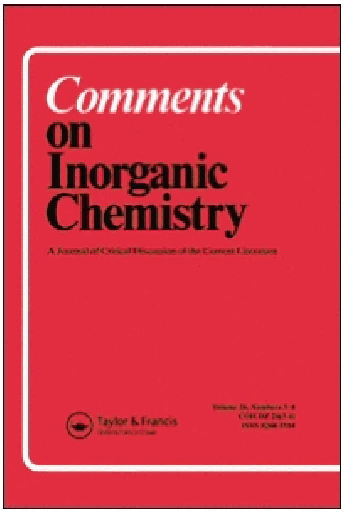

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Multiplet Splittings in Trigonal Cr(III) Complexes

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Multiplet Splittings in Trigonal Cr(III) Complexes

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The magnetic g factors and the zero field splittings of the $^4A_2$, ^2E, $^2T_1$ and $^2T_2$ states, all derived from the $(t_2)^3$ configuration, are re-examined. In particular the early work of Sugano and Tanabe, and the later, more precise analysis of Macfarlane are compared. The utility of the Hamiltonian applied to a Russell–Saunders multiplet is demonstrated. Some examples of trigonal Cr(III) complexes are used to illustrate outer sphere perturbations as well as limitations in the conventional ligand field model.

Key Words: *trigonal fields, effective Hamiltonian, multiplet splittings, g factors, Cr(III) complexes*

1. INTRODUCTION

Trigonally distorted metal complexes have played an important role in the development of coordination chemistry. It may come as a surprise to find that there are few examples for which the full set of trigonal field parameters are known with precision. The urgent need to establish relationships with molecular structure has tended to obscure the fact that the determination of these parameters is not a trivial matter. The trigonal potential, $v(t_{20})$, operating

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within the metal d manifold consists of two operators which transform as cubic harmonics of rank 2 and 4, $v(t_{20})^{(2)}$ and $v(t_{20})^{(4)}$, respectively. The trigonal field parameters are defined as[1]

$$v = -3K = \langle t_{20} \mid v(t_{20}) \mid t_{20} \rangle - \langle t_{2\pm} \mid v(t_{20}) \mid t_{2\pm} \rangle,$$

$$v' = -2^{1/2}K' = \langle t_{2\pm} \mid v(t_{20} \mid e_{u\pm} \rangle, \qquad (1)$$

where t_{2m} and e_m are the complex trigonal d orbitals which form the basis of the "general" effective Hamiltonian, the ligand field model.

The v and v' (or K and K') and the cubic parameter, Δ, derived from the cubic potential, $v(a_1)^{(4)}$, form a set of three independent parameters which determine the splitting of the d manifold in a trigonal site. All other models involve parameters whose interpretation may require additional assumptions. For example, in the angular overlap model (AOM)[2] the number of ligand field parameters is reduced by assuming a relationship between $v(a_1)^{(4)}$ and $v(t_{20})^{(4)}$. Furthermore, the AOM is frequently applied with the implicit assumption that the trigonal fields of the outer coordination spheres are negligible.

In 1958 it was not possible to diagonalize the full d^3 ligand field matrix and Sugano and Tanabe[3] applied the effective Hamiltonian model to individual Russell–Saunders multiplets in order to explain the electronic fine-structure as well as the electric dipole transition probabilities. Their work was mainly directed to states derived from the $(t_2)^3$ configuration viz. ${}^4A_2$, ${}^2E$, ${}^2T_1{}^a$ and ${}^2T_2{}^a$. These states have similar potential energy surfaces and the electronic transitions, ${}^2\Gamma \leftarrow {}^4A_2$, often give sharp lines. The half-filled subshell is resistant to Jahn–Teller distortions and to a good approximation Jahn–Teller coupling can be neglected. This approximation may not always be justified for the ${}^2T_2$ multiplet which is more strongly mixed with the ${}^4T_2(t_2{}^2e)$ state by spin-orbit coupling.[4]

The ${}^4T_2(t_2{}^2e)$ and ${}^4T_1(t_2{}^2e)$ states have first order trigonal splittings,[5]

$$D({}^4T_2) = E({}^2T_{2\pm}) - E({}^2T_{20}) \simeq -v/2,$$

$$D({}^4T_1{}^a) = E({}^2T_{1\pm}) - E({}^2T_{10}) \simeq -v/2 - v'. \qquad (2)$$

Although Eqs. (2) appear to provide a simple means of determining v and v', the excited states are subject to strong Jahn–Teller coupling through the stretching e_g vibration. Equations (2) may not be always reliable except in cases where the trigonal splittings are large.

