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Spin-Mixing and the Different Spin States of Ferric Ion in Tetragonal Symmetry

II. Localized Properties: Zero Field Splittings, Effective Magnetic Moments, Magnetic Field Energies and Electric Field Gradients of Ferric Ion

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We have used the wave functions generated from a strong crystal field model of ferric ion in complexes of tetragonal symmetry with spin-orbit coupling, to calculate the behavior of several localized properties of the ferric ion in parameter regions of different ground and low-lying ferric ion states. In the previous paper of this series we have shown with this model that ferric ion can exist in a doublet, sextet, quartet and substantially spin-mixed ground state. We have delineated such regions and described the changing nature of the wave functions. In the present study, we calculate the effective magnetic moments and their temperature dependence, the first order magnetic field energies, and the electric field gradients of ferric ion in these various spin states. Particular emphasis is placed on the properties of ferric ion in substantially spin-mixed states which have hitherto not been reported. Wherever possible, our results are compared with existing experimental data. In particular, with this model, we have been able to quantitatively account for the continuously varying values of magnetic moment for a series of 12 ferric hemoglobin derivatives, in the region from range of 5.92 to 2.26 Bohr magnetons.

Die im starken tetragonalen Feld mit Spin-Bahn-Kopplung erhaltenen Eigenfunktionen des Fe(III)-Ions werden benutzt, um effektive magnetische Momente und deren Temperaturabhängigkeit, Energien im magnetischen Feld und elektrische Feldgradienten für den Grundzustand und die niedrigsten angeregten Zustände zu berechnen. Je nach Parameterkombination ist der Grundzustand ein Sextett, Dublett, Quartett oder ein spin-gemischter Zustand; die oben genannten Eigenschaften werden besonders in den Gebieten des Parameter-Raums untersucht, in denen kein reiner Spinzustand vorliegt. Soweit möglich werden experimentelle Daten zum Vergleich herangezogen. Insbesondere kann dies Modell quantitativ die im Bereich von 2,26 bis 5,92 μ_B liegenden effektiven Momente von 12 Hämoglobinderivaten erklären.

Nous avons utilisé les fonctions d'onde engendrées à partir d'un modèle de champ cristallin fort pour les complexes de l'ion ferrique à symétrie tétragonale avec couplage spin-orbite, pour calculer le comportement de quelques propriétés localisées de l'ion ferrique dans des zones de paramètres correspondant à différents états fondamentaux et à différents états peu élevés. Dans l'article précédent de cette série nous avons montré à l'aide de ce modèle que l'ion ferrique peut exister dans quatre états fondamentaux: doublet, sextet, quartet et mixte. Nous avons définis ces zones et décrit les variations de nature des fonctions d'onde. Dans le travail ci-dessous nous calculons les moments magnétiques effectifs et leur variation avec la température, les énergies du champ magnétique au premier ordre, et les gradients de champ électrique de l'ion ferrique dans ces différents états de spin. On s'intéresse particulièrement aux propriétés de l'ion ferrique dans les états de spin mixtes qui n'ont pas été jusqu'ici étudiées. Nos résultats sont, lorsque cela est possible, comparés aux données expérimentales existantes. A l'aide de ce modèle nous avons pu en particulier rendre compte quantitativement de la variation continue des valeurs du moment magnétique pour une série de 12 dérivés ferriques de l'hémoglobine dans la zone de 5,92 à 2,26 magnétons de Bohr.

I. Introduction

In the first paper of this series [1], we have shown how it is possible for ferric ion to exist in a number of different ground states under varying conditions of perturbation by the local environment in its complex molecules.

Previous calculations of ferric ion in its complexes including heme compounds have been made, based on crystal field theory, primarily by Griffith and Kotani [1a]. However, these have been partial or more approximate attempts to characterize the behavior of the ferric ion. Thus, while we naturally consider our work in part as extensions or elaborations of these earlier works, particularly of Griffith, our investigations differ in that they include more electronic states, investigate a wider range of parameter variations including the conditions for all possible ground states of ferric ion, consider the physical meaning of these parameter variations, do not use the spin-Hamiltonian approximation to calculate spin-orbit coupling, and attempt to calculate and correlate more physical properties than heretofor.

Specifically, using the strong crystal field model with tetragonal symmetry and allowing spin-orbit coupling among the sextet, quartet and doublet states which are possible from the strong field configurations arising from the original $3d^5$ free ion configuration, we have delineated regions in crystal field parameter space in which ferric ion can exist as a sextet, quartet, doublet or spin-mixed state. Using the free ion values of the electrostatic Racah parameters B and C and the spin-orbit coupling parameters δ, we obtain the following results. For cubic field strengths $\Delta_{O_h} \leqq 31\,000\ \mathrm{cm}^{-1}$, a doublet ground state exists under conditions of strong axial fields. As the axial interactions decrease, there is a relatively narrow range of tetragonal parameter values in which ferric ion ground and low-lying states are substantially spin-mixed. This spin mixing is primarily among doublet and sextet states but has some quartet state character. As the axial field strength further decreases, pure sextet ground states occur. For cubic field strengths from 31 000 to 36 000 cm^{-1}, doublet ground states again occur at the high axial field interaction conditions, and the states become spin-mixed as this interaction decreases. However, in this region of cubic field strengths a pure sextet state is no longer possible for the weakest axial fields considered. This is due primarily to the increases quartet state mixing in the region of weaker axial fields at these higher overall field strengths. Thus in this cubic field parameter region there is a rather wide range of axial field conditions for which the ferric ion states are substantially spin-mixed states. Finally, at cubic field strengths $\geqq 36\,000\ \mathrm{cm}^{-1}$ only doublet and quartet states are possible; the former with strong and the latter with weak axial fields. There is also a transition region between these two pure spin regions in which ferric ion states are again substantially spin-mixed this time primarily a doublet-quartet mixing.

We have already discussed [1] how the wave functions vary through the spin-mixed and other regions for a series of values of Δ_{O_h} the cubic field parameter in the range of 29 000—38 000 cm^{-1}. We have specifically chosen values of $\Delta_{O_h} = 30\,000$, 32 000 and 38 000 cm^{-1} to illustrate the three different patterns of changing ground states we have just outlined.

As the nature of these perturbed ferric ion states changes, so will the behavior of all the localized properties of the complex which can be associated primarily with the electronic and spin states of the ferric ion. Specifically, the properties which we wish to investigate in this study are the effective magnetic moments of the ferric ion, the magnetic field energies, and the electric field gradients of the ferric ion, especially in the region of spin-mixed eigenfunctions which has heretofor not veen reported. Whith the results of these calculations, we hope to explain and predict the behavior of the zero field splittings, magnetic moments, electron spin resonance and the quadrupole splitting in Fe^{57} Mössbauer resonance spectra of a series of ferric heme compounds and other appropriate ferric complexes. The observed behavior of some of these properties in these compounds is still unexplained and rather interesting, for example the variation in magnetic moment in a series of ferric memoglobin derivatives in a continuous fashion from the high to low spin values [2]. From our previous assignment of parameters for the ferric heme complexes to explain other properties [3], it appears that a reasonable range of values for the average cubic field for them is 28 000—32 000 cm^{-1}, with the lower limit on firmer ground than the upper one which could be somewhat higher. Thus we may use the eigenfunctions and eigenvalues obtained for $\Delta_{O_h} = 30\,000\ cm^{-1}$ and $32\,000\ cm^{-1}$ as illustrative of the possible behavior of ferric ion in its heme complexes. The results at 38 000 cm^{-1} are then illustrative of ferric ion compounds where the quartet state can be the ground state.

In our previous calculation, we have described in detail the multicomponent eigenfunctions obtained from the solution of the spin-orbit coupling matrices of a set of 12 interacting sextet, quartet, and doublet basis states in each of these parameter regions. These 12 basic states are given in Table 4 of Ref. [1]. Each basic state is a Kramers doublet and so are the corresponding multi-component eigenfunctions after spin-orbit coupling. In tetragonal symmetry, these 12 states factor into two non-interacting blocks labelled by E' and E'', their representations in the double group of that symmetry. The double degenerate, spin-mixed eigenfunctions belonging to the E'' block are seven-component states of the form:

$$\psi_i(E'') = \sum_{j=1}^{1} a_{ij}\phi_j \tag{1}$$

where the $j = 1$—7 states are those listed sequentially in that order in Table 4 of [1]. Similarly, the state of the E' block are five-component, spin-mixed states of the form:

$$\chi_i(E') = \sum_{j=8}^{12} a_{ij}\phi_j \tag{2}$$

where the five states $j = 8$—12 are the remainder of the states given in Table 4 of [1].

Using the set of twelve doubly degenerate spin-mixed states as a basis set, we can calculate the expectation value of any property for any one state, provided we can write the equivalent operator for that property and know the coefficients of mixing, i.e., the eigenfunctions $\psi_i(E'')$ and $\chi_i(E')$. An expectation value is then simply the diagonal matrix element of that operator with the total state and represents the first order eigenvalue for that property in that state. In cases where the particular operator causes further interaction among the spin-mixed basis set, off-diagonal matrix elements with that operator might be desired, either to calculate eigenvalues by diagonalization of the operator matrix, or to calculate eigenvalues to second or higher order.

As we have just discussed, the total states $\chi_i(E')$ and $\psi_i(E'')$ are multicomponent, i.e., five and seven component stets of the form given in Eqs. (1) and (2). A general computer program for the Burroughs 5500 was devised which calculates the matrix elements of a given operator between any two such states, $\langle N|O_p|M\rangle$, given the matrix elements $\langle \varphi_j|O_p|\phi_i\rangle$ of that operator for the individual components, ϕ_j, and their coefficients of mixing a_j in the total states N and M. N and M are the $\chi_i(E')$ and $\psi_i(E'')$ states and ϕ_j's are the individual components of these states listed in Table 4 of [1]. Since each of these twelve states is a doublet, there are in all 24 such total states.

In our current study, we have used this formalism to calculate the magnetic moments, magnetic field energies and electric field gradient of the ferric ion. We turn now to a discussion of each of the properties of ferric ion in the different regions of changing ferric ion states particularly in the region of spin-mixed states. Wherever possible our results are compared with existing experimental observations. The remainder of our results then serve as predictions which can be used to compare with future experimental results.

