Spin-Mixed States of Ferric Ion in Complexes of Tetragonal Symmetry

I. Eigenfunctions and Eigenvalues of Different Spin States

GILDA HARRIS

Department of Physics, Pomona College, Claremont, California

Using a strong crystal field model for ferric ion complexes with tetragonal symmetry and allowing spin-orbit coupling between sextet, quartet, and doublet states, a mechanism is obtained whereby ferric ion can exist in four qualitatively different ground states: a sextet, a quartet, a doublet or a substantially spin-mixed state. We have delineated the regions in crystal field parameter space in which these various possible ground states prevail. Also, we have calculated the eigenfunctions and eigenvalues typical of each region. We discuss in detail the nature of the 5 lowest ferric ion functions in these different regions, particularly in the regions of spin-mixed states. With this model we obtain a picture of these various ferric ion states consistent with the behavior of known complexes of ferric ion, particularly of the ferric heme compounds. The results presented here will be used in a subsequent calculation of some of the observed properties of these compounds.

Das Fe(III)-Ion wird in einem starken tetragonalen Ligandenfeld unter Berücksichtigung der Spin-Bahn-Kopplung behandelt. Je nach Größe des kubischen Ligandenfeldes, der beiden Parameter der tetragonalen Verzerrung und des Spin-Bahn-Kopplungsparameters ist der Grundzustand ein Sextett, ein Dublett, ein Quartett oder ein spin-gemischter Zustand. Eigenwerte und Eigenfunktionen der fünf untersten Zustände in Abhängigkeit von den Parameterwerten werden eingehend diskutiert. Die Parameter werden physikalisch interpretiert. Die hier gewonnenen Resultate werden in den folgenden Arbeiten zur Berechnung der Eigenschaften von Eisen-Hämin-Komplexen herangezogen.

En utilisant un modèle de champ cristallin fort pour les complexes de l'ion ferrique à symétrie tétragonale et en tenant compte du couplage spin-orbite entre les états sextet, quartet et doublet, on obtient un mécanisme pour l'existence de l'ion ferrique dans quatre états fondamentaux qualitativement différents: un sextet, un quartet, un doublet et un état mixte. Nous avons délimité les zones de paramètre du champ cristallin où dominent ces différents états fondamentaux. Nous avons aussi calculé les fonctions et les valeurs propres typiques dans chaque zone. Nous discutons en détail la nature des cinq plus basses fonctions de l'ion ferrique dans ces différentes zones, en particulier dans les zones à états de spin mixtes. A l'aide de ce modèle nous obtenons une image de ces différents états de l'ion ferrique en accord avec le comportement des complexes ferriques connus, en particulier du type hémique. Les résultats présentés ici seront utilisés dans un calcul de propriétés observées de ces composés.

I. Introduction

Ferric ion has a $3d^5$ free ion ground state configuration with a ^6S ground state. When it is placed in a regular array of nearest neighbors to form a complex molecule or ion, free ion states are perturbed and mixed and there is the possibility that the lowest energy states of the ferric ion under certain conditions will be quartet or doublet states. In addition, if spin-orbit coupling is considered, it is also possible that the ground and low-lying states will be substantially spin-mixed states, i.e., states for which spin is no longer a good quantum number and which are compused of mixtures of sextet, quartet, and doublet components. There are

some properties of the complex which can be more or less associated with the local electronic distribution about the metal ion. These properties will change markedly from their free ion behavior, if the metal is perturbed a good deal by its environment in the complex, such that for example the nature of its ground and low lying states is changed markedly.

In many complexes of ferric ion, particularly in the prosthetic group of ferric hemoglobin and related heme proteins, there is ample evidence, by observation of the behavior of such properties, of large deviations from free ion behavior. For example, in all fairly stable ferric complexes, including those for which a sextet state is still the ground state, there is substantial zero field splitting, i.e., splitting of lowest energy states, while in the free ion, the ground state is six-fold degenerate and the zero field splitting is zero. In addition, the electric field gradients in such compounds as the heme proteins are substantial, causing large quadrupole splittings in the Mössbauer resonance of ^{57}Fe in these compounds, while in the free ion they are zero. Also, the value of magnetic moments vary from the sextet, spin only value of 5.92 Bohr magnetons to the low spin value of 2.26 in a continuous fashion in a series of ferric heme complexes. Finally, the electron spin resonance behavior is different in similar heme complexes and different from predicted free ion behavior.

Thus in all of these compounds there are strong perturbations from free ion behavior. Moreover, in all the ferric heme compounds the ferric ion must be under such perturbed conditions that small changes in the local environment can cause significant changes in the nature of the ground and low lying states. It becomes then a reasonable and challenging possibility that a simple localized model for the heme prosthetic group with parameters used in a consistent manner can explain and correlate some of the observed behavior of the ferric ion and its dependence on the local environment.

In most of its complexes ferric ion is 4, 5 or 6 coordinated. In the prosthetic group of the heme proteins the ferric ion is coordinated to 4 in-plane nitrogen ligands coming from a porphyrin ring structure. The skeleton of the porphyrin ring is shown in Fig. 1. In different heme proteins, the substituents on the porphyrin ring can be somewhat different. A key to these substituents and the common name of the corresponding porphyrin is given in a table accompanying Fig. 1. For hemoglobin or myoglobin the prosthetic group is the ferric protoporphyrin-IV ring structure. In addition to this four-coordination, ferric ion in intact heme proteins has two axial ligands. One is a fixed ligand coming from the protein part of the molecule. This ligand can also vary in different proteins. In hemoglobin it is an imidazole nitrogen from a histidine residue of the protein. The 6th position, the second axial position, can be reversibly occupied by a number of small atoms, ions and molecules. In vivo, it is to this position that the oxygen molecule attaches and detaches as ferrous hemoglobin performs its main biological function of transferring oxygen from lungs to tissues. In vitro, ferrous oxy-hemoglobin is readily oxidized to ferric with the simultaneous replacement of the oxygen molecule by a water molecule, forming what is called (acid) met-hemoglobin. The water in turn can be replaced by a series of small ligands such as F^-, N_3^-, CO, NO, acetate, formate, SCN^-, SH^-, etc. forming a series of derivatives. Similarly, one can form the same derivative, i.e., keep the 6th ligand the same for a series of similar heme

proteins differing only by small differences in their porphyrin ring substituents, or in the nature of the 5th ligand from the protein. Also, it is possible to prepare and observe the properties of the different prosthetic groups, i.e., ferric-porphyrin compounds completely detached from the protein part of the molecule and hence without the protein-attached 6th ligand.
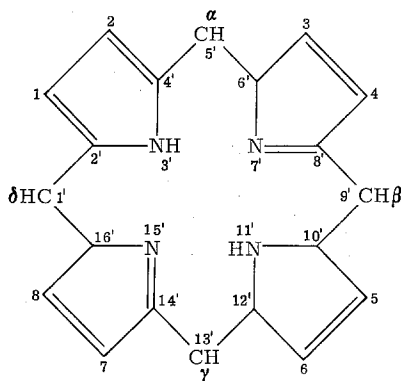
Substituents of different porphyrin ring compounds (Prefix-porphyrin IX-suffix)

	Proto-	Meso-	Deutero-	Deutero-Dimethyl Ester	2,4 Diacetyl Deutero-Dimethyl Ester	Cupro(III)-	Cupro(I)-
1	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
2	$CH=CH_2$	CH_2CH_3	H	H	$H_3C-C=O$	CH_2CH_2COOH	CH_2CH_2COOH
3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
4	$CH=CH_2$	CH_2CH_3	H	H	$H_3C-C=O$	CH_2CH_2COOH	CH_2CH_2COOH
5	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
6	CH_2CH_2COOH	CH_2CH_2COOH	CH_2CH_2COOH	$(CH_2)_2COOMe$	$(CH_2)_2COOMe$	CH_2CH_2COOH	CH_2CH_2COOH
7	CH_2CH_2COOH	CH_2CH_2COOH	CH_2CH_2COOH	$(CH_2)_2COOMe$	$(CH_2)_2COOMe$	CH_2CH_2COOH	CH_3
8	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_2CH_2COOH

Fig. 1. Porphyrin ring structure

In order to understand and explain the observed properties of ferric ion in these different ferric heme compounds, we have, in the past, considered the prosthetic group of these proteins as a complex ion with ferric ion coordinated in a regular array of 6 nearest neighbors. We have used as a model for this complex ion, the strong crystal field model with tetragonal symmetry and spin-orbit coupling among the lowest energy sextet, quartet, and doublet states in these strong crystal fields. This is the simplest model that could possibly explain the known properties of the heme compounds. Previous calculations with this model indicate that it can be used successfully to account for the localized properties of interest here for the high spin, intact heme proteins with values of parameters close to the conditions for a change in spin-state [1]. Examples of such complexes are the methemoglobin and the floride derivative. We have also shown now, with this model, a variation in crystal field parameters leads to changes in the nature of the ferric ion states and have previously delineated the conditions for high and low spin [2]. With very small changes in the crystal field parameter assignments for the high spin compounds, a low spin ground state is possible. Such conditions simulate in a reason-

able fashion the effect of a change in one ligand in a series of heme derivatives. Under low spin conditions, with the addition of a rhombic distortion, we have also previously accounted for the properties of low spin intact ferric heme derivatives examplified by the N_3^- derivative [2]. In these previous calculations we made certain simplifying assumptions that reduce the problem from three to two crystal field parameters in tetragonal symmetry. More recently, we have again used this model, with an extended treatment of crystal field parameters to successfully account for the recent direct measurements of the zero field splittings [3], i.e., first energy intervals, in a series of ten, high-spin, isolated ferric porphyrin compounds [4]. In the strong crystal field model single orbital energies are expressed in terms of crystal field parameters which are treated as "phenomenological parameters." In our latest treatment of the tetragonal crystal field parameters, however, we use all three parameters and impose restraints on their variation in a series of related compounds which corresponds to possible physical variations in the local environment in these compounds. These restraints lead to a self-consistent use of parameters and give more physical meaning to the single orbital energies used to explain observed behavior.

Encouraged by the reasonable success of our model in our previous work with high and low spin ferric heme compounds, and noting the possibility of other ferric ion states, we have continued to use the same model, a strong crystal field of tetragonal symmetry with spin-orbit coupling, together with our latest, extended and physically-correlated treatment of parameters for a more general analysis of the behavior of the ferric ion under a wider range of variation of its perturbed electronic states than heretofor studied. In the work to be discussed here we have delineated the conditions in terms of crystal field, electrostatic, and spin-orbit coupling parameters, under which the ground and low lying electronic states of ferric ion are in each of four possible conditions: almost pure sextet (high spin) states, almost pure doublet (low spin) states, almost pure quartet (intermediate) states, and substantially spin-mixed states. Our results clearly indicate that all of these conditions are possible for ferric ion in strong fields of axial symmetry and there is evidence that all of them occur in different ferric ion complexes. Since all of the states are somewhat spin mixed, due to spin-orbit coupling, in order to define terms, we shall designate a pure or "almost" pure spin state as one for which the components are composed of 98 % or more of the components of one total spin state or another, i.e., sextet, doublet or quartet. The remainder of the states are then "substantially" spin-mixed, i.e., more than 2 %.

In our present calculations, we particularly emphasize the interesting behavior of ferric ion in the parameter regions of spin-mixed and quartet ground states, regions which have heretofor not been discussed.

Our results show the mechanism of the change from one spin state to another and that such changes can occur with internally consistent and rather small variations in crystal field parameters. In addition, the physical significance of these variations is indicated, using the crystal field model as a guide, but with generalized results applying to all models of interactions in these complexes. Since the crystal field model is non-specific in its treatment of ligands, the results obtained from our present calculations are applicable, with appropriate changes in parameter values, to any $3d^5$ metal in strong fields of tetragonal symmetry.

In the next section we discuss the details of our calculations of eigenfunctions and eigenvalues. It is followed by a mapping of the regions in parameter space where the sextet, doublet, quartet and spin-mixed states exist. Then there is a rather detailed discussion of the nature of the eigenfunctions and eigenvalues and their variations with field strength in each region, in particular in the region of spin-mixed states.

In the subsequent paper of this series we shall use the eigenfunctions and eigenvalues calculated and discussed here as the basis for the calculation of some of the localized properties of interest especially the behavior of these properties in the narrow regions of rapidly changing, spin-mixed eigenfunctions.

II. Calculation of Eigenvalues and Eigenfunctions

A) Crystal Field Energy of Single d Orbitals

1. Single Orbital Energies

In the crystal field model of a metal complex, the effect of bonding on the central metal ion is treated as an electrostatic perturbation of its outer or valence electrons. This so-called crystal field potential created by the geometric array of nearest atoms or ions is added to the free ion Hamiltonian so that the total Hamiltonian becomes:

$$H = \sum_i p_i^2/2m_i - \sum Ze^2/r_i + \sum_{i>j} e^2/r_{ij} + \sum_i \delta_i(r_i)\, l_i \cdot s_i + V_c. \tag{1}$$

It is assumed that a central field solution of the Schrödinger equation including the one electron terms of the Hamiltonian has been obtained in some approximation. These then give energies of various configurations of the free ion. For the Fe^{+3} ion the $3d^5$ configuration is the ground state, and will be regarded as the zero of energy for the problem. The next three terms in the Hamiltonian can be considered all together or one at a time, in a perturbation sequence, with some predetermination of their order of importance. Experimental observation for the heme group complexes, as discussed, indicates that ferric ion is strongly perturbed from its free ion states and that the bonding in these metal-porphyrin compounds is very strong. We translate this then to the so-called strong field approximation, i.e., we consider that

$$V_c > \sum_{i>j} e^2/r_{ij} > \sum_i \delta_i(r_i)\, l_i \cdot s_i$$

and consider crystal field effects first. As a first step in this calculation then we wish to know how the single orbital energies, i.e., the free ion configurations, are perturbed by the crystal field term. We limit consideration to the $3d^5$ configuration and hence ask what the energies of the $5d$ orbitals, degenerate in the spherically symmetric free ion, are in the crystal field of axial symmetry, D_4.