2. $^2E(t_2{}^3)$ MULTIPLET

Sugano and Tanabe derived a perturbation expression for the zero field splitting of the ^2E multiplet,[3]

$$D(^2E) = E(E) - E(2A) \simeq -4\zeta v/(3E(^2T_2{}^a - {}^2E)) \qquad (3)$$

where ζ is the one-electron spin-orbit coupling, $|E_\pm\rangle = |\mp 1/2u_\pm\rangle$ and $|2A_\pm\rangle = |\pm 1/2u_\pm\rangle$ are the complex trigonal spin-orbit basis. Similar expressions were derived for g factors as well as zero field splitting for $^2T_1$ and $^2T_2$ states. In all cases their calculations were restricted to perturbation loops involving only the v parameter. By diagonalizing the full d^3 ligand field matrix Macfarlane showed that most of the perturbation expressions of Sugano and Tanabe are in general not valid.[5,6] The parameter $D(^2E)$ is the only one that is largely independent of v' (except when v' is large[9]) and (3) provides an excellent method for estimating v. However, the simple perturbation formulae are useful in the special cases where $v' \simeq 0$. We now proceed to show that the effective Hamiltonian generates symmetry parameters which are useful not only for ordering empirical data but also in making predictions.

The g values for the ^2E multiplet in a trigonal site are,

$$g_z(2A) = ((g_1 + 2k)^2 + 2g_2{}^2)^{1/2} \simeq g_1 + 2k,$$

$$g_z(E) = -g_1 + 2k \qquad (4)$$

where g_1 and g_2 are the first and second order g factors for a cubic Γ_8 state. The parameter g_2 consists solely of second order contributions from spin-orbit coupling. The latter also causes g_1 to deviate from the spin-only value of 2.0023. The effective orbital parameter k for the ^2E multiplet vanishes in the cubic limit.

For $B \perp z$ the two states, $|2A\rangle$ and $|E\rangle$, are connected by an off-diagonal Zeeman term, $\langle 2A_{\pm}|H_x|E_{\mp}\rangle = (1/2)g_2\mu_B B_x$. If the trigonal splitting quenches the off-diagonal Zeeman interaction then $g_x(2A) = 0$ and $g_x(E) = g_2$.

The perturbation formula for k in the special case $v' = 0$ is[3]

$$k(^2E) = -(2v^2/3E(^2T_2 - {}^2E)) \cdot (2/E(^2T_1 - {}^2E) + 1/E(^2T_2 - {}^2E)). \quad (5)$$

Equation (5) implies that k has a negative sign and gives $k \simeq -0.2$ for ruby, in agreement with experiment (see Table I). However, Wood[7] found $g_z(E) \simeq 0$ for Cr^{3+} doped in the spinel, $ZnAl_2O_4$, a result which is inconsistent with (4) and (5). The theory of Macfarlane[5] was able to reproduce the value $g_z(E) \simeq 0$ but the calculated value $g_z(2A) \simeq 3.72$ disagreed with the experimental value of 1.85 (Table I).

Now if we use (4) and assume $g_1 \simeq 2$ then the observed value $g_z(E) \simeq 0$ requires that $k \simeq +1$ and the effective Hamiltonian predicts that $g_z(2A) \simeq 4$, in agreement with the theoretical value, 3.72, of Macfarlane. Both theoretical numbers disagree with experiment. The origin of the discrepancy lies in the analysis of the Zeeman data.[7] The definition of the orbital g value employed by

TABLE I

Spectroscopic data for Cr^{3+} ion in trigonal sites

	$D(^2E)$	$g_z(2A)$	$g_z(E)$	$D(^4A_2)$	g_z	g_x
Ruby[a]	−29.1	1.48	−2.45	0.38	1.984	1.987
Emerald[a]	62.7	1.04	−2.71	1.78	1.974	1.979
$ZnAl_2O_4$[a]	6.7	1.85	0	−1.86	1.981	1.977
$ZnGa_2O_4$[a]	40	2.23	−0.95	−1.05	1.977	1.976
$Rh(bpy)_3(PF_6)_3$[b]	−19.5	2.08	−1.75	1.03	1.984	1.976
$Cr(NH_3)_6(ClO_4)_2Cl \cdot KCl$[c]	4.2	1.7	−2	0.35		

[a] Taken from Macfarlane.[5,6]

[b] Taken from Hauser *et al.*[17] See Section 5.