II. Effective Magnetic Moments

A) General Expressions for Tetragonal Symmetry

The operators for calculating the effective magnetic moment of a paramagnetic ion in tetragonal symmetry are:

$$H_z=(L_z+2S_z)\,,\qquad H_x=(L_x+2S_x)\,,\qquad H_y=(L_y+2S_y)\,. \tag{3}$$

The matrix elements of the H_x and H_y operators between any two total states labeled by the four "quantum numbers" total spin S, z component of spin M, irreducible representation to which the state belongs in D_4 symmetry, h, and the component of that representation, θ, i.e.,

$$\langle ShM\theta|L_x+2S_x\,|S'h'M'\theta'\rangle=H_x(J,K)\,,\quad \langle ShM\theta|L_y+2S_y\,|S'h'M'\theta'\rangle=H_y(J,K)$$

have the same value. Hence in D_4 symmetry, in the expressions for the magnetic moment twice the value of one of these matrix elements can be used.

The first order contribution to the total effective magnetic moment of paramagnetic ion with half integral spin-like ferric ion is:

$$\mu^2_{\mathrm{eff}}(1)=\Big(\sum_N H_z^2(N,N)+2H_\perp^2(N,N'')\Big)\,\exp(-E_N/kT)/\sum_N e^{-E_N/kT} \tag{4}$$

and the second order contribution is:

$$\mu^2_{\mathrm{eff}}(2)=2kT\left(\sum_N\sum_{M\neq N}\frac{H_z^2(N,M)+H_\perp^2(N,M'')+H_\perp^2(N'',M)}{E_M-E_N}\right)\times \\ \times\exp(-E_N/kT)/\sum_N\exp(-E_N/kT) \tag{5}$$

where N, N'' are α and β degenerate partners of state N, which is a Kramer's doublet, N, M'' are α and β partners of states N and M respectively, $E_N=$ energy of state N relative to the ground state, sum over N is for all states for which $E_N\leqq 2000\ \mathrm{cm}^{-1}$, sum over M for a given state N is until the second order contribution of state $M\leqq 0.01$.

Using the set of twelve doublet eigenfunctions obtained for each set of value of parameters chosen, values of the appropriate operators and the effective magnetic moments to second order were calculated at three different temperatures: $T=293°$, $77°$, and $4°$ K.

Table 1. *Properties of ferric ion in regions of spin-mixed states: region I (sextet-doublet states)*

$C' = f \cdot u'$	2000	2300	2400	2500	2600	2650	2700	2750	2800	2850	2900	2950	3000	3200
μ_{eff} (293 °K)	2.42	2.48	2.61	2.91	3.50	3.89	4.31	4.71	5.06	5.32	5.51	5.64	5.73	5.86
(77 °K)	2.04	2.05	2.06	2.07	2.10	2.16	2.37	3.08	4.35	5.27	5.63	5.75	5.80	5.86
(4 °K)	1.84	1.86	1.88	1.88	1.91	1.91	1.94	2.04	2.39	3.10	3.97	4.99	5.48	5.36
ΔE_1	564	558	555	545	451	355	254	158	78	31	12	3.66	.78	7.3
ΔE_2	398	461	372	172	49	41	40	39	39	38	38	38	38	30.85
g_z (0)	3.30	3.40	3.44	3.50	3.54	3.60	3.69	3.90	4.44	5.24	5.63	5.81	2.00 (5.86)	1.99
$g_\perp$ (0)	1.02	0.92	0.89	0.85	0.80	0.85	0.77	0.60	0.69	0.30	0.41	0.39	5.94 (0.34)	5.96
g_z (1)	.00846	.0244	.0526	.240	1.632	1.874	1.940	1.964	1.98	1.982	1.986	1.988	5.86	5.94
$g_\perp$ (1)	.0294	.0754	.1584	.718	4.88	5.60	5.80	5.86	5.90	5.92	5.94	5.94	.350	.194
g_z (2)	1.328	1.884	1.952	5.30	4.88	3.44	2.98	8.50	9.54	9.80	9.88	9.92	9.94	9.98
$g_\perp$ (2)	.870	1.020	5.84	1.74	2.20	3.20	4.34	2.50	1.41	.924	.664	.508	.404	.206
q_{lat} (293 °K)	.747	.859	.897	.934	.972	.990	1.01	1.03	1.05	1.06	1.08	1.10	1.12	1.20
q_{val} (77 °K)	11.0	10.6	10.5	10.3	10.3	10.1	10.0	9.64	8.82	6.80	4.81	3.36	2.49	1.10
(4 °K)	10.2	9.86	9.76	9.58	9.52	9.28	8.99	8.27	6.55	3.66	2.05	1.44	1.27	.905
	10.2	9.86	9.76	9.58	9.52	9.28	8.98	8.20	6.20	3.07	1.54	1.11	1.13	.540
$\lvert q_{\mathrm{tot}} \rvert$ (293 °K)	11.7	11.5	11.4	11.3	11.3	11.1	11.0	10.7	9.87	7.86	5.90	4.46	3.61	2.30
(77 °K)	10.9	10.7	10.7	10.5	10.5	10.3	10.0	9.30	7.50	4.72	3.13	2.55	2.39	2.10
(4 °K)	10.9	10.7	10.7	10.5	10.5	10.3	9.99	9.22	7.50	4.14	2.63	2.21	2.25	1.74

$B = 1100\ \mathrm{cm}^{-1}, C = 3750\ \mathrm{cm}^{-1}, \Delta_{O_h} = 30\,000\ \mathrm{cm}^{-1}, \delta = 420\ \mathrm{cm}^{-1}, f = 1$ ($\Delta E_1, \Delta E_2$ = first and second energy intervals in cm^{-1}. $g(i); i = 0, 1, 2$ refers to the ground, first and second excited states. $q_{\mathrm{lat}}, q_{\mathrm{val}}$ in $10^{15}\ \mathrm{esu} \cdot \mathrm{cm}^{-3}$. μ_{eff} in Bohr magnetons).

For each value of Δ_{O_h} and f considered, three effective magnetic moments were calculated for the range of values of C'('$= u'$) which allows substantially spin-mixed eigenfunctions. This, of course, is the same range of C' for which we have already plotted, tabulated and discussed the energy and spin mixing behavior of the five lowest ferric ion states in the previous paper in this series.

B) Region of Possible Ferric-Heme Assignments ($\Delta_{O_h} = 30\,000$ *and* $32\,000\ \text{cm}^{-1}$)

For $\Delta_{O_h} = 30\,000\ \text{cm}^{-1}$ the lowest C' considered was in the low spin region and the highest C' considered was well within the high spin region. Thus the values of μ_{eff} calculated at room temperature span the range of 2.40 to 5.89 Bohr magnetons. Table 1 gives these results for $\Delta_{O_h} = 30\,000\ \text{cm}^{-1}$, $f = 1$, and they are plotted in Fig. 1 for three different temperatures. The measured values of 12 ferric hemoglobin compounds at room temperature is given in Table 2 and are shown as experimental points on our theoretical room temperature curve in Fig. 1. We see at once that we are able to completely account for the measured values of the effective magnetic moments for this entire series [2], including not only the two high spin and two low spin compounds at each end but the eight compounds with magnetic moment values intermediate between these two ends. We have done so with extremely small variations in the value of the axial field parameter. The values of C' for each compound wich explains its measured magnetic moment value is also given in Table 2. The SH^- compound value of $\mu_{\text{eff}} = 2.26$ was well within the low spin region and is not shown on the graph. This small range of values corresponds in a physically reasonably fashion to the fact that only one ligand is changing in going from one of these compounds to another. From the values of the effective magnetic moments alone it appears that the division between high and low spin is quite arbitrary since the values decrease smoothly and continuously over the entire range from high to low spin. However, a distinction between pure sextet, pure doublet and substantially spin-mixed states can easily and naturally be made. As we can see clearly from Fig. 1, the inate differences in the wave functions are translated into the manner in which μ_{eff} varies in these different regions.

Table 2. *Effective magnetic moments of ferric ion in hemoglobin derivatives*

	Ligand	μ_{eff} (exp)			C'(theor.)
		Ref. [1]	Ref. [2]	Ref. [3]	
1	F^-	5.76	5.92	5.92	3150
2	H_2O	5.65	5.80	5.84	3010
3	$HCOO^-$	5.44			2870
4	OCN^-	5.40			2860
5	SCN^-	5.06			2800
6	OH^-	4.66	5.11		2740
7	NO_2^-	4.13			2680
8	$SeCN^-$	3.88			2650
9	Imidazole	2.87			2490
10	CN^-	2.50	2.50		2320
11	Acide$^-$	2.35	2.84	2.84	2390
12	SH^-	2.26			

The shape of our μ_{eff} curve is remarkable like an acid-base titration curve with the region of rapidly changing spin-mixed wave functions reflected by rapidly changing values of μ_{eff} over the narrow range of substantial spin mixing; where spin-mixing becomes negligible the values of μ_{eff} level off into their respective low and high spin limits. The success of this model in accounting for the observed room temperature magnetic moment behavior of a series of ferric heme proteins is rather marked. Spin-mixed states going to the appropriate high and low spin limits seem then to be a rather reasonable explanation of the changes occuring in the ferric ion in these complexes due to the small changes in the local environment.

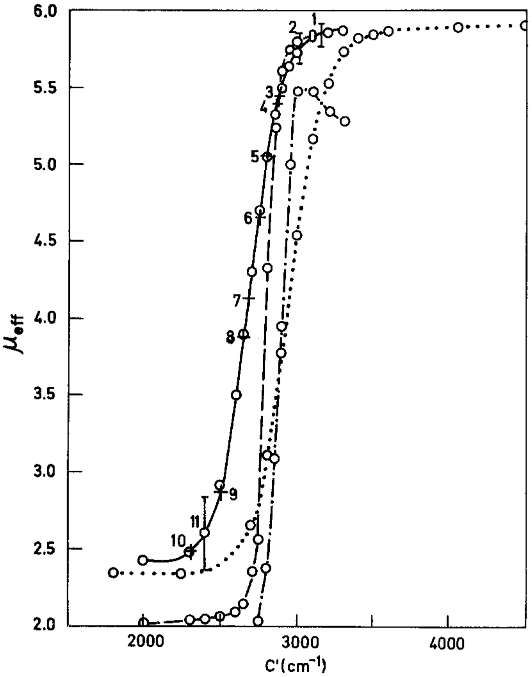

Fig. 1. Effective magnetic moment μ_{eff} of ferric ion as a function of axial field distortion C' ($\Delta_{O_h} = 30\,000\ \text{cm}^{-1}$). ——— $f=1, kT=214\ \text{cm}^{-1}$, – – – $f=1, kT=56\ \text{cm}^{-1}$, —·—· $f=1, kT=3\ \text{cm}^{-1}$, ······ $f=9,\ kT=214\ \text{cm}^{-1}$

In our calculations, we have also included the contribution to the effective magnetic moments of all states within 2000 cm^{-1} of the ground state assuming a thermal equilibrium of population among these states as well as allowing each state to be spin-mixed. Thermal equilibrium cannot account for the variation in effective magnetic moment in going from one compound to the other at the same temperature. These variations must be due to changes in the nature of the ferric ion eigenfunctions and eigenvalues such as we have postulated here. Certainly if the states are close enough to be in thermal equilibrium, they are close enough for substantial spin-orbit interaction. Both possibilities are included in our calculation of magnetic moments. The results themselves indicate the regions where each of these effects are important. A thermal equilibrium among the lowest lying states, spin-mixed or not, accounts for the temperature dependence of the values of μ_{eff} for any one compound. From Fig. 1, which gives the values of μ_{eff} for three temperatures and also the experimental points of the 12 derivatives at room temperature, the predicted temperature dependence of μ_{eff} for these compounds can be deduced.