In its most general form the crystal field potential can be expanded as an infinite series of spherical surface harmonics

$$V_c = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_l^m r^l y_l^m(\theta, \varphi)$$

where the Y_l^m's are ortho-normal sets of spherical harmonics

$$Y_l^m(\theta, \varphi) = \frac{N}{\sqrt{2\pi}}\, P_l^{|m|}(\cos\theta)\, e^{im\varphi}$$

and P_l^m are associated Legendre polynomials, N are normalization factors, C_l^m are constants whose value depends on the symmetry and strength of the potential. The symmetry of this so-called crystal field is that of the actual geometric array of these ligands about the central metal ion, taken as the origin of the coordinate system. The point group of the electric field is then the symmetry of this nuclear framework and the crystal field potential belongs to the totally symmetry representation of this group. Each orbital can also be expressed as a product of a radial function and a spherical harmonic

$$\psi_m = d_m R_{3d}(r) \qquad d_m = Y_2^m(\cos\theta, \varphi).$$

By specifying the symmetry of the crystal field and applying the selection rules for integrals of products of three spherical harmonics, the C_l^m which are zero or which do not enter into crystal field energy terms, can be deduced. For the geometric array of four equivalent ligands in the xy-plane, each placed at $\pm x$ and $\pm y$, acting on d electrons, the form of the potential is:

$$V_{D_{4h}} = C_0^0 s + C_2^0 r^2 d_0 + C_4^0 r^4 g_0 + C_4^4 r^4 (g_4 + g_{-4}).$$

For two equivalent axial ligands, placed at $\pm z$, the added potential is:

$$V_{\text{axial}} = B_0^0 s + B_2^0 r^2 d_0 + B_4^0 r^4 g_0.$$

Combining the two we obtain for a six coordinated complex of axial symmetry:

$$V_{D_4}(6) = (B_0^0 + C_0^0)s + (B_2^0 + C_2^0)r^2 d_0 + (B_4^0 + C_4^0)r^4 g_0 + C_4^4 r^4 (g_4 + g_{-4}). \quad (2)$$

We wish to calculate the single orbital energies:

$$E(V_{D_4}, 6) = \int \psi_0 V_{D_4}(6) \psi_0.$$

Let the set of ψ_0 be the d electron symmetry orbitals for D_4 point group representations:

$$a_1 = d_{z2} = R_{3d} d_0$$
$$b_1 = d_{x2-y2} = R_{3d} 1/\sqrt{2}(d_2 + d_{-2})$$
$$b_2 = d_{xy} = R_{3d} 1/\sqrt{2}(d_2 - d_{-2})$$
$$e(\theta) = d_{xz} = R_{3d} - 1/\sqrt{2}(d_1 - d_{-1})$$
$$e(\varepsilon) = d_{yz} = R_{3d} 1/\sqrt{2}(d_1 + d_{-1})$$

Let $\int R_{3d}^* r^n R_{3d} r^2 dr = \langle r^n \rangle$, $\int Y_m^1 Y_m^1 \sin\theta \, d\theta \, d\varphi = 1$. Then the orbital energies in terms of the coefficients in the potential and the expectation value of r^n can be written in the form

$$\varepsilon_d = a(B_0^0 + C_0^0) + b(B_2^0 + C_2^0)\langle r^2 \rangle + c(B_4^0 + C_4^0)\langle r^4 \rangle + d(C_4^4)\langle r^4 \rangle. \quad (3)$$

Table 1 gives the values of the a, b, c, and d coefficients determining the energy of each of the d orbitals, and their point group representation labels in D_4 symmetry.

Table 1. *d-orbital crystal field energy in tetragonal symmetry*
$$(\varepsilon_d = aA_0^0 + bA_2^0 + cA_4^0 + dA_4^4)$$

d-orbital	Γ_{O_h}	ΓD_4	a	b	c	d
d_z^2	e_g	a_1	$1/2\sqrt{\pi}$	$\sqrt{5}/7\sqrt{\pi}$	$3/7\sqrt{\pi}$	0
d_{x2-y2}	e_g	b_1	$1/2\sqrt{\pi}$	$\sqrt{5}/7\sqrt{\pi}$	$1/14\sqrt{\pi}$	$\sqrt{5}/\sqrt{14\pi}$
d_{xy}	t_{2g}	b_2	$1/2\sqrt{\pi}$	$-\sqrt{5}/7\sqrt{\pi}$	$1/14\sqrt{\pi}$	$-\sqrt{5}/\sqrt{14\pi}$
d_{xy}, d_{yz}	t_{2g}	e	$1/2\sqrt{\pi}$	$\sqrt{5}/14\sqrt{\pi}$	$-2/7\sqrt{\pi}$	0

Thus we see a D_4 symmetry splits the originally five-fold degenerate d orbitals into four distinct energy levels, one two-fold and three one-fold degenerate states.

The spherically symmetry term $a(B_0^0 + C_0^0)$ is the same for each state and hence does not contribute to the relative ordering of the orbitals, and is ignored here. Thus for this symmetry we are left with five crystal field parameters, C_4^4, B_4^0, C_4^0, B_2^0 and C_2^0, and two undetermined radial integrals. All of these can be treated as parameters which are a measure of the strength of axial and inplace binding as
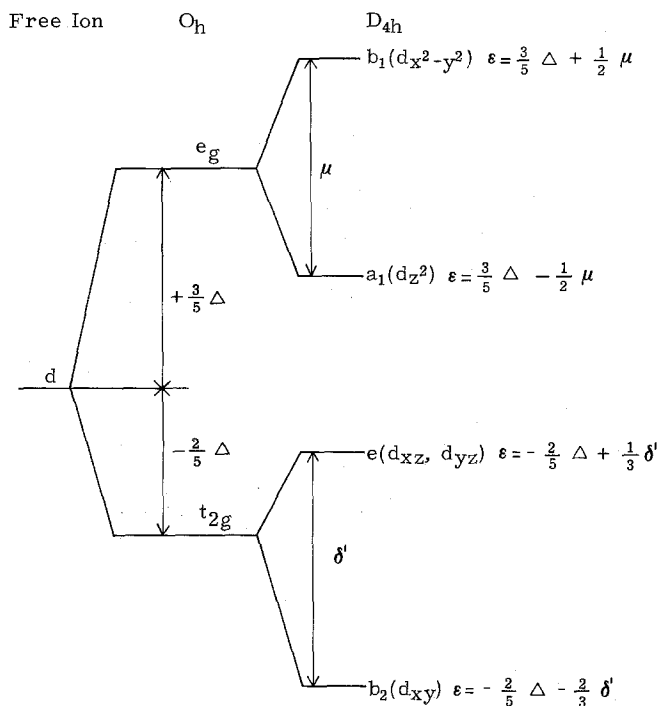
Fig. 2. Single orbital crystal field energies in D_{4h} symmetry

translated to the crystal field model. In our calculations we combine the B's and C's and r^n into three parameters and express the single orbital energies in terms of them: If we let

$$A_4^0 = (B_4^0 + C_4^0) \langle r^4 \rangle \tag{4a}$$

$$A_4^4 = C_4^4 \langle r^4 \rangle \tag{4b}$$

$$A_2^0 = (B_2^0 + C_2^0) \langle r^2 \rangle \tag{4c}$$

then the single orbital energy differences as shown in Fig. 2 are:

$$\Delta = 7/6 \frac{5}{14\sqrt{\pi}} A_4^0 + 5/6 \sqrt{\frac{5}{14\pi}} A_4^4 \tag{5a}$$

$$u = -4 \frac{\sqrt{5}}{14\sqrt{\pi}} A_2^0 - \frac{5}{14\sqrt{\pi}} A_4^0 + \sqrt{\frac{5}{14\pi}} A_4^4 \tag{5b}$$

$$\delta' = 3 \frac{\sqrt{5}}{14\sqrt{\pi}} A_2^0 - \frac{5}{14\sqrt{\pi}} A_4^0 + \sqrt{\frac{5}{14\pi}} A_4^4. \tag{5c}$$

9*

Each individual orbital energy ε in D_4 symmetry can be written as a function of Δ, u and δ' as shown in Fig. 2. Thus, for this symmetry the single orbital strong crystal field energies are each a function of three parameters, either the direct crystal field coefficients A_2^0, A_4^0, A_4^4, or equivalently, the relative values of the single orbital energies Δ, u and δ'. These single orbital energies and the corresponding pure d eigenfunctions serve then as the zero order basis for the consideration of the remaining terms in the Hamiltonian.

2. Treatment of Crystal Field Parameters

In previous calculations, using a strong crystal field of axial symmetry, the problem has been further simplified by using only two crystal field parameters, one cubic parameter and one tetragonal parameter. This was done by assuming that the parameter Δ always had its limiting octahedral value, Δ_{O_h}, uncorrected for different axial ligands, and in addition by considering only the effect of the A_2^0 term in the potential on the tetragonal splittings u and δ'. From Eqs. (5 b) and (5 c) it may be seen that in this approximation u and δ' are proportional with a fixed proportionality constant of 4/3, leaving only one free tetragonal parameter. There is no a priori justification for this assumption, and we do not make it in the present calculation.

We wish now to redefine our crystal field parameters somewhat to make more obvious their link to actual variations in different ligands in different ferric ion complexes. For this purpose we consider the behavior of the A_l^m parameters in the limit of octahedral symmetry. There, all six ligands are equal and:

$$A_2^0 = 0, \qquad A_4^0 = \sqrt{14/5}\, A_4^4.$$

hence

$$u = 0, \qquad \delta' = 0, \qquad \Delta \to \Delta_{O_h} = (2\sqrt{5/14\pi}\, A_4^4). \tag{6a}$$

The orbital energies in this limit are:

$$\varepsilon(b_2) = \varepsilon(e) = \varepsilon(t_{2g}) = -(2/5)\,\Delta_{O_h},$$
$$\varepsilon(a_1) = \varepsilon(b_1) = \varepsilon(e_g) = (3/5)\,\Delta_{O_h},$$

i.e. $\varepsilon(e_g) - \varepsilon(t_{2g}) = \Delta_{O_h}$, which is also called $10D_q$.

As an axial distortion is introduced, the value of A_4^0 changes. Consequently, as seen from Eq. (5a), the value of Δ deviates from Δ_{O_h}. We have then what might be called a tetragonal correction to the octahedral splitting, i.e., a correction due to the inequivalence of axial and in-plane ligands reflected in a changing value of A_4^0. Writing $\Delta = \Delta_{O_h} + \Delta_c$ and comparing equations (5a) for Δ and (6a) for Δ_{O_h} we obtain

$$\Delta = \Delta_{O_h} + 7/6 \left[\frac{5}{14\sqrt{\pi}} A_4^0 - \sqrt{\frac{5}{14\pi}} A_4^4 \right]. \tag{6b}$$

Referring to Eqs. (5 b) and (5 c) for u' and δ' we see that they become zero in the O_h limit for two reasons: A_2^0 is zero and the term in A_4^0 balances the one in A_4^4. Thus there are two true tetragonal parameters, A_2^0 and a change in A_4^0. The values of these and the third parameter Δ are all affected by axial distortion.

We now define two new parameters:

$$u' = \frac{-4\sqrt{5}}{14\sqrt{\pi}} A_2^0, \tag{6c}$$

$$C' = \frac{\sqrt{5}}{\sqrt{14\pi}} A_4^4 - \frac{5}{14\sqrt{\pi}} A_4^0. \tag{6d}$$

Substituting these expressions into Eqs. (6 b), (5 b), and (5 c) for Δ, u and δ' we obtain:

$$\Delta = \Delta_{O_h} - 7/6\, C' , \tag{7a}$$

$$u = u' + C' , \tag{7b}$$

$$\delta' = -3/4\, u' + C' . \tag{7c}$$

If we now use Δ_{O_h}, u' and C' as parameters we have separated the effects of the crystal field on the orbital energies into two tetragonal parameters, u' and C', both of which go to zero in the limit of octahedral symmetry and a third parameter, Δ_{O_h}, which has its "cubic field" value throughout the calculation.

To gain further insight into a reasonable variation of these parameters, we can . for the moment take the crystal field model literally. If we assume that each in-plane ligand is replaced by an effective point charge q placed at a distance R along the $\pm x$ and $\pm y$ axes and that each axial ligand is replaced by another effective point charge p at Z along the $\pm z$ axis, we can calculate expressions for the B_l^m and C_l^m coefficients in the potential and hence of the A_l^m coefficients in terms of effective charges and average radial distances:

$$A_4^{0\star} = \sqrt{\pi}(4/3\, p/Z^5 + q/R^5)\langle r^4\rangle , \tag{8a}$$

$$A_4^4 = \sqrt{35\,\pi}/3\sqrt{2}(q/R^5)\langle r^4\rangle , \tag{8b}$$

$$A_2^0 = 4\sqrt{\pi}/\sqrt{5}(p/Z^3 - q/R^3)\langle r^2\rangle . \tag{8c}$$

Using the definitions of Δ_{O_h}, u', and C' in terms of the A_l^m's in Eqs. (6 b), (6 c) and (6 d) we can write:

$$\Delta_{O_h} = 5/3(q/R^5)\langle r^4\rangle , \tag{9a}$$

$$u' = 8/7(q/R^3 - p/Z^3)\langle r^2\rangle , \tag{9b}$$

$$C' = 10/21(q/R^5 - p/Z^5)\langle r^4\rangle . \tag{9c}$$

We see that Δ_{O_h} depends only on the value of an average, total six-ligand interaction while u' and C' are both related to differences in the in-plane and axial field strengths.

Equations (7 a), (7 b), and (7 c) for the relative orbital energies in terms of u', and C', and Δ_{O_h} are general and independent of our interpretations of u', C' and Δ_{O_h} in terms of the point charge expressions (9 a), (9 b), and (9 c). However, by using these latter expressions we have a fairly obvious link between changes in the complex and changes in the parameters. We can therefore hope to use these parameters in a self-consistent way to explain observed changes in a given property in a series of heme complexes. In making these correlations, we use the points charge model simply as a guide and do not take the electrostatic aspects literally. Instead we make the following generalization: We correlate the value of q/R with the strength of the in-plane bonding and of p/Z with the axial bonding. Then a change in q/R means a change in in-plane bonding, for example q/R increases as bonding inter- action increases. Similarly, a change in p/Z is associated with a change in axial bonding, for example p/Z increasing means axial bond strength is increasing.

★ For positively charged central metal ion, if the ligands have a net negative charge, p and q should be taken as absolute values in the above expressions. If the ligands have a net positive charge the sign of each coefficient should be changed.

Using Eqs. (9a, b, c) with the general interpretation of them just described, we arrive at a set of rules for parameter values and variations consistent with actual physical situations and their variations. These are:

a) Both u' and C' relate to differences between axial and in-plane field strengths or bonding interactions. For complexes in which the in-plane interactions exceed the axial ones, u' and C' are positive, and where the converse is true, both are negative. In either case, it is not consistent with this model to allow u' and C' to have opposite signs. The relative magnitudes of u' and C' cannot be predicted a priori. However, they do increase and decrease together with the same changes in the physical system. Since u' and C' vary together, no generality is lost if we make one proportional to the other and define $C' = f u'$ with f positive. The magnitude of f then is a measure of the relative magnitude of the t_{2g} and e_g tetragonal splittings u and δ', i.e.,

$$\frac{u}{\delta'} = \frac{(1+f)}{(-3/4+f)} = \sigma .$$

We have then 2 tetragonal parameters, one (u') which measures the magnitude of the tetragonal orbital splitting and the other (f) which determines the ratio of the 2 tetragonal splittings.

b) The expression for Δ_{O_h} can be interpreted in two ways: q/R^5 can be regarded as being the value for the in-plane ligands only, assuming six such ligands. In this case, as the axial ligand varies Δ_{O_h} remains constant. Alternately it can be regarded as an average effect of all six ligands of a given complex, then Δ_{O_h} varies with any change in the complex, since the average value of q/R^5 will be changed. While either behavior can be selected as a definition, we tend to favor the latter as being closer to the actual physical situation.

c) Since the Δ_{O_h} parameter depends only on the average behavior of all six ligands assumed equivalent, and both the u' and C' parameters depend on the differences between axial and in-plane ligands, the relative magnitude of Δ_{O_h} vs. u' and C' is determined by the amount of axial distortion that is present in any given compound. C' should never exceed Δ_{O_h} since it represents the difference in axial and in-plane interactions to the same order as Δ_{O_h} does the total average interactions. u', a quadratic tetragonal term could possibly exceed Δ_{O_h} but then it would be more reasonable to restate the whole problem in terms of a strong axial field and not terms of corrections to cubic symmetry.

With these guidelines then we have completely defined what we call a self-consistent variation of the parameter u', C' and Δ_{O_h} for given variations in the in-plane and axial interactions of the ferric ion with its nearest neighbors. These may be summarized as follows: If the in-plane interaction is kept constant, and the axial field varied, then as the axial field increases Δ_{O_h} increases while u' and C' decrease. If, on the other hand, the in-plane ligands are varied and the axial ligands kept constant, then as the "in-plane" interactions increase, Δ_{O_h} increases but u' and C' also increase.

It is these three parameters which we vary extensively in our calculations of eigenfunctions and eigenvalues.

