-spin $^1A_1$ forms of [Fe(tpen)]$^{2+}$. If an isosbestic point occurs at the same wavelength in the transient spectrum, one may argue that the same two states, and only those two, are present. Furthermore, an isosbestic point is as sharp and characteristic a feature as we could hope to find in solution spectra of such compounds. A similar feature observed in related com-

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(19) Chang, H.-R.; McCusker, J. K.; Toftlund, H.; Wilson, S. R.; Trautwein, A. X.; Winkler, H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 6814–6827.

(20) McCusker, J. K.; Hendrickson, D. N., submitted for publication.

(21) Xie, X.; Simon, J. D. *Optics Commun.* **1989**, *69*, 303.

(22) Jongeward, K. A.; Magde, D.; Taube, D. J.; Marsters, J. C.; Traylor, T. G.; Sharma, V. S. *J. Am. Chem. Soc.* **1988**, *110*, 380.

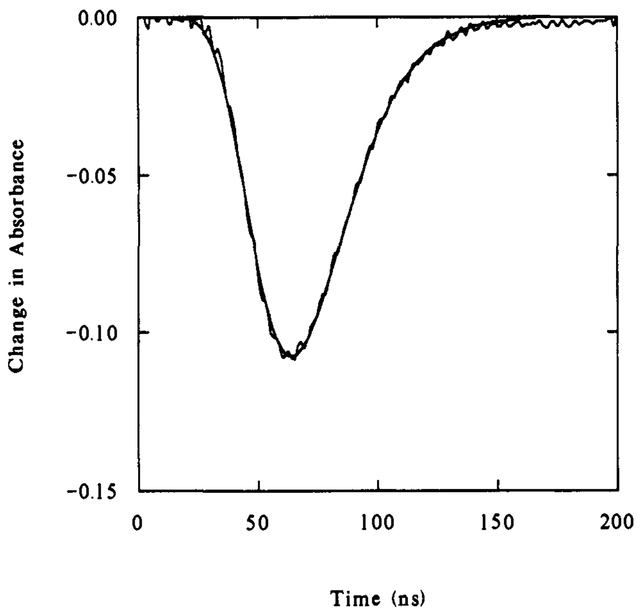

Figure 2. Plot of the change in absorbance versus time for an aqueous solution of [Fe(tpen)](ClO$_4$)$_2$ monitored at λ = 430 nm following excitation at 440 nm with a 24-ns laser pulse. The smooth solid line represents a convolution of the known instrument response function with a single exponential decay (τ_{obsd} = 18 ± 5 ns).

Table I. Variable Probe-Wavelength Studies for [Fe(tpen)](ClO$_4$)$_2$ and [Fe(tptn)](ClO$_4$)$_2$[a]

probe wavelength (nm)	nature of transient	
	[Fe(tpen)](ClO$_4$)$_2$	[Fe(tptn)](ClO$_4$)$_2$
266	absorption	absorption
290	absorption	absorption
300	absorption	absorption
313	bleach	bleach
320	bleach	bleach
325	bleach	bleach
380	bleach	bleach
385	bleach	bleach
440	bleach	bleach
460	bleach	bleach

[a] Data were collected following excitation at 355 nm with a ~80-ps laser pulse.

pounds would be persuasive, albeit not absolutely compelling, evidence for the conclusion that the $^5T_2$ state is the long-lived excited state formed upon ^{1}MLCT ← $^1A_1$ excitation.

In Figure 2 are shown data for an aqueous solution of [Fe(tpen)](ClO$_4$)$_2$ (3.36 × 10^{-4} M) following excitation of the sample with a 24-ns pulse at 440 nm. Transient bleaching was monitored at λ = 430 nm. It should be noted that the observed kinetics in these complexes have invariably been found to be independent of both the pump and probe wavelengths across the entire charge-transfer band. The relaxation was modeled by a single exponential decay with an observed rate constant of k_{obs} = (5.6 ± 0.6) × 10^7 s^{-1} (τ_{obs} = 18 ± 2 ns). Kinetic traces out to 2 μs reveal no additional transients. Since the transient is fairly long lived and since it is clear that the lowest-energy ligand-field excited state in [Fe(tpen)](ClO$_4$)$_2$ is the $^5T_2$ state, it is reasonable to assign the (18 ± 2)-ns state as the $^5T_2$ state. Using the values of K_{eq} calculated from the variable-temperature susceptibility data determined previously,[19] this would give a $^5T_2$ → $^1A_1$ relaxation rate of (5.0 ± 0.5) × 10^7 s^{-1} (τ = 20 ± 2 ns). However, confidence in the assignment would be greatly increased if we could detect the isosbestic point for the spin-equilibrium in this complex, so we attempted to determine the wavelength at which the transient changed from a bleach to an absorption.

The nanosecond instrumentation is limited to $\lambda_{\text{probe}} > 350$ nm, so the variable probe-wavelength measurements were made using a mode-locked Nd:YAG and a synchronously-pumped dye laser to enable probe wavelengths from 266 to 460 nm. In Figure 3 are presented kinetic traces covering delays of 0–3 ns in steps of 25 ps for two different probe wavelengths following 355-nm excitation of a 1.57 × 10^{-3} M aqueous solution of [Fe(tpen)](ClO$_4$)$_2$. The upper panel corresponding to λ_{probe} = 313 nm occurs to the red side of the static isosbestic point and accordingly shows a transient bleach of the ground-state spectrum similar to that found in the nanosecond experiment, Figure 2. However, when the probe wavelength is tuned to the blue side of the static isosbestic point (λ_{probe} = 290 nm, lower panel), the data reveal a transient absorption. Thus, an isosbestic occurs at 290 nm $< \lambda_i <$ 313 nm. In Figure 4 is presented a plot of the change in absorbance versus time for [Fe(tpen)](ClO$_4$)$_2$ with λ_{probe} = 300 nm; the data reveal a weak transient absorption at this probe wavelength.[23] We