While the excellent fit or our calculated values of μ_{eff} with the experimental values lends credence to our assumed physical basis for this model it does not determine uniquely the values of the crystal field parameters.

To illustrate the dependence of the results on the parameter f, which gives the ratio of quartic to quadrate corrections to the cubic field strengths, Table 3 lists the values of $\mu_{\text{eff}}(T)$ obtained for $\Delta_{O_h} = 30\,000\ \text{cm}^{-1}$ and $f = 9$. It appears from results shown in this table, that they are quite similar to those obtained for $f = 1$ for slightly different values of $C'(= fu')$. Thus it seems that, just as for the high spin region, the results obtained are much more sensitive to the values of the parameters Δ_{O_h} and C' then they are to f. A fit to the experimental values was also obtained for other values of Δ_{O_h} in the range $= 29\,000$ to $32\,000\ \text{cm}^{-1}$ as well. In Table 4 are given the values of the three $\mu_{\text{eff}}(T)$ through the spin mixed regions of C' for $\Delta_{O_h} = 32\,000\ \text{cm}^{-1}$ and $f = 1$. The room temperature behavior is shown in Fig. 2, and it may be seen that the values of the room temperature effective magnetic moments span the same range and figure as at $30\,000\ \text{cm}^{-1}$. What we have shown is that, in the narrow range of values of Δ_{O_h} which we have already determined as reasonable for the ferric porphyrin compounds from other experimental data, it is possible to explain not only the observed high and low spin ferric heme compounds but all those of intermediate effective magnetic moment as well. By appropriate variation of both Δ_{O_h} and C' we can also explain changes in magnetic moment as the in-plane ring changes and the axial field remains constant. To further pin down the exact variation of C' and Δ_{O_h} occuring through

Table 3. *Properties of ferric ion in regions of spin-mixed states: region I (sextet-doublet states)*

$C' = fu'$	1800	2700	2800	2900	3000	3100	3200	3300	3400	3500	4500
μ_{eff} (293 °K)	2.34	2.69	3.11	3.77	4.54	5.16	5.54	5.73	5.82	5.85	5.89
(77 °K)	2.11	2.13	2.15	2.21	2.78	4.85	5.68	5.81	5.84	5.85	5.87
(4 °K)	1.97	2.00	2.01	2.04	2.13	2.78	4.36	5.52	5.45	5.34	5.10
ΔE_1	497	489	474	366	191	51.7	8.25	1.89	5.77	7.78	12.6
ΔE_2	1476	301	129	47.5	44.0	41.4	40.4	38.1	34.1	32.1	29.5
$g_z(0)$	3.86	3.97	3.99	4.03	4.20	5.07	5.79	2.00	1.99	1.99	2.00
$g_\perp(0)$	.48	.32	.37	.28	.22	.03	.15	5.94	5.95	5.96	5.97
$g_z(1)$	.004	.075	.415	1.74	1.94	1.97	1.98	5.92	5.95	5.97	5.99
$g_\perp(1)$	.017	.224	1.23	5.19	5.89	5.90	5.93	.127	.101	.082	.022
$g_z(2)$	1.90	1.93	5.94	5.83	9.14	9.95	9.97	9.98	9.98	9.98	9.99
$g_\perp(2)$	1.46	5.76	.277	.656	1.92	.403	.220	.150	.112	.088	.022
q_{lat} (293 °K)	0.0747	.112	.116	.120	.125	.127	.134	.137	.141	.145	.187
q_{val} (77 °K)	8.79	8.67	8.68	8.67	8.50	7.06	4.02	2.21	1.40	1.06	.767
(4 °K)	8.06	7.91	7.89	7.80	7.34	4.62	1.75	1.14	.937	.854	.733
	8.06	7.91	7.89	7.80	7.31	4.13	1.27	.880	.584	.536	.491
$\lvert q_{\text{tot}}\rvert$ (293 °K)	8.86	8.69	8.80	8.79	8.62	7.18	4.15	2.35	1.54	1.21	.953
(77 °K)	8.13	8.02	8.00	7.92	7.47	4.75	1.89	1.28	1.08	1.00	.920
(4 °K)	8.13	8.02	8.00	7.92	7.43	4.26	1.40	1.02	.725	.681	.677

$B = 1100\ \text{cm}^{-1}$, $C = 3750\ \text{cm}^{-1}$, $\Delta_{O_h} = 30\,000\ \text{cm}^{-1}$, $\delta = 420\ \text{cm}^{-1}$, $f = 9$. See too footnote of Tab. 1.

Table 4. *Properties of ferric ion in regions of spin-mixed states: region II (sextet-doublet-quartet mixed states)*

$C' = fu'$	3000	4100	4200	4300	4400	4500	4600	4700	4800	4900	5000	6000	10 000
μ_{eff} (293 °K)	2.40	2.48	2.65	3.02	3.64	4.39	5.02	5.40	5.60	5.69	5.74	5.80	5.81
(77 °K)	2.07	2.11	2.13	2.16	2.26	2.78	4.30	5.25	5.52	5.61	5.64	5.70	5.70
(4 °K)	1.90	1.97	1.99	2.01	2.06	2.22	2.67	3.59	5.21	4.83	4.71	4.57	4.54
ΔE_1	540	542	535	497	367	202	73.9	15.5	6.11	15.7	20.9	32.4	37.0
ΔE_2	627	510	316	175	115	123	122	119	111	101	94.8	82.9	83.0
g_z (0)	3.57	3.81	3.85	3.91	4.04	4.33	5.04	5.63	1.98	1.99	1.99	1.99	1.99
$g_\perp$ (0)	.88	.651	.623	.578	5.26	.383	.126	.041	5.80	5.81	5.82	5.85	5.85
g_z (1)	.007	.100	.232	.853	1.70	1.90	1.95	1.97	5.84	5.91	5.99	5.99	5.99
$g_\perp$ (1)	.023	.231	.631	2.43	4.95	5.55	5.71	5.77	.065	.059	.050	.012	.001
g_z (2)	1.56	1.93	1.80	5.86	5.73	1.79	9.91	9.97	9.99	9.98	9.98	9.99	9.99
$g_\perp$ (2)	1.09	5.67	5.32	.412	.665	3.55	.527	.228	.137	.094	.040	.013	.001
q_{lat} (293 °K)	1.12	1.53	1.57	1.61	1.64	1.68	1.72	1.76	1.79	1.83	1.87	2.24	3.74
q_{val} (77 °K)	9.94	9.83	9.97	10.2	10.5	10.9	10.2	8.08	6.23	5.12	4.57	3.71	3.55
(4 °K)	9.22	9.16	9.24	.934	9.39	9.06	7.56	6.10	5.11	4.25	3.87	3.20	3.02
	9.22	9.16	9.24	9.34	9.39	8.97	6.82	4.21	2.81	2.39	2.34	2.24	2.20
$\lvert q_{tot}\rvert$ (293 °K)	11.1	11.4	11.5	11.8	12.2	12.6	11.9	9.83	8.03	6.95	6.44	5.96	7.29
(77 °K)	10.3	10.7	10.8	10.9	11.0	10.7	9.28	7.86	6.91	6.08	5.74	5.44	6.76
(4 °K)	10.3	10.7	10.8	10.9	11.0	10.7	8.54	5.97	4.61	4.22	4.22	4.48	5.94

$B = 1100\ \mathrm{cm}^{-1}$, $C = 3750\ \mathrm{cm}^{-1}$, $\Delta_{O_h} = 32\,000\ \mathrm{cm}^{-1}$, $\delta = 420\ \mathrm{cm}^{-1}$, $f = 1$. See too footnote of Table 1.

either of these series, changing axial ligand or changing porphyrin ring, it would be necessary to correlate the measured values of room temperature effective magnetic moment with some other physical properties which can be calculated from this model.

C) Magnetic Moment Behavior in Region where Quartet Ground State is Possible

At $\Delta_{O_h} = 38\,000\ \mathrm{cm}^{-1}$ the spin-mixed region is between a pure doublet state and a pure quartet ground state. In Table 5 the variation of μ_{eff} with C' from the pure doublet to the pure quartet region is given and this behavior is plotted in Fig. 2 for room temperature. At the low spin end, μ_{eff} remains close to 2.36 from $C' = 5000$ to $7200\ \mathrm{cm}^{-1}$. This is because the ground state is essentially a pure $^2E(\mp 1/2, \pm 1)$ state and as seen from values of ΔE_1 in Table 5 the first excited state remains the same distance away from the ground state in this range of values of C'.