The parameters that are finally chosen to fit a series of compounds can be translated immediately into single orbital energies. In terms of Δ, u and δ', the single

orbital energies are those given in Fig. 2. In terms of u, C' and Δ_{O_h} the energies are:

$$\varepsilon(b_2) = -2/5\,\Delta_{O_h} + 1/2\,u' - 1/3\,C', \tag{10a}$$

$$\varepsilon(e) = -2/5\,\Delta_{O_h} - 1/4\,u' + 2/3\,C', \tag{10b}$$

$$\varepsilon(a_1) = 3/5\,\Delta_{O_h} - 1/2\,u' - 6/5\,C', \tag{10c}$$

$$\varepsilon(b_1) = 3/5\,\Delta_{O_h} + 1/2\,u' - 1/5\,C'. \tag{10d}$$

By this latter treatment of crystal field parameters, a fair amount of physical significance can be given to the single orbital energies obtained to agree with experimental observations, for example, of the zero-field split $^6A_1$ transitions. These single orbital energies correspond to the anti-bonding partners of metal-ligand molecular orbitals and the energies obtained from our calculations can be compared with those from a molecular orbital calculation. The single orbital functions themselves however will be pure metal d orbitals.

B) Total Five-Electron States: Crystal Field and Electrostatic Energies

1. Electrostatic Energies

In a strong field, the orbitals t_{2g} and e_g form the basis for five electron configurations $t_2^n e^{5-n}$, all derived from the original free ion configuration d^5. When further split by tetragonal distortion, the a_1, b_1, b_2, and e symmetry orbitals form the basis for a much larger number of configurations. In order to construct total five-electron states in tetragonal symmetry, we shall use the five cubic field configurations. These five configurations lead to 43 total five-electron multiplets, each labeled in the following manner:

$$|t_2^n(S_1 h_1),\ e^{5-n}(S_2 h_2);\ Sh\rangle$$

where $t_2^n e^{5-n}$ is the configuration from which the total state of spin S and symmetry h is constructed. Griffith [5] gives detailed procedures for constructing such total states from sub-states from configuration t_2^n with spin S_1 and symmetry h_1 and e^m with spin S_2 and symmetry h_2. These total states are the strong field analogues of the free ion multiplets, labeled by a total spin and the representation of the cubic group to which they belong. Griffith has also calculated the electrostatic energies matrix elements between these states, i.e., matrix elements of the operator e^2/r, in terms of the Racah coefficients B and C. We have used these electrostatic energies to first order as an estimate of the ordering of the total strong field states before spin-orbit mixing, and in the limit of allowing the crystal field parameters to go to zero.

In previous calculations of energy eigenvalues and eigenfunctions for the high and low spin ferric ion complexes [1, 2], we have varied the number of the 43 multiplet states included in the calculation from 1 to 12. Our results indicated that only two of these strong field multiplets interact significantly with the $^6A_1$ ground state by spin-orbit coupling. These are the lowest lying quartet state $4T_1(t_2^4 e)$ and the unique doublet state $2T_2(t_2^5)$ which is particularly stabilized by the crystal field because of its configuration. Thus in our present calculation of the properties of the ferric ion states due to a strong tetragonal crystal field and spin-orbit coupling, we have considered only these 24 states, the 12 components of the $^4T_1(t_2^4 e)$ state, the six components of the $^2T_2(t_2^5)$ state, and the six $^6A_1(t_2^3 e^2)$ com-

ponents. The relative first order electrostatic energies of these three multiplet states are then in terms of the Racah parameters, B and C:

$$^6A_1 = 0, \tag{11a}$$

$$^4T_1 = 10B + 6C, \tag{11b}$$

$$^2T_2 = 15B + 10C. \tag{11c}$$

B and C are used as parameters in this calculation.

2. Crystal Field Energies of Total States

The $^4T_1(t_2^4 e)$ state is split into two states, a four-fold degenerate $^4A_2$ state and an eight-fold degenerate ^4E state, by the tetragonal field. Similarly, the $^2T_2(t_2^5)$ state is split into a two-fold degenerate $^2B_2$ state and a four-fold degenerate

Table 2. *Correspondence of octahedral and tetragonal representations*

$O_h|h\theta\rangle$[a]	$D_4|h\theta\rangle$
$T_1(0)$	$^4A_2$
$T_1(\pm1)$	E
$T_2(0)$	B_2
$T_2(\pm1)$	E
$E(e)$	B_1
$E(\theta)$	A_1
A_2	B_1
A_1	A_1

[a] h = irreducible representation, θ = component of irreducible representation.

^2E state. The state appropriate to D_4 symmetry can be formed from a linear combination of the octahedral states. Correspondingly, the configurations in D_4 symmetry can be formed from a linear combination of O_h configurations. To obtain the state and orbital labels in D_4 corresponding to the labeling in $O_h(t_{2g}^n e_g^m)$ notation, we have used the procedure outlined in Griffith and Tables 20 and 24 of his book [5], and Table 2 indicating how components of representations in O_h correspond to components of representations in D_4 symmetry.

Applying the methods outlined by Griffith and using the orbital energies shown in Fig. 2, we obtain the crystal field energies of each total state used in the present calculations. These are given in Table 3 along with the original O_h states from

Table 3. *Crystal field energies of total electronic states in D_4 symmetry*

$|Sh\rangle_{O_h}$	$|Sh\rangle_{D_4}$	D_4 Configuration	Crystal field energy
$^6A_1$	$^6A_1$	$(e)^2(b_2)(a_1)(b_1)$	0
$^4T_1$	$^4A_2$	$(e)^2(b_2)^2(a_1)$	$-\Delta - 2\delta'/3 - u/2$
$^4T_1$	^4E	$[-1/2(e)^3(b_2)(a_1) + \sqrt{3}/2(e)^3(b_2)(b_1)]$	$-\Delta + \delta'/3 + u/4$
$^2T_2$	$^2E_2$	$(e)^3(b_2)^2$	$-2\Delta - \delta'/3$
$^2T_2$	$^2B_2$	$(e)^4(b_2)$	$-2\Delta + 2\delta'/3$

which the D_4 states come and the electron configurations in D_4 symmetry of each state. Fig. 3 is a schematic representation of the total energy of each state to first order. The relative electrostatic and crystal field energy in an octahedral field is shown in the first column, followed by the additional splitting caused by a tetragonal field. At this stage there are then five multiplet states, $^6A_1$, $^4A_2$, ^4E, $^2B_2$, and ^2E. We see from this figure the significant result that the tetragonal splitting of the $^4T_1$ state depends only on one of the tetragonal parameters, i.e., $E(^4E)$

O_h D_4 D_4*

$^2B_2$ E''

$^2T_2$

$\delta' = -\frac{3}{4}u' + C'$ E' $\varepsilon = \frac{1}{2}\delta$

^2E E'' $\varepsilon = -\frac{1}{2}\delta$

$(15\,B + 10\,C - 2\Delta)$

E' $\varepsilon = \frac{1}{4}\delta$

E' $\varepsilon = \frac{1}{12}\delta$

^4E E'' $\varepsilon = -\frac{1}{12}\delta$

E'' $\varepsilon = -\frac{1}{4}\delta$

$^4T_1$

$(\delta' + \frac{3}{4}u) = \frac{7}{4}C'$

$^4A_2$ $E'(\alpha, \beta)$, $E''(\alpha, \beta)$

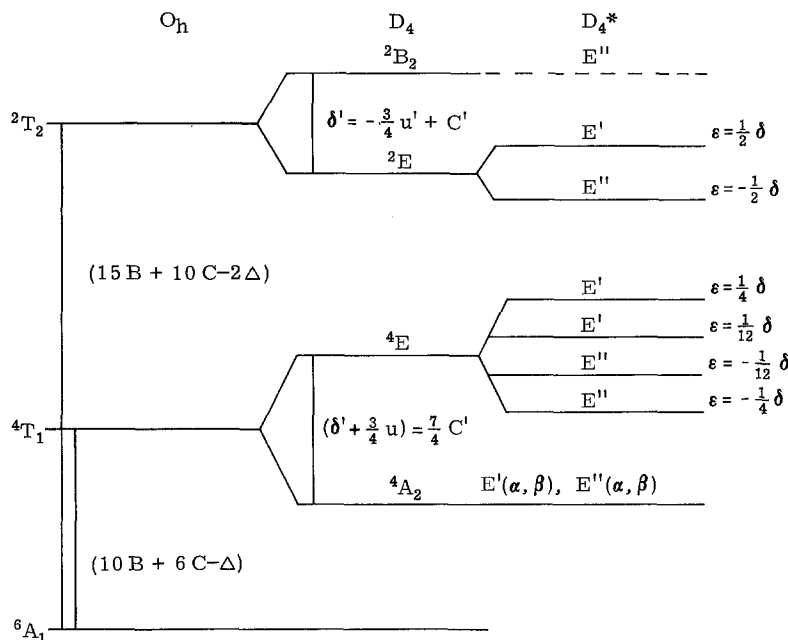$(10\,B + 6\,C - \Delta)$

$^6A_1$

Fig. 3. First order electrostatic, crystal field, and spin-orbit coupling energies of the sextet, quartet and doublet states

$- E(^4A_2) = 7/4\,C'$, while the splitting of the doublet state depends on both u' and C'. The quartet states are the only ones which interact directly with the sextet states through spin-orbit interaction. They also interact directly with the doublet state which then interact indirectly with the sextet state. In the high spin region, where sextet-quartet interaction dominates, we would expect the magnitude of zero field splitting and other properties resulting from spin-orbit coupling to depend only on the value of the one tetragonal parameter C' in addition to the cubic field parameter. The problem in this region reduces to a two parameter problem then, without any further approximations. These two parameters are, however, coupled and vary according to Eqs. (7a) and (7b) and the rules for self-consistency.

C) Spin-Orbit Coupling Interaction

1. Matrix Elements

Spin-orbit matrix elements of the form $H_{ij} = N\delta$ were calculated using the operator $H = \sum_i \delta_i(r_i)\,l_i \cdot s_i$ by second order irreducible tensor methods first developed for the many electron atom by Racah, Fano and others, and extended to

atoms of lower than spherical symmetry by Griffith [6]. To do this the 24 basic states were labeled by the four "quantum numbers" $|ShM\theta\rangle$, where S is the total spin of the state, M is the z component of the total spin, h is the irreducible representation of the group to which they belong, and θ is the component of that representation. Complex components 1, 0, and -1 were used for the three fold degenerate T_i representations. Alternately these functions were labeled by the spinor representation and component $|t\tau\rangle$ to which they belong in D_4^*. The spin-

Table 4. *Basis set for spin-orbit coupling interactions*

A. $E''(7\cdot 7)$ matrix

φ_i	$|t\tau\rangle = E''\alpha''$ $|M_s$	$\theta\rangle$	$|Sh\,O_h\rangle$	$|Sh\,D_4\rangle$	$|t\tau\rangle = E''\beta''$ $|M_s$	$\theta\rangle$
1	5/2	i	$^6A_1$	$^6A_1$	$-5/2$	i
2	$-3/2$	i	$^6A_1$	$^6A_1$	3/2	i
3	$-3/2$	0	$^4T_1$	$^4A_2$	3/2	0
4	3/2	1	$^4T_1$	^4E	$-3/2$	-1
5	$-1/2$	-1	$^4T_1$	^4E	1/2	1
6	$-1/2$	1	$^2T_2$	^2E	1/2	-1
7	1/2	0	$^2T_2$	$^2B_2$	$-1/2$	0

B. $E'(5\cdot 5)$ matrix

φ_i	$|t\tau\rangle = E'\alpha'$ $|M_s$	$\theta\rangle$	$|Sh\,O_h\rangle$	$|Sh\,D_4\rangle$	$|t\tau\rangle = E'\beta'$ $|M_s$	$\theta\rangle$
8	1/2	i	$^6A_1$	$^6A_1$	$-1/2$	i
9	1/2	0	$^4T_1$	$^4A_2$	$-1/2$	0
10	$-1/2$	1	$^4T_1$	^4E	1/2	-1
11	3/2	-1	$^4T_1$	^4E	$-3/2$	1
12	$-1/2$	-1	$^2T_2$	^2E	1/2	1

orbit coupling operator is diagonal in this representation. The result of spin-orbit coupling then is to yield a set of 12 doubly degenerate functions. For D_4^* symmetry these functions factor into two sets of non-interacting blocks, a $5\cdot 5$ labeled by E' (α' or β') and a $7\cdot 7$ labeled by E'' (α'' or β''). The E' and E'' states are listed in Table 4 with both $|ShM\theta\rangle$ and $|Sh\,t\tau\rangle$ labeling. Also shown is the representation h in both O_h and D_4 to which these states belong. There are some spin-orbit coupling matrix elements H_{ij} linking states of the same D_4 multiplet. These represent, then, first order energies of the partners of these multiplet states and a first order spin-orbit energy splitting among them results. This is also shown in Fig. 3 under D_4^* double group symmetry labeling: E' and E''. Thus, this last column represents the total first order energy of the 12 doublet states. We now allow these states to spin-orbit interact to all orders. The spin-orbit matrix elements calculated for these E' and E'' states by the methods outlined by Griffith [6] are given in Table 5. For the system at hand, the contributions to the zero field splitting of the sextet state from interactions with the $^4A_2$ multiplet just balance those from interactions with the ^4E state in the limit that the energy of these two excited states are equal, i.e., in the

cubic field limit. Thus to obtain a fair estimate of the effect of tetragonal distortion on the magnitude of zero field splitting of the sextet states, the contributions from both the $^4A_2$ and ^4E multiplet must both be included. If the ^4E partner is omitted as it has been in some previous calculations [5], the zero field splitting calculated for each set of values for parameters will be too large, since the ^4E state has a balancing effect.

Table 5

A. E'' $(7 \cdot 7)$ spin-orbit coupling matrix elements[a]

	$^6A_1(\pm\frac{5}{2})$	$^6A_1(\pm\frac{3}{2})$	$^4A_2(\pm\frac{3}{2})$	$^4E(\mp\frac{3}{2},\mp 1)$	$^4E(\pm\frac{1}{2},\pm 1)$	$^2E(\pm\frac{1}{2},\mp 1)$	$^2B_2(-\frac{1}{2},0)$
$^6A_1(\pm 5/2)$	0	0	0	$-\sqrt{2}$	0	0	0
$^6A_1(\mp 3/2)$	0	0	$-2/\sqrt{5}$	0	$-\sqrt{6/5}$	0	0
$^4A_2(\pm 3/2)$	0	$-2/\sqrt{5}$	0	0	$-1/2\sqrt{6}$	$\sqrt{3/2}$	0
$^4E(\pm\frac{3}{2},\mp 1)$	$-\sqrt{2}$	0	0	$-1/4$	0	0	$\sqrt{3/2}$
$^4E(\pm\frac{1}{2},\pm 1)$	0	$-\sqrt{6/5}$	$-1/2\sqrt{6}$	0	$-1/12$	1	$-1/\sqrt{2}$
$^2E(\pm\frac{1}{2},\mp 1)$	0	0	$\sqrt{3/2}$	0	1	$-1/2$	$1/\sqrt{2}$
$^2B_2(-\frac{1}{2},0)$	0	0	0	$\sqrt{3/2}$	$-1/\sqrt{2}$	$1/\sqrt{2}$	0

B. E' $(5 \cdot 5)$ spin-orbit coupling matrix elements[a]

	$^6A_1(\pm 1/2)$	$^4A_2(\pm 1/2)$	$^4E(\pm\frac{1}{2},\mp 1)$	$^4E(\mp\frac{3}{2},\pm 1)$	$^2E(\pm\frac{1}{2},\pm 1)$
$^6A_1(\pm 1/2)$	0	$-\sqrt{6/5}$	$-\sqrt{3/5}$	$-1/\sqrt{5}$	0
$^4A_2(\pm 1/2)$	$-\sqrt{6/5}$	0	$-1/3\sqrt{2}$	$-1/2\sqrt{6}$	$-1/\sqrt{2}$
$^4E(\pm\frac{1}{2},\mp 1)$	$-\sqrt{3/5}$	$-1/3\sqrt{2}$	$1/12$	0	-1
$^4E(\mp\frac{3}{2},\pm 1)$	$-1/\sqrt{5}$	$-1/2\sqrt{6}$	0	$1/4$	0
$^2E(\pm\frac{1}{2},\pm 1)$	0	$-1/\sqrt{2}$	-1	0	$1/2$

[a] Matrix elements have the form $H_{ij}=N_{ij}\delta$, where N_{ij} are the numbers in the table, and δ = spin-orbit coupling parameter.