[c] Zero field splittings taken from Wilson and Solomon[11] and g values from Dubicki *et al.*[14]

Wood[7] differs from the standard definition by a factor of two. If this is corrected then the experimental value $g_z(2A)$ becomes 3.70.

Thus the first order expressions for the effective $g(^2E)$ factors have predictive value. Indeed, inspection of Table I shows that $g_z(2A) - g_z(E) \simeq 4$ in all cases except for $Cr^{3+}:ZnGa_2O_4$.[8] Here the significant departure from the value of 4 has been traced to higher order corrections which become large in the regime where both v and v' are large and both have a negative sign.[9]

3. $^2T_1$, $^2T_2(t_2^3)$ MULTIPLETS

The effective Hamiltonian for the $^2T_1$ and $^2T_2$ multiplets in a trigonal site is[3]

$$H(^2T) = \Delta(^2T)(L_z^2 - 2/3) + \lambda_z S_z L_z + \lambda_x(S_x L_x + S_y L_y) + \mu_B(g_1\,\mathbf{S} + k\mathbf{L}) \cdot \mathbf{B} \tag{6}$$

where $g_1 \simeq 2$ and $k = 1$ for pure d orbitals. In this paper we ignore higher order Zeeman terms which should be considered in a more precise analysis. We follow the notation of Sugano and Tanabe[3] and write for the eigenfunctions of the $^2T_1$ multiplet,

$$\begin{aligned} |2A_\pm\rangle &= |\pm 1/2\ a_\pm\rangle, \\ |E_{a\pm}\rangle &= \cos(\alpha)|\mp 1/2\ a_\pm\rangle + \sin(\alpha)|\pm 1/2\ a_0\rangle, \\ |E_{b\pm}\rangle &= -\sin(\alpha)|\mp 1/2\ a_\pm\rangle + \cos(\alpha)|\pm 1/2\ a_0\rangle \end{aligned} \tag{7}$$

where $\tan(2\alpha) = 2^{1/2}\lambda_x/(\Delta - \lambda_z/2)$ and $0 \le \alpha \le \pi/2$.
The corresponding eigenvalues are

$$\begin{aligned} E(2A) &= \Delta/3 + \lambda_z/2, \\ E(E_a) &= \Delta/3 - \lambda_z/2 + \lambda_x \tan(\alpha)/2^{1/2}, \\ E(E_b) &= \Delta/3 - \lambda_z/2 - \lambda_x \cot(\alpha)/2^{1/2}. \end{aligned} \tag{8}$$

The expressions for the first order g values[3] are easily derived from (7),

$$\begin{aligned} g_z(2A) &= g_1 + 2k, \\ g_z(E_a) &= -g_1 \cos(2\alpha) + 2k \cos^2(\alpha), \\ g_z(E_b) &= g_1 \cos(2\alpha) + 2k \sin^2(\alpha), \\ g_x(2A) &= 0, \\ g_x(E_a) &= g_1 \sin^2(\alpha) + 2^{1/2}\, k \sin(2\alpha), \\ g_x(E_b) &= g_1 \cos^2(\alpha) - 2^{1/2}\, k \sin(2\alpha). \end{aligned} \tag{9}$$

The expressions for the $^2T_2$ multiplet corresponding to (7), (8) and (9) are obtained by replacing $|a_m\rangle$ by $|x_m\rangle$ and λ_z, λ_x and k by $-\lambda_z$, $-\lambda_x$ and $-k$, respectively.

The multiplet splitting of a ^2T state involves three parameters, $\Delta(^2T)$, λ_z and λ_x. Since only two energy separations are observed the model is over-parameterized. The assumption that $\lambda_z \simeq \lambda_x$ is, in general, not justified. This problem may be overcome by estimating the value of λ in the cubic limit. Then the trigonal anisotropy in the effective spin-orbit coupling should follow the barycenter rule,

$$\begin{aligned} \lambda_z &= \lambda_{\mathrm{Oh}} - 2\lambda(v, v'), \\ \lambda_x &= \lambda_{\mathrm{Oh}} + \lambda(v, v'). \end{aligned} \tag{10}$$