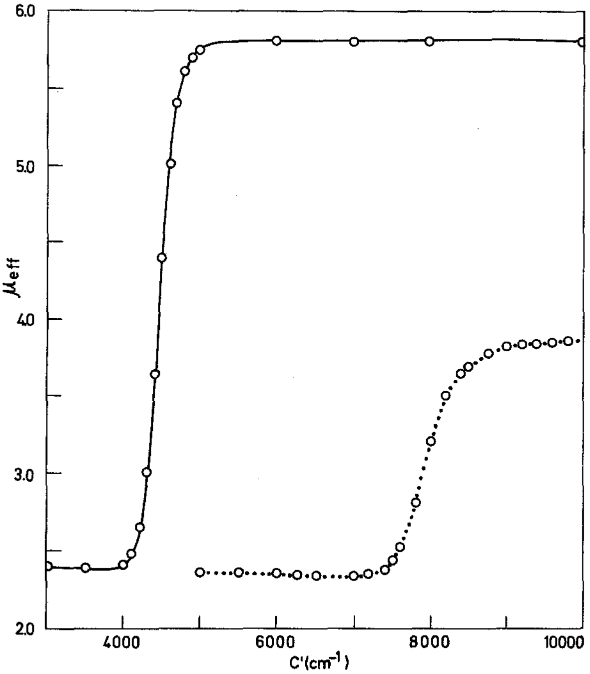

Fig. 2. Effective magnetic moment μ_{eff} of ferric ion as a function of axial field distortion C' ($f = 1$, $kT = 214\ \mathrm{cm}^{-1}$). ——— $\Delta_{O_h} = 32\,000\ \mathrm{cm}^{-1}$, ······ $\Delta_{O_h} = 38\,000\ \mathrm{cm}^{-1}$

As C' increases further, i.e., the axial field strength decreases, the first excited state energy decreases, spin mixing increases and μ_{eff} increases from its doublet state value towards the value for a spin-only quartet state of 3.88 Bohr magnetons. The lowest quartet state is the $^4A_2(\pm 3/2)$ state with zero orbital angular momentum. Thus the variation of μ_{eff} between these two limits from $C' = 7200$ to $9000\ \mathrm{cm}^{-1}$ as seen in Fig. 3 is a measure of the substantial quartet-doublet state mixing which occurs in the wave function in this region of parameters. At $C' = 15\,000\ \mathrm{cm}^{-1}$ the two doubly degenerate components of the $^4A_2$ state cross and the $^4A_2(\pm 1/2)$ state becomes the ground state. This does not affect the value of the calculated effective moment at room temperature but rather the temperature dependence of that value. This cross-over of quartet states does, however, affect some other properties which we calculate.

Table 5. *Properties of ferric ion in regions of spin-mixed states: region III (doublet, quartet and spin-mixed states)*

$C' = fu'$	5000	7400	7500	7600	7800	8000	8200	8400	8500	8750	9000	9800	15000	20000
μ_{eff} (293 °K)	2.36	2.38	2.43	2.51	2.81	3.20	3.49	3.66	3.70	3.78	3.82	3.86	3.89	3.89
(77 °K)	2.10	2.20	2.24	2.30	2.51	2.84	3.18	3.44	3.53	3.67	3.75	3.85	3.89	3.89
(4 °K)	1.95	2.11	2.15	2.21	2.40	2.63	2.81	2.91	2.95	3.02	3.06	3.21	3.76	3.56
ΔE_1	506	544	537	516	410	274	180	124	105	74.2	55	25.6	4.79	9.28
ΔE_2	1101	851	708	618	629	783	1071	1430	1624	2136	2666	44.13	4532	4530
g_z (0)	3.79	4.18	4.23	4.40	4.77	5.23	5.56	5.75	5.80	5.88	5.92	5.97	1.99	1.99
$g_\perp$ (0)	.605	.347	.321	.289	.205	.116	.058	.029	0	.011	0	.002	4.02	4.02
g_z (1)	.004	.288	.463	.749	1.44	1.78	1.99	1.94	1.95	1.97	1.98	1.99	5.99	5.99
$g_\perp$ (1)	.011	.596	.951	1.53	2.92	3.59	3.82	3.91	3.93	3.97	3.99	4.00	.00003	.000006
g_z (2)	1.78	1.71	1.53	1.25	5.08	4.64	4.32	4.14	4.09	2nd excited state energy > 2000 cm^{-1}				
$g_\perp$ (2)	1.38	2.43	3.08	2.50	2.51	.322	.366	.382	.384					
q_{lat} (293 °K)	1.87	2.77	2.80	2.84	2.91	2.99	3.06	3.14	3.18	3.27	3.36	3.66	5.60	7.47
q_{val} (77 °K)	9.06	11.6	12.8	14.5	20.3	28.9	37.0	42.8	44.9	48.7	51.2	55.1	58.1	57.5
(4 °K)	8.35	10.7	11.6	12.9	16.7	21.5	25.9	29.8	31.7	35.9	39.5	47.6	56.3	54.3
	8.35	10.7	11.6	12.9	16.7	21.3	24.8	26.7	27.3	28.2	28.6	29.1	35.3	30.7
$\lvert q_{tot}\rvert$ (293 °K)	10.9	14.4	15.6	17.3	23.3	31.9	40.0	45.9	48.1	52.0	54.5	58.8	63.7	65.0
(77 °K)	10.2	13.5	14.4	15.7	19.6	24.5	29.0	33.0	34.8	39.2	42.9	51.3	61.9	61.8
(4 °K)	10.2	13.5	14.4	15.7	19.6	24.3	27.9	29.9	30.5	31.5	32.0	32.8	40.9	38.1

$B = 1100\ \mathrm{cm}^{-1}$, $C = 3750\ \mathrm{cm}^{-1}$, $\Delta_{O_h} = 38\,000\ \mathrm{cm}^{-1}$, $\delta = 420\ \mathrm{cm}^{-1}$, $f = 1$. See too footnote of Table 1.

III. Magnetic Field Energies and Predicted Electron Spin Resonance Spectra

A) General Ferric Ion Tetragonal Field Results

The twelve doubly degenerate states are each split by an applied magnetic field. The first order magnetic field energy of each state is given by the expectation value:

$$E_N = \langle N|\vec{L} + 2\vec{S}|N\rangle \cdot \vec{H} \tag{6}$$

where L and S are the orbital and spin angular momenta for an ion with Russell Saunders coupling and H is the applied magnetic field, and $|N\rangle$ is any one of the E' or E'' states.

Magnetic-dipole induced transitions can occur between the magnetically split states and it is these transitions which are observed in the electron spin resonance spectra of paramagnetic complex ions.

In tetragonal symmetry, two magnetic field directions are defined, an xy plane, which in the case of the heme complexes would be approximately the plane of the porphyrin ring, and a z axis, perpendicular to the plane.

If a magnetic field is applied along the molecular z axis, the observed resonance energy for each split state is:

$$\Delta E_z = g_z H_z \text{ Bohr magnetons,} \tag{7}$$

where

$$g_z = \langle\beta|H_z|\beta\rangle - \langle\alpha|H_z|\alpha\rangle = 2\langle\alpha|H_z|\alpha\rangle\,, \tag{8}$$

$$H_z = (L_z + 2S_z)\,. \tag{9}$$

For the multicomponent states: $\psi_i(E'')$ or $\chi_i(E') = |\alpha\rangle = \sum_j a_{ij}\phi_j$, where $j = 1$—7 for the 7-component $E''\alpha''$ states, and $j = 8$—12 for the 5-component $E'\alpha'$ states, and the j index identifies the basis states as given in Table 4, Ref. [1]. The total value of g_z is the sum of the contributions to the operator H_z from all the component states. Since each of the basis states $|\phi_j\rangle$ are $|ShM_s\theta\rangle$ states, the H_z operator has only diagonal elements among the component states. Then the total value of $\langle\alpha_i|H_z|\alpha_i\rangle$ is:

$$\langle\alpha_i|H_z|\alpha_i\rangle = \Sigma\, a_{ij}^2 H_z(jj)$$

where $H_z(jj) = \langle\phi_j|H_z|\phi_j\rangle$.

Thus we see that the actual values of g_z depend on two factors: The values of $H_z(jj)$, the component matrix elements, and the mixing coefficients. The $H_z(jj)$ need only be calculated once for the twelve basis functions ϕ_j used. When this is done the expression for g_z for the 7-component E'' states is:

$$g_z(E'') = |-10A^2 + 6B^2 + 6C^2 - 7D^2 + 3E^2 + 4F^2 - 2G^2| \tag{10}$$

where A, B, C, etc. are the coefficients a_{ij}, $j = 1$—7, and for the 5-component E'' states is:

$$g_z(E'') = |-2H^2 - 2I^2 + J^2 - 5K^2| \tag{11}$$

where H, I, etc. are the coefficients a_{ij}, $j = 8$—12. For a given basis set, each of these g_z values is then a function of the extent of mixing of the component states. The values of g_z for different total states of the same sub-set, E' or E'', will be different only because of the different extent of mixing of components.

For an applied magnetic field in the xy plane in tetragonal symmetry, $H_x = H_y = H_\perp$. The $H_\perp$ field mixes all six components of the ${}^6A_1$ state. To first order only, the two degenerate α and β states are mixed. There are no diagonal elements of $H_\perp$ for either the α or β states. Hence the first order magnetic field energy of each mixed state is $\pm H_\perp\langle\alpha|H_\perp|\beta\rangle\beta_m$ (β_m = Bohr magneton) and the observed splitting between two Kramer partners by an applied field in this direction is:

$$\Delta E_\perp = g_\perp H_\perp \beta_m \quad \text{when } H = \text{applied field}\,, \tag{12}$$

$$g_\perp = 2\langle\alpha|H_\perp|\beta\rangle \quad \text{for transitions between any two split doublets} \tag{13}$$

$$\text{and} \quad H_\perp = (L_x + 2S_x) = (L_y + 2S_y)\,, \tag{14}$$

that is, the matrix elements of these two operators with wave functions belonging to irreducible representations of point groups with tetragonal symmetry are equal.

In terms of component contributions, the total value of $\langle\alpha|H_\perp|\beta\rangle$ for each pair of multicomponent α and β states is:

$$\langle\alpha_i|H_\perp|\beta_i\rangle = \sum_{jk} a_{ij}(\alpha)\, a_{ik}(\beta)\, \langle\phi_j|H_\perp|\phi_\kappa\rangle \tag{15}$$

(j, $k = 1$, 7 for E'' states, j, $k = 8$, 12 for E' states).

Computing the $\langle\phi_j|H_\perp|\phi_k\rangle$ for all combinations of component states we obtain for E'' states

$$g_\perp(E'') = |2\sqrt{5}AB + 2\sqrt{3}DE + 1\sqrt{2}CD - 2\sqrt{F}G + 2G^2| \tag{16}$$

and for the E' states

$$g_\perp(E') = |6H^2 + 4I^2 + 1\sqrt{3}IJ + 2\sqrt{3}JK|\,. \tag{17}$$

Table 6a. *g Values of 12 unmixed Kramer's doublets*

Pure state	g_z	$g_\perp$
$^6A_1(\pm 1/2)$	2	6
$^6A_1(\pm 3/2)$	6	0
$^6A_1(\pm 5/2)$	10	0
$^2E(E'')$	4	0
$^2B_2(E'')$	2	0
$^2E(E')$	0	0
$^4A_2(\pm 1/2)$	2	4
$^4A_2(\pm 3/2)$	6	0
$^4E(\pm 3/2, \pm 1)$	7	0
$^4E(\pm 1/2, \pm 1)$	3	0
$^4E(\pm 1/2, \pm 1)$	1	0
$^4E(\pm 3/2, \pm 1)$	5	0

The g values defined in Eqs. (8) and (13) apply to transitions between originally degenerate Kramer's doublets, and to first order only, i.e., not allowing the states to mix in a $H_\perp$ applied field. In this approximation, we can use the expressions for g_z and $g_\perp$, Eqs. (10), (11), (16), and (17) to tabulate the two g values for all twelve unmixed Kramer's doublets. This is done in Table 6a. We see from this table that only two pure states have non-zero values of $g_\perp$ to first order. Thus with a single crystal sample and an rf-field in the plane of the porphyrin ring, only the $^6A_2(\pm 1/2)$ and the $^4A_2(\pm 1/2)$ transitions would be observed.

