

APPRAISAL OF EXPERIMENT AND THEORY IN THE SPECTRA OF COMPLEXES

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INTRODUCTION

The methods of crystal field (CF) and ligand field (LF) theories have now been quite generally applied to a study of the spectra of transition metal complexes for a little over ten years, and it seems to be a suitable time and occasion to appraise the progress made during that time. Many of the predictions made by the use of these theories have been in the nature of suggesting the assignments for very many absorption spectra and it is at least pertinent to inquire just how firmly these assignments stand in terms of spectroscopic theory as distinct from ligand and crystal field theories.

ELECTRONIC SPECTRA

If the discussion is initially restricted to electronic spectra then it is possible to sum up what sort of information has been obtained by spectroscopy in the allied field of organic polyatomic molecules¹ and then to see how far similar methods might succeed, and have succeeded in the inorganic realm. The "organic" spectroscopist may examine molecules in one of three phases

- (a) the gas phase
- (b) the solid phase (crystalline)
- (c) in solution.

Most of the detailed information obtained concerns the moments of inertia and the directions of the transition dipole moments of the molecule under study, thus enabling each electronic state to be classified according to the electronic symmetry and elastic constants of the molecule in this state. Such information is obtained from a study of the rotational fine structure of the vibrational bands making up the electronic transition and so the molecules are investigated in the gas phase. In those cases where the moments of inertia are too large for the rotational structure to be resolved or where the vapour pressure of the molecule is too small, recourse is had to the spectra of crystals², either pure crystals or else optically transparent crystals containing small amounts of the molecule to be studied. It is not possible to obtain moments of inertia from such studies but it is still possible to discover the direction of the transition dipole moments for the various transitions and so to characterize the excited states by their electronic symmetry properties.

For the most part, solutions yield little or no information unless used comparatively to determine trends³, and the same applies for spectra of

inorganic species in solution. In fact, the organic spectroscopist usually has the advantage of knowing the formula and approximate structure of his compounds whereas this information is all too often lacking in the inorganic field. This, coupled with the difficulty of working with many of the inorganic compounds in the gas phase due to lack of vapour pressure, has restricted information almost exclusively to assignments of the transition moment directions in solid complexes and in host-guest lattices.

In the case of atomic spectra⁴, all the work is gas phase, the main source of information about a particular transition being its g_J value (Landé spectroscopic splitting factor) obtained from Zeeman studies. This g value allows the J , L and S values to be assigned to the levels involved since

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

the symbols having their usual significance⁵.

Resumé of crystal field theory

The main concepts of CF and LF theories are by now very well known⁶⁻⁸ but it is necessary to draw attention to the nature of the methods usually used to make assignments of ground and excited state energy levels. The fundamental idea behind CF theory is that the one electron d orbital set is split by an octahedral field to give the well known t_{2g} and e_g pair and that the transitions can be regarded, in a one electron sense, as involving $e_g \leftrightarrow t_{2g}$ excitation (see *Figure 1*).

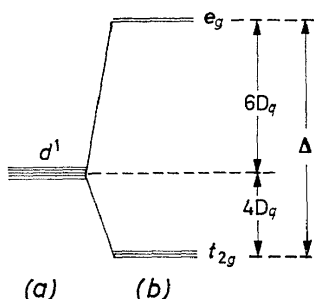


Figure 1. Diagrammatic representation of the energy levels of the electron configuration d^1
 (a) In a field-free atom or ion (fivefold degenerate)
 (b) In an ion perturbed by an octahedral field

Thus, for the configuration d^1 the excitation $e_{2g} \leftarrow t_{2g}$ gives rise to a transition ${}^2E_g \leftarrow {}^2T_{2g}$ as represented on an Orgel diagram⁸ (*Figure 2*). Ilse and Hartmann's contribution⁹ was to identify this transition with the 20,300 cm^{-1} (4900 Å) band in the complex ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. This assignment cannot be proved at an empirical level and all that can be said is that there is an absorption region 20,300 cm^{-1} . When the theory is extended to two

