

# Photochemically-induced Perturbation of the $^1A \rightleftharpoons ^5T$ Equilibrium in $Fe^{II}$ Complexes by Pulsed Laser Irradiation in the Metal-to-ligand Charge-transfer Absorption Band

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Rapid perturbation of the  $^1A \rightleftharpoons ^5T$  equilibrium in several  $Fe^{II}$  complexes occurs upon irradiation in the metal-to-ligand charge-transfer absorption region of the low-spin state, providing primary evidence for the formation of a  $^5T$  ligand field state from the initially populated charge-transfer state and permitting study of the dynamics of the spin change in a wide range of solvents.

The recent literature contains frequent references to the significance, in the context of photophysics and electron-transfer, of spin-state interconversions in transition metal complexes,<sup>1,2</sup> especially of  $Fe^{II}$  and  $Fe^{III}$ . We now report the first examples of the photochemically-induced perturbation of the equilibrium between  $^1A$  and  $^5T$  ligand field (LF) states of some  $Fe^{II}$  complexes in solution.

Nanosecond laser irradiation<sup>3</sup> of the complexes<sup>4†</sup>  $Fe(biz)_3^{2+}$ ,  $Fe(ppa)_2^{2+}$ , and  $Fe(pyimH)_3^{2+}$  in solution<sup>‡</sup> at 530 nm, a wavelength which lies within the metal-to-ligand charge-transfer (MLCT) ( $t_{2g} \rightarrow \pi^*$ ) absorption bands of the low-spin forms, resulted in a ground state depletion, occurring within the pulse rise-time. The ground state recovery times ( $\tau_{GSR}$ ) varied with temperature but were independent of monitoring  $\lambda$  (Table 1) and of concentration over a 5-fold range. Argon- or air-saturated solutions yielded identical results.<sup>‡</sup> The data are summarised in Table 1. Also shown are the relaxation times,  $\tau_{AD}$ , for  $Fe(ppa)_2^{2+}$  from transients monitored in the  $\lambda$  range 270–330 nm where an absorbance increase was observed, also within the pulse rise-time, followed by a return to the ground state level. An isosbestic point for this system was observed at ca. 330 nm. Intense ground state absorption

at  $\lambda < 340$  nm prevented measurements in this region for the other two complexes.

The three complexes exhibit a  $^1A \rightleftharpoons ^5T$  spin equilibrium in solution, as shown by Wilson *et al.*<sup>2</sup> for  $Fe(pyimH)_3^{2+}$  and in the present work, for the biz and ppa complexes, from temperature-dependent magnetic moments by means of the Evans method.<sup>1,5</sup> Pronounced thermochromism observed in  $Fe(biz)_3^{2+}$  solutions provided further evidence for the equilibrium in this complex. We assign the ground state recovery observed for all three complexes, following the extremely rapid depletion induced by the laser pulse, to relaxation of the spin-state equilibrium. The assignment is strongly supported by the absorbance transients detected in  $Fe(ppa)_2^{2+}$  solutions in the range 270–330 nm, attributable to ligand-centred  $\pi \rightarrow \pi^*$  transitions of the  $^5T$  isomer,<sup>6</sup> and by the close agreement between  $\tau_{GSR}$  and  $\tau_{AD}$  (Table 1). The isosbestic point at 330 nm is a further indication that the assignment is correct. The apparent absence of  $O_2$ -enhancement of the decays in  $Fe(ppa)_2^{2+}$  and  $Fe(pyimH)_3^{2+}$  lends additional support to the conclusions. The most significant evidence is provided by the results for  $Fe(pyimH)_3^{2+}$  where  $\tau_{GSR} = 50 \pm 3$  ns at 296 K is seen to be in excellent agreement with  $\tau = 48 \pm 9$  ns at 295 K for the singlet  $\leftrightarrow$  quintet interconversion in this complex measured by Wilson *et al.*<sup>2</sup> using the quite independent laser Raman temperature-jump technique. The temperature-dependent  $\tau_{GSR}$  data in the present work together with the published<sup>2</sup> thermodynamic data permit calculation of the activation parameters, not previously available for this system. For the singlet(1)  $\rightarrow$  quintet(5) transition the data yield:  $\Delta H_{15}^\ddagger = 27 \pm 3$  kJ mol<sup>-1</sup>,  $\Delta S_{15}^\ddagger = -12 \pm 8$  J K<sup>-1</sup> mol<sup>-1</sup>. They are in the range observed<sup>7</sup> for other  $Fe^{II}$  spin-state transitions in solution.

The laser irradiation wavelength (530 nm) lies within the intense CT( $t_{2g} \rightarrow \pi^*$ ) absorption band of these complexes, and perturbation of the  $^1A \rightleftharpoons ^5T$  equilibrium occurs within the shortest laser pulse duration used. To our knowledge, the present observations provide the first direct evidence of the formation of a LF state ( $^5T$ , assuming  $O_h$  symmetry) from an initially populated CT state. A CT  $\rightarrow$  LF intersystem crossing (ISC) rate  $\geq 10^9$  s<sup>-1</sup> is implied by our results which therefore support recent proposals<sup>8,9</sup> of strong coupling between CT and LF excited states of low-spin  $Fe^{II}$  complexes and a suggested<sup>6,10</sup> ISC rate of ca.  $10^{11}$  s<sup>-1</sup>.