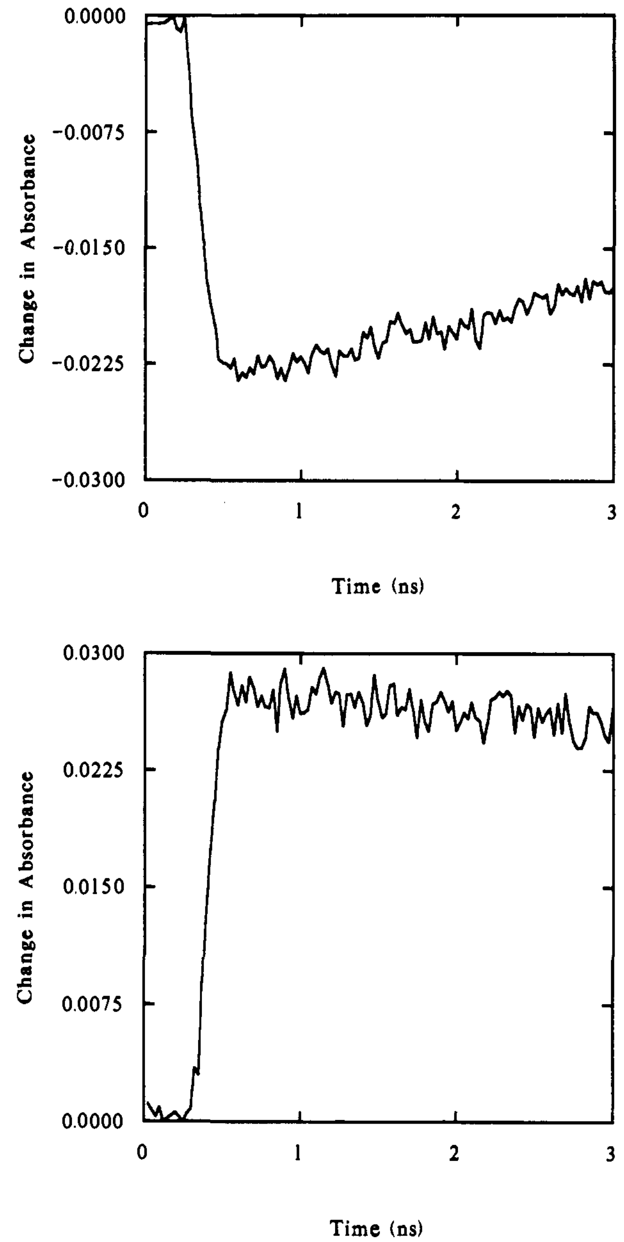

Figure 3. Plot of the change in absorbance versus time of a 1.49 × 10^{-3} M aqueous solution of [Fe(tpen)](ClO$_4$)$_2$ following excitation at 355 nm with a ~80-ps laser pulse. Upper panel: λ_{probe} = 313 nm. Lower panel: λ_{probe} = 290 nm.

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[23] Since, different dyes were used for the three wavelengths examined, the nominal probe pulse energies were not identical. However, since the data collection required attenuation of the probe beam intensity to the same level for all three wavelengths to avoid PMT saturation, a semiquantitative comparison of absolute ΔOD is appropriate. The 355-nm excitation pulse energy was not measured, but it typically exhibits a ±5% fluctuation under normal operating conditions (cf. ref 21).

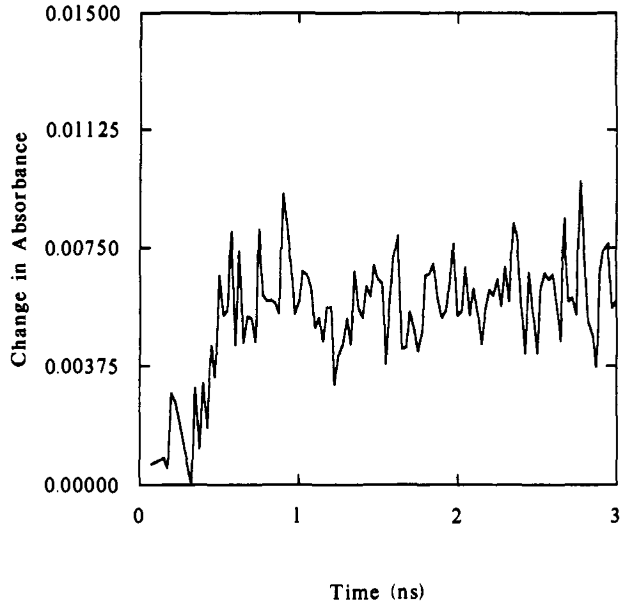

Figure 4. Plot of the change in absorbance versus time of a 1.49 × 10^{-3} M aqueous solution of $[Fe(tpen)](ClO_4)_2$ following excitation at 355 nm with a ~80-ps laser pulse. The probe wavelength used was 300 nm. See text for details.

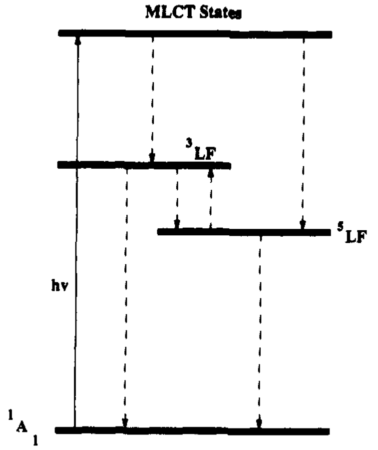

Figure 5. Excited-state decay mechanism proposed by Sutin and co-workers[14] following $^1MLCT \leftarrow {}^1A_1$ excitation of low-spin Fe^{II} polypyridyl complexes in aqueous solution. The abbreviation LF denotes a ligand-field electronic state. This figure was adapted from Figure 2 of ref 14.

conclude that 300 nm is very close to but slightly blue of the isosbestic. Unfortunately, experimental limitations did not allow for data collection at probe wavelengths between 300 and 313 nm, but it is clear that the crossing point occurs at some wavelength λ_i where 300 nm $< \lambda_i <$ 306.5 nm (i.e., to the blue side of the 300-/313-nm midpoint), in excellent agreement with the expected value of 302 ± 2 nm for the isosbestic point. In Table I are listed the types of transient observed (i.e., either bleach or absorption) for all of the probe wavelengths examined for $[Fe(tpen)](ClO_4)_2$. Besides locating the isosbestic wavelength, the complete set of data establish that the state observed in this experiment is the same as that detected at longer times in the nanosecond experiment since only one kinetic component is observed. Based on these data, we believe that conclusive evidence has been presented to show that the $^5T_2$ state is the long-lived excited state formed following picosecond charge-transfer excitation of $[Fe(tpen)](ClO_4)_2$ on both the nanosecond and picosecond time scales.

As an example of a non-spin-crossover molecule that should be very similar to $[Fe(tpen)](ClO_4)_2$ we selected $[Fe(tptn)](ClO_4)_2$. Despite the fact that $[Fe(tptn)](ClO_4)_2$ is not a spin-crossover molecule and therefore cannot exhibit a $^1A_1/^5T_2$ isosbestic point in variable-temperature optical spectroscopy, we might anticipate that "transient inversion" will occur in approximately the same spectral region as was found for $[Fe(tpen)](ClO_4)_2$. Variable probe–wavelength studies were therefore performed on $[Fe(tptn)](ClO_4)_2$ in the range of 266–460 nm; these data are summarized in Table I. As with the data on $[Fe(tpen)](ClO_4)_2$, it is clear that the ground-state and excited-state spectra cross a couple of nanometers to the red of 300 nm. This is consistent with an assignment of $^5T_2$ as the lowest-energy excited state.

Assignments of the longest-lived excited states in molecules such as $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ have evolved over the years from charge-transfer-based to triplet ligand-field and/or quintet ligand-field. Arguments by Sutin and co-workers[13,14] (vide supra) that the excited states are not charge-transfer-based are persuasive, but distinguishing between the $^3T_1$ (and/or $^3T_2$) and $^5T_2$ in these systems is not easy. Hauser[17] has indicated that, although $[Fe(bpy)_3]^{2+}$ is a low-spin complex, it is still fairly close to the spin-crossover point. Based on the similarity of spectra and kinetics of all six compounds treated here, we agree with this assessment and believe that the $^5T_2$ state is the lowest-energy excited state in most if not all low-spin octahedral Fe^{II} complexes. This is consistent with other lines of argument, including (i) the lack of any observable emission from low-spin Fe^{II} complexes suggests that the excited state is not radiatively-coupled to the $^1A_1$ ground state to any significant extent (vide infra); (ii) the lifetimes previously reported[13] for the excited states of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$, in conjunction with the data on $[Fe(tptn)](ClO_4)_2$, are qualitatively consistent with the trend in relaxation times observed for spin-crossover compounds given the expected increase in ligand-field strength (i.e., consistent with the energy gap law); and (iii) the markedly different photoactivity of $[Co(CN)_6]^{3-}$ relative to other low-spin Co^{III} complexes such as $[Co(en)_3]^{3+}$ has led researchers to assign a $^3T_{1g}$ state as the lowest-energy excited state in this complex. Given the increase in ligand-field strength anticipated on going from a Fe^{II} complex to an analogous Co^{III} complex, one would presumably need a ligand with a stronger ligand-field than CN^- to cause the $^3T_1$ state to drop below the $^5T_2$ state in energy in a Fe^{II} complex having pseudooctahedral symmetry. We are therefore reasonably confident in our assignment of the $^5T_2$ state as the lowest-energy excited state in *all* low-spin, non-spin-crossover Fe^{II} polypyridyl complexes and proceed from this assumption.