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electrons¹⁰⁻¹² it might appear that the predictions rest upon firmer foundations but this is not really so. In the strong field limit the theory predicts four levels¹³ arising from the possible configuration

$$\begin{aligned} t_{2g}^2 &\rightarrow {}^3T_{1g} \\ t_{2g}e_g &\rightarrow {}^3T_{1g} + {}^3T_{2g} \\ e_g^2 &\rightarrow {}^3A_{2g} \end{aligned}$$

with the first ${}^3T_{1g}$ level lying lowest. The weak field approximation using the maximum spin multiplicity terms of the free ion 3F , and 3P also gives

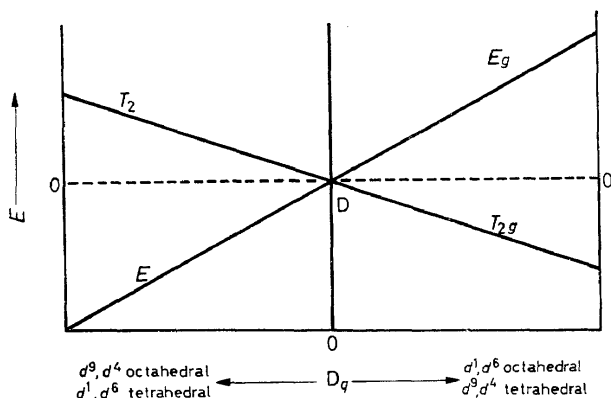


Figure 2. Orgel diagram showing the splitting of a field-free ion D term (arising from configurations d^1 , d^4 , d^6 and d^9) by a cubic perturbing field of magnitude E . The notation on the right-hand side of the diagram refers to an octahedral perturbation, and that on the left-hand side to a tetrahedral perturbing field. (The energy zero corresponds to the field-free ion ground term energy with addition of the spherically symmetrical term in the perturbation energy)

four levels¹⁰ and three transitions are predicted. However, only two bands are usually observed and if theory is used to predict the position of the bands then two parameters are required, Dq and the 3P - 3F interval pertinent to the complex, before this can be done (see Figure 3). In fact, the situation does not really become very convincing until the d^5 configurations are treated^{14, 15} e.g. Mn^{2+} .

In this case, the number of parameters to data is either 5 to 10 or 4 to 7 (see Figures 4 and 5) dependent upon whether the group of levels arising from 4F is observed or not. (These parameters are Dq , and the 4G - 6S , 4P - 4G , 4D - 4P and 4F - 4D intervals, which are not the same as for the free ion). These data, particularly when coupled with the extra data on line widths¹⁵, as well as the behaviour of the d^5 spectra of Fe^{3+} ion¹⁶, make the theoretical predictions seem good. Support is also found in a study of the effects of substitution in the octahedron upon the spectra¹⁷, although the number of bands predicted is seldom seen due to their broadness.

It is, however, comforting to the spectroscopist, and to the theoretician, to be able to show unambiguously that at least one of the assignments made

