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# Electronic and magnetic properties of trigonal fivefold-coordinated Fe(III) molecules with high-spin($^6A_1$)–intermediate-spin($^4E$) transitions

Kuang Xiao-Yu, Irène Morgenstern-Badarau,* and Marie-Carmen Rodriguez
*Laboratoire de Chimie Bioorganique et Bioinorganique, Université de Paris-sud, Bâtiment 420, 91405 Orsay, France*

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The electronic structure of trigonal fivefold-coordinated Fe(III) molecules has been studied. The ligand-field model that we use takes into account the covalency effect which modifies the ligand-field parameters. The complete matrices for electron-electron repulsion, ligand-field, and spin-orbit coupling, have been diagonalized, including the Zeeman interaction in the case of magnetic-property calculations. The energy levels position can be expressed as a function of the ratio $\Delta/\zeta$, $\Delta$ being the energy gap $^6A_1$-$^4E$, and $\zeta$ the spin-orbit-coupling parameter. It is shown that, by varying this ratio, the intermediate spin level $^4E(^4T_1)$ can be stabilized as the ground state, instead of the $^4A_2(^4T_1)$ level in the case of a tetragonal distortion. Near the crossover point ($^6A_1$-$^4E$ transition), strong quantum admixtures and large zero-field splittings occur: the ground Kramers doublet contains 41% high-spin state and 59% intermediate-spin state; the corresponding ground-state wave functions are associated with $M_J=\pm\frac{5}{2}$; the first-excited low-lying Kramers doublet associated with $M_J=\pm\frac{3}{2}$ is located at 102.5 cm$^{-1}$. Characteristic temperature dependences of the effective magnetic moment are calculated as a function of $\Delta/\zeta$. Taking into account the effect of the temperature on the considered parameters, the magnetic moment can vary more or less sharply from a high-spin value to an intermediate-spin value.

The Fe(III) molecules with spin-transition effects, which have received considerable attention in the last decade, are found in chemical and biochemical systems. This interesting phenomenon arises when the ligand-field splitting energy becomes comparable with the mean spin-pairing energy. At the molecular scale, it is possible to understand the spin transition as an intraionic transfer with spin flip of the transferred electrons. For the Fe(III) molecules this transfer, depending on the coordination and distortion of the molecules, may involve either two electrons or one electron, the former being associated with the high-spin–low-spin transition ($\Delta S=2$) and the latter with the high-spin–intermediate-spin transition or the intermediate-spin–low-spin transition ($\Delta S=1$). Recently, we have established a theoretical model for the high-spin–low-spin transition.[1] In the following we will present the electronic and magnetic properties associated with the high-spin ($^6A_1$)–intermediate-spin($^4E$) transitions.

The high-spin–intermediate-spin transitions for Fe(III) ion in complexes include both the $^6A_1 \Longrightarrow {}^4A_2$ transition and the $^6A_1 \Longrightarrow {}^4E$ transition depending on the coordination and distortion of the system. The $^6A_1 \Longrightarrow {}^4A_2$ transition for Fe(III) complexes with tetragonal symmetry has been investigated by Maltempo and Moss.[2] Herein we will describe a theoretical model of the $^6A_1 \Longrightarrow {}^4E$ transition, which may occur in the five coordinated Fe(III) complexes with a trigonal distortion.

According to the ligand-field theory the Hamiltonian of the Fe(III) ion in a trigonal ligand field can be written as

$$\mathcal{H}=\mathcal{H}_{\text{atomic}}+\mathcal{H}_{\text{trig}}+\mathcal{H}_{\text{s.o.}}\ , \tag{1}$$

where $\mathcal{H}_{\text{atomic}}$, $\mathcal{H}_{\text{trig}}$, and $\mathcal{H}_{\text{s.o.}}$ represent the free-ion Hamiltonian, the trigonal ligand-field potential, and the spin-orbit coupling interaction, respectively. The complete matrices for the above Hamiltonian have been constituted and checked in our previous works.[3-7] For the sake of simplicity, we introduce the covalency parameter $N$ and use the following relationship:[8-10]