We have previously verified this result, by making calculations with and without the ^4E state. Since there is no physical reason for leaving this state out, it is included in the calculation.

In general then, we would expect the zero field splitting and other effects of spin-mixing in the sextet state to increase with the magnitude of Δ_{O_h} which brings the quartet state components closer to the sextet ground state and with the value of the tetragonal splitting of the quartet states which is equal to $7/4\,C'$. In the limit of very large C' the ^4E energy is much larger than the $^4A_2$ and then the approximation of neglecting the ^4E state contribution becomes valid. The calculations themselves indicate this region, however, since the magnitude of the zero field splittings becomes independent of C' for large C' and hence no a priori change in the model need be made to include this possibility.

2. Parameter Variation

The spin-orbit matrix elements given in Table 5 together with diagonal elements for each state which include the electrostatic and crystal field energies given by Eqs. (11 a, b, c), and Table 3, and shown schematically in Fig. 3, were used in a matrix diagonalization program written for the Burroughs 5500 to obtain sets of 12 eigenvalues and 12 doubly degenerate eigenfunctions, resulting from the

solution of a $7 \cdot 7 (E'')$ and a $5 \cdot 5 (E')$ spin-orbit matrix. This calculation is a function of six parameters, the two electrostatic parameters B and C, three crystal field parameters Δ_{O_h}, u' and C', and the spin-orbit coupling parameter δ. In addition the results depend on the number of excited states included in the calculation. Previous calculations, varying the number of excited states included from 1 to 33 total E'' and E' states, led to the conclusion that the states included in the present calculation are the most important in explaining the effects of spin-orbit coupling.

Since both electrostatic and crystal field energies are considered to first order only, and appear in an additive fashion in the diagonal element, a decrease in the value of electrostatic parameters used would mean a corresponding decrease in the value of Δ_{O_h} at which any observed property occurred. For example, for smaller values of B and C, a smaller value of the maximum Δ_{O_h} above which a sextet ground state could not occur would be obtained. We have made such a trial calculation varying B and C and such was the case. We found we could scale most of the results to the relative values of B, C, and Δ_{O_h}. Hence the absolute values of all cubic field parameters we specify for a certain value of a certain property are dependent on the value of B and C chosen and so do not have by themselves great physical significance. However the relative values of all parameters, their variation from compound to compound, and the fact that regions of changing ground states do exist are all quite significant.

In previous calculations the spin-orbit coupling parameter was varied from 150 to 600 cm^{-1}, the free ion value being 420 cm^{-1}. In this calculation we fix the value at 420 cm^{-1}. Again, experience has shown that decreasing the spin-orbit coupling strengt simply increases the values of crystal field parameters at which agreement with experiment is obtained and all properties follow a consistent pattern. It did not then seem a worthwhile endeavor to vary this parameter extensively.

In this calculation then we are thus left with the three crystal field parameters, the variation of which in a consistent manner as just outlined is of particular interest here.

We turn now to a discussion of the results obtained from these calculations.

III. Results: Delineation of Different Ground State Regions in Parameter Space
A) Before Spin-Orbit Coupling

The effect of a strong crystal field of tetragonal symmetry without spin-orbit coupling can cause a doublet or quartet state to become the ground state. In this approximation, it is possible to establish simple crystal field parameter conditions for such changes.

1. Doublet Ground State

For a doublet ground state, for conditions where the axial perturbation is smaller than the in-plane one, it is the $^2E(\mp\frac{1}{2}, \pm 1)$ state, i.e., component φ_6 in Table 4, that becomes the ground state. The condition for this change to occur is $E(^2E) - E(^6A_1) \leqq 0$. From Fig. 3, Eqs. (11a, b, c) and Table 3 we see that this condition in terms of first order electrostatic and crystal field energy parameters is:

$$15B + 6C - 2\Delta_{O_h} + 14C'/6 - 1/3(-3/4u' + C') \leqq 0 \qquad (12a)$$

with the three crystal field parameters Δ_{O_h}, C' and u' defined as in Eqs. (6a), (6c), and (6d). For the values of the two Racah parameters B and C used in the present calculation this condition becomes

$$(2\Delta_{O_h} - 2fu' + u'/4) \geqq 54\,000 \text{ cm}^{-1} \tag{12b}$$

where $C' = fu'$.

Thus the conditions for a doublet ground state depend on all three crystal field parameters. Several useful observations can be made from Eq. (12b). Since f is always positive, for values of $\Delta_{O_h} \leqq 27\,000$ cm^{-1}, u' must be negative to have a doublet ground state, i.e., the axial field must be stronger than the in-plane field. In such a case, the $^2B_2$ state, i.e., φ_7 of Table 4, is the ground state. For values of $\Delta_{O_h} \geqq 27\,000$ cm^{-1} however, a doublet state can occur for axial fields weaker than in-plane fields, and the ^2E state is the ground state. This latter result agrees with our previous calculations for low spin ferric heme complexes with a more approximate two parameter treatment of tetragonal parameters. In that calculation only

Table 6. *Doublet ground state conditions without spin-orbit coupling*
for $f = 1/2$; $54\,000$ cm$^{-1} = 2\Delta_{O_h} - 5/4\,\mu'$
for $f = 1$; $54\,000$ cm$^{-1} = 2\Delta_{O_h} - 9/4\,\mu'$
for $f = 4$; $54\,000$ cm$^{-1} = 2\Delta_{O_h} - 33/4\,\mu'$
for $f = 9$; $54\,000$ cm$^{-1} = 2\Delta_{O_h} - 73/4\,\mu'$
Maximal μ' for which a doublet is a ground state

f	Δ_{O_h} [cm^{-1}]				
	28 000	30 000	32 000	35 000	40 000
0.5	1 600	4 800	8 000	12 800	20 800
1	900	2 680	4 445	7 100	11 555
4	250	750	1 250	2 000	3 250
9	110	330	555	800	1 445

the case for axial fields weaker than in-plane was treated, the minimum octahedral field strength needed was $27\,000$ cm^{-1}, and the ^2E state was the ground state. That this state is the ground state in low spin heme complexes appears to be borne out by the electron spin and magnetic succeptibility measurements. Therefore the possibility of axial fields stronger than in-plane fields in the heme complexes seems to be eliminated.

The actual numerical value of $27\,000$ cm^{-1} for the minimum cubic field strength which allows a doublet ground state with axial field weaker than in-plane field is dependent on the value of B and C chosen, as we have already discussed to some extent. However, the existence of such a minimum appears to be real and accounts for possible variations in ferric ion ground states with small changes in field strength conditions. Table 6 gives the field strength conditions for a low spin ground state, before spin orbit coupling, in terms of the three crystal field parameters. For a given value of cubic field strength, Δ_{O_h}, and a given ratio of quartic to quadratic tetragonal corrections, f, this table lists the maximum values of u', i.e., minimum axial field strengths for which a doublet can still be the ground state. For values of $u' \leqq u_{\max}$ given in this table, the axial field is strong enough, relative to the in-plane field to allow a doublet ground state. For values of u' greater than

those in this table, i.e., weaker axial fields, a doublet ground state can no longer exist. We see from this table that the larger the quartic correction, i.e., the larger the value of f, the smaller the quadratic one, u', must be to maintain a doublet ground state. As Δ_{O_h} increases, for a given value of f, the weaker the relative axial field, i.e., the larger the value of u' that will sustain a doublet ground state.

2. Quartet Ground State

There is recent evidence that in ferric bis-NN-diethyl-dithiocarbamato-chloride $Fe[S_2C-NR_2]_2Cl$, where $R=C_2H_5$, ferric ion is in a $^4A_2$ ground state [7]. Without spin-orbit coupling, the crystal field condition of such a ground state is:

$$^4A_2 - {}^6A_1 = 10B + 6C - \Delta_{O_h} + 7C'/6 - 2\delta'/3 - u/2 \leq 0 \qquad (13\,a)$$

where all quantities have been previously defined.

Substituting the expression for δ' and u in terms of C' and u', all dependence on the tetragonal parameters cancels out and we obtain a simple quartet ground state criteria:

$$\Delta_{O_h} \geq 33\,500 \text{ cm}^{-1}. \qquad (13\,b)$$
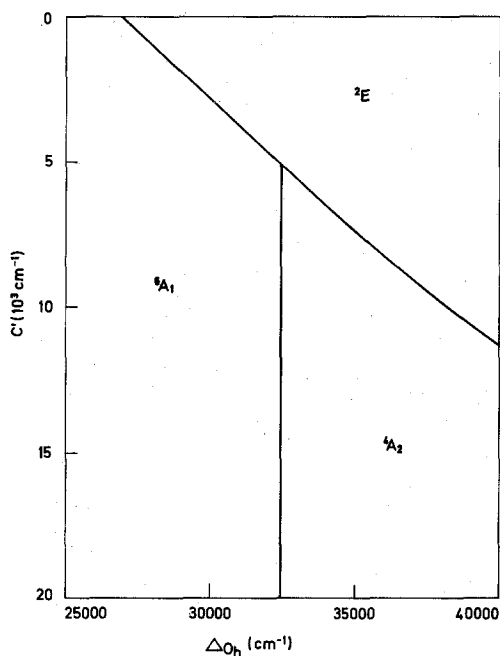
Fig. 4. Pattern of changing ferric ion ground state without spin-orbit coupling ($f = 1$, $B = 1100 \text{ cm}^{-1}$, $C = 3750 \text{ cm}^{-1}$)

Without spin-orbit coupling then, the pattern of changing ground state is shown schematically in Fig. 4. For cubic field strengths weaker than $33\,500 \text{ cm}^{-1}$, the ground state changes from a doublet to a sextet state as the axial strength decreases. For cubic field strengths greater than $33\,500 \text{ cm}^{-1}$, the ground state changes from a doublet to a quartet state as the axial field weakens. For cubic fields less than $27\,000 \text{ cm}^{-1}$ and all values of axial field less than in-plane field, only the sextet ground state is possible.

B) Effects of Spin-Orbit Coupling

1. Method of Boundary Delineation

Let us now examine the effect of spin-orbit coupling among the twelve Kramer's doublets listed in Table 4. In addition to sextet, quartet and doublet ground states as before, there is also the added possibility of substantially spin-mixed ferric ion states. In fact, all states will be spin-mixed to some extent. We therefore define a pure spin state as one with less than 2 % mixing of any other spin component, and all other states as spin-mixed. With these definitions we have written a program to search for the boundaries in parameter space along which these conditions hold. The range of values of crystal field parameters chosen were: Δ_{O_h} from 10 000 to 40 000 cm^{-1}, f from 0.5 to 9, and u' from $-12\,\Delta_{O_h}/7f$ to $+6\,\Delta_{O_h}/7f$. The lower limit of u' was chosen to insure axial fields large enough to detect doublet ground state conditions for all values of cubic strength selected. The upper limit is that which makes the corrected value of Δ_{O_h} go to zero. The cubic field parameter range was chosen to cover all reasonable possibilities of five and six coordinated compounds. The range of f, the quartic/quadratic tetragonal corrections, is more arbitrary and simply represents a possible spectra of this ratio. Within this range of parameters for a given value of Δ_{O_h} and f, values of u' and C' $(= fu')$ were found which delineate the boundaries of the pure spin regions in the following fashion:

a) A maximum value of u' was found for which a doublet state can exist, i.e., spin mixing $\leq 2\%$ for $u' \leq u'_{max}$. The minimum value of u' considered for each Δ_{O_h} and f gave a doublet state and hence the total doublet state region was delineated.

b) A minimum value of u' was found for which a pure sextet ground state was possible. The maximum value of u' considered for each Δ_{O_h} was tested. If a sextet state was still a ground state, these two values delineated the high spin region. If a sextet state was no longer the ground state, then the upper boundary of the sextet was located.

c) The minimum value of u' for quartet ground state was obtained. For values of Δ_{O_h} and f where such a value of u' was discovered, the quartet state persisted to the highest value of u' considered.

Fig. 5 shows the results of the search procedure in delineating regions of differing ground state for $f = 1$. For $f \leq 3/4$ the order of doublet states is reversed. There is no evidence of a $^2B_2$ ground state in low spin heme complexes, therefore we eliminate this possibility. For the remaining range of f, there are quantitative differences in the regions delineated for different f, but the nature of these regions remains similar. We shall therefore discuss in most detail the results for $f = 1$ as an example of the possible ferric ion behavior.

2. Low Spin Region

We see from Fig. 5 that for all values of the cubic field strength considered it is possible to have a low spin state if the axial field is strong enough. For each value of Δ_{O_h}, the doublet ground state occurs in the strong axial field strength region. To have a doublet ground state at cubic field values $\Delta_{O_h} \leq 27\,300$ cm^{-1}, u' must be negative, that is, the axial field must be stronger than the in-plane field. This is consistent with the results obtained without spin-orbit coupling which gave a value of 27 000 cm^{-1} for this condition. The effect of spin-orbit coupling is then to

change the value of crystal field parameters needed for a doublet ground state by the same order of magnitude as the additional interaction.

We see also from Fig. 5 that the smaller the cubic field strength, the larger the axial field needed for a doublet ground state. We may use the point charge model
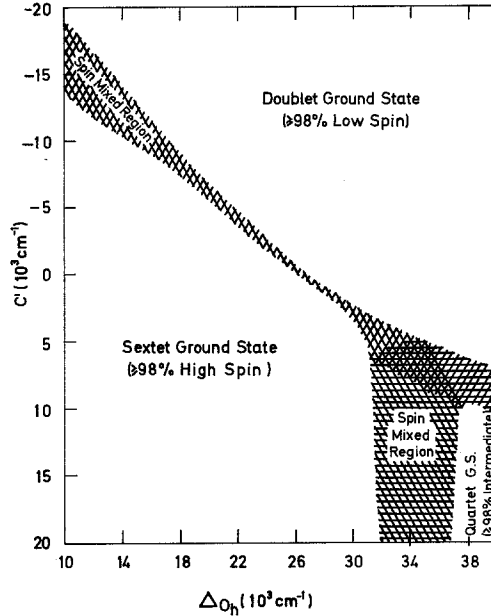
Fig. 5. Delineation of regions of different Fe^{+3} ground states as a function of cubic and tetragonal field strength ($B = 1100 \text{ cm}^{-1}$, $C = 3750 \text{ cm}^{-1}$, $\delta = 420 \text{ cm}^{-1}$, $f = 1$)

to illustrate the conditions on the in-plane and axial interactions that cause a doublet ground state. Using the relationships

$$3/5 \, \Delta_{O_h} = (q/R^5) \langle r^4 \rangle , \tag{14a}$$

$$(21/10) \, C' = [q/R^5 \langle r^4 \rangle - p/Z^5 \langle r^4 \rangle] , \tag{14b}$$

where q/R^5 represents the average strength of interaction in the octahedral limit, and p/Z^5 represents the effective axial interaction, and $C' = fu'$, we can find the values of these interaction parameters at the boundary of the low spin conditions. For example, at $\Delta_{O_h} = 10\,000 \text{ cm}^{-1}$, the minimum value of C' needed for a doublet state is approximately $-20\,000 \text{ cm}^{-1}$. Using the above equations, this corresponds to a value of $q/R^5 \langle r^4 \rangle = 6000 \text{ cm}^{-1}$ and a value of $p/Z^5 \langle r^4 \rangle = 48\,000 \text{ cm}^{-1}$. Thus the axial field must be eight times the average in-plane field to have a doublet ground state. At $\Delta_{O_h} = 20\,000 \text{ cm}^{-1}$, the ratio of axial to in-plane strength is reduced to $14\,070/12\,000$ and at $\Delta_{O_h} = 30\,000 \text{ cm}^{-1}$, the axial field can be weaker, its ratio to the average in-plane field being $13/18$ at that point. These results, shown in Fig. 5, are qualitatively similar for different values of f.

