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Temperature-dependent magnetic moments of Fe(III) complexes with high-spin–low-spin transitions

Kuang Xiao-Yu, Irène Morgenstern-Badarau,* and Isabelle Malfant
Laboratoire de Chimie Bioorganique et Bioinorganique, Université de Paris–Sud,
Bâtiment 420, 91405 Orsay, France

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A theoretical model of the ground state and the magnetic moment of spin crossover of Fe(III) in a cubic ligand field has been established by diagonalizing the complete matrices for electron-electron-repulsion, ligand-field, spin-orbit-coupling, and Zeeman interactions. It is shown that the temperature dependence or unusual magnetic moment of Fe(III) in molecules is due to a large zero-field splitting and an asymmetrically high-order Zeeman effect of the electronic states between the high-spin ${}^6A_1$ and the low-spin ${}^2T_2$ states.

It is well known that Fe(III) molecules can exist either in the high-spin (${}^6A_1$) or in the low-spin (${}^2T_2$) ground state, depending on the ligand-field strength. These two states can also be nearly degenerated when the ligand field is comparable to the mean spin-pairing energy. At the crossover condition, a thermally induced spin transition can then be observed. Various methods of investigation have been carried out to investigate this interesting phenomenon.[1–3] For instance, a number of recent publications focus on the unusual temperature dependence of the effective magnetic moment.[4–6]

To reproduce the reported physical properties, molecular models have been suggested that take into account intramolecular and structural features. They mainly consider either a thermal spin-equilibrium situation, or a quantum-mechanical mixture of the energy levels. In the first case, generally two different species exist, in the second case one species is supposed to exist with changing properties when the temperature varies. It has also been shown that intramolecular effects and lattice properties are important to influence the spin transition.[7] However, the real situation may often be complicated, and, at present, this phenomenon does not seem satisfactorily interpreted.

The aim of the present research is to propose a theoretical model that involves an electron-electron repulsion, ligand-field, spin-orbit coupling, and Zeeman interactions in order to give a reasonable interpretation of the reported unusual magnetic properties exhibited by "spin-crossover" molecules. We will show that due to these interactions, quantum mixing of the energy levels is important and induces large zero-field splitting of the ground state in the crossover region. Then, we will emphasize the following point: The magnetic behavior is governed by the two factors, (i) the magnitude of the ligand-field parameter and (ii) the variation of this parameter with the temperature, those changes being at the origin of changes in the energy levels.

From the Van Vleck expression[8] and using the relationship between the magnetic moment μ and the magnetic susceptibility χ, $\mu^2=(3kT/N)\chi$, we get

$$\mu^2=3kT\frac{\sum_i (W_1^2/kT-2W_2)\exp(-W_0/kT)}{\sum_i \exp(-W_0/kT)} . \tag{1}$$

k is the Boltzman constant; W_1, W_2, and W_0 are defined from the following expression of the Zeeman energy E_i:

$$E_i=W_0+W_1H+W_2H^2 . \tag{2}$$

Then, as far as we find the values of W_1, W_2, and W_0 we can determine the magnetic moment μ.

The W_0 is associated with the zero-field splitting, and it can be calculated by diagonalizing the complete matrices of the Hamiltonian[9]

$$H=H_{\text{atomic}}+V_{\text{cubic}}+H_{\text{s.o.}} . \tag{3}$$

H_{atomic} represents the free-ion Hamiltonian; V_{cubic} and $H_{\text{s.o.}}$ represent the cubic ligand-field potential and the spin-orbit coupling, respectively. All energy-level positions depend only on the two parameters Dq and N when we use the following relationship:[10–12]

$$\begin{gathered} B=N^4B_0,\quad C=N^4C_0,\quad \alpha=N^4\alpha_0 , \\ \beta=N^4\beta_0,\quad \zeta=N^2\zeta_0 , \end{gathered} \tag{4}$$

where B_0, C_0, α_0, β_0, and ζ_0 are the free-ion parameters, and their values have been reported for Fe^{3+} and Mn^{2+} in recent works.[10,13] After considering the spin-orbit coupling, the high-spin state ${}^6\mathrm{A}_1$ and the low-spin state ${}^2T_2$ will be split into a quartet state Γ_8 and a doublet state Γ_7, respectively. When the two doublet states, ${}^6A_1(\Gamma_7)$ and ${}^2T_2(\Gamma_7)$, are close to each other, a strong quantum admixture in two states would happen. The physical mechanism of the quantum admixture is simple, due to an indirect interaction between the high-spin and low-spin states:

$$\mathrm{HS}\leftarrow H_{\text{s.o.}}\rightarrow \mathrm{MS}\leftarrow H_{\text{s.o.}}\rightarrow LS , \tag{5}$$

where HS, MS, and LS represent the high-spin, intermediate-spin, and low-spin states, respectively. If we

TABLE I. Energy level of spin transition between high-spin $^{6}A_1$ and low-spin $^{2}T_2$; all values are in units of cm^{-1}.