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

$B_0$, $C_0$, $\alpha_0$, $\beta_0$, and $\zeta_0$ are free-ion parameters and for the Fe$^{3+}$ ion their values have been determined in recent works.[6] The ligand-field parameters, which are of the form[3,5]

$$\begin{aligned} Y_1&=(5/196\pi)^{1/2}\nu_{20}\langle r^2\rangle\ ,\\ Y_2&=(1/196\pi)^{1/2}\nu_{40}\langle r^4\rangle\ ,\\ Y_3&=(5/56\pi)^{1/2}\nu_{43}^{c}\langle r^4\rangle\ ,\\ Y_4&=i(5/56\pi)^{1/2}\nu_{43}^{s}\langle r^4\rangle\ , \end{aligned} \tag{3}$$

where $\langle r^2\rangle$ and $\langle r^4\rangle$ are the expectation values of $r^2$ and $r^4$, respectively, and the values of $\nu_{20}$, $\nu_{40}$, $\nu_{43}^{c}$, and $\nu_{43}^{s}$ are concerned with the charge of the ligands and the distortion of the molecule. From the point-charge model these ligand-field parameters may be determined by three parameters: $Q_2$, $Q_4$, and $\theta$. The $Q_2$ and $Q_4$ parameters are as defined by Norgett, Thornley, and Venanzi for the fivefold coordinated complex with $C_{3V}$ symmetry,[11] and $\theta$ is the angle of distortion as used by Bencini and Gatteschi.[12] Thus, all energy-level positions are a function of the four parameters $N$, $Q_2$, $Q_4$, and $\theta$. In this paper the calculations have been performed for fixed values of $N$ ($N=0.76$) and $\theta$ ($\theta=83.33°$), and various values of the $Q_2$ and $Q_4$ parameters (for $Q_2/Q_4=2$).

In the case of the spin transition, the main features of

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the energy-level positions and the magnetic moments can be described by two parameters $\zeta$ and $\Delta$. $\zeta$ being the spin-orbit coupling coefficient and $\Delta$ the energy gap between the $^6A_1$ and $^4E$ states for the system without the spin-orbit coupling perturbation, we have

$$\zeta=\zeta(N),\quad \Delta=\Delta(N,Q_2,Q_4,\theta)\ . \tag{4}$$

Taking $N=0.76$ (which leads $\zeta=271.5\ \mathrm{cm}^{-1}$) and $\Delta/\zeta=0,\pm1,\pm2,\pm3,\pm4$, we have derived the energy-level diagram of the high-spin($^6A_1$)-intermediate-spin($^4E$) transitions by diagonalizing the complete matrices of the Hamiltonian (1), as shown in Fig. 1. In the range of the spin transition, two interesting results are worth noting: (1) The quantum admixture in the ground-state Kramers doublet is sensitively dependent on the value of $\Delta/\zeta$; near the crossover point ($\Delta/\zeta=0$) the ground-state Kramers doublet is a strong quantum mixed state which contains a 41% high-spin ($S=\frac{5}{2}$) state and a 59% intermediate-spin state ($S=\frac{3}{2}$). The corresponding ground-state wave functions are associated with $M_J=\pm\frac{5}{2}$. (2) There are large zero-field splittings; the first-excited low-lying Kramers doublet associated with $M_J=\pm3/2$ is located at 102.5 $\mathrm{cm}^{-1}$, which is comparable with the thermal energy kT and will induce magnetic behavior depending on the temperature.

The molecular magnetic moments are associated with the energy-level positions and the first- and the second-order Zeeman coefficients. We start from the well-known Van Vleck formula[13]

$$\mu^2=3kT\frac{\sum_i (W_1^2/kT-2W_2)\exp(-W_0/kT)}{\sum_i \exp(-W_0/kT)}\ , \tag{5}$$

$k$ is the Boltzmann constant, $W_0$ denotes the energy levels, and $W_1$ and $W_2$ represent the Zeeman coefficients defined in the following expression:

$$E_i=W_0+W_1H+W_2H^2\ . \tag{6}$$

The coefficients of $W_1$ and $W_2$ may be found by diagonalizing the complete matrices of the following Hamiltonian:

$$\mathcal{H}=\mathcal{H}_{\mathrm{atomic}}+\mathcal{H}_{\mathrm{trig}}+\mathcal{H}_{\mathrm{s.o.}}+\mathcal{H}_{\mathrm{Zeeman}}\ . \tag{7}$$