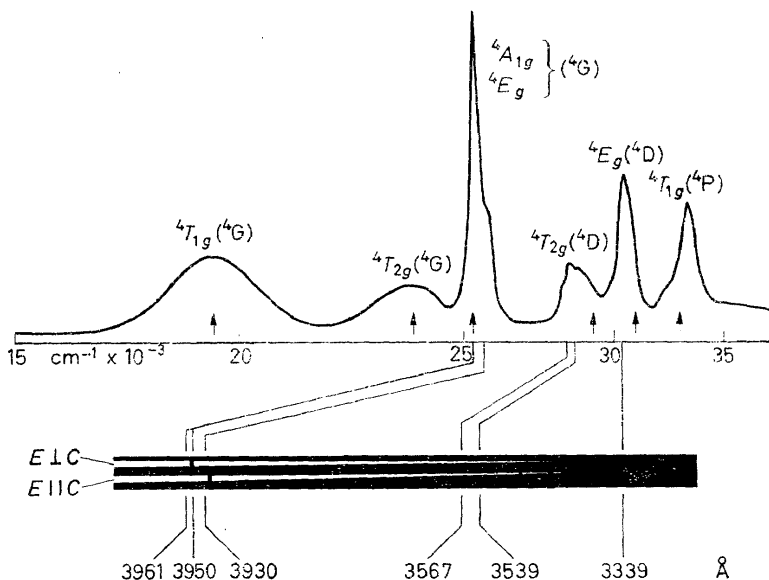


Figure 5. The absorption spectrum of MnF_2 . The upper spectrum is a low-resolution record made at room temperature. The lower spectrum was photographed at 20°K using a single crystal and polarized light. The calculated positions of the peaks are shown by the short arrows. The parameters used in the calculation are: $Dq = 740 \text{ cm}^{-1}$; and the ${}^6\text{S}-{}^4\text{G}$ separation was reduced by $1,500 \text{ cm}^{-1}$ from the value for the free ion (Reproduced by courtesy of J. W. Stout. *J. Chem. Phys.* 31, 709 (1959))

Polarized spectra

The use of this method depends upon the fact that the direction of the transition dipole moment in the molecule is different for different electronically allowed transitions (provided that the molecule is not perfectly cubic), and so may be distinguished between, and identified by, examining a crystal of the complex with plane-polarized light. It is possible to investigate such polarization properties.

- (a) in the pure crystal
- (b) in optically dilute form in host crystals
- (c) in host crystals containing impurity (guest) ions.

(a) *The pure crystal*—Many of the earliest measurements in this field were made by Tsuchida and the Japanese school, and good examples are afforded by the spectra of trisethylenediamine cobalt (III) and chromium (III) complexes¹⁸ and of the spectrum of *trans* bisethylenediamine dichloro-cobalt (III) ion¹⁹ which has also been discussed in detail by Ballhausen and Moffitt^{6,20}. Many other polarized spectra have been done²¹⁻²³ but most of the advantages of the method apply equally to the following method (b) and so the pure crystal will not be discussed in detail. Also, many of the conclusions are not completely certain due to incomplete crystal structure data.

(b) *Optically dilute form in host crystals*—Certain difficulties arise in the study of pure crystals, in particular those involving interactions of like neighbouring ions, as well as the purely experimental difficulty of getting well formed microcrystals thin enough to carry out the measurements *e.g.* if $\epsilon_{\max} \sim 100$ then the crystal needs to be only $\sim 10\text{--}50 \mu$ thick for light to penetrate it. These difficulties are overcome to a large extent by applying the methods used in studying rare earth crystals in a magnetically dilute form²⁴ by introducing a small amount of the complex into a colourless, diamagnetic host crystal of similar structure.

Piper and Carlin²⁵ have examined the spectra of the $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ ions in the host lattice²⁶ $\text{NaMg Al}(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ at 77°K . The host crystal belongs to the space group $\text{P}\bar{3}1c$ with two molecules per unit cell, but the aluminium ion itself has a site symmetry of D_3 (no centre of symmetry). Chromi- and cobaltioxalate ions are assumed to replace the aluminioxalate groups and the crystal field at each chromium (or cobalt) ion is, therefore, mainly octahedral with a small trigonal component. The selection rules for electric dipole radiation are given in *Table 1* for the point group D_3 , the

Table 1
(a) D_3 and C_{3v} character tables

D_3			E	2C_3	$2\text{C}_2'$
	C_{3v}		E	2C_3	$3\sigma_v$
z, R_z	z	A_1	1	1	1
x, y	R_x	A_2	1	1	-1
$R_x R_y$	x, y	E	2	-1	0
	$R_x R_y$				