δ	-20	-10	-5	0	5	10	15	20	30	40
State										
$^{6}A_1(\Gamma_7)$	0	0	0	0	210	289	376	466	651	837
$^{6}A_1(\Gamma_8)$	11	26	50	103	180	267	356	445	600	841
$^{2}T_2(\Gamma_7)$	341	182	137	150	0	0	0	0	0	0
$^{2}T_2(\Gamma_8)$	972	798	728	686	669	662	659	659	689	633

define the Dq_0 that is associated with the transition point between the $^{6}A(\Gamma_7)$ and $^{2}T_2(\Gamma_7)$, the energy-level positions of the spin crossover can be described by introducing the parameter δ, and we have

$$Dq = Dq_0 + \delta \; , \tag{6}$$

where $\delta \leq 0$ and $\delta > 0$ are concerned with the high spin $^{6}A_1(\Gamma_7)$ and low-spin $^{2}T_2(\Gamma_7)$ ground Kramers doublet, respectively. According to our previous works,[13–17] a calculation of the energy-level positions (or the values of W_0; see Table I and Fig. 1) of $^{6}A_1(\Gamma_7)$, $^{6}A_1(\Gamma_8)$, $^{2}T_2(\Gamma_7)$, and $^{2}T_2(\Gamma_8$, the quantum admixture in $^{6}A(\Gamma_7)$ and $^{2}T_2(\Gamma_7)$ have been carried out by diagonalizing our complete matrices (where $N = 0.84$ and $Dq_0 = 1337$ cm^{-1}). We find two interesting results: (1) The zero-field splitting and the quantum admixture in $^{6}A_1$ state are sensitively dependent on the δ; at the transition point the splitting is equal to 103 cm^{-1} and approximate 40% low-spin ($S = \frac{1}{2}$) state has been mixed into the $^{6}A_1(\Gamma_7)$ state. (2) The splitting in the $^{2}T_2$ state is also sensitively dependent on the δ and the $^{2}T_2(\Gamma_7)$ is a mixed state of low spin and intermediate spin; for $\delta > 0$, approximate 10% ^{4}P state has been mixed into $^{2}T_2(\Gamma_7)$.

In order to calculate the W_1 and W_2 we introduce the Zeeman interaction in the system and rewrite the Hamiltonian as

$$H = H_{\text{atomic}} + V_{\text{cubic}} + H_{\text{s.o.}} + H_{\text{Zeeman}} \; , \tag{7}$$

where

$$H_{\text{Zeeman}} = \beta H (L + 2S) \; .$$

By utilizing the $|J, M_J\rangle$ basis functions of d^5 configuration, we have constituted the matrices of the Zeeman interaction. Diagonalizing the complete matrices of the above Hamiltonian for a weak magnetic field ($\beta H \leq 0.5$ cm^{-1}) we can obtain the eigenvalues of the

TABLE II. Magnetic moment of electronic states in the range of spin transition as a function of δ and T. μ is in units of μ_B.

δ (cm^{-1})	-20	-10	0	10	15	20	40	60
T (K)								
10	5.4469	4.3593	2.3615	1.9756	1.8690	1.8296	1.8403	1.8106
20	5.7023	5.1101	2.6040	2.0735	1.8876	1.8319	1.8677	1.8176
30	5.7553	5.3701	2.8632	2.1670	1.9061	1.8342	1.8948	1.8246
50	5.7853	5.5373	3.4516	2.3493	1.9430	1.8389	1.9478	1.8385
70	5.7950	5.5828	3.9376	2.5613	1.9906	1.8457	1.9994	1.8523
80	5.7972	5.5888	4.1187	2.6880	2.0269	1.8527	2.0247	1.8592
100	5.7975	5.5843	4.3846	2.9729	2.1399	1.8847	2.0744	1.8726
120	5.7936	5.5683	4.5625	3.2688	2.3071	1.9534	2.1234	1.8851
140	5.7862	5.5473	4.6859	3.5456	2.5108	2.0630	2.1730	1.8959
150	5.7815	5.5358	4.7336	3.6717	2.6187	2.1308	2.1985	1.9003
160	5.7764	5.5241	4.7741	3.7888	2.7272	2.2052	2.2249	1.9039
170	5.7708	5.5121	4.8086	3.8967	3.8342	2.2841	2.2523	1.9066
180	5.7649	5.5000	4.8381	3.9957	2.9383	2.3658	2.2811	1.9083
190	5.7587	5.4879	4.8634	4.0862	3.0384	2.4486	2.3112	1.9090
200	5.7523	5.4757	4.8849	4.1689	3.1338	2.5311	2.3429	1.9088
210	5.7457	5.4635	4.9031	4.2444	3.2242	2.6123	2.3763	1.9075
220	5.7390	5.4513	4.9185	4.3132	3.3094	2.6912	2.4112	1.9054
230	5.7322	5.4391	4.9314	4.3760	3.3894	2.7672	2.4477	1.9024
240	5.7254	5.4269	4.9420	4.4335	3.4644	2.8399	2.4855	1.8985
250	5.7184	5.4146	4.9506	4.4860	3.5345	2.9090	2.5246	1.8939
260	5.7115	5.4024	4.9574	4.5342	3.6002	2.9744	2.5649	1.8888
270	5.7045	5.3901	4.9625	4.5784	3.6614	3.0360	2.6061	1.8832
280	5.6975	5.3779	4.9661	4.6191	3.7187	3.0938	2.6479	1.8771
290	5.6904	5.3656	4.9683	4.6566	3.7723	3.1480	2.6904	1.8706
300	5.6833	5.3532	4.9692	4.6912	3.8224	3.1986	2.7332	1.8639