3. The Sextet Ground State Region

For a given value of Δ_{O_h} (and f) as the value of u' is increased, i.e., as the axial field strength is decreased, the ferric ion goes from a low spin to a high spin ground

state. As can be seen from Fig. 5, this is true for all values of $\Delta_{O_h} \leqq 31\,000$ cm^{-1}. Above $31\,000$ cm^{-1} a pure sextet state, i.e., one that is less than 2% spin-mixed, cannot exist.

The sextet state which is the first to become the ground state as the axial distortion is decreased from the low spin conditions is the $^6A_1$ ($\mp 3/2$) state. This is because it is the one which interacts most strongly with the doublet state which is the ground state, this interaction decreasing with decreasing axial strength. As the axial strength continues to decrease, the $^6A_1$ ($\pm 1/2$) state becomes the sextet ground state. Thus there is crossing of two sextet spin states, with different values of $\pm M_s$ in the high spin region of field parameter. Under most conditions, when the $^6A_1$ ($\mp 3/2$) state is the ground state it is not completely pure, i.e., it has more than 2% spin mixing from the doublet and quartet states. Thus the true boundary of the high spin region coincides more properly with the region of $^6A_1$ ($\pm 1/2$) ground state, in agreement with most of the direct observations of the high spin ferric heme complexes.

4. Quartet Ground State

As the axial field strength continues to decrease at a given value of Δ_{O_h} (and f) from the conditions under which a pure sextet state occurs, more and more mixing of the sextet state with the quartet state components occurs. However, a pure high spin state persisted, to the weakest axial fields considered, for all values of $\Delta_{O_h} \leqq 31\,000$ cm^{-1}. For $\Delta_{O_h} > 31\,000$ cm^{-1}, a completely pure sextet state does not occur. For a given Δ_{O_h} in this range, as the axial field decreases from the doublet ground state conditions, the mixing of the sextet into the doublet states increases but reaches a maximum short of 98%. This is because at a certain point, quartet state mixing also begins to be significant and increases as the axial field decreases. Thus for value of Δ_{O_h} between $31\,000$ and $36\,000$ cm^{-1}, from the boundary of the doublet ground state region to the maximum value of axial distortion considered, the region is truly a spin-mixed ground state region. For values of $\Delta_{O_h} \geqq 36\,000$ cm^{-1}, this spin mixing gives way to a pure quartet ground state at the weakest axial fields. An idea of the relative in-plane and axial field interactions which lead to a quartet ground state may be obtained by using the point charge analogy. At $\Delta_{O_h} = 38\,000$ cm^{-1} the quartet becomes the ground state at $C' = 9000$ cm^{-1}. Using eqs. (14a) and (14b) we find $q/R^5 \langle r^4 \rangle = 22\,800$ cm^{-1} and $p/Z^5 \langle r^4 \rangle = 3900$ cm^{-1}. Thus we see that for the relatively small axial/in-plane interaction ratio of about 1/5.5 a quartet ground state is possible in tetragonal symmetry.

The quartet ground state conditions without spin-orbit coupling was $\Delta_{O_h} = 33\,500$ cm^{-1} independent of tetragonal field parameters. We see that spin-orbit coupling causes a significantly large spin-mixed region for weak axial fields. Thus, a larger cubic field strength is required for a pure quartet ground state and this condition now depends on the tetragonal parameter also.

5. Spin-Mixed Ground State Conditions

For values of $\Delta_{O_h} \leqq 31\,000$ cm^{-1}, spin mixing of ground and low lying wave functions occurs as the axial field strength is decreased from the pure doublet to the pure sextet ground state conditions. As can be seen from Fig. 5, the parameter region in which substantial spin-mixed functions exist, at a given Δ_{O_h} (and f) is

narrow compared to the range under which either of the pure spin states, i.e., sextet or doublet, can exist. This doublet-sextet spin-mixed region, defined as the range of values of C' between the minimum required for low spin and the maximum needed for a high spin ground state, becomes narrower the larger the cubic field strength up to about 31 000 cm^{-1}. For example, at $\Delta_{O_h} = 10\,000$ cm^{-1} the spin-mixed region is from $C' = -19\,675$ to $-13\,950$ cm^{-1}, a range of about 5 700 cm^{-1}, while at $\Delta_{O_h} = 30\,000$ cm^{-1} the region of spin-mixed wave functions is narrowed down to values of C' between 2338 and 3325 cm^{-1}, barely 1000 cm^{-1} in scope.

We have just seen that for values of Δ_{O_h} between 31 000 and 36 000 cm^{-1}, and values of C' from the doublet ground state condition to the maximum value, there is appreciable spin mixing of sextet, doublet and quartet states. As Δ_{O_h} increases from 31 000 to 36 000 cm^{-1} the ground states wave function, at a given value of u', has decreasing sextet and increasing quartet character. For example, at $u'_{max} = 6\Delta_{O_h}/7 = 31\,000$ cm^{-1} the ground state has 96% $^6A_1$ ($\pm 1/2$) character, while at 35 000 cm^{-1} the ground state has 94.5% $^4A_2$ ($\mp 3/2$) character.

Finally, for $\Delta_{O_h} = 36\,000$ cm^{-1} up to the limit we have considered 40 000 cm^{-1}, there is a rather substantial spin-mixed region between the pure doublet and pure quartet state. The span of C' for this quartet-doublet spin mixed region seems to increase as the cubic field strength increases.

The present calculations have then established the existence of and conditions for a spin-mixed ferric ion ground state in complexes of tetragonal symmetry, in addition to sextet, quartet, and doublet ground states. For this symmetry, which of these ground states actually occurs in a given complex is determined by the magnitude of the average cubic field strength and the axial distortions present. All of the them, it seems, are possible.

In ferric heme complexes both high and low spin compounds have been observed. From the magnetic moment data of a series of heme derivatives it also seems likely that a number of these exist in substantially spin-mixed states. The gradual decrease in the measured room temperature effective moments from 5.92 for the floride to 5.44 for the formate, then to 2.87 through a series of 8 compounds to the imidazole continuing down to the low spin azide and SH compound, cannot be explained on the basis of thermal equalbrium between sextet and doublet states alone. No quartet states of ferric heme compounds have been observed. In previous calculations, we have explained the observed zero field splittings of a number of isolated ferric porphrin compounds with cubic field strengths in the range 28 000—32 000 cm^{-1}. Our present calculations indicate that in this range, it is possible to have sextet, doublet and spin-mixed states only. No quartet ground state is possible. Thus we appear to have accounted for all the observed behavior of the ferric heme compounds in an internally consistent and physically resonable manner. The five coordinated compounds would be expected to have the weakest axial fields. These are well within the high spin region. For hemin, the compounds with the same prosthetic group as the intact heme proteins the value of C' obtained, which was both internally consistent with the other assignments and also explained its observed zero field splitting, was 6200 cm^{-1}. We could expect that in the intact heme complexes, though the in-plane interactions would still be stronger than the axial ones, i.e., C' and u' would be still positive, these interactions would be greater than in the isolated prosthetic group. For the H_2O and

F^- derivative this binding is still not strong enough to cause substantial change in the spin state while for ions like N_3^-, CN^- and SH^-, where stronger binding is expected, low spin ferric ion behavior is observed.

Having thus mapped the regions of the various possible ground states of ferric ion, we turn now to an examination of the eigenfunctions and eigenvalues obtained in these regions, particularly in those with spin-mixed and quartet ground states.

IV. Results: Spin-Mixed Eigenfunctions and Eigenvalues
A) General Behavior of Multi Component Eigenfunctions

The spin-orbit matrices, using the twelve pairs of basis functions listed in Table 5, factor into two non-interacting, doubly degenerate blocks: Two $7 \cdot 7 E''(\alpha)$ and $E''(\beta)$ and two $5 \cdot E'(\alpha)$ and $E'(\beta)$ matrices, which yield twelve doubly degenerate eigenvalues each with an α and β eigenfunction. The degeneracy can be further split by the application of a magnetic field. In zero magnetic field, the resulting doubly degenerate spin-mixed eigenfunctions belonging to the E'' block are seven-component states of the form:

$$\Psi_{ij} = \sum_{j=1}^{8} a_{ij}\varphi_j \tag{15}$$

where the φ_j $(j = 1$—$7)$ are the two sextet, three quartet and two doublet states listed in Table 4.

Similarly, the states of the E' block are five-component, spin-mixed states of the form:

$$X_{ij} = \sum_{j=8}^{12} a_{ij}\varphi_j \tag{16}$$

where the five states with $j = 8$—12 are the sextet, three quartet and one doublet state listed in Table 4.

The specific definition which we have used to establish the boundaries of the different pure spin states discussed in the previous section is: A pure spin state is one in which the sum of the squares of the coefficients of all components of one spin in the total wave function is $\geq 98\%$. Having delineated these areas, we wish now the focus attention on the behavior of the eigenfunctions and eigenvalues through the spin-mixed regions of parameters. These are the regions for which the above criteria do not hold and where there is a rapid change in the nature of the ground and low lying states over a fairly narrow range of parameters as the system goes from one pure spin state to another. We have already shown that ferric ion in some intact heme complexes can, from the observed values of the magnetic moment, be assumed to exist in such a state. In order to possibly explain the known magnetic moment behavior and predict others, we wish to illustrate the behavior of the ferric ion in as general a manner as possible. We have chosen three values of Δ_{O_h} each of which illustrate one of the three possible patterns of changing ground state: a value of $\Delta_{O_h} = 30\,000$ cm^{-1} illustrative of the region in which only doublet, spin-mixed and sextet ground states are possible; a value of $\Delta_{O_h} = 32\,000$ cm^{-1} which is in the range where only doublet and spin-mixed ground states are possible; and a value of $\Delta_{O_h} = 38\,000$ cm^{-1} where doublet, spin-mixed and quartet ground states are possible. For each of these three values of cubic field parameters, we have varied the ratio $f = C'/u'$. To illustrate the effect of this parameter on the eigenfunctions and eigenvalues, we discuss the results at $\Delta_{O_h} = 30\,000$ cm^{-1} for two

values of f, 1 and 9. For the other two cubic field parameters, the value of f is fixed at 1 i.e. $C' = u'$. For each value of Δ_{O_h} and f, we calculate the spin-orbit-coupled eigenfunctions and eigenvalues as a function of $C' = (fu')$ through the spin-mixed and other regions of interest. Within each of the three "behavior regions" of Δ_{O_h}, the eigenfunction mixtures and eigenvalues obtained are quantitatively similar.

As we have mentioned, previous calculations for the series of 10 high spin-ferric porphyrin compounds for which the zero-field splittings have been measured [3], place the value of the cubic field parameters for ferric heme compounds in the region of 28 000—32 000 cm^{-1} [4]. Thus we may consider that the results discussed here for $\Delta_{O_h} = 30\,000$ and 32 000 cm^{-1} are applicable to heme proteins. It is doubtful that small changes in either axial or in-plane field strengths would increase the average cubic field strength to as high a value as 38 000 cm^{-1}. If it did, this value would be caused by a very strong axial field which would lead to a doublet ground state. Since we have shown in previous work that the results for low spin compounds are quite insensitive to the value of the cubic field parameter, provided it is large enough to allow such a ground state to occur, this would not then be an interesting region to explore. Much more interesting, is the combination of high cubic fields, i.e., $\Delta_{O_h} \geqq 36\,000$ cm^{-1} and low axial fields, which are inconsistent for heme compounds, but which could apply to ferric complexes in tetragonal symmetry which could exist in a quartet ground state.

We turn now to a discussion of the behavior of the five lowest eigenfunctions for the sets of values of Δ_{O_h} and f which differ qualitatively.

1. Region I: $\Delta_{O_h} = 30\,000$ cm^{-1}. The Low Heme Protein Region

At $\Delta_{O_h} = 30\,000$ cm^{-1} and $f = 1$, the region of spin-mixed wave functions is from $u = 2300$ to 3300 cm^{-1}. Fig. 6a shows the variation in eigenfunctions and eigenvalues of the five lowest lying states of ferric ion as a function of u' through this spin mixed region. Table 7 gives the eigenvalues as well as
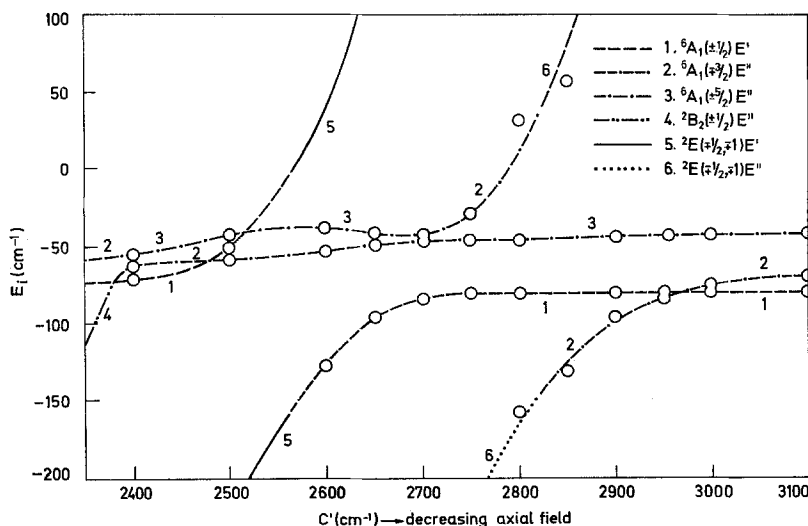

Fig. 6a. Energies and changing natures of the five lowest ferric ion states in spin-mixed region
$(\Delta_{O_h} = 30\,000$ cm^{-1}, $f = 1)$

Table 7a. *Energies and eigenfunctions for the five lowest lying ferric ion states*
$(\Delta_{O_h} = 30\,000 \text{ cm}^{-1}, f = 1)$