(b) C_3 character table

C_3		E	C_3
z, R_z	A	1	1
$xy, R_x R_y$	E	2	-1

(c) Electric and magnetic dipole selection rules for D_3 point group (identical for both)

D_3	A_1	A_2	E
A_1	forb.	π	σ
A_2		forb.	σ
E			σ, π

(d) Electric dipole selection rules for $\text{C}_3, \text{C}_{3v}$ points groups

C_3		A	A	E
	C_{3v}	A_1	A_2	E
A	A_1	π	forb.	σ
A	A_2		π	σ
E	E			σ, π

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σ direction being perpendicular to the c crystal axis (which is also the trigonal axis of the molecule) and π is parallel to this axis.

Both complexes (as well as some others) were examined and their low frequency bands, with $\epsilon_{\max} \sim 100$, were found to be neither strongly σ - or π -polarized. In the chromium complex the absorption maximum is at slightly lower frequencies in the π beam than in the σ , whereas for the cobalt complex the reverse is true. The high frequency bands in each complex (which also have $\epsilon_{\max} \sim 100$) have a large polarization preference in favour of σ absorption (see *Figure 6*). The way in which the various irreducible representations of the point group O_h break up upon reduction of

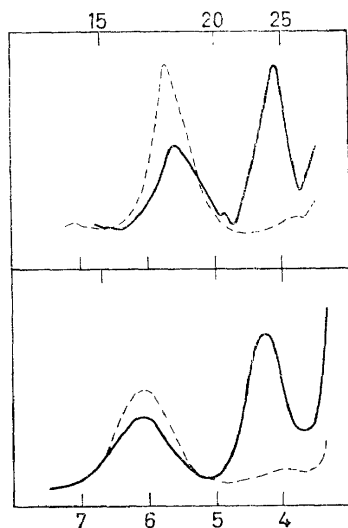


Figure 6. The upper curve is the spectrum of the chromium complex and the lower that of the cobalt complex (Reproduced by courtesy of T. S. Piper and R. L. Carlin. *J. Chem. Phys.* 35, 1809 (1961))

the symmetry is given in *Table 2* and it will be observed that for the point group D_3 , $T_{1g} \rightarrow E + A_2$ and $T_{2g} \rightarrow E + A_1$.

If the ground term for Cr^{3+} is assumed for the moment to be 4A_2 (and this can be confirmed by e.s.r. and magnetic anisotropy experiments; see below)

Table 2

$C_3 - A_1(z)$	$A_1(z)$	$E(xy)$	E, A	E, A
↑	↑	↑	↑	↑
$C_{3v} - A_1(z)$	A_2	$E(xy)$	E, A_2	E, A_1
↑	↑	↑	↑	↑
$O_h - A_{1g}$	A_{2g}	E_g	T_{1g}	T_{2g}
↓	↓	↓	↓	↓
$T_d - A_1$	A_2	E	T_1	$T_2(xy_2)$
↓	↓	↓	↓	↓
$D_3 - A_1$	$A_2(z)$	$E(xy)$	$E, A_2(z)$	E, A_1

then the experimental results are explicable only if the 4A_1 level lies lower than the E_a in the low frequency band, while in the high frequency band,

the high polarization ratio in favour of the σ beam indicates only an $E_b \leftarrow A_2$ transition, its partner transition $A_2 \leftarrow A_2$ being forbidden. Exactly the same type of data are obtained for the cobalt complex except that in this case the ground term is 1A_1 , the low frequency band is split into an E_a and A_2 , the E_a lying slightly lower, while the high frequency band splits to give an E_b and A_1 , transitions to the latter being once again forbidden (see *Figure 1*).