Zeeman energy levels as a function of βH. By employing Eq. (2) to fit the eigenvalues we have found the coefficients W_1 and W_2 for various δ. We note that the high-order Zeeman effect is asymmetrical for each of the Kramers levels $^6A_1(\Gamma_7)$, $^6A_1(\Gamma_8)$, $^2T_2(\Gamma_7)$, and $^2T_2(\Gamma_8)$ in the range of spin transition [i.e., if we use W_{2+}, W_{2-} to represent the second-order Zeeman coefficients in one Kramers doublet, we have $W_{2+}+W_{2-}\neq 0$ and $\sum_i (W_{2+}+W_{2-})_i \approx 0$, where i denotes the different Kramers state]. Substituting the values of W_0, W_1, and W_2 into the formula (1) we have derived the magnetic moment as a function of δ and temperature T. As shown in Table II and Fig. 2, the magnetic moment depends sensitively on the δ and T.

For spin transition the structure of molecule is also sensitively dependent on the temperature.[6] The high-spin form has a significantly longer average metal-ligand bond

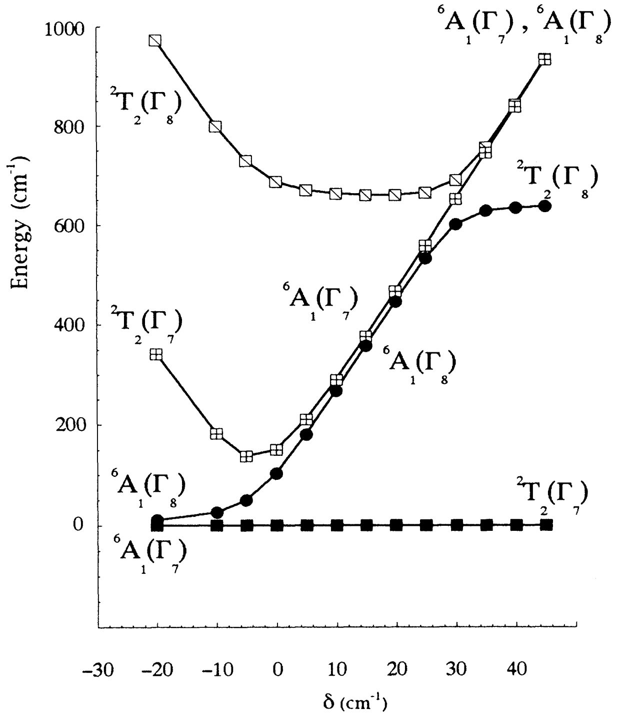

FIG. 1. Energy level of the electronic states of spin crossover between high spin and low spin.

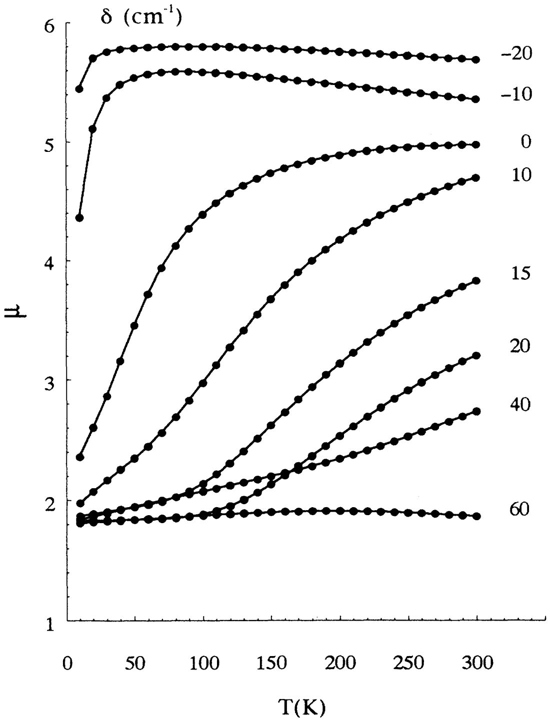

FIG. 2. Magnetic moment of electronic states as a function of δ and T. μ in units of μ_B.