$C'(\text{cm}^{-1})$	$E_i(\text{cm}^{-1})$	Main comp.	$a_{i1}(8)$	$a_{i2}(9)$	$a_{i3}(10)$	$a_{i4}(11)$	$a_{i5}(12)$	a_{i6}	a_{i7}
Ground state									
2000	−1895.4	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.006	.032	.092	.020	.058	.933	.341
2300	−1221		.009	.056	.108	.019	.060	.939	.316
2500	−775.0		.015	.097	.123	.019	.062	.939	.297
2600	−554.9		.020	.144	.133	.019	.065	.934	.290
2650	−446.7		.025	.187	.140	.019	.067	.927	.285
2700	−341.2		.033	.258	.149	.019	.070	.910	.276
2750	−242.2		.047	.389	.160	.019	.074	.865	.258
2800	−160.6		.065	.617	.168	.018	.078	.731	.215
2850	−113.1	$^6A_1(\mp 3/2)$	.072	.836	.159	.014	.076	.494	.142
2900	−92.9		.062	.928	.144	.010	.069	.319	.008
2950	−83.7		.051	.960	.134	.007	.065	.224	.061
3000	−79.5	$^6A_1(\pm 1/2)$	.989	.133	.040	.022	.054		
3100	−78.6		.989	.132	.039	.022	.044		
3200	−77.9		.990	.132	.038	.021	0.37		
3300	−77.3		.990	.132	.037	.021	.032		
First excited state									
2000	−1331.1	$^2E, E'(\mp\frac{1}{2}, \mp 1)$	.036	.066	.052	.001	.996		
2300	−662.7		.084	.081	.055	.003	.992		
2500	−230.4		.329	.117	.063	.009	.935		
2600	−104.0		.891	.151	.059	.022	.924		
2650	−91.8	$^6A_1(\pm 1/2)$	.957	.145	.052	.023	.245		
2700	−86.9		.974	.141	.048	.023	.167		
2750	−84.3		.981	.138	.046	.023	.125		
2800	−82.7		.984	.136	.044	.023	.100		
2900	−80.7		.987	.134	.040	.022	.071		
2950	−80.0		.988	.134	.041	.022	.061		
3000	−78.7	$^6A_1(\pm 3/2)$	.042	.973	.128	.006	.062	.170	.045
3100	−73.4		.030	.984	.121	.004	.058	.114	.029
3200	−70.5		.022	.987	.177	.003	.055	.085	.021
3300	−68.6		.017	.989	.115	.002	.054	.067	.016
Second excited state									
2000	−932.8	$^2B_2(\pm 1/2)$	.041	.008	.040	.065	.016	.340	.936
2300	−301.2		.237	.055	.048	.080	.115	.305	.916
2400	−70.1	$^6A_1(\pm 1/2)$	.981	.115	.034	.025	.152		
2500	−58.9	$^6A_1(\mp 3/2)$	.197	.968	.091	.020	.050	.089	.070
2600	−54.5		.253	.951	.082	.023	.046	.134	.069
2650	−51.2		.391	.899	.073	.034	.0	.160	.018
2700	−47.2	$^6A_1(\pm 5/2)$	.743	.644	.049	.055	.026	.140	.080
2750	−45.0		.949	.293	.022	.072	.011	.067	.058
2800	−44.0		.983	.159	.012	.073	.006	.035	.044
2900	−42.6		.994	.074	.006	.071	.002	.015	.031
2950	−42.0		.995	.057	.004	.070	.002	.011	.028
3000	−41.5		.996	.045	.003	.070	.001	.009	.025
3100	−40.5		.997	.031	.003	.068	.001	.006	.020
3200	−39.6		.997	.023	.002	.067	.0	.004	.017
3300	−38.8		.998	.018	.001	.065	.0	.003	.015
Third excited state									
2000	−78.0	$^6A_1(\pm 1/2)$	.990	.125	.044	.027	.046		
2400	−63.6	$^6A_1(\mp 3/2)$	.503	.824	.089	.055	.042	.005	.224

Table 7a (Continuation)

C' (cm^{-1})	E_i (cm^{-1})	Main comp.	a_{i1} (8)	a_{i2} (9)	a_{i3} (10)	a_{i4} (11)	a_{i5} (12)	a_{i6}	a_{i7}
2500	$-$ 58.0	$^6A_1(\pm 1/2)$	.934	.093	.021	.023	.343		
2600	$-$ 45.6	$^6A_1(\pm 5/2)$	.962	.248	.016	.074	.012	.075	.035
2650	$-$ 44.1		.915	.380	.025	.068	.016	.111	.010
2700	$-$ 40.8	$^6A_1(\mp 3/2)$	.663	.710	.044	.045	.027	.222	.044
2750	$-$ 29.4		.301	.866	.037	.015	.025	.382	.109
2800	$+$ 26.2		.153	.762	.007	.0	.005	.604	.178
2850	$+$ 64.1	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.082	.526	.064	.009	.021	.810	.237
2900	$+$ 155.2		.048	.347	.099	.013	.036	.894	.258
2950	$+$ 257.2		.032	.250	.119	.014	.043	.923	.263
3000	$+$ 363.1		.024	.195	.131	.015	.047	.934	.263
3100	$+$ 579.1		.015	.138	.150	.015	.051	.943	.253
3200	$+$ 796.6		.011	.109	.166	.015	.053	.945	.253
3300	$+1014$		.009	.092	.184	.015	.054	.945	.246

Fourth excited state

2000	$-$ 66.9	$^6A_1(\mp 3/2)$	.012	.992	.099	.001	.063	.046	.004
2300	$-$ 62.5		.056	.989	.094	.006	.058	.081	.021
2400	$-$ 56.3	$^6A_1(\pm 5/2)$	.797	.547	.040	.075	.034	.126	.203
2500	$-$ 48.4		.971	.198	.012	.079	.011	.065	.082
2600	$+$ 39.5	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.434	.020	.030	.010	.900		
2650	$+$ 139.1		.257	.051	.041	.005	.964		
2700	$+$ 245.9		.179	.065	.045	.003	.981		
2750	$+$ 355.1		.138	.074	.047	.002	.986		
2800	$+$ 465.1		.113	.081	.048	.002	.989		
2900	$+$ 686.1		.085	.092	.050	.001	.991		
2950	$+$ 796.7		.077	.098	.051	.001	.991		
3000	$+$ 907.4		.070	.103	.051	.001	.991		
3100	$+1129$		.062	.114	.052	.0	.990		
3200	$+1350$		.056	.127	.053	.0	.989		
3000	$+1570$		.053	.142	.053	.0	.987		

the corresponding values of the coefficients of the components in each of these five wave functions as a function of $C' (= u')$. The graph was made from this table. The rules for labeling the states in the graph and table are as follows: If states belong to the different spin-orbit matrices, E'' and E', they can cross. If states belong to the same spin-orbit matrix they interact and mix and do not cross. The label on the state corresponds to the component which is present to an extent $\geqq 50\%$. The label of a state changes then as its dominant components changes due to spin-orbit interaction.

From both Fig. 6a and Table 7a, we see that the ground state at the low spin end, i.e., low values of u', high axial field, is predominantly the $^2E, E''(\mp\frac{1}{2}, \pm 1)$ state φ_6. As $C' (= u')$ increases, this component spin-mixes, primarily with the sextet component $^6A_1(\mp 3/2)$. The amount of $^6A_1(\mp 3/2)$ character in the ground state increases, until at about $C' = 2850$ cm^{-1} it becomes the dominant component of the ground state. As the amount of $^6A_1(\mp 3/2)$ character continues to increase, at $C' = 3000$ cm^{-1} it becomes the first excited state, crossing the lowest of the non-interacting E' block of states, just before it becomes a pure sextet state. It remains the first excited state from then on into the region of pure sextet ground state.

The complement to the state we have just been describing is the one which at low values of C' starts as the pure sextet state $^6A_1(\mp 3/2)$, the fourth excited state. It ends at high values of C' as the pure doublet state $^2E(\mp\frac{1}{2}, \pm 1)$, the third excited state. This state can also interact with the $^6A_1(\pm 5/2)$. At low values of C' the two E'' sextet states are close to one another, and they interact strongly with one another in the region $C' = 2400—2700$ cm^{-1} as can be seen from the behavior of the curves marked 2. and 3. in Fig. 6a in this region. At $C' = 2700$ cm^{-1} the state which is predominantly $^6A_1(\mp 3/2)$ is the second excited state and begins to interact more and more with the doublet state becoming the third excited state. At $C' = 2850$ cm^{-1} this state assumes predominant doublet character as its compliment, the ground state, assumes predominantly sextet character.

The first excited state is the lowest of the five-component E' states. From Table 7a or Fig. 6a, it may be seen that at low C' it is primarily the $^2E(\mp 1/2, \mp 1)$ state. As C' increases it begins to mix substantially with the $^6A_1(\pm 1/2)$ component. This mixing continues until at about $C' = 2750$ cm^{-1} this state is a pure sextet state. Its energy increases less rapidly with C' than the $^6A_1(\mp 3/2)$ state and it becomes the ground state at 3000 cm^{-1}. Thus there is a crossing of essentially high spin components. Since the $^6A_1(\mp 3/2)$ E'' state is not quite 98% pure at the cross point, the official, rigorously defined, high spin region may be said to begin at this cross point.

The interacting partner of the lowest E' state is the one which begins as almost pure $^6A_1(\pm 1/2)$ under low spin ground state conditions, and is the third excited state. As C' increases, it interacts more and more with the $^2E(\mp 1/2, \mp 1)$ state that is the first excited state and becomes the fourth excited state as the doublet character becomes dominant.

The fifth state, whose behavior we have tabulated and drawn, is the one which becomes the pure $^6A_1(\mp 5/2)$ state under high spin ground state conditions. This state can mix with the other doublet component of the E'' block, the $^2B_2(\pm\frac{1}{2})$ state. Thus at low values of C' this state starts out as the predominantly $^2B_2$ state and is the second excited state. At 2400 cm^{-1} it becomes predominantly $^6A_1(\pm 5/2)$, and it is the fourth excited state. At intermediate values of C' between 2400 and 2750 cm^{-1} the $^6A_1(\mp 3/2)$, $^6A_1(\pm 5/2)$ and $^2B_2$ and $^2E(1/2, -1)$ all interact. The labels maintain the rule of showing the main component at any value of C'. The state which is predominantly $^6A_1(\pm 5/2)$ shows considerable interaction and ends as the 2nd excited state for $C' \geq 2750$ cm^{-1}. The behavior we have just described then is, in general, what is happening to the five lowest energy states as ferric ion passes through a spin-mixed region consistent with its low and high spin limits. At the low spin end, then, the order of states is

$$^2E(E'') < {}^2E(E') < {}^2B_2(E'') < {}^6A_1(\pm\tfrac{1}{2}) < {}^6A_1(\mp 3/2)$$

while at the high spin end the order of states is

$$^6A_1(\pm\tfrac{1}{2}) < {}^6A_1(\mp 3/2) < {}^6A_1(\pm 5/2) < {}^2E(E'') < {}^2E(E') \,.$$

We see that the correct ordering of doublet and sextet components, i.e., agreement with experimental observation is obtained in each limit, and that the properties of the ferric ion in the spin mixed region, where these five eigenfunctions are changing so rapidly, can differ considerably from either pure spin region and can change markedly with a small change in ferric ion-ligand interaction.

We have made this same calculation for a value of $f = 9$ and $\Delta_{O_h} = 30\,000$ cm^{-1}. The resulting eigenvalues and eigenfunctions of the five lowest energy states are given in Table 7b and plotted in Fig. 6b. The general pattern of energies and changing eigenfunctions as a function of the parameter C'
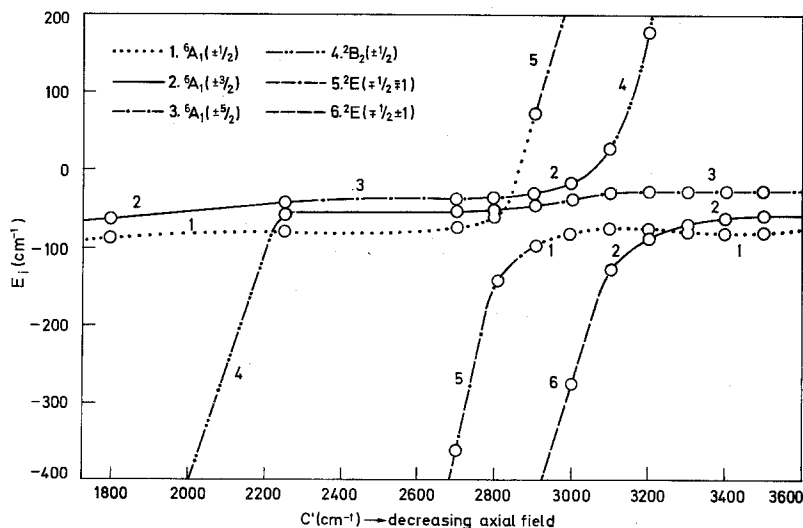

Fig. 6b. Energies and changing natures of the five lowest ferric ion states in spin-mixed region
$(\Delta_{O_h} = 30\,000$ cm^{-1}, $f = 9)$

Table 7b. *Energies and eigenfunctions for the five lowest lying ferric ion states*
$(\varDelta_{O_h} = 30\,000 \text{ cm}^{-1}, f = 9)$

$C'(\text{cm}^{-1})$	$E_i(\text{cm}^{-1})$	Main Comp.	$a_{i1}(8)$	$a_{i2}(9)$	$a_{i3}(10)$	$a_{i4}(11)$	$a_{i5}(12)$	a_{i6}	a_{i7}
Ground state									
1800	−2673	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.002	.020	.084	.009	.051	.982	.158
2250	−1761		.003	.035	.100	.008	.052	.984	.131
2700	− 857		.005	.084	.124	.007	.055	.981	.111
2800	− 659		.006	.115	.132	.007	.056	.977	.107
2900	− 463		.008	.175	.143	.006	.059	.967	.103
3000	− 276.1		.014	.325	.160	.006	.065	.925	.096
3100	− 133.4	$^6A_1(\mp 3/2)$	.024	.726	.170	.005	.071	.660	.067
3200	− 88.0		.021	.941	.143	.003	.063	.299	.031
3300	− 78.60	$^6A_1(\pm 1/2)$	.988	.133	.038	.021	.057		
3400	− 77.74		.989	.133	.037	.020	.047		
3500	− 77.07		.990	.132	.036	.020	.039		
First excited state									
1800	−2177	$^2E, E'(\mp\frac{1}{2}, \mp 1)$	.019	.054	.048	.0009	.997		
2250	−1268		.037	.067	.050	.0014	.996		
2700	−3682		.172	.097	.055	.005	.979		
2800	−1844		.439	.128	.061	.011	.887		
2900	− 97.6	$^6A_1(\pm 1/2)$	.921	.149	.053	.021	.355		
3000	− 85.3		.976	.140	.045	.002	.160		
3100	− 81.63		.984	.136	.042	.002	.100		
3200	− 79.78		.987	.135	.040	.002	.073		
3300	− 76.72	$^6A_1(\mp 3/2)$	.016	.975	.128	.002	.058		
3400	− 71.97		.012	.984	.121	.001	.054		
3500	− 69.29		.009	.987	.118	.001	.052	.090	.009
Second excited state									
1800	− 701	$^2B_2 E''(\pm 1/2)$	.063	.011	.018	.075	.031	.016	.098
2250	− 76.8	$^6A_1(\pm 1/2)$	.990	.125	.042	.026	.048		
2700	− 67.2		.976	.112	.030	.023	.185		
2800	− 55.4	$^6A_1(\pm 3/2)$	.031	.986	.087	.003	.048	.129	.011
2900	− 50.1		.074	.975	.077	.006	.043	.188	.018
3000	− 41.2	$^6A_1(\pm 5/2)$	.971	.221	.014	.067	.008	.064	.018
3100	− 40.2		.997	.045	.003	.067	.001	.018	.012
3200	− 39.4		.997	.025	.001	.066	.0	.005	.010
3300	− 38.6		.997	.016	.001	.065	.0	.003	.009
3400	− 37.9		.998	.013	.0	.064	.0	.002	.008
3500	− 37.2		.998	.009	.0	.062	.0	.001	.007
Third excited state									
1800	− 80.1	$^6A_1(\pm 1/2)$	.990	.126	.048	.029	.028		
2250	− 65.1	$^6A_1(\mp 3/2)$	.013	.992	.099	.001	.060	.049	.006
2700	− 58.4		.018	.989	.092	.002	.051	.098	.007
2800	− 49.4	$^6A_1(\pm 1/2)$	.888	.078	.013	.020	.452		
2900	− 41.9	$^6A_1(\pm 5/2)$	.995	.071	.004	.070	.003	.024	.012
3000	− 36.3	$^6A_1(\mp 3/2)$	.230	.912	.049	.014	.032	.332	.029
3100	+ 20.86		.040	.677	.035	.001	.002	.731	.070
3200	+ 175.07	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.014	.319	.011	.004	.032	.937	.089
3300	+ 362.73		.007	.192	.137	.004	.040	.967	.090
3400	+ 556.28		.005	.140	.154	.004	.043	.973	.088
3500	+ 751.08		.003	.112	.168	.004	.045	.975	.086

Table 7b (Continuation)

$C'(cm^{-1})$	$E_i(cm^{-1})$	Main Comp.	$a_{i1}(8)$	$a_{i2}(9)$	$a_{i3}(10)$	$a_{i4}(11)$	$a_{i5}(12)$	a_{i6}	a_{i7}
Fourth excited state									
1800	— 69.5	$^6A_1(\pm 3/2)$	.038	.991	.102	.004	.067	.031	.013
2250	— 50.3	$^6A_1(\pm 5/2)$	.994	.014	.003	.084	.0	.010	.060
2700	— 43.9		.997	.018	.0	.074	.002	.009	.018
2800	— 42.9		.997	.030	.001	.072	.002	.012	.015
2900	+ 65.3	$^2E, E'(\mp\frac{1}{2}, \mp 1)$	.365	.032	.032	.008	.930		
3000	+ 254.4		.173	.067	.043	.003	.982		
3100	+ 451.8		.114	.080	.045	.001	.989		
3200	+ 650.8		.087	.091	.047	.001	.991		
3300	+ 850.2		.072	.100	.048	.0	.991		
3400	+1049.6		.063	.110	.048	.0	.991		
3500	+1248.7		.057	.121	.049	.0	.990		

is the same as for $f = 1$ with small quantitative differences. For example, the cross-over of the $^6A_1(\pm 1/2) - {}^6A_1(\pm 3/2)$ states occurs at $C' = 3000$ cm^{-1}. The region of spin mixing is about the same but the values at which states change labels are also somewhat different. These small differences are translated into small differences in the calculated properties at given values of field parameters. It is quite clear that the two important parameters in this calculation are Δ_{O_h} and $C'(= fu')$ rather than the two individual tetragonal parameters. The results are more sensitive to variations in these and quite intensitive to variations of the individual values of the two tetragonal parameters, through adjusting their ratio f. Thus the three parameter tetragonal problem reduces fairly accurately to a two parameter one, with parameters treated as we have indicated here.