The non-zero values of $g_\perp$ for all other Kramer's doublets of ferric ion in tetragonal symmetry is due to spin mixing of states. Because of this mixing there are added cross terms in the expression for $g_\perp$, as can be seen from Eqs. (16) and (17), which do not vanish. Depending then on the magnitude of various products of coefficients of components, $g_\perp$ can vary greatly over regions where several coefficients of mixing are important. The g_z values of these twelve doublets vary from 0—10. Since all the functions used are eigenfunctions of H_z, the value of g_z for any given spin-mixed state is the weighted average of the individual g_z values and hence can be anywhere in the 0—10 range.

B) Region of Possible Heme Assignments ($\Delta_{O_h} = 30\,000$ *and* $32\,000\ \text{cm}^{-1}$)

If we include the spin-mixed region as well as the high and low spin state regions, then, it would seem that a wide range of both g_z and $g_\perp$ can occur in the region of parameters suitable for ferric heme compounds. We have calculated these values for all Kramer's doublets within 2000 cm^{-1} of the ground state and have tabulated the g values for the three Kramer's doublets for $\Delta_{O_h} = 30\,000$ and 32 000 cm^{-1} for values of C' through the region of spin-mixed wave functions.

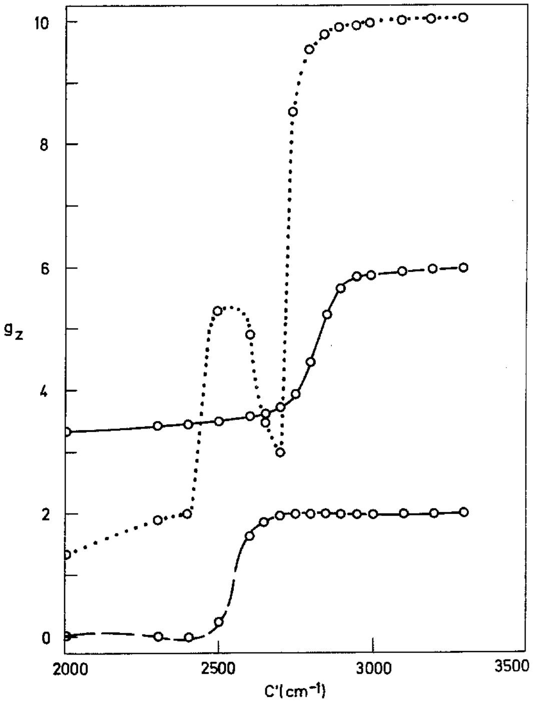

Fig. 3. Effects of spin-mixing on the "g_z" values of the three lowest ferric ion states, as a function of axial field strength ($\Delta_{O_h} = 30\,000$ cm^{-1}, $f = 1$). ——— ground state, – – – first excited state, · · · · · second excited state

These results are given in Tables 1, 3 and 4 which also list the magnetic moment values and the first two energy intervals for the excited states ΔE_1 and ΔE_2.

Again, as a typical example of ferric heme complex behavior, let us examine in some detail the electron spin resonance results predicted at $\Delta_{O_h} = 30\,000$ cm^{-1} and $f = 1$. The g_z and $g_\perp$ values for the three lowest Kramer's doublets are plotted as a function of axial distortion in Fig. 3 and 4 respectively. At the low spin end, i.e., $C' = 2000$ cm^{-1}, $g_z = 3.30$. This value is a reflection of the fact that the ground state is a pure doublet but with a mixture of the ^2E and ^2B states, i.e., $F = .933$ and $G = .341$. The value of $g_\perp = 1.02$ is due to the last two terms in Eq. (16), $|-\sqrt{2}FG + 2G^2|$. As C' increases, mixing with the $^6A_1(\pm 3/2)$ state increases, i.e., the coefficient B increases, while the coefficients F and G decrease. From Eq. (10) and from our results in Fig. 3, we see that this has the effect of increasing g_z towards the pure $^6A_1(\pm 3/2)$ value of 6. The value of $g_\perp$, as seen in Fig. 4 on the other hand diminishes, since the contribution from the sextet state is subtracted from that of the main doublet contribution and $g_\perp$ approaches the limit of zero for the pure ${}^6A_1(\pm 3/2)$ state. We see that the ground state g_z values in a region of sextet-doublet spin-mixed states can vary from 3 to 6 and $g_\perp$ from 1 to 0 through the spin-mixed region. At 3000 cm^{-1} the pure ${}^6A_1(\pm 1/2)$ state becomes the ground state and values of g_z and $g_\perp$ of 2 and 5.94 reflect this change as noted by a discontinuity in the ground state values of g_z and $g_\perp$.

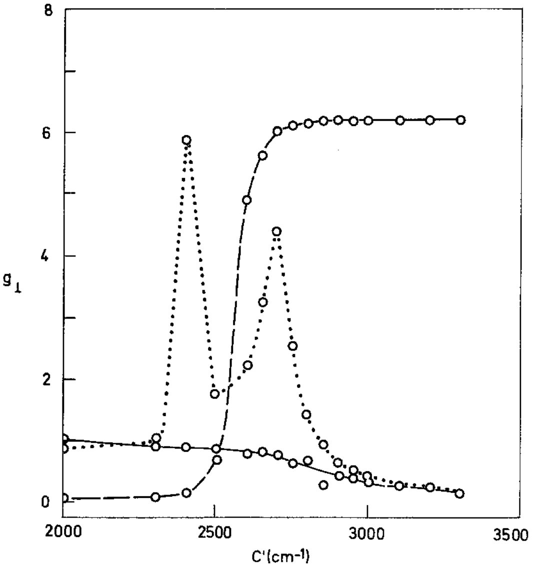

Fig. 4. Effects of spin-mixing on the "$g_\perp$" values of the three lowest ferric ion states, as a function of axial field strength ($\Delta_{O_h} = 30\,000$ cm^{-1}, $f = 1$). ——— ground state, – – – first excited state, ····· second excited state

The first excited state at $C' = 2000$ cm^{-1} is an almost pure ${}^2E(\pm 1/2, \pm 1)$ state, i.e., $L = .996$. Therefore, as can be seen from Figs. 3 and 4 both g_z and $g_\perp$ are close to zero and would be exactly zero if there was no spin mixing at all. As C' increases, the ${}^6A_1(\pm 1/2)$ state mixes, H increases and L decreases. Thus g_z increases from 0 to 2 and $g_\perp$ from 0 to 6. Again, even more than for the ground state, the first excited state values of g_z and $g_\perp$ vary over a very wide range in the doublet-sextet, spin-mixed region. Over most of this region, as can be seen from values of ΔE_1 in Table 1, the first excited state is several hundred wave numbers above the ground state. On the other hand, the ground state doublet transition has a much lower probability of occurring, due to the smaller value of $g_\perp$. Therefore, it is possible that both of these interdoublet transitions could be seen with g values ranging from 0 to 6 in some of the ferric heme compounds with intermediate values of magnetic moment.

The second excited state at $C' = 2000$ cm^{-1} is the complement of the ground state, a pure doublet with the two doublet state E'' components mixed so that $F = .340$ and $G = .936$. Since F contributions substract from G the value of g_z is therefore less than 2, namely 1.33, and the value of $g_\perp$, given mainly by the last two terms in Eq. (16), is .870. At $C' = 2400$ cm^{-1} the second excited state becomes the almost pure $^6A_1(\pm 1/2)$ state and the values of $g_z = 1.952$ and $g_\perp = 5.84$ reflect this shift. At $C' = 2500\,\text{cm}^{-1}$, the second excited state becomes the interacting counterpart of the ground state with some $^6A_1(\pm 3/2)$ and some $^2E(\pm 1/2, \pm 1)$ character. Since the ground state at this point is still predominantly doublet, this second excited state is still predominantly $^6A_1(\pm 3/2)$, i.e., $B = .968$, and $g = 5.30$ while $g_\perp = 1.74$. The rather high value of $g_\perp$ comes from a substantial value of $A = .197$ in this function, i.e., mixing of the $^6A_1(\pm 3/2)$ and $^6A_1(\pm 5/2)$ states so that the first term in Eq. (16) for $g_\perp$ accounts for most of its non-zero value. As C' increases, the amount of $^6A_1(\pm 5/2)$ in this state increases and the amount of $^6A_1(\pm 3/2)$ character decreases, i.e., A increases and B decreases while all other components are negligible throughout this C' variation. From Eq. (10) for g_z, it may be seen that A and B contribute oppositely to g_z, so that first g_z decreases from 6 and then begins to increase towards 10 as it approaches the pure $^6A_1(\pm 5/2)$ state, as can be seen from Fig. 4. The value of $g_\perp$ determined by the product AB first increases and then decreases towards zero as B approaches zero.

The value of ΔE_2 given in Table 1 is the energy difference between the first and second excited state. We see from this table that for some of the spin-mixed region this interval is only a small fraction of the first energy interval. The $g_\perp$ value for the second excited doublet electron spin resonance transition is substantially larger than for the ground state, indicating a larger transition probability. Therefore, if it were possible to see both the ground and first excited doublet transition, it might also be possible to see the second excited doublet transition with very little less probability.

Our calculations of the g_z and $g_\perp$ values for the first three Kramer's doublets of ferric ion through a region of heavily spin-mixed states have clearly indicated that these values can vary markedly over a wide range of values, specifically shown in Table 1, and summarized in Table 6b. This is by far much more variation than is both observed and calculated for the high spin region where the ground state is $^6A_1(\pm 1/2)$, and $g_z \cong 2$ and $g_\perp \cong 6$ [4] only are observed since the first two excited states, the other sextet state doublets, both have $g_\perp = 0$. It is also in contrast to the pure doublet state, where so far g values from 2.8 to 1.72 [4] have been observed for the azide derivative. Due to the mixing of the $^2B_2$ and ^2E states in the $\psi_i(E'')$ state which is the ground state in low spin compounds, we would expect more of a variation in the observed "g" values for low spin than for high spin compounds.

