

Dynamics and Mechanism of Spin-State Interconversion in Transition Metal Complexes

James K. McCusker

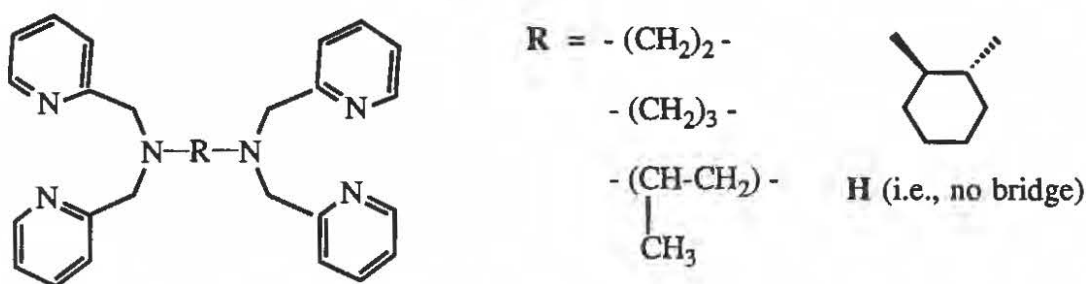
Final Seminar

July 7, 1992

The study of excited electronic states in chemical systems represents a vast area of research in inorganic chemistry [1]. Intersystem crossing, the mechanism by which chemical systems can alter their total net unpaired spin density, is a central feature of most processes that involve excited states of transition metal complexes. In few other subsets of chemical systems is the study of intersystem crossing more accessible than in spin-crossover complexes. A spin-crossover molecule is one that, by virtue of having a ligand-field splitting (Δ) that is comparable to the effective spin-pairing energy (P), has its lowest-lying excited electronic state within thermal accessibility of the ground state (i.e., $|\Delta - P| \approx k_B T$). For complexes of Fe^{II} , this means that a low-spin 1A_1 compound can be thermally excited to the high-spin 5T_2 excited state. This interconversion represents a $\Delta S = 2$ intersystem crossing that has attracted considerable interest for a variety of reasons over the last two decades [2].

Although there is a considerable body of work in the spin-crossover literature pertaining to effects in the solid state (e.g., cooperativity) [3], there has been surprisingly little effort aimed at understanding the intramolecular factors important in the spin-crossover transformation. Given the large change in metal-ligand bond length that accompanies the spin-crossover transition, researchers have assumed that the symmetric breathing mode of the first coordination sphere is coupled to spin-state interconversion. However, certain experimental [4] and theoretical [5] studies suggest that torsional modes are better candidates for effecting spin state changes in metal complexes.

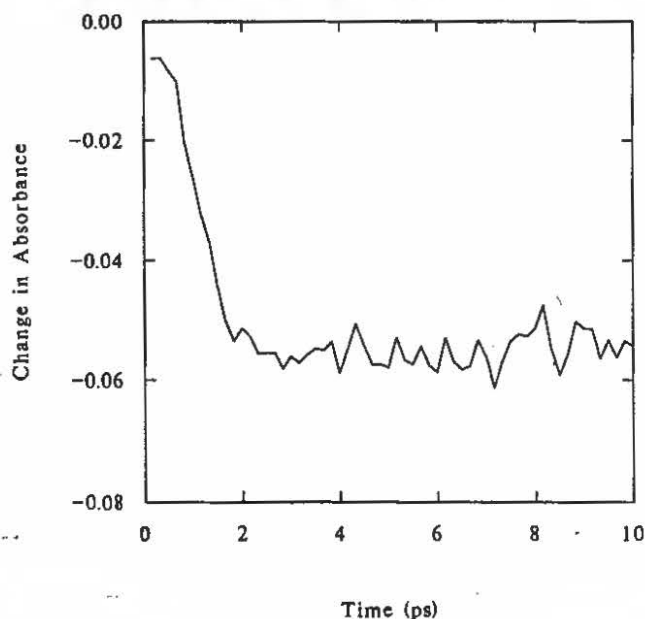
Our work in a general sense is geared at examining the molecular reaction coordinate for spin-crossover. We are particularly interested in the role of low-frequency torsional modes in controlling the kinetics of spin-state interconversion. To study this, we have examined a series of molecules with ligands having the general form



The nature of the backbone R is varied to yield a systematic variation in molecular geometry with respect to torsional modes in the molecule. Variable-temperature kinetic data from nano-second time-resolved laser photolysis studies establish an empirical correlation between molecular flexibility in this series and the activation energy for $^5T_2 \rightarrow ^1A_1$ relaxation. Specifically, the data indicate that the more labile the molecule is along torsional coordinates, the smaller the barrier is for spin-crossover. In addition, examination of the intrinsic rates of spin-state interconversion suggests that conformational preferences of the ligand framework may influence the kinetics of spin-state interconversion by modulating the extent to which the molecule proceeds along the reaction coordinate.