Sugano and Tanabe[3] have determined $\lambda(v, v')$ for the special case $v' = 0$ and for the $^2T_1$ state,

$$\lambda(v, v' = 0) = -v\zeta/3E(^2T_2 - {}^2T_1). \tag{11}$$

In their analysis of ruby they omitted the important cubic term which takes the values $\lambda_{\mathrm{Oh}}(^2T_1) \sim -40\ \mathrm{cm}^{-1}$ and $\lambda_{\mathrm{Oh}}(^2T_2) \sim +63\ \mathrm{cm}^{-1}$ for Cr^{+3} in $\mathrm{M_gO}$.[5]

Application of the effective Hamiltonian to the $^2T(t_2{}^3)$ multiplets in metal oxide systems reveals several interesting features. First of all, the eigenvalues obtained from the full d^3 calculations[5] indicate that the trigonal splitting tends to quench the effective spin-orbit coupling and the angle α tends towards the limiting values 0° and 90°. Equations (7) and (8) give for $\alpha = 0°$, $E(2A) \simeq \Delta/3 + \lambda_z/2$, $E(E_a) \simeq \Delta/3 - \lambda_z/2$ and $E(E_b) \simeq -2\Delta/3$, and for $\alpha = 90°$, $E(2A) \simeq \Delta/3 + \lambda_z/2$, $E(E_a) \simeq -2\Delta/3$ and $E(E_b) \simeq \Delta/3 - \lambda_z/2$.

Inspection of Table II shows that

$$\Delta(^2T_1) \simeq v'/3 \quad \text{and} \quad \Delta(^2T_2) \simeq -v'. \tag{12}$$

The largest deviation from (12) occurs for the $^2T_2$ state in ruby and this discrepancy can be reduced by allowing $\alpha > 0°$. Thus the effective trigonal field for the ^2T multiplets is dominated by v'. However, the simple perturbation expressions for $\Delta(^2T)$ given by Sugano and Tanabe should be useful in the special cases where $v' \simeq 0$.

The analysis of the eigenvalues by the effective Hamiltonian is confirmed by comparing the computed g values with those pre-

TABLE II

Application of the effective Hamiltonian to $^2T_1$ and $^2T_2$ multiplets for Cr^{3+} doped in metal oxides

	Ruby	Emerald	$ZnAl_2O_4$	$ZnGa_2O_4$
ζ[a]	180	225	250	250
v	800	−2000	−200	−650
v'	680	2000	−1700	−1100
$^2T_1/\alpha$[b]	90°	90°	0°	0°
λ_z	−20	−50	−110	−90
$\Delta(^2T_1)$	200	790	−610	−450
$^2T_2/\alpha$	0°	0°	90°	90°
λ_z	110	30	80	3
$\Delta(^2T_2)$	−330	−1600	1510	1060

[a] The theoretical values of ζ, v and v' (all in units of cm^{-1}) used by Macfarlane.[5]

[b] The angle α is defined in the text and λ_z and Δ (all in units of cm^{-1}) are the effective spin-orbit and trigonal field parameters, respectively, for ^2T multiplets.

TABLE III

Comparison between the ligand field and the first order effective g values for the $^2T_1$ and $^2T_2$ multiplets

$^2T_1$	$\alpha = 90°$	Ruby[a]	Emerald[a]	$\alpha = 0°$	$ZnAl_2O_4$[a]
$g_z(2A)$	$g + 2k$	4.23	4.07	$g + 2k$	2.02
$g_z(E_a)$	g	1.92	1.90	$-g + 2k$	−2.40
$g_z(E_b)$	$-g + 2k$	0.23	−0.11	g	1.94
$g_x(E_a)$	g	2.19	2.35	0	0.12
$g_x(E_b)$	0	0.14	0.15	g	2.00
$^2T_2$	$\alpha = 0°$			$\alpha = 90°$	
$g_z(2A)$	$g - 2k$	0.58	1.11	$g - 2k$	0.27
$g_z(E_a)$	$-g - 2k$	−3.39	−2.82	g	2.00
$g_z(E_b)$	g	1.97	2.07	$-g - 2k$	−3.67
$g_x(E_a)$	0	0.17	0.11	g	1.87
$g_x(E_b)$	g	2.14	2.11	0	0

[a] Theoretical g values computed by Macfarlane.[5]

dicted by the first order equations (9). Table III shows good agreement in most cases. The major deviation occurs for the $^2T_1$ state for Cr^{3+}:$ZnAl_2O_4$. This is the case where v' is large and negative in sign. In this regime the mixing of ^2E and $^2T_1$ becomes large and higher order mechanisms involving v' increase k from 0 to +1 for ^2E and decrease k from 1 to 0 for $^2T_1$.[9] Thus a careful analysis of the $^2T_1$ and $^2T_2$ multiplets may give a measure of the v' parameter.