Table 6b. *Effect of spin-orbit coupling on g values of the three lowest spin-mixed Kramer's doublets*

	g_z	$g_\perp$
Ground state	3.30—5.81	1.02— .39
First excited state	0.00—1.988	.03—5.94
Second excited state	1.33—9.92	.87—4.34—.508

The electron spin resonance spectra then of single crystals of ferric heme proteins in tetragonal symmetry with intermediate values of magnetic moment would be characterized by four to six transitions spanning the magnetic field range corresponding to $g = 1$—10. The powder spectra might resolve some of these transitions also, and would in general give weaker and broader resonance than either a high spin or low spin compound. Thus the intermediate magnetic moment complexes should have a characteristic electron spin resonance which verifies the spin-mixed nature of their ground and low-lying excited states. These are the conclusions and predictions of our calculation. Because of these predictions, we have begun in our laboratory a modest experimental program to measure the electron spin resonance of some of these intermediate-magnetic-moment hemoglobin derivatives. Our preliminary results for powder of the SCN^-, $ScCN^-$ and OH^- derivatives (methemoglobin at a pH of 10) seem to verify the general characteristics predicted.

These spectra have four to six resonance transitions, are broader and weaker than the high spin hemoglobin signals and span the g value range from 2—6. Also the $SeCN^-$ spectra resemble a low spin ferric compound much more than the SCN^- spectra does. Since the magnetic moment of $SeCN^-$ is lower than the SCN^- derivative, this result is in qualitative agreement with the observed magnetic moment values. The hydroxide and SCN^- spectra seem quite similar in nature. We are continuing to investigate and analyze these spectra in more detail and will discuss the results at a later time.

Another characteristic of the spin-mixed region is that it predicts much larger zero field splittings than for the high spin compounds and lower values than for the low spin compounds as seen from Table 1. For example, all of the crystal field parameter assignments which corroborate the value of $\mu_{\mathrm{eff}} = 3.88$ for the $SeCN^-$ derivative also predict values of ΔE_1 of about $350\,\mathrm{cm}^{-1}$ to $100\,\mathrm{cm}^{-1}$, allowing for the variation in fitting μ_{eff} only.

As we have previously discussed, we can fit the series of measured effective magnetic moment values for a number of different values of crystal field parameters between $\Delta_{O_h} = 29\,000$ and $32\,000\,\mathrm{cm}^{-1}$. The calculated values of g_z and $g_\perp$, ΔE_1 and ΔE_2 for the other possible assignments of magnetic parameters for ferric heme complexes are given in Tables 3 and 4 for $\Delta_{O_h} = 30\,000\,\mathrm{cm}^{-1}$, $f = 9$ and $\Delta_{O_h} = 32\,000\,\mathrm{cm}^{-1}$, $f = 1$, respectively, which also list the magnetic moment variation with C' previously discussed. The calculated g_z and $g_\perp$ values for the first three Kramer's doublets follow the same qualitative behavior as we have just discussed for $\Delta_{O_h} = 30\,000\,\mathrm{cm}^{-1}$, $f = 1$. From all these tables and graphs the following conclusions can be drawn.

All the results are most affected by the two parameters Δ_{O_h} and $C' (= u'f)$ and are much more insensitive to f variation. Comparing values of the calculated quantities μ_{eff}, ΔE_1, ΔE_2, g_z and $g_\perp$, we see that the main difference using these different combinations of parameters is small differences in the set of actual numerical values for all of these quantities at any one point for which a desired value of μ_{eff} is obtained. For example, for $SeCN^-$, the four assignments that fit the observed value of $\mu_{\mathrm{eff}} = 3.88$, differ somewhat in the value of ΔE_1, ΔE_2, g_z, and $g_\perp$ they predict. Thus, in order to sort out the different parameter assignments, the zero field splittings or very careful electron spin resonance spectra would have to be obtained. However, all of the values of parameters that corroborate the measured values of effective magnetic moments for this as well as the other ferric heme compounds predict the same type of ESR spectra, quite different from either pure sextet, quartet, or doublet states, and values of ΔE_1 much larger than the high spin values and lower than low spin values.

Our success in explaining the measured values of magnetic moments already implies heavily that ferric ion exists in a mixed spin ground state in all of these compounds, even though for example the value of μ_{eff} for the SeCN$^-$ compound coincides exactly with the spin-only value for the quartet state. We have, by our calculation and its agreement with all continuously varying values of μ_{eff}, shown that this agreement with quartet ground state values is a coincidence and that ferric ion in SeCN$^-$ heme as well as the order heme compounds probably exists in a spin-mixed state. Electron spin resonance and direct zero field splitting measurements would further corroborate our spin-mixed model for this series of ferric heme compounds.

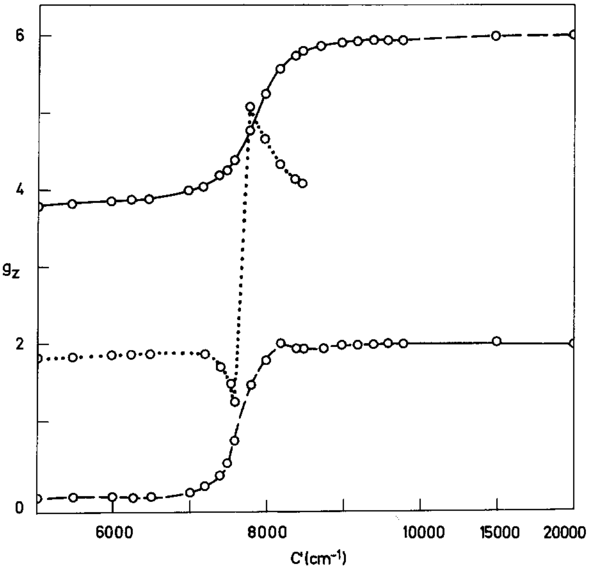

Fig. 5. Effects of spin-mixing on the "g_z" values of the three lowest ferric ion states, as a function of axial field strength (Δ_{O_h} = 38 000 cm^{-1}, $f = 1$). ——— ground state, – – – first excited state, · · · · · second excited state

C) Region of Quartet Ground State Possibility

As we have been discussing, for $\Delta_{O_h} \geqq 36\,000$ cm^{-1}, a quartet ground state becomes possible for small axial field strengths. The results at $\Delta_{O_h} = 38\,000$ cm^{-1} and $f = 1$ are typical of the behavior of ferric ion in this region where only a doublet ground state, a spin-mixed quartet-doublet, and quartet ground states are possible. Table 5 lists the g values of the three lowest Kramer's doublets as a function of C' from the low spin through the spin-mixed to the quartet ground state conditions and the 3 values of g_z and $g_\perp$ are shown in Figs. 5 and 6 respectively. Also listed in Table 5 are the zero field splittings i.e., the first two energy intervals between the three lowest lying ferric ion states in this region. At $C' = 5000$ cm^{-1}, the strong axial field, the value of μ_{eff}, also given in this table, is a typical low spin value of 2.36. The ground state is primarily the ${}^2E(E'')$ state mixed with some of the other doublet ${}^2B_2(E'')$ component, i.e., $F = .977$ and $G = .193$. The values of $g_z = 3.79$ and $g_\perp = .605$ reflect this small mixing of doublet components. The first excited state is the doublet state of the E' series ${}^2E(E')$, i.e., $L = .998$ and therefore both g_z and $g_\perp$ are essentially zero. The second excited state is primarily the third doublet component ${}^2B_2(E'')$ with some ${}^2E(E'')$, i.e., $G = .980$ and $F = .192$, and $g_z = 1.78$ while

$g_\perp = 1.38$. The zero field splitting between these three doublet states is very large, $\Delta E_1 = 506$ and $\Delta E_2 = 1101\ \text{cm}^{-1}$. This is typical of low spin ferric ion compounds, since there is first order spin-orbit coupling among the three doublet components. As the axial field decreases, C' increases and the ${}^4A_2(\pm 3/2)$ state mixes into the ground state doublet, i.e., the coefficient C increases while F and G decrease. Since this state has $g_z = 6$, as it becomes the dominant component in the ground state, the value of g_z increases from 3.79 to 6. Simultaneously, the value of $g_\perp$ decreases to zero which is the value for this pure quartet state. The first excited state, similarly starting as ${}^2E(E')$, $L \cong 1$, becomes more and more mixed with the ${}^4A_2(\pm 1/2)$ component, i.e., I increases and L decreases, causing g_z to increase from 0 to 2, and $g_\perp$ from 0 to 4. The second excited state, which starts as the almost pure ${}^2B_2$ component, changes character several times as C' increases. At $C' = 7500\ \text{cm}^{-1}$ it is predominantly the ${}^4A_2(\pm 1/2)$ state mixed with ${}^2E(E')$, i.e., $I = .871$ and $L = .482$. It is the interacting partner of the first excited state, which at this value of C' is still predominantly the ${}^2E$ state, i.e., $L = .876$ and $C = .480$. Here the value of g_z for this state is 1.53 and $g_\perp = 3.08$. At $C' = 7800\ \text{cm}^{-1}$ however, the state which is the interacting partner of the ground state, i.e., the $\langle {}^2E(E'') - {}^4A_2(\pm 3/2)\rangle$ state, becomes the second excited state and remains so until about $C' = 9800\ \text{cm}^{-1}$. At $C' \cong 7800\ \text{cm}^{-1}$ when it crosses the non-interacting E' state and becomes the second excited state, $C = .608$, $F = .781$ and $G = .129$ so that it has about 36 % quartet and 64 % doublet character. Because of the state crossing, g_z increases abruptly to 5.08 and $g_\perp$ decreases .251. This state remains the second excited state and, as its doublet character increases, i.e., F increases and C decreases, g_z increases towards 6 and $g_\perp$ stays between 0 and 1. For $C' \geqq 9000\ \text{cm}^{-1}$, the state energy is more than $2000\ \text{cm}^{-1}$ from the ground state and its g values are no longer calculated.