Both these results confirm the assignment of the lowest frequency band of an octahedral Cr^{3+} complex as ${}^4T_{2g} \leftarrow {}^4A_{2g}$ with ${}^4T_{1g} \leftarrow {}^4A_{2g}$ for the higher frequency band. The cobalt results are identical, except that the spin multiplicity and subscript 1's and 2's are interchanged, and confirm the CF and LF predictions completely. Similar experiments²⁷ have been carried out with $[\text{Co}(\text{acc})_3]^{3-}$ and the results are also in complete accord with the conclusions set out above.

(c) *Host crystals containing impurity (guest) ions*—Instead of using metal complexes it is possible to use transparent crystal lattices as a matrix and to add "impurity" transition metal ions and observe the polarized spectra of these. Some of the common lattices used are given in *Table 3*, together with

Table 3

Host lattice	Formula	Site symmetry	
		Octahedral	Tetrahedral
Corundum	Al_2O_3	+	
Magnesium oxide	MgO	+	
Rutile	TiO_2	+	
	ZnF_2	+	
Perovskite	BaTiO_3	+	
	LaAlO_3	+	
*Yttrium-gallium garnet (Y.G.G.)	$\text{Y}_3\text{Ga}_2\text{Ga}_3\text{O}_{12}$	+	+
Aluminium spinel	MgAl_2O_4	+	+
Zinc blende	ZnO		+
Wurzite	ZnO		+
Cadmium sulphide	CdS		+

* Dodecahedral sites also occur in Y.G.G.

the predominant symmetry of the sites which the impurity ions may occupy. Many of the crystal matrices have smaller, less symmetric, components of the crystal field and these are very valuable in an interpretation of the spectra. (Polarization measurements cannot be made on cubic crystals).

One such typical material is corundum with Cr^{3+} as an impurity (artificial ruby). McClure,^{2, 28} and others,^{29, 30} have investigated the spectra obtained, from room temperature down to 4°K. The aluminium ions in corundum³¹ lie in a site of almost octahedral symmetry in which the oxygen octahedra are slightly stretched along the 111 (c) axis, *i.e.* a trigonal distortion. In addition, one "triangle" of oxygens is slightly larger than the other and closer to the aluminium ion, the two being rotated by 2° 8·5' away from the σ_v planes of the C_{3v} point group (see *Figure 7*). The site symmetry is therefore C_3 , although it is not far from C_{3v} and it might be expected that the C_{3v} selection rules (*Table 1*) would almost apply.

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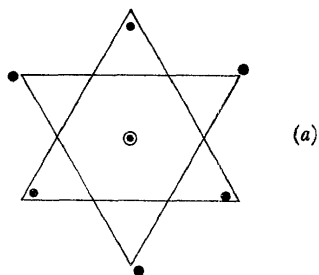


Figure 7. (a) Corundum "octahedron" viewed along C_3 axis showing difference in size of oxygen triangles and rotation of one triangle with respect to the other

(b) Corundum lattice showing displacement of aluminium ion along the three fold axis (Reproduced by courtesy of D. S. McClure. *J. Chem. Phys.* **36**, 2757 (1962))

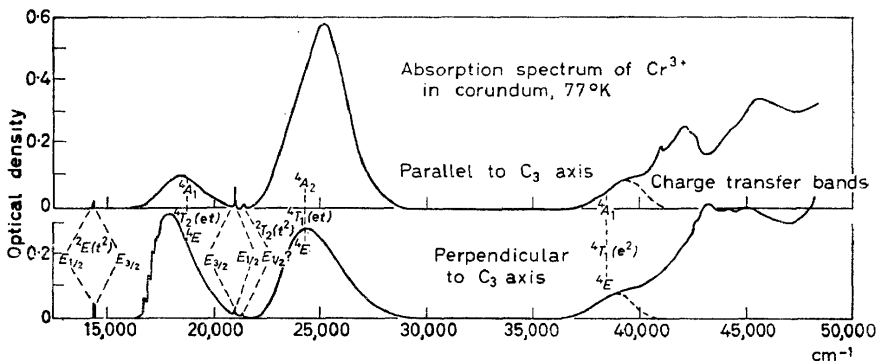
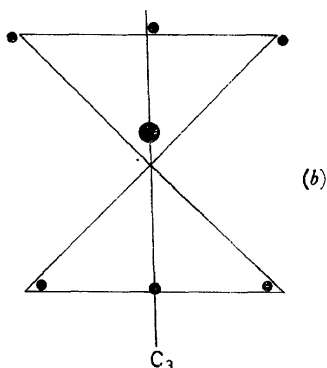