2. The Region: $\Delta_{O_h} = 32\,000$ cm^{-1}. The High Heme Protein Region

At $\Delta_{O_h} = 32\,000$ cm^{-1} and $f = 1$, the limit of the low spin region is $C' = 3500$ cm^{-1}. In the low spin regions, for example at $C' = 3000$ cm^{-1}, the ground state is the seven component E'' state, primarily $^2E_2(\mp 1/2, \pm 1)$, just as it is at 30 000 cm^{-1}. This is shown in Table 7c and Fig. 6c, where the behavior of the five lowest energy eigenfunctions is illustrated. As the axial field decreases, this doublet state mixes
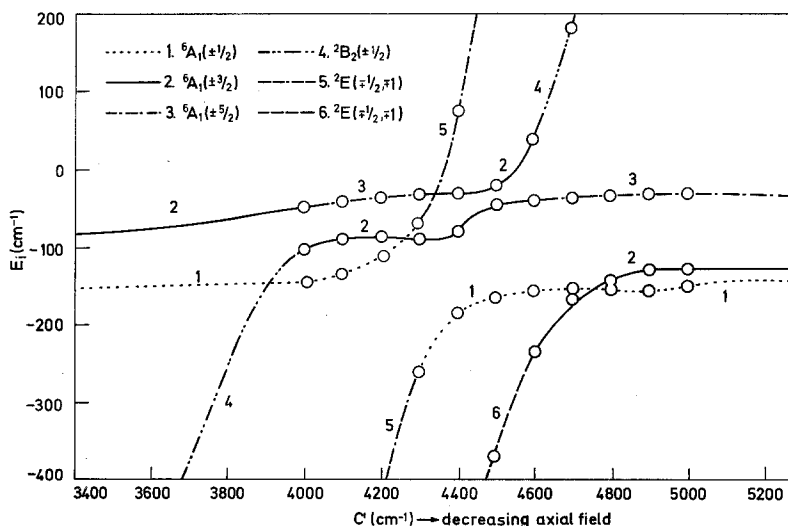

Fig. 6c. Energies and changing natures of the five lowest ferric ion states in spin-mixed region
$(\Delta_{O_h} = 32\,000$ cm^{-1}, $f = 1)$

Table 7c. *Energies and eigenfunctions for the five lowest lying ferric ion states*
$(\Delta_{O_h} = 32\,000 \text{ cm}^{-1},\ f = 1)$

$C'(\text{cm}^{-1})$	$E_i(\text{cm}^{-1})$	Main Comp.	$a_{i1}(8)$	$a_{i2}(9)$	$a_{i3}(10)$	$a_{i4}(11)$	$a_{i5}(12)$	a_{i6}	a_{i7}
Ground state									
3000	− 3618.8	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.0022	.016	.098	.014	.048	.956	.273
4000	− 1397.4		.0050	.065	.180	.012	.052	.955	.218
4100	− 1180.5		.0058	.083	.196	.012	.053	.952	.213
4200	− 966.2		.0070	.109	.216	.011	.054	.946	.207
4300	− 755.9		.0087	.154	.241	.011	.056	.936	.199
4400	− 553.2		.012	.235	.274	.011	.059	.911	.189
4500	− 368.8		.016	.400	.315	.101	.063	.841	.169
4600	− 233.7		.020	.676	.339	.008	.066	.639	.123
4700	− 171.5	$^6A_1(\mp 3/2)$	.016	.859	.317	.005	.062	.391	.071
4800	− 153.6	$^6A_1(\pm 1/2)$	.954	.284	.037	.020	.086		
4900	− 152.0		.956	.282	.036	.020	.071		
5000	− 150.7		.957	.281	.035	.019	.061		
8000	− 140.9		.961	.274	.022	.013	.011		
10000	− 138.7		.962	.273	.018	.011	.006		
20000	− 134.4		.962	.272	.009	.006	.002		
First excited state									
3000	− 3078.4	$^2E, E'(\mp\frac{1}{2}, \mp 1)$	.015	.067	.044	.0	.997		
4000	− 854.8		.098	.145	.049	.003	.983		
4100	− 638.7		.149	.170	.051	.005	.973		
4200	− 431.2		.270	.212	.054	.007	.938		
4300	− 259.3		.589	.285	.056	.014	.754		
4400	− 186.2	$^6A_1(\pm 1/2)$	.870	.308	.050	.020	.381		
4500	− 167.2		.929	.298	.044	.021	.213		
4600	− 160.0		.945	.291	.041	.021	.144		
4700	− 156.0		.951	.287	.039	.020	.108		
4800	− 147.5	$^6A_1(\mp 3/2)$	.012	.920	.292	.003	.057	.253	.044
4900	− 136.25		.009	.942	.276	.002	.053	.182	.030
5000	− 129.8		.007	.952	.267	.001	.051	.141	.022
8000	− 105.1		.0	.972	.234	.0	.030	.017	.001
10000	− 101.6		.0	.972	.233	.0	.025	.011	.0
20000	− 95.2		.0	.973	.231	.0	.013	.004	.0
Second excited state									
3000	− 2451.0	$^2B_2(\pm 1/2)$	.013	.002	.035	.055	.018	.272	.960
4000	− 134.9	$^6A_1(\pm 1/2)$	.959	.249	.032	.023	.133		
4100	− 128.9		.952	.237	.029	.022	.189		
4200	− 115.2		.926	.208	.021	.021	.315		
4300	− 84.6	$^6A_1(\pm 3/2)$	.043	.963	.168	.006	.040	.191	.058
4400	− 71.6		.071	.946	.139	.009	.034	.272	.070
4500	− 44.2		.491	.780	.068	.037	.019	.368	.095
4600	− 38.1	$^6A_1(\pm 5/2)$	.995	.059	.005	.064	.0	.028	.027
4700	− 37.2		.997	.025	.002	.062	.0	.012	.020
4800	− 36.4		.998	.015	.002	.061	.0	.007	.016
4900	− 35.7		.998	.010	.001	.060	.0	.004	.014
5000	− 35.0		.998	.008	.0	.059	.0	.003	.012
8000	− 22.9		.9993	.0	.0	.039	.0	.0	.002
10000	− 18.7		.9995	.0	.0	.031	.0	.0	.0
20000	− 9.7		.9998	.0	.0	.016	.0	.0	.0

Table 7c (Continuation)

C'(cm^{-1})	E_i(cm^{-1})	Main Comp.	a_{i1}(8)	a_{i2}(9)	a_{i3}(10)	a_{i4}(11)	a_{i5}(12)	a_{i6}	a_{i7}
Third excited state									
3000	− 149.0	$^6A_1(\pm 1/2)$	.962	.266	.047	.029	.034		
4000	− 101.7	$^6A_1(\mp 3/2)$	.093	.958	.205	.016	.045	.070	.155
4100	− 96.9		.042	.970	.195	.007	.045	.112	.067
4200	− 92.0		.037	.969	.184	.006	.043	.144	.056
4300	− 66.7	$^6A_1(\pm 1/2)$	.764	.105	.0	.017	.636		
4400	− 39.4	$^6A_1(\pm 5/2)$	.995	.065	.004	.066	.002	.036	.023
4500	− 36.8		.868	.434	.030	.054	.010	.230	.029
4600	− 33.1	$^6A_1(\pm 3/2)$	.065	.707	.061	.004	.001	.688	.141
4700	+ 176.8	$^2E, E''(\mp\frac{1}{2}, \pm 1)$	.025	.471	.195	.007	.021	.843	.166
4800	352.9		.014	.342	.285	.008	.030	.879	.167
4900	533.7		.009	.281	.359	.008	.033	.875	.150
5000	707.8		.006	.253	.436	.008	.034	.850	.149
6000	−1450.6	$^4A_2(\pm 3/2)$	.0	.244	.932	.001	.008	.266	.023
8000	1548.7		.0	.235	.969	.0	.0	.080	.003
10000	+1565.5		.0	.233	.971	.0	.0	.047	.001
20000	+1581.3		.0	.231	.973	.0	.0	.015	.0
Fourth excited state									
3000	− 114.7	$^6A_1(\mp 3/2)$	.002	.973	.217	.0	.066	.041	.003
4000	− 55.7	$^6A_1(\pm 5/2)$	.916	.139	.002	.086	.015	.097	.354
4100	− 44.5		.991	.046	.0	.074	.004	.034	.100
4200	− 42.1		.995	.038	.001	.070	.003	.025	.055
4300	− 40.6		.996	.042	.002	.008	.002	.025	.036
4400	+ 79.1	$^2E, E'(\mp\frac{1}{2}, \mp 1)$	.418	.056	.027	.008	.907		
4500	+ 277.1		.264	.135	.036	.004	.954		
4600	+ 484.0		.206	.190	.039	.002	.959		
4700	+ 689.6		.184	.248	.040	.001	.950		
4800	889.0		.181	.322	.040	.0	.929		
4900	1075.5		.192	.421	.039	.0	.886		
5000	1238.2		.214	.551	.036	.001	.806		
6000	1590.9	$^4A_2(\pm 1/2)$	.277	.951	.006	.003	.135		
8000	1617.4		.274	.961	.002	.002	.043		
10000	1622.4		.273	.962	.0	.002	.026		
20000	1627.4		.272	.962	.0	.0	.009		

more and more with the $^6A_1(\mp 3/2)$ component. At the same time the $^4A_1(\pm 3/2)$ mixing increases to a maximum of .34 at $C' = 4600$ cm^{-1}. As C' increases further, the $^4A_2(\pm 3/2)$ state mixing decreases and the $^6A_1(\mp 3/2)$ increases but at the highest value of C' considered, i.e., $C' = 20\,000$ cm^{-1}, this state is not completely pure $^6A_1(\mp 3/2)$, that is, the coefficient of this component is .9733. This state crosses the predominantly $^6A_1(\pm 1/2)$ state at $C' = 4800$ cm^{-1} when decreasing quartet state mixing begins.

At the low spin limit the first excited state is the lowest of the five-component E' states and is pure $^2E(1/2, 1)$. This state mixes with the $^6A_1(\pm 1/2)$ state just as it does at the lower values of Δ_{O_h}, but also with the $^4A_2(\pm 1/2)$ state to a greater extent than at 30 000 cm^{-1}. Thus at $C' = 20\,000$ cm^{-1}, the state is almost but not quite pure sextet, i.e., $C(^6A_1(\pm 1/2)) = .962$. It is this state which becomes the ground state at 4800 cm^{-1} where its composition is .954 $^6A_1(\pm 1/2)$ and .284 $^4A_2(\pm 1/2)$ with negligible doublet character. Thus the main difference in the behavior of these states from the lower cubic field values is that they have more quartet character, leading at still higher values of Δ_{O_h} to a pure quartet state.

The partner of the ground state, at the low spin values of C' is the primarily $^6A_1(\mp 3/2)$ state which starts as the fourth excited state. It mixes with the ground ^2E state, and the $^4A_2(\pm 3/2)$ state becomes the second excited state at $C' = 4000$ cm^{-1}. It then becomes the third excited state at $C' = 4600$ cm^{-1} as its doublet character becomes dominant. The quartet character also increases at the same time. As C' increases beyond 4600 cm^{-1}, the energy of the state which is primarily $^2E(1/2, -1)$ increases

rapidly and the state with increasing quartet character becomes the third excited state at $C' = 8000 \text{ cm}^{-1}$, as seen in Table 7c.

A similar behavior occurs with the partner of the lowest five-component state. At the low values of C' it is the pure sextet state ${}^6A_1(\pm 1/2)$ and is the third excited state. It mixes with the first excited doublet state and becomes the second and again the third excited state as C' increases. At $C' = 4400 \text{ cm}^{-1}$, it is primarily a doublet ${}^2E(1/2, 1)$ state. As the amount of both doublet and quartet character continue to increase with C' it becomes the fourth excited state. Then as C' further increases the pure doublet state increases in energy and the state which is increasing in quartet character remains the fourth excited state.

The fifth state shown starts at the low values of C' as the third doublet component, the ${}^2B_2$ state, and ends as the pure ${}^6A_1(\mp 5/2)$ state, the second excited state. There is not much quartet state mixing into this state.

At this value of Δ_{O_h} then, for high values of C' the ground and first excited states are sextet with a substantial mixture of quartet character, the second excited state is the pure ${}^6A_1(\pm 5/2)$ state and the third and fourth excited states are predominantly quartet states with some sextet mixing. For example, at $C' = 8000 \text{ cm}^{-1}$, the order of states is

$$({}^6A_1(\pm 1/2) - {}^4A_2(\pm 1/2)) < ({}^6A_1(\mp 3/2) - {}^4A_2(\mp 3/2)) < ({}^6A_1(\pm 5/2))$$
$$< ({}^4A_2(\pm 3/2) - {}^6A_1(\mp 3/2)) < ({}^4A_2(\pm 1/2) - {}^6A_1(\pm 1/2)).$$

The quartet state contribution to the low lying states is substantially greater than at $30\,000 \text{ cm}^{-1}$. It is primarily this increased quartet state mixing at low axial fields that prevents a pure sextet ground state. In general, then at $\Delta_{O_h} = 32\,000 \text{ cm}^{-1}$, the entire weak axial-field-region beyond the doublet ground state is spin-mixed, starting as primarily sextet-doublet mixing and ending with sextet-quartet mixing as the axial field decreases, passing through a region where all three are important. The properties of ferric ion in this region, especially at very low axial fields, should be considerably different from the low heme region.