Subpicosecond Formation of the $^5T_2$ State. The second goal of this study was to learn how the $^5T_2$ state is formed. The conversion to the $^5T_2$ state following $^1MLCT \leftarrow {}^1A_1$ excitation corresponds to a $\Delta S = 2$ spin change. This is a highly forbidden process due to the fact that interaction between the $S = 0$ and $S = 2$ manifolds must occur via second-order spin–orbit coupling through the $S = 1$ manifold. The conventional thinking is that after formation of the ^1MLCT excited state, vibrational cooling would be fastest, followed by internal conversion (singlet to singlet, etc.), and then the slowest step would be intersystem conversion. It was our goal to determine how fast the $^1MLCT \rightarrow {}^5T_2$ process occurred and what intermediates are along the mechanistic pathway.

Sutin and co-workers[13,14] performed picosecond time-resolved transient absorption experiments on $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ following excitation into the ^1MLCT state and determined that the excited state present after 10 ps had a molar absorptivity of <900 M^{-1} cm^{-1}. Knowing that the ^3MLCT states of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ show strong absorptions in the visible region ($\epsilon \approx 5 \times 10^3$ M^{-1} cm^{-1}), they concluded that crossover to the ligand-field manifold occurs in <10 ps. Combining this insight with their observation of slower biphasic return to the ground state in a 4:1 EtOH/MeOH glass at 14 and 81 K,[14] data which Hauser has called into question (vide supra),[17] they propose the Jablowski diagram shown in Figure 5, which involves "metastable" populations of ^3LF and ^5LF. This remains the currently[15] accepted description of the photophysics of low-spin Fe^{II} polypyridyl complexes.

The $^{1,3}MLCT$ states carry enough oscillator strength that even a 10-ps lifetime should lead to detectable luminescence. Yet there has never been a report of emission being observed from any Fe^{II} complex. A great deal of effort was expended in our laboratory looking for emission from the complexes described in this work using a picosecond time-resolved single-photon counting apparatus.[24] Wavelength scans from 350 to 900 nm following excitation at various wavelengths within the ^{1}MLCT band did not reveal any emission from any of the Fe^{II} complexes discussed here. Based on the sensitivity of the apparatus, we place an upper limit on the radiative quantum yield for these complexs of $\sim 10^{-6}$ *in this wavelength range*. This effectively rules out any significant emission from charge-transfer states (e.g., ^{3}MLCT) but does not necessarily address the issue of ligand-field emission. Due to the small degree to which the $^1A_1$ and $^5T_2$ states must be coupled electronically, the transition moment integral describing radiative transitions between these two states (either absorptive or emissive) must be vanishingly small. Thus, we would not anticipate observing emission from the $^5T_2$ state even if it occurs at wavelengths short enough to be observed. There is a small degree of radiative coupling between the $^1A_1$ state and the $S = 1$ manifold, as evidenced by the observation of $^3T_{1,2} \leftarrow {}^1A_1$ absorptions in a number of Fe^{II} complexes.[25] Therefore, there can be, in principal, radiative emission from the $S = 1$ manifold which might be detectable if the ^{3}LF state lasts as long as nanoseconds. However, the absorption bands for the ^{3}LF absorptions, in general, occur at wavelengths $\lambda > 700$ nm. Given the strong Stokes shift anticipated, it is likely that emission, if any, would occur at $\lambda > 1000$ nm, where we were unable to look due to the lack of sensitive detectors.

There have been three studies addressing the issue of quantum yield for formation of the long-lived excited state in Fe^{II} complexes, now assigned as the $^5T_2$ state. Creutz et al.[13] studied [Fe(bpy)$_3$]$^{2+}$ and calculated the quantum yield on the basis of some assumptions regarding the pulse profile of the picosecond excitation source and absorption cross sections but neglecting attenuation of the excitation pulse propagating through the solution. They determined a quantum yield of $\Phi = 1.6 \pm 0.5$ at room temperature. Netzel and co-workers[16] performed a more detailed study of excited-state formation in [Fe(phen)$_3$]$^{2+}$ and obtained a value of $\Phi = 1.00 \pm 0.05$ (also at room temperature). It is remarkable that a $\Delta S = 2$ spin-conversion process occurs with 100% efficiency. Considering the number of electronic states which lie between the initially populated ^{1}MLCT state and the $^5T_2$ state, all of which are coupled to some extent to the $^1A_1$ ground state, it is surprising that there are no alternate decay pathways competing with the formation of the high-spin state. Netzel and co-workers[16] concluded that the decay pathway is a cascade: $^{1,3}\text{MLCT} \rightarrow {}^3\text{LF} \rightarrow {}^5\text{LF} \rightarrow {}^1A_1$. They could not rule out the possibility that the MLCT states directly populate the $^5T_2$ state but deemed it unlikely on the basis of energy gap and spin conservation considerations. They were unclear about why they chose to include a ^{3}MLCT state and exclude the ^{1}LF state in the decay scheme. Probably they had in mind that the energy gap and spin conservation considerations used to rule out direct MLCT → $^5T_2$ conversion would imply inclusion of singlet states in the decay process unless an assumption of 100% conversion efficiency from ^{1}MLCT → ^{3}MLCT is made, and they made the latter choice. In any event, the work by Netzel is important since it implies that repopulation of the $^1A_1$ ground state can only come about through $^5T_2 \rightarrow {}^1A_1$ relaxation.

The most recent quantum yield study comes from Hauser.[17] In a detailed examination of the LIESST (light-induced excited-state stabilization) properties of [Fe(ptz)$_6$](BF$_4$)$_2$ (ptz = 1-propyltetrazole), Hauser used CW photolysis to estimate the quantum yield of the various processes potentially present. The [Fe(ptz)$_6$](BF$_4$)$_2$ complex is convenient because all four of the ligand-field transitions ($^1T_2 \leftarrow {}^1A_1$, $^1T_1 \leftarrow {}^1A_1$, $^3T_2 \leftarrow {}^1A_1$, and $^3T_1 \leftarrow {}^1A_1$) are observed in the electronic spectrum of a single crystal.[25b] Hauser presents three main conclusions: (1) the fact that the $^5T_2$ state can be formed following excitation into either the singlet or triplet ligand-field states is proof that at least the $^3T_1$ state is directly involved in the intersystem crossing mechanism; (2) the branching ratio from the $^3T_1$ state to the $^1A_1$ and $^5T_2$ state is ≈ 1:4 [i.e., $\Phi(^3T_1 \rightarrow {}^1A_1) = 0.22$ (8) and $\Phi(^3T_1 \rightarrow {}^5T_2) = 0.78$ (8)]; and (3) the quantum yield of formation of the $^3T_1$ state following $^1T_1 \leftarrow {}^1A_1$ excitation is calculated to be 0.96 (11). He did not treat excitation into charge-transfer excited states.