Figure 8. Polarized absorption spectrum of Cr^{3+} in corundum (Al_2O_3) at $77^\circ K$. Both the cubic field and trigonal field designations of the upper levels are given. The ground state for all transitions is ${}^4A_2(g)$. The configuration designation is given incorrectly for each excited state; for the correct description add one t electron to each configuration shown in the figure. To convert optical density, ρ , to molar extinction coefficient, ϵ (where $\epsilon = \rho/cd$, c = conc. of Cr^{3+} in moles/l., d = thickness of sample in cm) multiply ρ by 150. The "charge transfer bands" are so-called because the crystal field states are all assigned (Reproduced by courtesy of D. S. McClure. *J. Chem. Phys.* **36**, 2757 (1962))

The spectra are taken with polarized light, one beam of which has its electric vector along the c axis (π) and the other its electric vector perpendicular to this axis (σ). The spectrum obtained is shown in *Figure 8* and certain differences are immediately apparent comparing it with the chromioxalate spectrum (*Figure 6*). The first of these is that the lowest frequency component of the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ octahedral spectrum is now in the ${}^4E \leftarrow {}^4A_2$ component indicating a trigonal field of opposite sign to that obtained in the oxalate. McClure has shown²⁸ that the sign of the field constant (K) is consistent with its dependence upon the O_3 -Cr- O_3 angle, a negative value ($\sim 500 \text{ cm}^{-1}$) being obtained for an angle $> 90^\circ$ while a positive value is obtained for chromioxalate where the angle is known²⁵ to be $< 90^\circ$. (This is also confirmed by a spectrum in rutile³² where the angle is also $< 90^\circ$). The obvious difference in the polarization ratios compared with the chromioxalate bands is mainly due to the changed site symmetry of the Cr^{3+} ion, the relative intensity of the high and low frequency σ components being caused by a tendency to follow C_{3v} selection rules, as reference to the differences between C_3 and C_{3v} show (*Table 1*).

From the assignment point of view, however, it is clear that the low frequency transition consists of a strong ${}^4E \leftarrow {}^4A_2$ component and a relatively weak ${}^4A_1 \leftarrow {}^4A_2$ component, which would be completely forbidden in C_{3v} selection rules but is allowed (π) in C_3 . The octahedral parentage is, therefore, clearly ${}^4T_{2g} \leftarrow {}^4A_{2g}$, as is predicted by theory. The prediction of ${}^4T_{1g} \leftarrow {}^4A_{2g}$ is also borne out by a similar analysis of the high frequency band.

A large number of such doped lattices have now been thoroughly examined by many workers³⁴⁻³⁸ and while it could not be said that everything has been explained, nevertheless it appears that the *electronic symmetries* predicted by crystal field theory and found by experiment do in fact coincide completely in those cases which have been carefully examined. Reference 31 should be consulted for a concise summary of the results.

Rotatory dispersion and circular dichroism measurements

A second, and what promises to be a most important, approach to the question of level identification has recently been emphasized by Mason^{39, 40}. This is the method of optical rotatory dispersion and circular dichroism. The principles involved have been set out clearly by Condon,⁴¹ Moffitt,⁴² Liehr,⁴³ Mason³⁹ and others⁴⁴ and will be only briefly mentioned here. Circular dichroism of an optically active compound refers to the fact that such a compound differentially absorbs left- and right-handed circularly polarized light (whence different refractive indices) in one or other of its absorption bands thus giving rise to the allied dispersion phenomenon of the rotation of plane polarized light through an angle⁴³. The actual rotational strength of a transition is given by⁴¹ the scalar product of the electric (ρ) and magnetic (μ) moments, whereas the electric dipole strength of a transition is equated to the square of its electric dipole transition moment.