The photochemical perturbation approach in the present work permits study of the spin interconversion dynamics in a wider range of solvents<sup>§</sup> than is generally possible for either time-<sup>1,2</sup> or frequency-<sup>1,7</sup> domain chemical relaxation techniques. Activation volumes for the spin-state change also become technically more accessible.

**Table 1.** Selected relaxation times<sup>a</sup> for  $Fe^{II}$  complexes at various temperatures.

Complex <sup>b</sup>	$Fe(biz)_3^{2+}$		$Fe(ppa)_2^{2+}$		$Fe(pyimH)_3^{2+}$	
	MeCN		H <sub>2</sub> O		MeCN(20%)–MeOH <sup>c</sup>	
Solvent	$\tau_{GSR}/ns$	$T/K$	$\tau_{GSR}/ns$	$T/K$	$\tau_{GSR}/ns$	$T/K$
	580	220	185	274	239	245
	295	235	135	281	168	257
	182	247	115	289	162	261
	134	256	102	296	128	266
	98	265	91	307	86.5	277
	27	288	67	318	54.5	290
			115 <sup>d</sup>	291	49	296
			105 <sup>d</sup>	293		

<sup>a</sup>  $\tau_{GSR}$  values, measured at a number of monitoring wavelengths in the ranges 410–600 nm for  $Fe(biz)_3^{2+}$  and 360–575 nm for  $Fe(ppa)_2^{2+}$  and  $Fe(pyimH)_3^{2+}$ , were independent of  $\lambda_{mon}$  within the experimental errors in each case. <sup>b</sup> Concentration range ca.  $10^{-3}$ – $10^{-4}$  mol dm<sup>-3</sup>. <sup>c</sup> Chosen for direct comparison with data in ref. 2.  $\tau_{GSR}$  is also measurable in acetone. Full details will be published later. <sup>d</sup>  $\tau_{AD}$  from absorbance decay monitored at  $\lambda$  300 nm.

† Ligand abbreviations: biz = 2,2'-bi-1,4,5,6-tetrahydropyrimidine; ppa = *N*-(2-pyridylmethyl)picolinamide; pyimH = 2-(2-pyridylimidazole).

‡ Solutions of the extremely  $O_2$ -sensitive complex  $Fe(biz)_3(CIO_4)_2$  were prepared *in vacuo*, in dry, degassed MeCN. Solutions of  $Fe(ppa)_2(CIO_4)_2$  and  $Fe(pyimH)_3(BPh_4)_2$  were freshly prepared in H<sub>2</sub>O and MeCN(20%)–MeOH, respectively. PyimH and its  $Fe^{II}$  complex were synthesized as in ref. 2.

§ We have also measured  $\tau_{GSR}$  for  $Fe(pyimH)_3^{2+}$  in MeCN and Me<sub>2</sub>CO, for  $Fe(biz)_3^{2+}$  in CH<sub>2</sub>Cl<sub>2</sub> and for  $Fe(ppa)_2^{2+}$  in MeCN and MeOH.

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### References

- 1 R. A. Binstead, J. K. Beattie, T. G. Dewey, and D. H. Turner, *J. Am. Chem. Soc.*, 1980, **102**, 6442 and references therein.
  - 2 K. A. Reeder, E. V. Dose, and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1071.
  - 3 An  $\text{Nd}^{3+}$  laser was used, with pulse energy of *ca.* 10 mJ and variable pulse duration, 5–25 ns; see G. Lockwood, J. J. McGarvey and R. Devonshire, *Chem. Phys. Lett.*, 1982, **86**, 127.
  - 4 The complexes  $\text{Fe}(\text{biz})_3(\text{ClO}_4)_2$  and  $\text{Fe}(\text{ppa})_2(\text{ClO}_4)_2$  were first prepared and their solid state magnetic properties described by Nelson *et al.*: M. G. Burnett, V. McKee, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1492 (biz); M. J. Boylan, S. M. Nelson, and F. A. Deeney, *J. Chem. Soc. A*, 1971, 976 (ppa).
  - 5 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
  - 6 C. Creutz, M. Chou, T. L. Netzel, M. Okumura, and N. Sutin, *J. Am. Chem. Soc.*, 1980, **102**, 1309.
  - 7 J. K. Beattie, R. A. Binstead, and R. J. West, *J. Am. Chem. Soc.*, 1978, **100**, 3044.
  - 8 A. J. Street, D. M. Goodall, and R. C. Greenhow, *Chem. Phys. Lett.*, 1978, **56**, 326.
  - 9 A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley, and M. W. Windsor, *Chem. Phys. Lett.*, 1976, **37**, 199.
  - 10 See also J. Ternner, T. G. Spiro, N. Nagumo, M. F. Nicol, and M. A. El-Sayed, *J. Am. Chem. Soc.*, 1980, **102**, 3238.
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