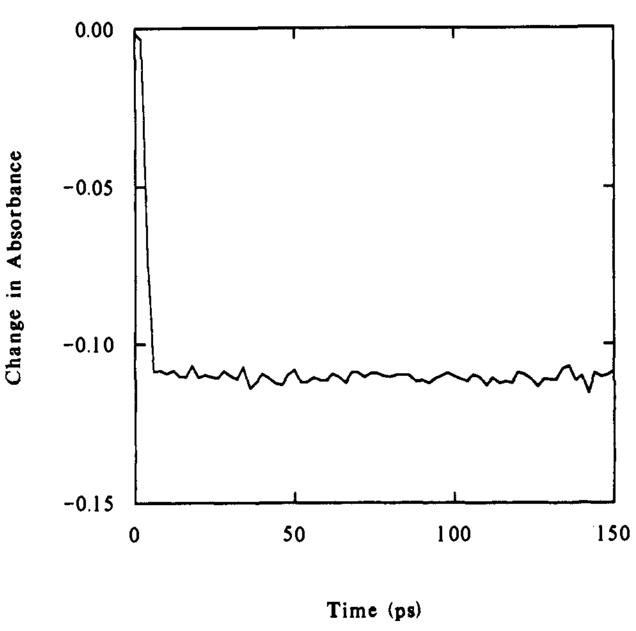

Figure 6. Plot of the change in absorbance versus time for a 1.52×10^{-3} M aqueous solution of [Fe(tpen)](ClO$_4$)$_2$ monitored at 425 nm. Data were collected in increments of 1 ps following excitation at 314 nm with a ~500-fs laser pulse.

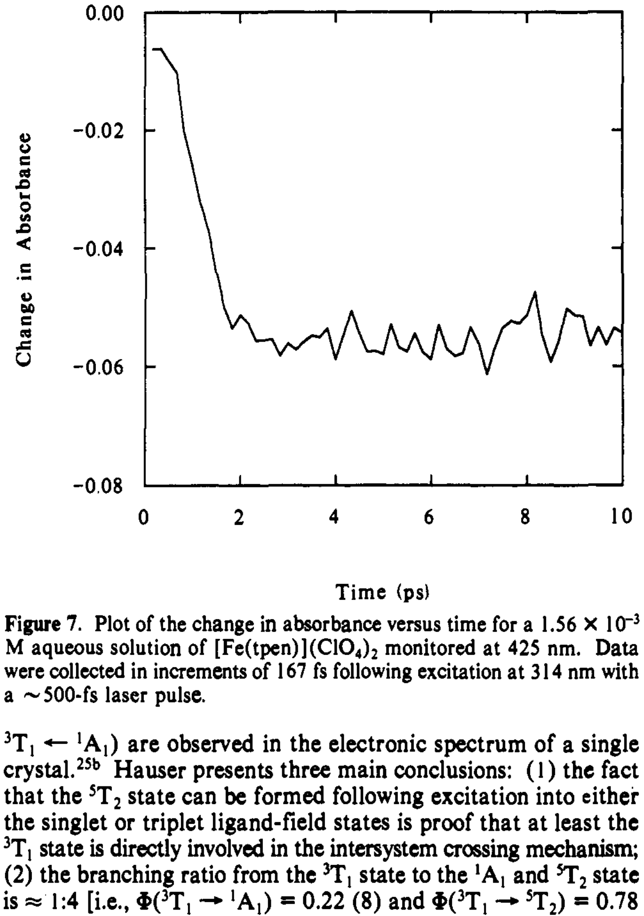

Figure 7. Plot of the change in absorbance versus time for a 1.56×10^{-3} M aqueous solution of [Fe(tpen)](ClO$_4$)$_2$ monitored at 425 nm. Data were collected in increments of 167 fs following excitation at 314 nm with a ~500-fs laser pulse.

Hauser's calculations were made on data at 20 K and conflict somewhat with the results of Netzel and co-workers.[16] Of course, the measurements were made on different systems. It is also possible that quantum yields in these systems are temperature-dependent, an idea suggested by both Hauser and Netzel. Note that Hauser's quantum yields are intimately tied to the proposed mechanism. They are extracted by simultaneously solving the

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(24) The picosecond emission spectrometer consisted of a mode-locked Ar$^+$ laser (Spectra-Physics Model 2020) synchronously pumping a cavity-dumped, ultrafast dye laser. The output of the dye laser was doubled to provide excitation on the high-energy side of the charge-transfer band. Alternatively, the output of the Ar$^+$ laser was used directly through the cavity dumper to effect excitation wavelengths in the visible region of the spectrum. Detection was via time-resolved, single-photon counting.

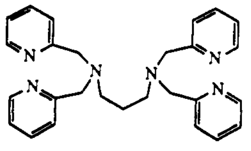
(25) (a) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864. (b) Hauser, A. *J. Chem. Phys.* **1991**, *94*, 2741.

kinetic equations for the decay scheme on the basis of his CW photolysis results with some processes assumed to have zero rate. We are not convinced by Hauser that formation of the $^5T_2$ state following excitation into either the $^1T_1$ or $^3T_1$ absorption bands constitutes proof that the latter is always involved in the intersystem crossing and that $^1T_1 \rightarrow {}^5T_2$ conversion can be neglected in the kinetic scheme presnted in Figure 7. This assumption may be justified less by experimental evidence than by a lingering bias that intersystem crossing is a "slow" process. This might be valid in a solid at 20 K, but we must question its extension to room temperature liquid solutions. The $^1T_1 \rightarrow {}^5T_2$ pathway is not incorporated into Hauser's model, and if it does contribute at 20 K this would call into question the values calculated for the quantum yields of ^3T and $^5T_2$ states' formation. In the remainder of this section we shall present results from kinetic studies designed to directly measure the rate of formation of the $^5T_2$ state following $^1MLCT \leftarrow {}^1A_1$ excitation of a low-spin Fe^{II} complex in order to determine whether this can in any sense be treated as a "slow" process and in the hopes of definitively establishing the mechanism of internal conversion/intersystem crossing in these transition-metal complexes.

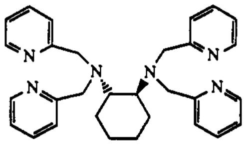
Since the ground- and excited-state properties of $[Fe(tpen)](ClO_4)_2$ are so well-determined, we used this complex as our prototype. As discussed above, experimental data like those in Figures 2 and 3 indicate that the $^5T_2$ state appears within some tens of picoseconds, while the lack of luminescence suggests that any CT state is depopulated much faster than that. We examined the shortest time behavior with subpicosecond transient absorption. Figure 6 is a plot of Δ(OD) versus time for a 1.52×10^{-3} M aqueous solution of $[Fe(tpen)](ClO_4)_2$ measured in increments of 1 ps following excitation at 314 nm with a ~500-fs laser pulse. This kinetic trace was taken at 425 nm, but the observed kinetics were found to be independent of probe wavelength throughout the range of 385–510 nm. It can be seen that the kinetics are essentially time-independent on this time scale. Since this trace overlaps temporally with the picosecond data in Figure 3, it is clear that there are no additional kinetics to be observed in the time window bridging the picosecond and subpicosecond experiments, i.e., only one state is kinetically important from the microsecond through the picosecond regimes. It is also apparent from the data in Figure 6 that the rise of the transient bleach is very rapid, even on this short timescale.