3. The Region of Quartet Ground State Possibility

At $\Delta_{O_h} = 38\,000 \text{ cm}^{-1}$ and $f = 1$, we see from Fig. 6d that a pure doublet ground state is possible up to $C' = 6284 \text{ cm}^{-1}$. A quartet ground state is possible for $C' \geqq 9000 \text{ cm}^{-1}$. No sextet ground state is possible. Thus for C' between these two values, the ground state is a quartet-doublet spin-mixed state. Table 7d shows this behavior and that of the first four excited states for $\Delta_{O_h} = 38\,000 \text{ cm}^{-1}$. A graph from this table is plotted in Fig. 6d. From this table and figure we see that the ground state at low
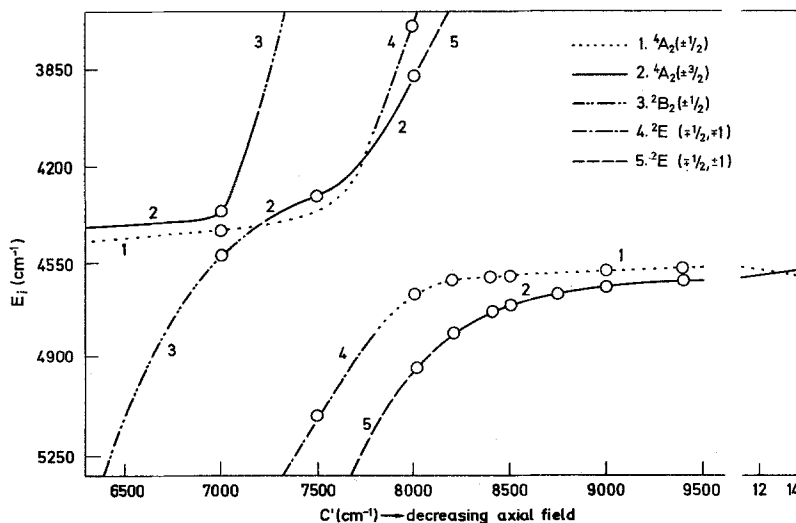

Fig. 6d. Energies and changing natures of the five lowest ferric ion states in spin-mixed region
$(\Delta_{O_h} = 38\,000 \text{ cm}^{-1}, f = 1)$

Table 7d. *Energies and eigenfunctions for the five lowest lying ferric ion states ($\Delta_{O_h} = 38\,000\ cm^{-1}, f = 1$)*

$C'(cm^{-1})$	$E_i(cm^{-1})$	Main Comp.		$a_{i1}(8)$	$a_{i2}(9)$	$a_{i3}(10)$	$a_{i4}(11)$	$a_{i5}(12)$	a_{i6}	a_{i7}
Ground state										
5000	-11072	$^2E, E''(\mp\frac{1}{2}, \pm 1)$		.0	.004	.077	.007	.031	.977	.193
7000	$-\ 6643$			.0	.016	.235	.005	.033	.961	.139
7500	$-\ 5630$			.0	.031	.421	.004	.033	.898	.117
8000	$-\ 4928$	$^4A_2(\pm 3/2)$		.0	.063	.789	.002	.026	.607	.065
8200	$-\ 4799$			.0	.071	.884	.001	.022	.459	.043
8400	$-\ 4725$			.0	.076	.933	.001	.018	.351	.020
8500	$-\ 4701$			.0	.077	.947	.001	.017	.310	.025
8750	$-\ 4659$			.0	.079	.968	.001	.015	.238	.017
9000	$-\ 4633$			.0	.081	.978	.0	.013	.192	.012
9400	$-\ 4608$			.0	.082	.986	.0	.011	.145	.008
9800	$-\ 4592$			.0	.082	.990	.0	.010	.116	.005
15000	$-\ 4553$	$^4A_2(\pm 1/2)$		.101	.995	.005	.004	.018		
20000	$-\ 4550$			.101	.995	.004	.003	.011		
First excited state										
5000	-10567	$^2E, E'(\mp\frac{1}{2}, \mp 1)$		.003	.050	.003	.0	.998		
7000	$-\ 6110$			.016	.188	.031	.001	.982		
7500	$-\ 5093$			.045	.480	.031	.004	.876		
8000	$-\ 4654$	$^4A_2(\pm 1/2)$		.094	.938	.019	.007	.332		
8200	$-\ 4619$			.098	.968	.015	.007	.230		
8400	$-\ 4601$			.100	.980	.014	.007	.173		
8500	$-\ 4595$			.100	.983	.013	.007	.154		
8750	$-\ 4585$			.100	.988	.012	.007	.120		
9000	$-\ 4578$	$^9A_2(\pm 1/2)$		.101	.990	.011	.007	.098		
9400	$-\ 4571$			.101	.992	.010	.007	.076		
9800	$-\ 4567$			.101	.993	.009	.006	.062		
15000	$-\ 4548$	$^4A_2(\pm 3/2)$		.0	.083	.996	.0	.008	.032	.001
20000	$-\ 4541$			.0	.081	.996	.0	.004	.019	.0
Second excited state										
5000	$-\ 9465$	$^2B_2(\pm 1/2)$		.002	.0	.070	.037	.015	.192	.980
7000	$-\ 4527$			.005	.041	.509	.037	.016	.0	.859
7500	$-\ 4383$	$^4A_2(\pm 1/2)$		.091	.871	.007	.007	.482		
8000	$-\ 3870$	$^2E, E''(\mp\frac{1}{2}, \pm 1)$		.001	.056	.608	.005	.022	.781	.129
8200	$-\ 3548$			.001	.045	.459	.005	.026	.877	.132
8400	$-\ 3171$			.001	.037	.350	.005	.029	.926	.132
8500	$-\ 2970$			.001	.035	.309	.005	.029	.941	.131
8750	$-\ 2449$			.001	.031	.237	.005	.031	.962	.128
9000	$-\ 1911$			.002	.030	.190	.005	.032	.973	.125
9400	$-\ 1035$			.003	.037	.142	.005	.032	.981	.120
9800	$-\ 153.0$			.022	.165	.102	.006	.028	.974	.113
15000	$-\ 16.3$	$^6A_1(\pm 5/2)$		.999	.00	.0	.027	.0	.0	.001
20000	$-\ 11.6$			.999	.0	.0	.020	.0	.0	.0
Third excited state										
5000	$-\ 4535$	$^4A_2(\pm 1/2)$		.102	.993	.013	.012	.050		
7000	$-\ 4491$			.101	.977	.004	.008	.188		
7500	$-\ 4298$	$^4A_2(\pm 3/2)$		.001	.078	.901	.005	.007	.409	.120
8000	$-\ 3698$	$^2E, E'(\mp\frac{1}{2}, \mp 1)$		.039	.330	.027	.003	.943		
8200	$-\ 3283$			.029	.228	.029	.002	.973		
8400	$-\ 2851$			.024	.172	.030	.001	.984		
8500	$-\ 2632$			.023	.153	.030	.001	.988		

Table 7d (Continuation)

$C'(\text{cm}^{-1})$	$E_i(\text{cm}^{-1})$	Main Comp.	$a_{i1}(8)$	$a_{i2}(9)$	$a_{i3}(10)$	$a_{i4}(11)$	$a_{i5}(12)$	a_{i6}	a_{i7}
8750	− 2080		.022	.119	.031	.001	.992		
9000	− 1524		.023	.097	.031	.001	.995		
9400	− 632		.031	.073	.032	.001	.996		
9800	− 28.2	$^6A_1(\pm 5/2)$	.999	.015	.001	.047	.0		
15000	+ 21.7	$^6A_1(\pm 3/2)$	.0	.996	.083	.0	.021	.003	.0
20000	+ 24.4		.0	.996	.083	.0	.015	.002	.0
Fourth excited state									
5000	− 4491	$^4A_2(\pm 3/2)$	.0	.084	.993	.0	.011	.080	.004
7000	− 4363		.003	.072	.824	.021	.011	.274	.490
7500	− 3231	$^2B_2(\pm 1/2)$	.008	.010	.060	.043	.020	.158	.984
8000	− 1987		.014	.010	.027	.045	.021	.142	.988
8200	− 1489		.018	.012	.021	.046	.021	.138	.989
8400	− 991		.028	.017	.017	.047	.022	.134	.989
8500	− 742		.039	.022	.015	.048	.022	.133	.989
8750	− 127		.281	.106	.005	.060	.026	.123	.944
9000	− 33	$^6A_1(\pm 5/2)$	.997	.017	.001	.055	.002	.008	.050
9400	− 30		.999	.007	.0	.051	.001	.005	.016
9800	+ 19.0	$^6A_1(\pm 3/2)$	.012	.982	.100	.0	.041	.152	.023
15000	+ 40.5	$^6A_1(\pm 1/2)$	.995	.101	.014	.008	.002		
20000	+ 42.3		.995	.101	.010	.006	.001		

values of C' is predominantly the $^2E(\mp 1/2, \pm 1)$ state mixed somewhat with the other doublet component, $^2B_2(\pm 1/2)$, i.e., $a_6 = .977, a_7 = .193$. As the axial field decreases, instead of mixing with the $^6A_1(\mp 3/2)$ state as it does at lower values of Δ_{O_h}, the doublet state mixes with the $^4A_2(\mp 3/2)$ state until at about 8000 cm^{-1} this quartet state becomes the dominant component in the ground state. As the axial field decreases the $^4A_2(\mp 3/2)$ character increases, becoming a pure quartet state at 9000 cm^{-1}. At $C' = 15\,000$ cm^{-1}, the pure $^4A_1(\mp 3/2)$ becomes the first excited state.

The interacting partner of this state starts as the almost pure $^4A_2(\mp 3/2)$ state at the low C', low spin end. There it is the fourth excited state. It interacts more and more with the $^2E_2(\mp 1/2, \pm 1)$ ground state as C' increases and at 7800 cm^{-1}, where $a_3 = .608$ and $a_6 = .708$ it becomes the second excited state. It stays so until at values of $C' = 9000$ cm^{-1} it becomes a highly excited pure doublet state.

The first excited state is the lowest of the five-component E' states. It starts, at $C' = 5000$ cm^{-1}, as an almost pure $^2E(\mp 1/2, \mp 1)$, state, mixes with the $^4A_2(\pm 1/2)$ state as C' increases, becomes a pure quartet state at 8400 cm^{-1} and crosses the $^4A_2(\pm 3/2)$ state to become the ground state at about $C' = 15\,000$ cm^{-1}. At lower values of Δ_{O_h}, the predominant interaction of this doublet state is with the $^6A_1(\pm 1/2)$ state and leads to a sextet ground state.

The partner of this lowest E' state is the almost pure $^4A_2(\pm 1/2)$ state. At low C' values it is the third excited state and interacts more and more with the first excited state $^2E(\mp 1/2, \mp 1)$ component, becoming the second excited state briefly, but ending as the third excited state, becoming pure doublet at 8400 cm^{-1}.

The fifth state shown begins as the third doublet component, the $^2B_2(\pm 1/2)$ state, at low C' and is the second excited state. It mixes primarily with the $^6A_1(\pm 5/2)$ state and becomes the fourth excited state at $C' = 7500$ cm^{-1}, and a pure sextet state at $C' = 9000$ cm^{-1}.

The region of quartet ground state then begins at about $C' = 9000$ cm^{-1}. There the ground state is the pure $^4A_2(\pm 3/2)$ state. The first excited state is the pure $^4A_2(\pm 1/2)$ state. The energy interval, ΔE_1, at this point, is 55 cm^{-1}, having decreased from 506 as the nature of these two states changed from doublet to quartet over the C' range of 5000—9000 cm^{-1}. This order of quartet states follows naturally from our model by the way which the quartet and doublet states mix under spin-orbit coupling and the order of the doublet component states in the low spin system. It seems then that a $^4A_2(\pm 3/2)$ ground state for ferric ion occurs in our model as a consequence of a decreasing axial field and spin-mixing with the doublet ground state. For the only example of a ferric complex for which a quartet ground state has been observed, i.e., ferric-(-NN-diethyl dithiocarbamato) chloride, there is

ample evidence from both electron spin resonance and Mössbauer ^{57}Fe resonance spectra that the $^4A_2(\pm 3/2)$ state is indeed the ground state in this compound and that the $^4A_1(\pm\frac{1}{2})$ state is the first excited state [7]. It is thus extremely gratifying that our model corroborates these quartet ground state results, in a manner consistent with our overall high-spin, low-spin and mixed spin investigations with no further approximations.

At the boundary of the quartet ground state conditions, the order of states is

$$^4A_2(\pm 3/2) < {}^4A_2(\pm 1/2) < {}^2E(\mp 1/2,\ \pm 1) < {}^2E(\mp 1/2,\ \mp 1) < {}^6A_1(\pm 5/2).$$

As C' increases from 9000 cm^{-1} within the quartet ground state regions, the first energy interval decreases from 55 cm^{-1} to 0 cm^{-1} at $C' = 15\,000$ cm^{-1} where the two quartet states cross. Above this value of C' then, the sign of ΔE_1, changes and its magnitude increases. Thus we would predict zero field splittings for a series of quartet ground state compounds in the range of 0–55 cm^{-1}, with the possibility also of the sign of ΔE_1, changing. Very recently, there is preliminary evidence that for the ferric-(NN-diethyl dithiocarbamato) complexes there might be a sign change of ΔE_1, in going from the Cl$^-$ to the Br$^-$ derivative [8]. These results are very enticing and it would be of interest to determine these energy intervals directly for a series of quartet ground state compounds. In the parameter region $C' \geqq 15\,000$ cm^{-1}, in addition to ground state-first excited state crossing, the doublet states increase greatly in energy and the three sextet components become the third, fourth and fifth excited state. Then the order of state energies in this region is:

$$^4A_2(\pm\tfrac{1}{2}) < {}^4A_2(\pm 3/2) \leqq {}^6A_1(\pm 5/2) < {}^6A_1(\mp 3/2) < {}^6A_1(\pm\tfrac{1}{2}).$$

We have thus seen how a decreased axial field from the low spin values and spin mixing lead at $\Delta_{O_h} \geqq 36\,000$ cm^{-1} to ferric ion states which are doublet-quartet, spin-mixed and finally to the correct order of quartet ground state components in so far as can be determined.

V. Conclusion

Since it is possible for ferric ion with its $3d^5$ free ion ground state configuration to form total states of different spin and orbital angular momentum, i.e., sextet, quartet and doublet states, it has always appeared possible for these ferric ion states perturbed by complex formation to both mix and change their energy ordering. Indeed examples of both high and low spin ferric complexes have been known for quite some time. Using a simple strong crystal field model for such complexes with tetragonal symmetry, and allowing spin-orbit coupling of the sextet, quartet and doublet state components which are the lowest energy states in strong cubic fields, we have shown how by small variations in cubic field and axial field parameters it is possible to obtain not only sextet and doublet ground state functions but also substantially spin-mixed and quartet ground states as well. We have given in detail a quantitative description of a mechanism by which these states interact and change from one to the other as a function of the crystal field parameters. We have also delineated regions in parameters space where these four possible ground-state conditions prevail and discussed the nature of the eigenfunctions in each region. We obtain a picture of high, low and spin-mixed states consistent with the known behavior of many ferric heme complexes and a description of the evolution to a quartet state which both shows why ferric heme complexes are not found in these states and give an ordering of the states in the quartet limit consistent with the only known ferric complex in a quartet ground state. Having obtained these generally satisfying results, in subsequent work, to be reported in the following paper in this series, we use the eigenfunctions calculated and described here as the basis for the calculation of several physical properties of the ferric complexes in tetragonal symmetry.

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Professor Gilda M. Harris
Department of Physics
Pomona College
Claremont, California 91711, USA