4. $^4A_2(t_2{}^3)$ MULTIPLET

The zero field splitting of the ground state of Cr^{3+} is defined as $D(^4A_2) = -2D = E(E) - E(2A)$, where D is the parameter commonly used in EPR spectroscopy. The origin of D has been a controversial subject. The early work of Van Vleck led to the perturbation expression[10]

$$D(^4A_2) = -4v\zeta^2/9E(^4T_2)^2. \tag{13}$$

This model could not account for the sign of D in ruby and Sugano and Tanabe[3] considered trigonal anisotropy in spin-orbit coupling. They introduced the second order perturbation,

$$D(^4A_2) = -8(\zeta_x^2 - \zeta_z^2)/9E(^4T_2). \qquad (14)$$

Anisotropy in spin-orbit coupling also produces anisotropy in the g values,[3]

$$g_z = 2.0023 - 8\zeta_z k_z/3E(^4T_2),$$

$$g_x = 2.0023 - 8\zeta_x k_x/3E(^4T_2). \qquad (15)$$

Their analysis was superseded by the work of Macfarlane[5,6] who obtained excellent agreement with the experimental values of $D(^4A_2)$ by using isotropic ζ and k in his ligand field calculations. He showed that third order perturbation loops, linear in v' and quadratic in ζ, account for ~80% of the observed zero field splitting. He derived,

$$D(^4A_2) = (8^{1/2}/3)\zeta^2 v'\{2/E(^4T_2)E(^4T_1^a) + 3/E(^2T_2^a)E(^2T_2^b)$$

$$+ 3/E(^2T_2^a)E(^4T_1^a)\}. \qquad (16)$$

Similarly, most of the observed trigonal anisotropy in the $g(^4A_2)$ values was attributed to third order perturbations,

$$g_z - g_x = (4\zeta k/E(^4T_2))(v/3E(^4T_2) - 2^{1/2}v'/E(^4T_1^a)). \qquad (17)$$

Notwithstanding the success of Macfarlane's analysis, closer inspection of his results (Table IV in Ref. 5) shows that the agreement in the $g_z - g_x$ values is excellent for emerald and $ZnAl_2O_4$ but the error increases for $ZnGa_2O_4$ and becomes more significant for ruby. In addition, the theoretical values of the isotropic spin-orbit parameter vary over a remarkably large range, 180 cm^{-1} for ruby and up to 250 cm^{-1} for the spinels (Table II).

The neglect of trigonal anisotropy in λ (and k) is certainly not justified in principle. Unfortunately it is not easy to go beyond the conventional ligand field model without introducing a large number of additional parameters. Even in cubic symmetry there are two spin-orbit parameters $\zeta(t_2, t_2)$ and $\zeta(t_2, e)$, usually denoted by ζ and ζ', as well as $k(t_2, t_2)$ and $k(t_2, e)$. Equation (16) should be adjusted, with ζ^2 replaced by $\zeta\zeta'$. A systematic and consistent method of incorporating the cubic and trigonal anisotropy of ζ and k into the ligand field analysis trigonal Cr(III) complexes has not been achieved so far. Incidently, expression (14) is incomplete and the full second order contribution is

$$D(^4A_2) = (1/9)(\zeta_x^2 - \zeta_z^2)(6/E(^2T_2^a) - 8/E(^4T_2) + 8/E(^2T_2^b)). \quad (18)$$

5. SOME EXAMPLES

The complex $Cr(NH_3)_6(ClO_4)_2Cl \cdot KCl$[11] and the related $CdCl_5^{3-}$ salts[12] have sharp line absorption spectra and are suitable for a more penetrating study of the trigonal field parameters. The magnitude and the sign of $D(^2E)$ and $D(^4A_2)$ are known for the mixed salt[11] (Table I). If we assume an isotropic spin-orbit coupling of $\zeta \simeq 220\ \mathrm{cm}^{-1}$, then the full d^3 matrix gives $v' \simeq 630\ \mathrm{cm}^{-1}$ and $v \simeq -180\ \mathrm{cm}^{-1}$.