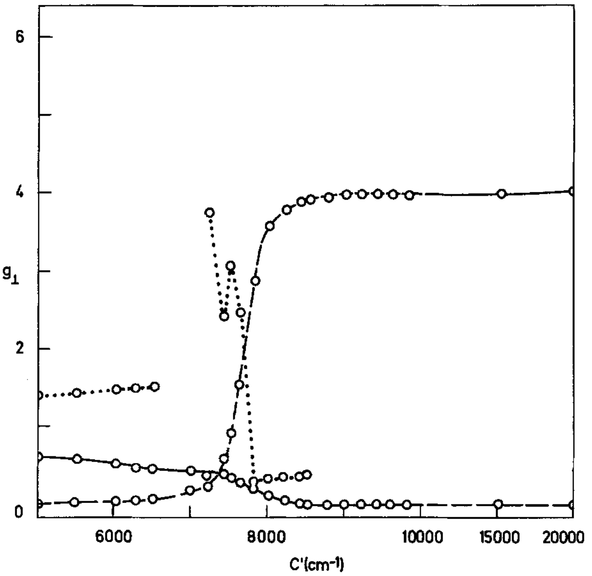

Fig. 6. Effects of spin-mixing on the "$g_\perp$" values of the three lowest ferric ion states, as a function of axial field strength ($\Delta_{O_h} = 38\,000\ \text{cm}^{-1}, f = 1$). ——— ground state, – – – first excited state, ····· second excited state

Our calculations predict then that through the doublet-quartet spin-mixed region, the g_z value of the ground state varies from 3.79—5.92 and $g_\perp$ from .605 to 0. Then for ferric ion compounds in this region, since the transition probability for the electron spin resonance with an rf-field in the porphyrin ring plane is proportional to $g_\perp^2/2$, only a very weak transition would be observed with possible g values in the above range. The first energy interval, ΔE_1, ranges from 506 to $55\ \text{cm}^{-1}$ as the states go from doublet to quartet character. The values of g_z and

$g_\perp$ for the first excited state range from 0 to 2 and 0 to 4, respectively. Therefore, for some values of C' in the spin-mixed region where ΔE_1 is not too large and $g_\perp$ has a substantially larger value than 0, it should be possible to see this first excited state doublet transition for spin-mixed states. It is possible that the increased transition probability times the decreased population would lead to a stronger signal for this state than for the ground state transition. A typical quartet-doublet mixed spin ferric ion electron spin resonance spectra then might have one or two broad and weak transitions with some resolution, for example, at a g between 4 and 6 and again at $g \cong 1$ to 4. Such compounds would have μ_{eff} values from 2.80 to 3.82. It does not seem as if any of our list of ferric heme derivatives fall within this category. Nor, to the best of our knowledge, have any examples of such doublet-quartet spin-mixed, ferric complexes been reported. For the pure quartet ground state region, the ESR predicted in tetragonal symmetry would be only one transition between the excited state doublet with $g_z \cong 2$ and $g_\perp \cong 4$. The intensity of this transition should be temperature dependent and also vary for a series of quartet ground state compounds since the value of ΔE_1 varies. The only known quartet state compound was found to have some rhombic character so that $g_z = 2.20$ and the $g_\perp$ value of 4.00 was symmetrically split to the two values 3.72 and 4.18. In the tetragonal limit these simple electron spin resonance results then are verified experimentally.

IV. Electric Field Gradient: Quadrupole Splitting of Mössbauer Resonance Spectra

A) General Formulation

In the Mössbauer resonance spectra of the Fe^{57} nucleus, there is a splitting of the excited $I = 3/2$ state into two states with $M_I = \pm 3/2$ and $M_I = \pm 1/2$ due to the interaction of its quadrupole moment with a residual electric field gradient at the nucleus. As a consequence, a doublet is observed in the transition to the ground state $I = 1/2$. In the assumed tetragonal symmetry of this model calculation, only the z component of the electric field gradient makes a non-zero contribution at the ferric ion nucleus. In such a case the observed splitting is [9]:

$$\Delta E_Q = E(\pm 3/2) - E(\pm 1/2) = 1/2\, eqQ\,, \tag{18}$$

where $q = -V_{zz} = \left(\dfrac{3z_i^2 - r_i^2}{r_i^5}\right)\varepsilon_i$, ε_i = effective charge at lattice site (x, y, z), and Q = nuclear quadrupole moment of the excited $I = 3/2$ state of Fe^{57}. If one assumes two separate contributions to q, a lattice contribution coming directly from the assumed distribution of the 6 ligands about the ferric ion, and a valence contribution from the ground and low lying electronic state of the ferric ion itself, then the total value of q is given by [9]:

$$q = (1 - R)q_{\text{val}} - (1 - \gamma_\infty)q_{\text{lat}}\,, \tag{19}$$

where q_{val} = contribution of all electronic states within kT of the ground state to the z component of the electric field gradient.

$$q_{\text{val}} = V_{zz}(T) = \sum_N V_{zz}(N)\exp(-E_N/kT)\,, \tag{20a}$$

$$V_{zz}(N) = \langle N | 3z^2 - r^2/r^5 | N\rangle\,, \tag{20b}$$

$$V_{zz}(N) = A(N)\,\langle r^{-3}\rangle\,, \tag{20c}$$

where $\langle r^{-3}\rangle$ is the expectation value of r^{-3} with the state N and $A(N)$ is the evaluated angular contribution to the *efg*. In terms of the tetragonal field strength parameter u':

$$q_{\text{lat}} = 7u'/2e\langle r^2\rangle \tag{21}$$

$(1-R)$ and $(1-\gamma_\infty)$ are the so-called antishielding factors which augment the effect of both lattice and valence contributions by a polarization of the inner core of electrons. Values of antishielding factors for atomic ferric ion have been calculated, as have the radial expectation values $\langle r^{-3}\rangle_0$ and $\langle r^2\rangle_0$ [6], using Hartree Fock wave functions. The most current values of these quantities are: $(1-R)\langle r^{-3}\rangle = 3.3$—$4.0$ atomic units; $\langle r^2\rangle = 1.4$ atomic units; $(1-\gamma_\infty) = 10.14$ atomic units [7]. Using these values in the expression for q, it becomes:

$$q = 3.737 \cdot 10^{11} u' + 1.298 \cdot 10^{16}\, V_{zz}(T)\,. \tag{22}$$

The matric elements $V_{zz}(N)$ between total spin-mixed states were calculated from the known coefficients of mixing in the eigenfunctions obtained and the values of the matrix elements V_{zz} between all components of the spin-mixed states, i.e., $\langle\phi_j|\, V_{zz}\,|\phi_k\rangle$. These individual matrix elements between basis set states ϕ_j need only be calculated once for all combinations of pairs of functions ϕ_j possible for the set of twelve states. Calculating these values for the twelve Kramer's doublets used here, we find the following expression for the total valence contribution to the *efg* from the α and β partners of a particular state. For the seven $|E''\rangle$ states the $V_{zz}(N)$ expression is:

$$V_{zz_{(\alpha+\beta)}}|E''\rangle = +(16/7)C^2 - (8/7)D^2 - (8/7)E^2 - (2/7)F^2 + (16/7)G^2\,, \tag{23}$$

where, as in the g_z and $g_\perp$ expression, the coefficients correspond to the coefficients a_{ij} with $j = 1$—8 in the total wave function. Correspondingly, for the five $|E'\rangle$ states with coefficients of mixing of components H, I, J, K, and L corresponding to $a_{ij}, j = 8$—12, the total contribution to the electric field gradient from the α and β partners of a given Kramer's doublet is:

$$V_{zz_{(\alpha+\beta)}}|E'\rangle = (16/7)I^2 - (8/7)J^2 - (8/7)K^2 - (2/7)L^2\,. \tag{24}$$

From Eqs. (23) and (24) for V_{zz} we see that it is only the doublet and quartet states which make a contribution to the electric field gradient in axial symmetry. In the limit of equal mixtures of all of the quartet components in a given state, the contribution to V_{zz} vanishes. This is not true of the two doublet state components in the E'' states. Using expressions (23) and (24) for $V_{zz}(N)$, we have calculated these quantities for all states within 2000 cm^{-1} of the ground state and included all these individual state contributions in the total valence contribution $V_{zz}(T)$ to the electric field gradient, using Eq. (20a) for $V_{zz}(T)$.

For convenience, we define the lattice contribution:

$$q_{\text{lat}} = 3.737 \cdot 10^{11}\, u' \tag{25}$$

and the valence contribution:

$$q_{\text{val}} = 1.298 \cdot 10^{16}\, V_{zz}(T)\,. \tag{26}$$

The valence contribution $V_{zz}(T)$ is a function of temperature since it involves a thermal average of the contributions from excited states. We have calculated $V_{zz}(T)$ for three temperatures, 293°, 77° and 4° K as well as the values obtained for the total $q = q_{\text{lat}} + q_{\text{val}}$ at each temperature.

The magnitude of the electric field gradient is manifest in the magnitude of the quadrupole splitting of the $I = 3/2$ state that it causes. Since the quadrupole moment of this excited nuclear state is not known, the equation $\Delta E_Q = 1/2\, eqQ$ represents one equation with two unknowns. Using experimental values of ΔE_Q and calculated values of q, the most we can do to determine the reasonability of our calculated values of q is to determine if, for a series of compounds of the same nucleus, the measured values of ΔE_Q and calculated values of q give a constant Q, i.e., if the ratio of $2\Delta E_Q eq$ is constant from compound to compound. The observed quadrupole splitting is usually measured in mm/sec and the quadrupole moment Q in Barns. Using these units, ΔE_Q becomes:

$$\Delta E_Q = 6.154 \cdot 10^{-15}\, qQ = CqQ\,. \tag{27}$$

B) Region of Possible Ferric Heme Complex Assignment ($\Delta_{O_h} = 30\,000$ *and* $32\,000\ \mathrm{cm}^{-1}$)

The values of q_{lat} and three values of $q_{\mathrm{val}}(T)$, together with the total $q(T)$ calculated at the three different temperatures are all given in Tables 1, 3, and 4. In these tables, which also give the zero field splittings, magnetic moments, and g values for the various values of Δ_{O_h} and f, q is tabulated also as a function of C' through the region of spin-mixing. Unfortunately, there have been no Mössbauer resonance spectra published of the ferric heme derivatives with intermediate values of magnetic moments. What we can do with our results then is examine the behavior of our calculated values of q in the spin-mixed region. For this we again take the results at $\Delta_{O_h} = 30\,000\ \mathrm{cm}^{-1}$, $f = 1$ as typical. The behavior of the lattice and valence contributions as a function of C' through the spin-mixed region is shown in Fig. 7. From the low to high spin region, q_{lat} increases monotonically as a function of C'. However, the valence contribution has an entirely different behavior reminiscent of the behavior of μ_{eff}. At the low spin end, i.e., low values of C', the valence contribution is very large and almost constant as a function of C', decreasing very slowly. In this region of doublet ground and low lying states, the valence contribution exceeds the lattice one by a factor of approximately 10. Then, as spin-mixing becomes significant, the value of the valence contribution decreases rapidly over a very small range of values of C'. This rapidly changing region is characteristic of spin-mixed behavior. In this region the valence contribution is reduced from a factor of ~ 10 larger to a value of somewhat smaller than the lattice contribution. In the high spin region of C' the valence contribution levels off and is the typically smaller value associated with an almost pure $^6A_1$ ground state. However, the value of the valence contribution is very sensitive to small amounts of mixing of other states and it never reduces to zero, remaining at least 10% of the lattice contribution.