This fact is more clearly evident in Figure 7, a plot of Δ(OD) versus time of data collected in increments of 167 fs over the first 10–15 ps following $^1MLCT \leftarrow {}^1A_1$ excitation. These data clearly indicate that the $^5T_2$ state in $[Fe(tpen)](ClO_4)_2$ is formed within the instrument response time of the subpicosecond experiment, that is, in ≤700 fs. The aforementioned lifetime estimate of ≤10 ps for the initially populated ^1MLCT state can now be revised. We conclude that the risetime of the $^5T_2$ state is *significantly less than 1 ps* and is very likely less than ~700 fs. This reduction of the upper limit of the lifetime of the ^1MLCT state by more than an order of magnitude has important mechanistic consequences with regard to the formation of the $^5T_2$ state, and these consequences will be discussed below.

Generalizing the Photophysics of Low-Spin Fe^{II} Systems. In order to ascertain how general the results obtained for the $[Fe(tpen)](ClO_4)_2$ system are, we examined aqueous solutions of several Fe^{II} polypyridyl complexes: $[Fe(tptn)](ClO_4)_2$, $[Fe(t\text{-}tpchxn)](ClO_4)_2$, $[Fe(bpy)_3](ClO_4)_2$, $[Fe(phen)_3](ClO_4)_2$, and $[Fe(terpy)_2](ClO_4)_2$. The ligands bpy, phen, and terpy are the well-known ligands 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′,6′,2″-terpyridine, respectively. The other two complexes have hexadentate ligands related to tpen.



(tptn)



(*t*-tpchxn)

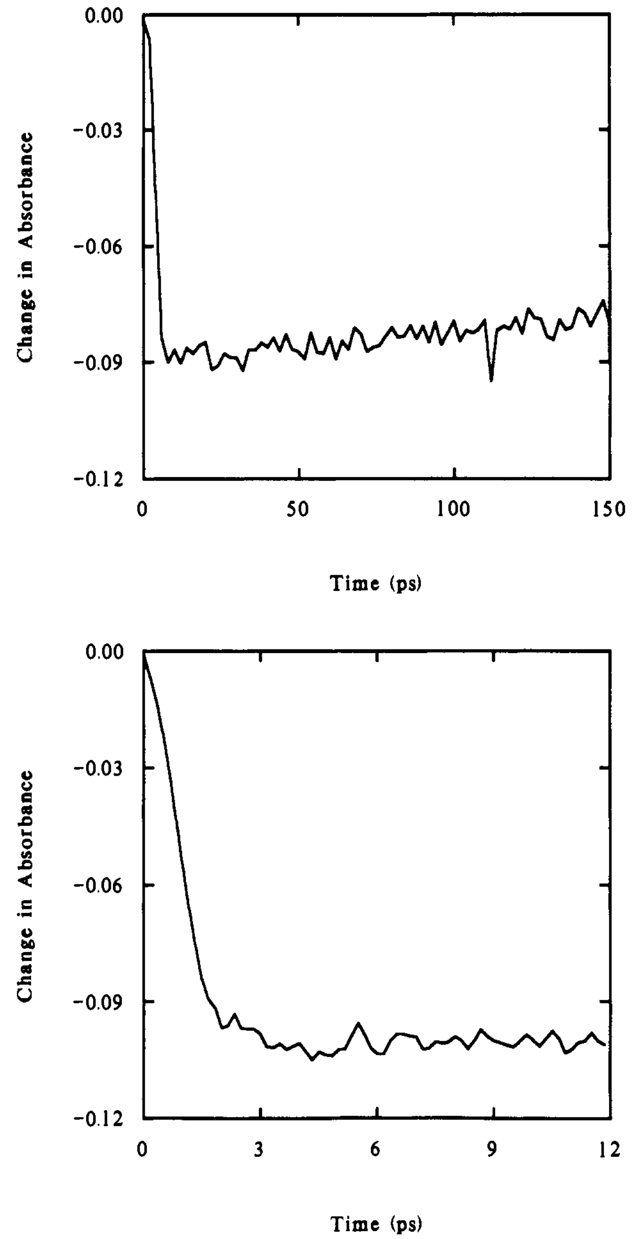


Figure 8. Plot of the change in absorbance versus time for aqueous solutions of $[Fe(tptn)](ClO_4)_2$ monitored at 439 nm following excitation at 314 nm with a ~500-fs laser pulse. Upper panel: data collected in increments of 1 ps (1.66×10^{-3} M). Lower panel: data collected in increments of 167 fs (1.49×10^{-3} M).

Transient kinetics relating to the $^5T_2 \rightarrow {}^1A_1$ relaxation of $[Fe(tptn)](ClO_4)_2$ have been presented in another paper.[20] The excited-state lifetime at room temperature in H_2O is $\tau_{obs} = 1.6 \pm 0.1$ ns, giving a $^5T_2 \rightarrow {}^1A_1$ relaxation rate constant of $k = (6.25 \pm 0.4) \times 10^8\ s^{-1}$ ($K_{eq} \ll 1$). Subpicosecond experiments were performed on an aqueous solution of $[Fe(tptn)](ClO_4)_2$ from 0 to 200 ps in 1-ps steps and from 0 to 15 ps in 167-fs steps; these data are presented as plots of Δ(OD) versus time in Figure 8. It is clear from the data, particularly in the lower panel of Figure 8, that the results found for $[Fe(tptn)](ClO_4)_2$ are identical to those obtained for $[Fe(tpen)](ClO_4)_2$ with respect to the lack of a risetime associated with the formation of the $^5T_2$ state. Thus, in $[Fe(tptn)](ClO_4)_2$ the $^5T_2$ state is formed in ≤700 fs following $^1MLCT \leftarrow {}^1A_1$ excitation at 314 nm.

The compound $[Fe(t\text{-}tpchxn)](ClO_4)_2$ was examined on the subpicosecond time scale and exhibited the same behavior as the other members of the tpen series, i.e., no risetime for the $^5T_2$ state. The lack of a risetime for $[Fe(t\text{-}tpchxn)](ClO_4)_2$ deserves special comment since it alone among all Fe^{II} complexes studied exhibits biphasic kinetics for the $^5T_2 \rightarrow {}^1A_1$ relaxation.[26] A plot of change