$\mathcal{H}_{\mathrm{Zeeman}}$ represents the Zeeman interaction. In the trigonal symmetry the Zeeman interaction must be expressed in two parts for parallel and perpendicular directions, respectively, which are

$$\begin{aligned}\mathcal{H}_{\parallel}&=\beta H_z(L_z+2S_z)\ ,\\ \mathcal{H}_{\perp}&=\beta H_x(L_x+2S_x)\ .\end{aligned} \tag{8}$$

Employing the $|J,M_J\rangle$ wave functions, we have constituted the Zeeman matrices for the $z$ and $x$ directions, respectively. The calculations of the values of $W_1$ and $W_2$ involve the diagonalizations of the complete matrices along the two directions. For the $z$ direction, the calculation includes three $84\times84$ matrices belonging to $\Gamma_4$, $\Gamma_5$, and $\Gamma_6$, respectively. For the $x$ direction, we neglect the low-spin states, the calculation includes one $102\times102$ matrix. According to the Van Vleck assumption all calculations are completed for a weak magnetic field approximation ($\beta H_i\leq0.5\ \mathrm{cm}^{-1}$, $i=x,y$). In fact, in this work

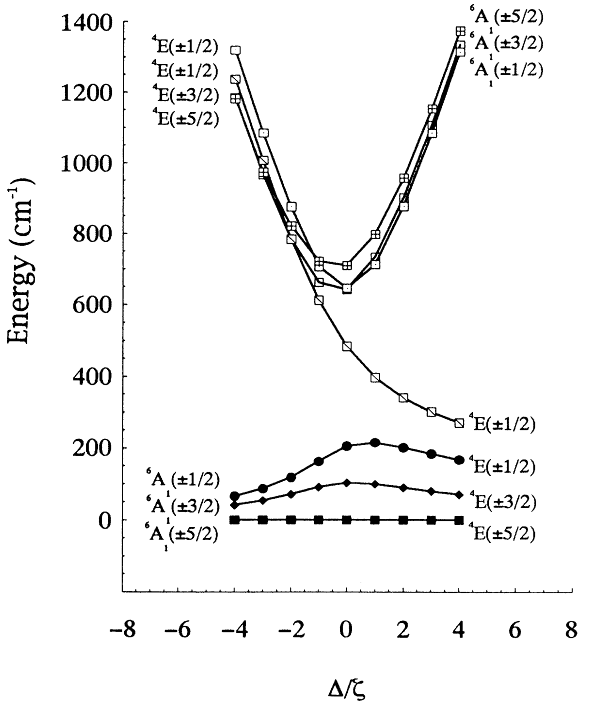

FIG. 1. The energy-level diagram of the high-spin($^6A_1$)-intermediate-spin($^4E$) transitions as a function of $\Delta/\zeta$.

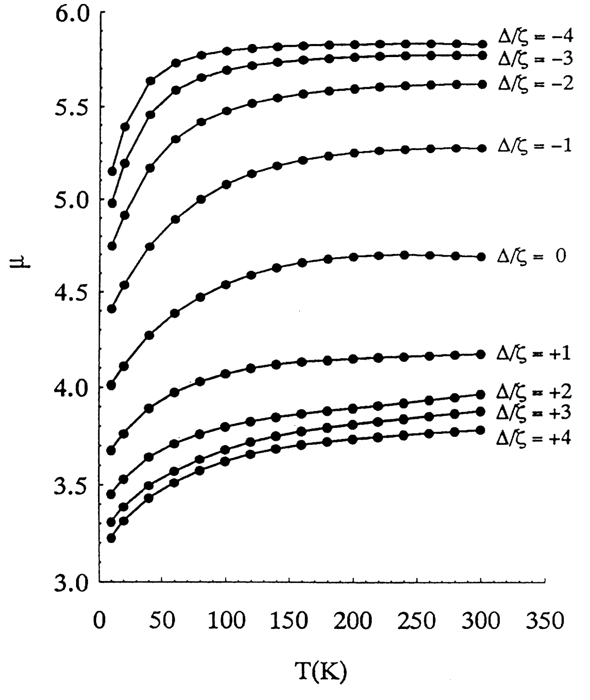

FIG. 2. Magnetic moments of the electronic states as a function of $\Delta/\zeta$ and $T$. $\mu$ is in units of $\mu_B$.