The importance of low-frequency modes is further supported by theoretical modeling of the ${}^5T_2 \longrightarrow {}^1A_1$ relaxation. Since in a formal sense an analogy can be drawn between the spin-crossover transition and unimolecular electron transfer, we can apply electron transfer theory to our systems. Fitting rate data for the ${}^5T_2 \longrightarrow {}^1A_1$ process in the representative molecule $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$ to classical [6], semi-classical [7], and quantum-mechanical [8] theories of electron transfer gave *identical* results. The convergence of the classical and quantum-mechanical solutions implies that the quantum nature of the vibrational mode coupled to spin-state interconversion is not manifested in the 160 - 300 K temperature range examined. This fact combined with the fitted value of ca. 65 cm^{-1} for the normal-mode frequency is inconsistent with the coupling to a ca. 300 cm^{-1} metal-ligand stretching mode, and is strong evidence that low-frequency modes are very influential in determining the kinetics of spin-state interconversion.

In addition to ${}^5T_2 \longrightarrow {}^1A_1$ relaxation, we also examined the mechanism of photo-induced formation of the high-spin ligand-field state following ${}^1\text{MLCT} \longleftarrow {}^1A_1$ excitation. Definitive evidence that the long-lived excited state formed following photolysis is the 5T_2 state was obtained from the observation of a transient bleach-to-transient absorbance transition coincident with the known ${}^1A_1/{}^5T_2$ isosbestic point of the system. The data below were collected on $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$ in H_2O following ${}^1\text{MLCT} \longleftarrow {}^1A_1$ excitation with a $\approx 500 \text{ fs}$ laser pulse. The lack of a measurable risetime for the 5T_2 state indicates that the net $\Delta S = 2$ intersystem



crossing occurs at a rate of $\geq 1.5 \times 10^{12} \text{ s}^{-1}$. The extremely short time scale of the spin conversion precludes the involvement of any thermalized excited states other than the 5T_2 state. Thus, excited state decay in Fe^{II} complexes *does not* follow the widely-believed scheme that scales the rates of excited state processes as $k_{\text{vib}} > k_{\text{ic}} > k_{\text{isc}}$; rather, we observe that $k_{\text{jsc}} > (k_{\text{vib}}, k_{\text{ic}})$. We postulate that formation of the 5T_2 state occurs via direct ${}^1\text{MLCT} \longrightarrow {}^5T_2$ conversion from the Franck-Condon state of the system following excitation, and that this gross "disregard" of spin-selection rules is likely a very general characteristic of excited-state dynamics in transition metal complexes.

References

1. (a) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; John Wiley & Sons: New York, 1988.
- (b) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979.
- (c) *Concepts in Inorganic Photochemistry*; Adamson, A. and Fleischauer, P., Eds.; Wiley-Interscience: New York, 1975.
- (d) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.
2. (a) Martin, R. L.; White, A. H. *Trans. Met. Chem.* **1968**, *4*, 113.
- (b) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293.
- (c) Gütlich, P. *Struc. Bond. (Berlin)* **1981**, *44*, 83.
- (d) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.
- (e) Bacci, M. *Coord. Chem. Rev.* **1988**, *86*, 245.
- (f) Maeda, Y.; Takashima, Y. *Comments Inorg. Chem.* **1988**, *7*, 41.
- (g) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 1.
- (h) Toftlund, H. *Coord. Chem. Rev.* **1989**, *94*, 67.
- (i) König, E. *Struc. Bond. (Berlin)* **1991**, *76*, 51.
- (j) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527.
- (k) Gütlich, P.; Hauser, A. *Pure Appl. Chem.* **1989**, *61*, 849.
- (l) Hauser, A. *J. Chem. Phys.* **1991**, *94*, 2741.
- (m) Hauser, A. *Coord. Chem. Rev.* **1991**, *95*, 275.
3. (a) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555.
- (b) König, R.; Ritter, G.; Kulshreshtha, S. K. *Chem. Rev.* **1985**, *85*, 219.
- (c) Rao, C. N. R. *Int. Rev. Phys. Chem.* **1985**, *4*, 19.
4. (a) Purcell, K. F.; Zapata, J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 497.
- (b) Perkovic, M. W.; Heeg, M. J.; Endicott, J. F. *Inorg. Chem.* **1991**, *30*, 3140.
- (c) Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R.; Ryu, C. K.; Brubaker, G. R. *Coord. Chem. Rev.* **1987**, *77*, 1.
- (d) Lessard, R. B.; Endicott, J. F.; Perkovic, M. W.; Ochromowycz, L. M. *Inorg. Chem.* **1989**, *28*, 2574.
5. (a) Purcell, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 5147.
- (b) Vanquickenborne, L. G.; Pierloot, K. *Inorg. Chem.* **1981**, *20*, 3673.
6. (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
- (b) Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.
- (c) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.
- (d) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.
7. (a) DeVault, D. *Quantum-Mechanical Tunneling in Biological Systems*, 2nd ed.; Cambridge University Press: New York, 1984.
- (b) Hopfield, J. J. *Proc. Natl. Acad. Sci. USA* **1974**, *71*, 3640.
8. (a) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148, and references therein.
- (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358.
- (c) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860.
- (d) Buhke, E.; Navon, G.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 2918.