The crystal structure of the neat Cr(III) complex is not known but the x-ray structures of the analogous Co(III)[13] and Os(III)[14] mixed salts have been determined. At room temperature, the M^{3+} ions reside on D_{3d} sites. The polar angles of the coordinating triangles of NH_3 groups with respect to the trigonal axis are $\theta \simeq 55.0°$ for Co(III) and 55.2° for Os(III). The bond lengths are Co–N = 1.959 Å and Os–N = 2.107 Å. Application of the linear ligator version of the AOM[15] with $e_{\pi c} = e_{\pi s} = 0$ cannot account for the large value of v' even if we assume $\theta \simeq 55.5°$. Furthermore, the same model predicts that v is small and has positive sign, in disagreement with (3). If we assume that the trigonal anisotropy in $g(^4A_2)$ is very small, then we must conclude that outer sphere contributions to v and particularly v' are significant.

The analysis of the trigonal splittings in the $CdCl_5^{3-}$ salt may not be as simple as described elsewhere.[12] The sign of $D(^4A_2)$ and

$D(^2E)$ have not been established experimentally. Our preliminary analysis of the Zeeman spectra suggest that if $D(^2E)$ has a positive sign then $g_z(2A) > |g_z(E)|$ and the sign of v' may be opposite to that in the mixed salt.[11]

The axial absorption spectrum[16] of a single crystal of Cr(bis-1,4,7-triazacyclononane)$Cl_3 \cdot 4H_2O \cdot 1/2HCl$ at 10 K shows no splitting of the $^4T_2$ band but it does show a pronounced shoulder on the $^4T_1^a$ band with $|D(^4T_1^a)| > 2000\ cm^{-1}$. From (2) we deduce that $|v'| \geq 1000\ cm^{-1}$ and predict that $|D(^4A_2)|$ is very large, of the order of 1 cm^{-1}. The very large v' is simply explained by the linear ligator AOM[15] which predicts a large v' with negative sign for a polar elongation, $\theta \simeq 50-52°$, of strong σ bands.

Recent work on Cr^{3+}:NaMgAl(oxalate)$_3 \cdot 8H_2O$ gives another example of a complex for which the AOM appears to provide a simple correlation between angular geometry and trigonal splittings.[17]

As a final example we comment on the trigonal fields in $Cr(bpy)_3(PF_6)_3$. A detailed spectroscopic study has been published[18] (Table I). Application of the conventional ligand field model produced a disturbing result. It was not possible to fit $D(^4A_2)$, $D(^2E)$ and the $g_z(^2E)$ values. The discrepancy was very large in this case because the $D(^4A_2)$ parameter required a large positive v' while the excited state g values required a smaller v' with negative sign.[17]

Our recent Zeeman studies[14] have shown that the measurement of g values by a scanning monochromator is fraught with many difficulties. Apart from the use of sharp calibration lines we have looked for absorptions which originate from different ground levels ($^4A_2$) and terminate in the same excited state, and used $g(^4A_2)$ obtained from EPR to calibrate internally the applied magnetic field. These precautions tend to be vitiated by large line widths, $\bar{\nu}_{1/2} > 2\ cm^{-1}$, as found in $Cr(bpy)_3$. It is very probable that the published $g_z(^2E)$ values[18] are incorrect.

Therefore, the parameters $D(^2E)$ and $D(^4A_2)$ (Table I) are used to deduce that v' is large and has a positive sign, $v' \geq 800\ cm^{-1}$. According to the comments in Section 3, we expect the $^2T_1$ multiplet to be split, $E(E_a) < E(2A) < E(E_b)$, and $\alpha \simeq 90°$. This order is indeed confirmed by the analysis[9] of the polarized absorption and Zeeman spectra of the $^2T_1 \leftarrow {}^4A_2$ transition (Figure 9 in Ref.

18). One interesting feature emerges. The analysis of the $^2T_1$ multiplet requires v' to be ~400 cm^{-1}.

This large discrepancy in the two derived values of v' may be strong evidence for trigonal anisotropy in ζ. The observed anisotropy in $g(^4A_2)$ (Table I) is large and cannot be explained by the conventional model (Eq. (17)). However, from Eq. (15) we obtain $\zeta_x k_x > \zeta_z k_z$. If $\zeta_i \sim k_i \zeta_0$, where ζ_0 is the free-ion spin-orbit coupling, then $\zeta_x > \zeta_z$ and (18) gives a positive contribution to $D(^4A_2)$. Accordingly, if one uses the conventional ligand field model, the observed $D(^4A_2)$ should be reduced by the anisotropic contribution arising from (18) and a smaller v' will emerge, thereby reducing the difference in the values of v' obtained from different multiplets.

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