On the same graph in Fig. 7 are shown the results for $f = 9$. In this case, both the lattice and valence contributions have the same quantitative behavior as just described, but the value of q_{lat} is reduced considerably. Since it is a small part of the total contribution to the electric field gradient over the spin-mixed region, the results obtained for the two values of f do not differ greatly.

Over the entire spin-mixed region, i.e., $\mu_{\mathrm{eff}} = 2.5$—5.5 Bohr magnetons, the total value of q at room temperature diminishes by a factor of approximately 2 for both $f = 1$ and 9. While, because of the large number of approximations made in these calculations of q, many more than in the other quantities calculated, we cannot take this quantitative variation literally; it is an indication of the trend and rate of change of the magnitude of quadrupole splitting one might except to see in the series of ferric heme complexes for which the magnetic moments have been measured. We would also expect the magnitude of the observed quadrupole splittings to be somewhere between the low and high spin values.

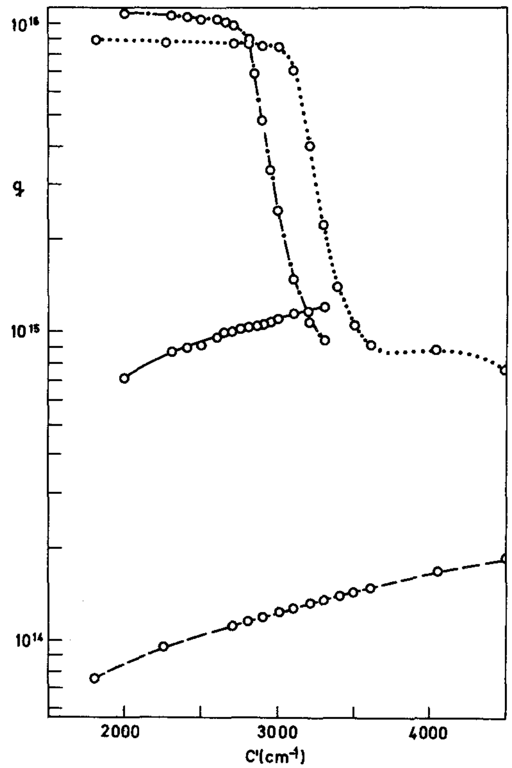

Fig. 7. Lattice and valence contributions to electric field gradient in spin-mixed region as a function of axial field strength ($\Delta_{O_h} = 30\,000$ cm^{-1}, $kT = 214$ cm^{-1}). ——— q_{lat}, $f = 1$, — · — · q_{val}, $f = 1$, — — — q_{lat}, $f = 9$, · · · · · q_{val}, $f = 9$

The results for $\Delta_{O_h} = 32\,000$ cm^{-1}, $f = 1$ are also in the realm of possible ferric heme assignments which give agreement with the measured values of magnetic moments. For this somewhat higher cubic field strength, there is more quartet state mixing. Thus, for larger axial distortions, the ground state is never quite pure sextet state. The effect of these differences on the calculated values of q are shown for q_{lat}, $q_{\text{val}}(T)$ and $q(T)$ in Table 4, and the room temperature behavior of q_{lat} and q_{val} as a function of C' is given in Fig. 8. We see from this figure that the region of very substantially spin-mixed states is again characterized by a rapid decrease in the value q_{val}. However, the valence contribution does not drop to as low a value as it does in the pure sextet limit at $\Delta_{O_h} = 30\,000$ cm^{-1} due to the increased mixing with the quartet state which persists to the lowest value of axial fields considered here. The slight rise in the q_{val} curve at the low spin end is also due to the quartet state mixing which occurs simultaneously with the sextet state mixing. The lattice contribution, a function only of the tetragonal field parameters, has the same behavior as for the lower value of Δ_{O_h}. At the low spin end, the valence contribution is again about a factor of 10 greater than the lattice, decreasing to about the same value at the higher values of axial distortion. In this case, the variation of the total value of electric field gradient over the entire spin-mixed region is much less than

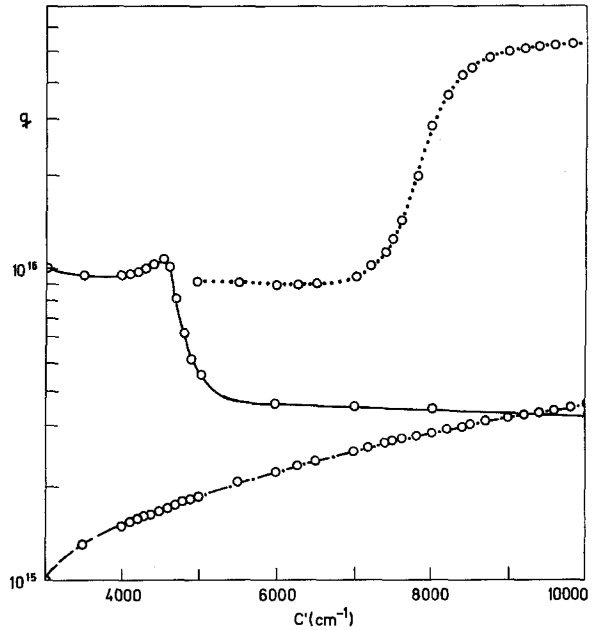

Fig. 8. Lattice and valence contributions to electric field gradient in spin-mixed region as a function of axial field strength ($kT = 214\ \text{cm}^{-1}$, $f = 1$). ——— q_{val}, $\Delta_{O_h} = 32\,000\ \text{cm}^{-1}$, ····· q_{val}, $\Delta_{O_h} = 38\,000\ \text{cm}^{-1}$, —·—· q_{lat}, $\Delta_{O_h} = 32\,000$ and $38\,000\ \text{cm}^{-1}$

at $\Delta_{O_h} = 30\,000\ \text{cm}^{-1}$. It is reduced by about 20% over the range from the low to high spin region. Which of these quantitative variations, if any, the one described at 30 000 or at 32 000 cm^{-1} more closely describes the ferric heme protein derivatives remains to be verified by experiment.

C) Region of Quartet Ground State Possibility ($\Delta_{O_h} = 38\,000\ \text{cm}^{-1}$)

Values of q_{lat}, $q_{\text{val}}(T)$ and $q(T)$ for a variation of C' from a doublet to a quartet ground state through the spin-mixed region, are given in Table 5 together with the other properties of ferric ion in this region. The room temperature results are also given in Fig. 8. We see from this figure that the valence contribution to the electric field gradient is larger in the quartet state than it is in the doublet state. This may also be seen from Eq. (23) for V_{zz} where it may be noted that the contribution to V_{zz} of an E'' state from the ${}^4A_2(\pm 3/2)$ state, which is the ground state in the pure quartet limit, is greater than that from the doublet states, i.e., the coefficient of C exceeds that of F. Similarly, from Eq. (24) for the E' states, it may be seen that the contribution from the ${}^4A_2(\pm 1/2)$ state exceeds that from the doublet state, i.e., the coefficient of I exceeds that of L. Thus, in the spin-mixed region, there is a rapid increase in the value of the valence contributions as C' increases from the doublet to the quartet state region. This is in contrast to the rapid decrease in the values of q_{val} with increasing C' over the doublet-sextet mixed region. From doublet to quartet ground state the valence contribution increases 5-fold, while the lattice contribution gradually increases. Therefore, in the quartet ground state limit for weak axial fields, i.e., large axial distortions, a much larger value of field gradient is expected than for any of the other states, doublet, sextet or spin-mixed. The ^4E components of the original $^4T_1$ cubic field state which balances the electric field gradient from the $^4A_2$ state in the cubic symmetry limit are at so high an energy in the limit of very weak axial fields that their contribution to the average value of electric field gradient is negligible. This would not be the case for rhombic symmetries which allow the ^4E and $^4A_2$ states to mix and hence would lower the value of total electric field gradient to be expected in a quartet ground state. For the one ferric ion compound known to be in a quartet ground state, extensive Mössbauer resonance measurements have been made, as well as measurements of the electron spin resonance [8]. The electron spin resonance results indicate a rhombic distortion and for this compound at 3 °K, the measure quadrupole splitting is about 3 mm/sec. This is 50% higher than for the sextet compound but much smaller than our calculations with axial symmetry alone predict.

V. Conclusions

In conclusion then, we may state that our simple strong crystal field model of ferric ion in complexes of tetragonal symmetry including spin-orbit coupling has indicated how, with a self-consistent and physically reasonable variation of crystal field parameters, ferric ion can have sextet, doublet, quartet and spin-mixed eigenfunctions.

We have discussed in detail the properties of the ferric ion in spin-mixed regions of parameters. We have seen how the nature of the wave functions vary and hence cause the zero field splittings and the magnitude of the effective magnetic moments to vary from the low spin to the high spin values. With these results we have successfully explained the observed magnetic moments for a series of ferric hemoglobin derivatives which vary continuously from high to low spin values. We have done so within a range of crystal field parameters consistent with both previous high and low spin ferric heme results. We have also predicted the behavior of the electron spin resonance spectra and electric field gradients for ferric ion in these spin-mixed regions.

In addition, at higher values of cubic field parameters, $\Delta_{O_h} \geqq 36\,000\ \text{cm}^{-1}$ we have calculated and discussed the behavior of ferric ion in a region where only a doublet and quartet ground state are possible. In this region, the spin-mixed states are doublet-quartet states. We have shown that the correct ground states in the quartet state limit are obtained for the only known example of ferric ion in a quartet state. We have also discussed the zero field splitting behavior, electron spin resonance and quadrupole splitting of Mössbauer resonance in this region.

Thus, as far as experimental knowledge for ferric complexes with near-axial symmetry will allow, we seem with our model to have accounted for the existence and behavior of ferric ion in sextet, quartet, doublet and spin-mixed states in a self-consistent way and to have shown at least one possible mechanism whereby ferric ion states undergo such changes.

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