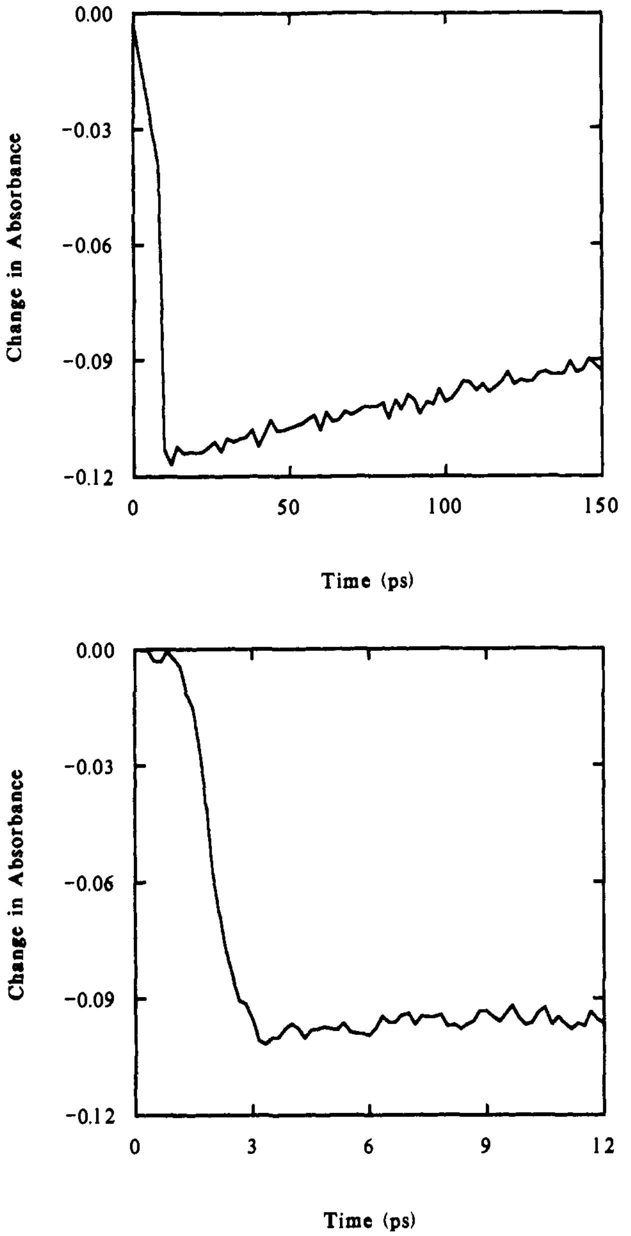


Figure 9. Plot of the change in absorbance versus time for aqueous solutions of $[Fe(bpy)_3](ClO_4)_2$ following excitation at 314 nm with a ~500-fs laser pulse. Upper panel: data collected in increments of 1 ps (1.52×10^{-3} M). Lower panel: data collected in increments of 167 fs (1.40×10^{-3} M).

in absorbance at early times is given in the supplementary material. It is clear that the $^5T_2$ state is formed in ≤700 fs, as observed for the other complexes. One might have expected to see more complex kinetics associated with the formation of the $^5T_2$ state in this system. It remains possible that this compound (or any other) might exhibit additional features if it were studied on even faster time scales so that the kinetics of ^{1}MLCT → $^5T_2$ conversion could be measured directly.

In a separate study,[20] we redetermined the $^5T_2 \rightarrow {}^1A_1$ relaxation data for aqueous solutions of $[Fe(bpy)_3](ClO_4)_2$, $[Fe(phen)_3](ClO_4)_2$, and $[Fe(terpy)_2](ClO_4)_2$ using the picosecond laser system described in this work. For the first two of these compounds, "textbook-like" relaxation profiles were obtained. The lifetime of the $^5T_2 \rightarrow {}^1A_1$ conversion was found to be 676 ± 30 ps at room temperature for $[Fe(bpy)_3](ClO_4)_2$ and 685 ± 30 ps for $[Fe(phen)_3](ClO_4)_2$. Data were reported[20] for $[Fe(terpy)_2](ClO_4)_2$ in H_2O in the range of 190–239 K, where, for example, the lifetime is 23 ± 2 ns at 190 K. Subpicosecond time-resolved kinetic studies reveal that for these three compounds there is again no indication of any risetime for the formation of the $^5T_2$ state distinguishable from the instrument-limited response time of the apparatus. Plots of change in absorbance versus time from 0 to 200 ps (1-ps steps) and from 0 to 15 ps (167-fs steps) are presented in Figure 9 for $[Fe(bpy)_3](ClO_4)_2$, and figures showing the data for the other two compounds are available in the supplementary material.

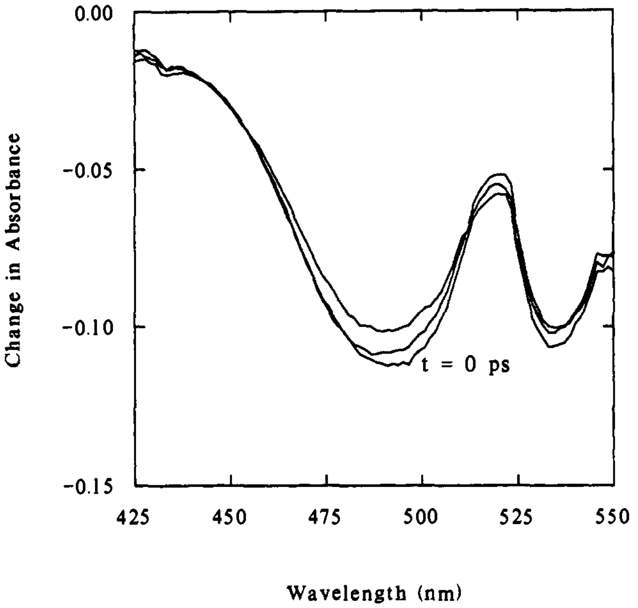


Figure 10. Transient absorption spectra for aqueous $[Fe(bpy)_3](ClO_4)_2$ following subpicosecond excitation at 314 nm. The time delay between each spectrum is approximately 20 ps.

In Figure 10 is presented a plot of transient absorption spectra of an aqueous solution of $[Fe(bpy)_3](ClO_4)_2$ at several time increments following excitation. The data indicate a marked bleach at approximately 495 and 540 nm with no excited-state absorption in the 400–450-nm range. These data are particularly interesting since Braterman[27] et al. have recently published a spectroelectrochemical study of the above three complexes in DMF solution. Upon one-electron reduction of $[Fe(bpy)_3]^{2+}$, the absorption spectrum of $[Fe(bpy^-)(bpy)_2]^+$ shows a transient absorption around 365 nm which tails into the 425–450-nm region and as well an absorption band around 550 nm. Both of these observations contrast with the excited-state absorption spectra of photoexcited $[Fe(bpy)_3]^{2+}$ and reaffirm that the MLCT chromophore is not present at any time ≥700 fs following excitation at 314 nm. The spectroelectrochemical data are less useful in the case of $[Fe(phen)_3]^{2+}$ since the singly-reduced complex exhibits a marked attenuation around 500 nm, where the maximum of the MLCT transition is centered. However, the available data for $[Fe(terpy)_2]^{2+}$ nicely support the notion that terpy$^-$ is not observed on the subpicosecond timescale. The singly-reduced complex $[Fe(terpy^-)(terpy)]^+$ in DMF exhibits a strong absorption ($\pi \rightarrow \pi^*$ of terpy$^-$, $\epsilon \approx 8000$ M^{-1} cm^{-1}) at around 600 nm. Subpicosecond transient absorption measurements were attempted in the probe wavelength region from 520 to 620 nm. *No transient spectrum was observed at any wavelength $\lambda > 550$ nm.* Although spectral shifts are possible on changing from DMF to H_2O, it is not likely that the spectra could have been shifted out of the probe region. It seems clear that subpicosecond formation of the $^5T_2$ ligand-field state following $^1\text{MLCT} \leftarrow {}^1A_1$ excitation is a general characteristic of low-spin Fe^{II} polypyridyl complexes.