The ratio of these strengths is expressed in terms of a coefficient g , (not to be confused with the spectroscopic splitting factor) termed the dissymmetry factor by Kuhn⁴⁵. If ϵ_1 , ϵ_T and ϵ are the molar extinction coefficients for

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left- and right-hand circularly polarized light and for unpolarized light respectively, then^{41, 45}

$$g = \frac{(|\epsilon_1 - \epsilon_r|)}{\epsilon} \approx \frac{4\rho\mu \cos \theta}{\rho^2}$$

where θ is the angle between the directions of the electric and magnetic transition moments. Mason argued³⁹ that for fully allowed electric and magnetic dipole transitions, g will take values <0.01 and >0.01 , respectively, and he proposes this as a criterion of transitions being magnetic dipole allowed or not. It is clear that the highest g values require $\theta \sim 0$, *i.e.* that the electric and magnetic moments should be parallel. It is also clear that both μ and ρ must be non zero so that some electric dipole strength is required. These conditions are well met in the case of the optically active molecules belonging to the dihedral point groups D_2 ,⁴⁴ of which D_3 is a member, and includes complexes of the trisethylenediamine, trisoxalato and tristartrato metal complexes of chromium and cobalt.

Just as the symmetry properties of an electric dipole depend upon charge translation along a line and transform according to the irreducible representation T_{1u} of the point group O_h so the formation of a magnetic dipole moment depends upon charge rotation and the magnetic dipole therefore transforms like T_{1g} of the O_h point group⁴⁴. It is easy to show in complexes possessing either a centre of symmetry or reflection planes that if one type of moment is allowed then the other must vanish, *i.e.* it is only in those complexes which have neither symmetry element that circular dichroism is to be found.

It is a result of crystal field theory that all of the lowest energy spin allowed $d-d$ transition are magnetic dipole allowed (but electric dipole forbidden for perfectly octahedral fields) whilst most of the higher frequency transitions are both magnetic and electric dipole forbidden. In complexes of the trisethylenediamine type the centre of symmetry has been removed and transitions may become electric dipole allowed whilst retaining their magnetic character. According to crystal field predictions the lowest frequency transitions in octahedral $Cr(III)$ and low spin $Co(III)$ complexes are ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^1T_{1g} \leftarrow {}^1A_{1g}$ respectively, and are magnetic dipole allowed (since $\Gamma_{(A_{2g})x} \Gamma_{(T_{2g})} \supset \Gamma_{(T_{1g})}$ and $\Gamma_{(A_{1g})x} \Gamma_{(T_{1g})} \supset \Gamma_{(T_{1g})}$) whilst the higher frequency transitions are ${}^4T_{1g} \leftarrow {}^4A_{2g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ respectively and are magnetic dipole forbidden. ($\Gamma_{(A_{2g})x} \Gamma_{(T_{1g})} \supset \Gamma_{(T_{2g})}$ *etc.*).

Treating these low frequency transitions as though the actual energy splitting on going from O_h to D_3 is small the results are shown in *Table 4*. A more complete analysis for the chromium complexes taking the splitting into account⁴⁰ shows that the T state splits into A and E states

$$\begin{aligned} T_{2g} &\rightarrow A_1 + E_a \\ T_{1g} &\rightarrow A_2 + E_b \end{aligned}$$

with the transformation properties given in *Table 1*. Thus the ${}^4E \leftarrow {}^4A_2$ transitions are both electric and magnetic dipole allowed as also is the ${}^4A_1 \leftarrow {}^4A_2$, whilst ${}^4A_2 \leftarrow {}^4A_2$ is both magnetic and electric dipole forbidden.