TABLE I. Magnetic moments of the electronic states in the range of the spin transition as a function of $\Delta/\zeta$ and $T$.

| $\Delta/\zeta$<br>$T$ (K) | $-4$ | $-3$ | $-2$ | $-1$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 5.1456 | 4.9784 | 4.7451 | 4.4109 | 4.0117 | 3.6770 | 3.4517 | 3.3072 | 3.2236 |
| 20 | 5.3879 | 5.1887 | 4.9124 | 4.5364 | 4.1094 | 3.7605 | 3.5298 | 3.3860 | 3.3137 |
| 40 | 5.6346 | 5.4558 | 5.1637 | 4.7426 | 4.2722 | 3.8923 | 3.6433 | 3.4954 | 3.4314 |
| 60 | 5.7282 | 5.5856 | 5.3197 | 4.8910 | 4.3871 | 3.9747 | 3.7110 | 3.5695 | 3.5110 |
| 80 | 5.7705 | 5.6524 | 5.4148 | 4.9980 | 4.4730 | 4.0310 | 3.7594 | 3.6303 | 3.5738 |
| 100 | 5.7930 | 5.6908 | 5.4751 | 5.0752 | 4.5391 | 4.0712 | 3.7964 | 3.6797 | 3.6222 |
| 120 | 5.8064 | 5.7153 | 5.5159 | 5.1318 | 4.5897 | 4.0996 | 3.8249 | 3.7187 | 3.6585 |
| 140 | 5.8150 | 5.7321 | 5.5449 | 5.1739 | 4.6278 | 4.1195 | 3.8471 | 3.7494 | 3.6857 |
| 160 | 5.8209 | 5.7443 | 5.5663 | 5.2052 | 4.6555 | 4.1334 | 3.8652 | 3.7739 | 3.7065 |
| 180 | 5.8250 | 5.7533 | 5.5823 | 5.2284 | 4.6748 | 4.1433 | 3.8807 | 3.7940 | 3.7229 |
| 200 | 5.8278 | 5.7599 | 5.5943 | 5.2452 | 4.6873 | 4.1507 | 3.8948 | 3.8110 | 3.7362 |
| 220 | 5.8296 | 5.7646 | 5.6031 | 5.2568 | 4.6943 | 4.1566 | 3.9085 | 3.8262 | 3.7474 |
| 240 | 5.8305 | 5.7676 | 5.6094 | 5.2643 | 4.6970 | 4.1618 | 3.9222 | 3.8401 | 3.7573 |
| 260 | 5.8305 | 5.7691 | 5.6135 | 5.2685 | 4.6963 | 4.1666 | 3.9365 | 3.8535 | 3.7664 |
| 280 | 5.8296 | 5.7694 | 5.6159 | 5.2700 | 4.6932 | 4.1712 | 3.9513 | 3.8667 | 3.7751 |
| 300 | 5.8279 | 5.7684 | 5.6168 | 5.2695 | 4.6881 | 4.1759 | 3.9669 | 3.8799 | 3.7837 |

the eigenvalues are obtained for three values of $\beta H_i$, $\beta H_i = 0$, 0.2, and 0.5 $\mathrm{cm}^{-1}$, respectively. Employing expression (6) to fit these eigenvalues, we have determined the first- and the second-order Zeeman coefficients. Introducing the values of $W_0$, $W_1$, and $W_2$ into Eq. (5), we have obtained the magnetic moments for the two directions, respectively. The magnetic moments display a significant anisotropy. The average values of $\mu^2$ have been calculated by the following formula:

$$\mu^2 = \tfrac{1}{3}(\mu_{\parallel}^2 + 2\mu_{\perp}^2) . \qquad (9)$$

The final results are given in Table I and Fig. 2. We see that the average magnetic moments sensitively depend on the values of $\Delta/\zeta$ and temperature $T$, which may be attributed to the variance of the large zero-field splitting and the nonvanishing second-order Zeeman effect in the range of spin transition.