Mechanistic Implications. The lower limit of $k = 1.4 \times 10^{12}$ s^{-1} set by the subpicosecond data for the rate of formation of the $^5T_2$ state after excitation into the ^{1}MLCT state is certainly consistent with the report by Bergkamp et al.[16] of 100% quantum

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(26) McCusker, J. K.; Toftlund, H.; Rheingold, A. L.; Hendrickson, D. N., submitted for publication.

(27) Braterman, P. S.; Song, J.-l.; Peacock, R. D. *Inorg. Chem.* **1992**, *31*, 555.

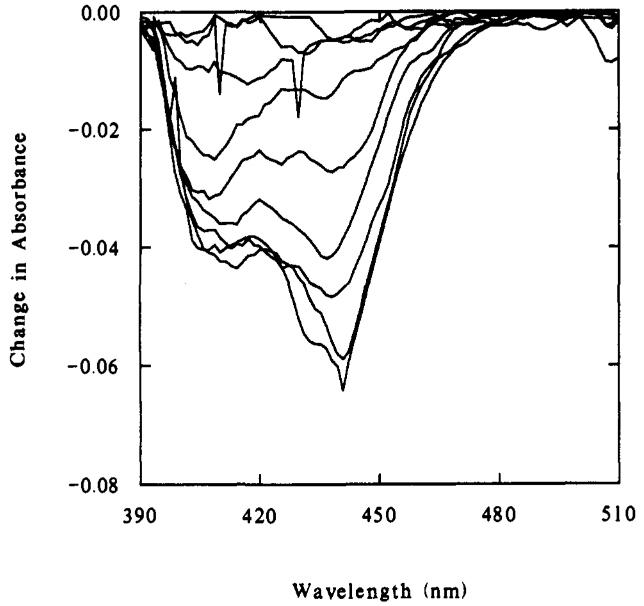

Figure 11. Plot of transient absorption spectra of [Fe(tpen)]$(ClO_4)_2$ following excitation at 314 nm. The time interval between each successive spectrum is approximately 333 fs. The data suggest that the $^5T_2$ state is thermally relaxed within approximately 3 ps following $^1MLCT \leftarrow {}^1A_1$ excitation. See text for details.

yield, since any competing process would require a rate constant on the order of 10^{12} s^{-1}. The question now is the following: given this lower limit on the rate of formation of the high-spin state and 100% quantum efficiency, what can be said about the mechanism of ^1MLCT excited-state decay?

Consider first the conventional picture of transition-metal photophysics. This assumed that the fastest process following excited-state formation is vibrational relaxation in the excited state to generate the "thexi" state (thermally-equilibrated excited state) introduced by Adamson.[28] The next process in terms of timescale is considered to be internal conversion, that is, decay within a particular spin manifold, for which decay is spin-allowed. Intersystem crossing (ISC) is spin-forbidden and, therefore, the slowest process. Given this picture, the excited-state decay following $^1MLCT \leftarrow {}^1A_1$ excitation would occur by vibrational cooling in the ^1MLCT state, followed by internal conversion to either the $^1T_1$ state or, if the $^1T_2$ state lies below the ^1MLCT state, to the $^1T_2$ state followed by internal conversion to the $^1T_1$ state. Vibrational cooling in the $^1T_1$ state would occur next and be followed by intersystem crossing to either the $^3T_1$ or $^3T_2$ states (both lie below the $^1T_1$ state). Vibrational cooling and internal conversion, if necessary, would produce the thexi form of the lowest triplet prior to intersystem crossing to the $^5T_2$ state of the $S = 2$ manifold. The molecule would then thermalize in the high-spin state prior to relaxation back to the $^1A_1$ ground state.

Based on the fact that the $^5T_2$ state is formed in ≤700 fs, we believe that *the "conventional" decay scheme following* $^1MLCT \leftarrow {}^1A_1$ *excitation cannot be accurate for low-spin* Fe^{II} *complexes.* Our suggestion is not so much that the time is too short for all the steps to occur in neat succession but more that one should not even distinguish the processes as separable events. The separation of coordinates in the Born–Oppenheimer approximation is not well justified. Photoexcitation produces a strongly mixed state having energy that exceeds not only the minima of all the lower states in Figure 12 but also the crossings between them. The nuclear motions invoked to discuss vibrational reorganization and cooling are probably coincident with changes in the electronic wave function that would distinguish various CT and LF states, and torsional rearrangement of the spatial wave function is intimately coupled to spin flips. As the molecule loses energy to its surroundings, it finds itself in the potential minimum associated with $^5T_2$ but it does not sample other potential surface minima along the way.

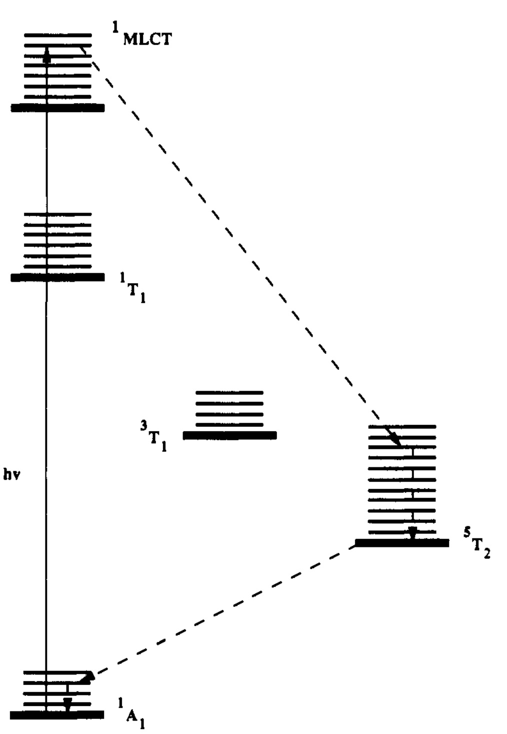

Figure 12. Proposed mechanism for $^1A_1 \leftrightarrow {}^5T_2$ interconversion following $^1MLCT \leftarrow {}^1A_1$ excitation of low-spin Fe^{II} polypyridyl complexes.

Several workers have studied vibrational relaxation in dissolved organic molecules.[29a–c] For example, Hochstrasser and co-workers have recently reported[29c] a two-color time-resolved infrared study of N_3^- in which vibrational relaxation in the ground electronic state was found to occur with a relaxation time on the order of ~3 ps. The time scale for complete vibrational relaxation is thus typically several picoseconds for room temperature liquid solutions. There have been markedly fewer studies on vibrational energy transfer/relaxation for photoexcited transition-metal systems.[29d–f] Hopkins and co-workers have studied[29e] the vibrational dynamics of $Cr(CO)_6$ in *n*-hexane with time-resolved Raman spectroscopy. A 381-cm^{-1} band assigned to a metal–ligand vibration was found to relax with $\tau = 145 \pm 25$ ps following photodissociation of CO. More recently, Zhang and Harris have reported[29f] on the photodissociation of $Mn_2(CO)_{10}$. Vibrationally hot $Mn(CO)_5$ was observed to relax within 10 ps, whereas $Mn_2(CO)_9$ exhibited biphasic vibrational relaxation with lifetimes of ca. 10–15 and 145–170 ps, depending somewhat on the identity of the solvent. However, no *general* patterns of behavior have yet been established for metal complexes. In an absolute sense, a lower limit to vibrational relaxation times is set by the period of pertinent vibrations. Using the metal–ligand coordinate as a typical (not the lowest-frequency) motion,[30] we note that the Fe–N stretching frequency for low-spin Fe^{II} and Fe^{III} pyridyl-based ligand systems is approximately 380 cm^{-1}.[31] This corresponds to a vibrational

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[28] *Concepts in Inorganic Photochemistry*, Adamson, A.; Fleischauer, P., Eds.; Wiley-Interscience: New York, 1976.