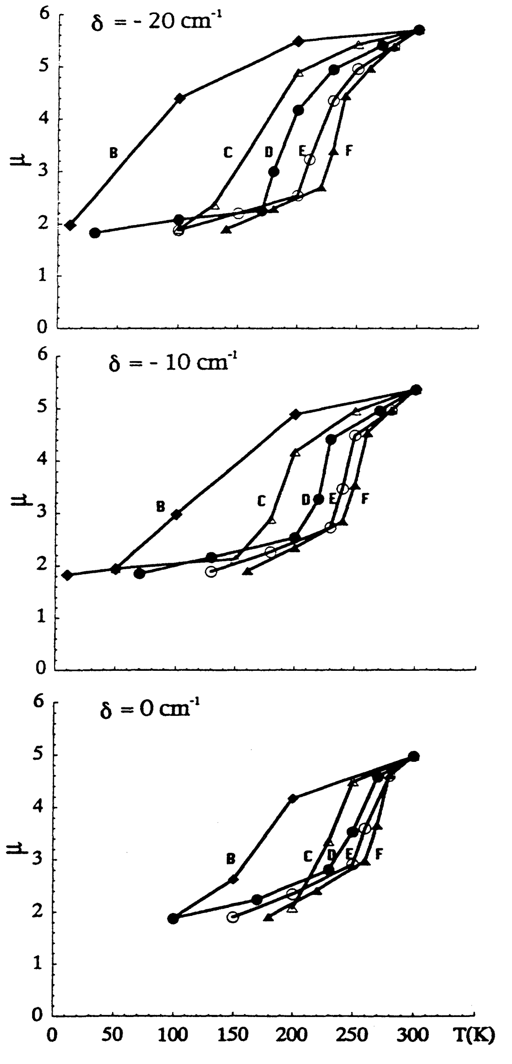

FIG. 3. Magnetic moment of spin crossover as a function of p, where $\delta=-20$, -10, and 0 cm^{-1}; μ in units of μ_B. B, C, D, E, and F are associated with p equal to 0.1, 0.2, 0.3, 0.4, and 0.5 (cm^{-1} K^{-1}), respectively.

length than the low-spin form. The greater distance in the high-spin complex results from the somewhat antibonding character of the e_g orbitals, which are occupied only in the high-spin complexes. According to the point charge model ($Dq = -eq\langle r^4\rangle/6R^5$

$$Dq = Dq_0 + \delta + \Delta Dq \ , \tag{8}$$

where $\Delta Dq \approx -p\Delta T$ and

$$p = -\frac{eq\langle r^4\rangle}{6R^5}\left[\frac{5}{R}\frac{\partial R}{\partial T} - \frac{1}{\langle r^4\rangle}\frac{\partial\langle r^4\rangle}{\partial T}\right] .$$

R is the bond length, $\langle r^4\rangle$ is the expectation value of r^4. Using Eq. (8) and Table II, we can discuss the magnetic moment of spin transition. In our model the magnetic moment of spin transition depends only on two parameters, δ and p. The δ describes the electronic state at initial temperature T_0 and p describes the temperature-dependent electronic state. A calculation of the magnetic moment of spin transition has been completed for $\delta = -20$, -10, and 0 cm^{-1} and $p = 0.1$, 0.2, 0.3, 0.4, and 0.5 cm^{-1}K^{-1}), respectively (where $T_0 = 300$ K). As shown in Fig. 3, the magnetic moment decreases gradually from the value of high spin to that of the low spin. Therefore, in our model the various temperature-dependent magnetic moments can be understood using different values of δ, p, and T_0.

We can draw the following conclusions: (1) A theoretical model of the magnetic moment of spin crossover has been established by diagonalizing the complete matrices for an electron-electron repulsion, ligand-field, spin-orbit coupling, and Zeeman interaction. (2) The large zero-field splitting and the strong quantum admixture in the $^6A_1$ state is due to an indirect interaction between the high-spin and low-spin states via the intermediate-spin states. (3) The temperature-dependent magnetic moment of Fe(III) molecules can be interpreted by a large zero-field splitting and an asymmetrically high-order Zeeman effect in the range of spin transition between the high-spin $^6A_1$ and the low-spin $^2T_2$ states.

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*Author to whom correspondence should be addressed.

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