In order to describe the spin-transition phenomenon in a more extensive way, we take into account the influence of the temperature: the structure of molecules is sensitively dependent on it, due to the different bond lengths and covalence between the high-spin and intermediate-spin states. In the range of the spin transition we suppose that the electronic state positions depend on the temperature and that they can be estimated by a linear relationship:

$$\delta/\zeta = \Delta_0/\zeta - p(T - T_0) . \qquad (10)$$

$\Delta_0/\zeta$ refers to the electronic state at the initial temperature $T_0$. The parameters $p$ represents the temperature-dependent electronic states. For example, we have plotted $\mu$ versus $T$ for $\Delta_0/\zeta = -4$, $T_0 = 300$ K and $p = 0.03$,

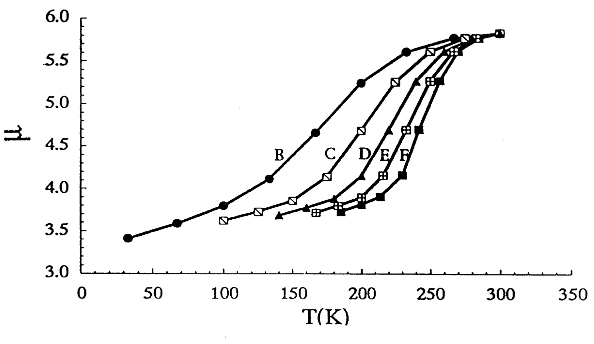

FIG. 3. Magnetic moments of the high-spin($^6A_1$)–intermediate-spin($^4E$) transitions; $B$, $C$, $D$, $E$, and $F$ are associated with $p = 0.03$, 0.04, 0.05, 0.06, and 0.07 ($\mathrm{K}^{-1}$), respectively. $\mu$ is in units of $\mu_B$.

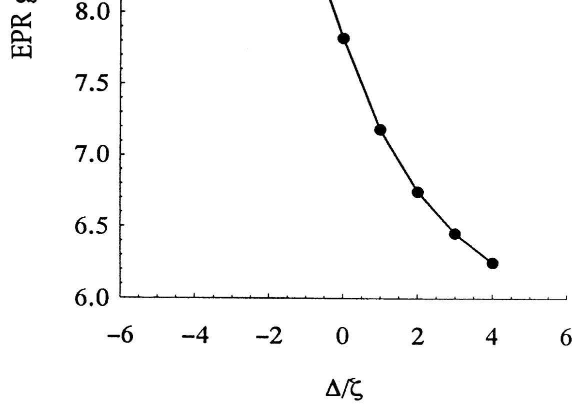

FIG. 4. EPR $g$ factor of the ground-state Kramers doublet as a function of $\Delta/\zeta$.

0.04, 0.05, 0.06, and 0.07 ($\mathrm{K}^{-1}$), respectively. As shown in Fig. 3, the magnetic moments may be varied more or less sharply from the value of the high spin to that of the intermediate spin.

Another interesting result is that the spin transition is also EPR detectable. The EPR effective *g* factor of the ground-state Kramers doublet is also sensitive depending on the values of the $\Delta/\zeta$. In the range of the spin transition we find that $g_x \approx 0$, $g_y \approx 0$, and $g_z$ changes gradually from 9.7 to 6.2, which are in good agreement with a ground-state doublet associated with $M_J = \pm\frac{5}{2}$, as presented in Fig. 4.

In conclusion, the theoretical model of the high-spin($^6A_1$)-intermediate-spin($^4E$) transition has been established by considering electron-electron repulsion, ligand-field, spin-orbit coupling, and Zeeman interactions; this transition can occur in a fivefold-coordinated Fe(III) complex with a trigonal distortion. In the range of the spin transitions there are variable effective *g* factors, a strong quantum admixture, a large zero-field splitting, and a nonvanishing second-order Zeeman effect, which lead to characteristic effective magnetic moment temperature dependences.

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## APPENDIX: QUANTUM ADMIXTURE FOR HS ⟺ MS AND HS ⟺ LS TRANSITIONS

$$\langle \Psi_g | \Psi_g \rangle = a^2(S=5/2) + b^2(S=3/2) + c^2(S=1/2)$$

| | | $a^2\%$ | $b^2\%$ | $c^2\%$ |
|---|---|---|---|---|
| HS ⟺ MS | | | | |
| $\Delta/\zeta=0$ | : | 41.0 | 58.6 | 0.4 |
| HS ⟺ LS | | | | |
| $\delta=0$ | : | 26.8 | 3.2 | 69.9 |

$\Psi_g$ is the eigenfunction of the ground Kramers doublet; *a*, *b*, and *c* are mixed coefficients. The coefficients for $\delta=0$ in our previous work[1] contains a typographical error.

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*Author to whom correspondence should be addressed.

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