[29] (a) Todd, D. C.; Jean, J. M.; Rosenthal, S. J.; Ruggiero, A. J.; Yang, D.; Fleming, G. R. *J. Chem. Phys.* **1990**, *93*, 8658 and references therein. (b) Sension, R. J.; Repinec, S. T.; Hochstrasser, R. M. *J. Chem. Phys.* **1990**, *93*, 9185 and references therein. (c) Owrutsky, J. C.; Kim, Y. R.; Li, M.; Sarisky, M. J.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1991**, *184*, 368. (d) Beckerle, J. D.; Casassa, M. P.; Cavanagh, R. R.; Heilweil, E. J.; Stephenson, J. C. *Chem. Phys.* **1992**, *160*, 487 and references therein. (e) Yu, S.-C.; Xu, X.; Lingle, R., Jr.; Hopkins, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 3668. (f) Zhang, J. Z.; Harris, C. B. *J. Chem. Phys.* **1991**, *95*, 4024.

[30] The metal–ligand coordinate is used here for convenience, even though lower-frequency modes may be involved as well. Since the lower-frequency modes will have longer vibrational periods, their inclusion would only serve to strengthen the arguments to follow.

[31] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986.

period of ~88 fs. Coupling to solvent necessary to dissipate energy (~10000 cm^{-1} worth of energy) is presumably weaker than this.

If thermal equilibration requires a picosecond or more, we might expect to see some evidence in the transient spectrum. Figure 11 presents time slices of the absorption spectra for [Fe(tpen)](ClO$_4$)$_2$ in increments of 333 fs corresponding to the kinetic data presented in Figure 7. It can be seen that the spectra are evolving in time. First to appear is a transient bleaching in the blue end of the probe region (λ = 410 nm) that eventually gives way to a stronger bleach at approximately 440 nm. The profile of the last few spectra are consistent with expectations from the variable-temperature optical spectra discussed above with a pronounced drop in spectral intensity on the low-energy side of the charge-transfer band upon formation of the high-spin state. The evolution of the spectra over the first 1–2 ps are "contaminated" in the original data by a spectral shift from blue to red that is the result of group velocity dispersion. However, the spectra in Figure 11 have been corrected for this, and we believe that the spectral shift displayed in Figure 11 is not a GVD artifact. It would be difficult to draw any inferences regarding specific modes of vibrational relaxation from broad-band optical spectra. However, what the transient spectra do indicate is that thermalization of the $^5T_2$ state appears to be complete within ~2–3 ps.

Using all of the above data and the fact that the vibrational period of a high-spin Fe^{II}–N bond is ~145 fs,[31] we can now present our picture of the $^1A_1 \leftrightarrow {}^5T_2$ interconversion process as it occurs following ^{1}MLCT ← $^1A_1$ excitation of low-spin Fe^{II} polypyridyl complexes. The proposed mechanism is presented in Figure 12. We assert that, since the $^5T_2$ state is formed in ≤700 fs following initial excitation in the ^{1}MLCT state, vibrational cooling in the initially excited state or any intermediate *does not* occur. Rather, we believe that population of the $^5T_2$ state occurs with 100% efficiency via "direct" ^{1}MLCT → $^5T_2$ conversion at or near the Franck–Condon configuration of the charge-transfer state. We suspect that any charge-transfer character is lost in tens of femtoseconds. Nor is there reason to invoke intermediate $S = 1$ states (either $^3T_1$ and/or $^3T_2$) in the sense of thexi states which are passed through in order to form the $^5T_2$ state, at least in liquid solution at ambient conditions. The fact that the $^5T_2$ state appears to be completely relaxed within 2–3 ps suggests that, in addition to being formed very rapidly, vibrational cooling in the $^5T_2$ state is extremely fast. One may propose that over this time a mixed state is evolving through different admixtures of (^{1}T, ^{3}T, ^{5}T) character, but one should not retain classical thexi states. The exact mechanism for vibrational relaxation in the $^5T_2$ state is not clear, but it seems likely that the solvent plays a vital role in the kinetics of $^5T_2$ formation insofar as providing a heat sink for the rapid dissipation of vibrational energy. The issue of whether or not the solvent is involved to an even greater extent, i.e., completely controlling the kinetics of the overall process,[32] can only be addressed with additional experiments on shorter timescales.

Concluding Comments

The data presented above have established several points: (1) the $^5T_2$ state is the excited state that is formed following photoexcitation of low-spin Fe^{II} complexes; (2) the $^5T_2$ state is formed in ≤700 fs following ^{1}MLCT ← $^1A_1$ excitation of low-spin Fe^{II} complexes; and (3) the mechanism of $^5T_2$ formation likely occurs via "direct" ^{1}MLCT → $^5T_2$ conversion at or near the Franck–Condon configuration for the ^{1}MLCT ← $^1A_1$ excitation. Apparently, the rate of intersystem crossing is at least equal to the rates for both internal conversion and vibrational relaxation. There is no observation in room temperature liquid solution requiring that states in the $S = 1$ manifold be directly involved in the spin conversion process as intermediates in the conventional sense. The time scale on which the $^5T_2$ state is formed clearly prohibits the involvement of any additional, well-defined excited states other than the ^{1}MLCT and $^5T_2$ states. By "well-defined" we refer to a state which exists long enough for the wavepacket to be localized near a potential minimum. We are accustomed to thinking in terms of very well-defined potential surfaces, but in doing so we are usually considering the energetics of systems near potential minima. The spin-state conversion process under consideration corresponds to a highly excited configuration of the system, and it is very unclear what the nature of the anharmonic potentials are under these conditions. It is possible that the $S = 0$, $S = 1$, and $S = 2$ states are all highly mixed in these excited states relative to their ground-state descriptions and that the "spin-forbidden" ^{1}MLCT → $^5T_2$ merely represents conversion along the steepest energetic slope of the potential surface, i.e., direct conversion to the lowest-energy excited state. This represents a significant change in the way one must think about how photoexcited transition-metal complexes undergo electronic relaxation. While concepts such as spin conservation and energy gap are useful in some contexts, they are not necessarily correct for describing the excited-state properties of metal complexes.

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Supplementary Material Available: Four figures showing plots of change in absorbance versus time from 0 to 200 ps (1-ps steps) and from 0 to 15 ps (167-fs steps) for [Fe(phen)$_3$](ClO$_4$)$_2$ and [Fe(terpy)$_2$](ClO$_4$)$_2$ in H$_2$O, from 0 to 3 ns for [Fe(tptn)](ClO$_4$)$_2$ in aqueous solution, and from 0 to 15 ps (167-fs steps) for [Fe(t-tpchxn)](ClO$_4$)$_2$ (5 pages). Ordering information is given on any current masthead page.

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[32] For a recent review of dynamical solvent effects on electron transfer, see: Weaver, M. J. *Chem. Rev.* **1992**, *92*, 368.