Figure 9 shows the spectrum for unpolarized light, the circular dichroism spectrum and the rotatory dispersion curve of potassium chromium tartrate

in aqueous solution, and it can be seen that the onset of the dichroism curve shows a negative value of $\epsilon_l - \epsilon_r$ changing to positive and becoming negative again. This has been interpreted⁴⁰ as favouring the ${}^4A_1 \leftarrow {}^4A_2$ component lowest in energy followed by the more intense ${}^4E_g \leftarrow {}^4A_2$ with the ${}^4E_g \leftarrow {}^4A_2$

Table 4

Species	Absorption		Circular dichroism		g	Transition for O_h
	ν_{\max}	ϵ_{\max}	ν_{\max}	$\epsilon_l - \epsilon_r$		
Chromioxalate	17,400	90	18,000	2.88	0.045	${}^4T_{2g} \leftarrow {}^4A_{2g}$
	24,100	110	24,100	-1.00	0.009	${}^4T_{1g} \leftarrow {}^4A_{2g}$
Cobaltioxalate	16,400	143	16,200	1.80	0.043	${}^1T_{1g} \leftarrow {}^1A_{1g}$
	23,900	210	25,000	-0.20	0.001	${}^1T_{2g} \leftarrow {}^1A_{1g}$

higher still, the ${}^4A_2 \leftarrow {}^4A_2$ being forbidden and not being observed. Further, the small peak in the onset of the curve coincide with the position of a band which is usually assigned as 2E or ${}^2T_1 \leftarrow {}^4A_2$ and the sign of the dichroism possibly favours the assignment ${}^2E \leftarrow {}^2A_2$. For further details the original papers should be consulted^{39, 40}.

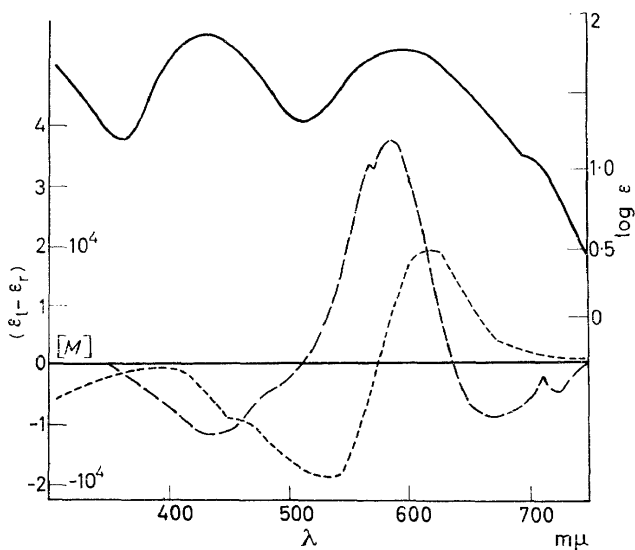


Figure 9. Spectra of chromium tritartrate complex
 —: ordinary absorption spectrum (unpolarized)
 - - - - -: circular dichroism spectrum
: optical rotatory dispersion curve

The evidence is, therefore, clear that the order of the T_{2g} and T_{1g} levels is as predicted by even relatively crude crystal field theory. It is interesting to note that the application of the above ideas also confirms the assignments made^{46, 47} for the spectrum of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and for Ni^{2+} ions in a magnesium

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oxide lattice^{35, 36}. It has been known for many years that $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystallizes in an optically active form (α)⁴⁸⁻⁵⁰ and the optical rotatory dispersion and circular dichroism spectra have been determined⁵¹ (see Figure 10). As the figure shows there is a maximum in the circular dichroism curve at $\sim 116\mu$, *i.e.* $8,600\text{ cm}^{-1}$ with a further small inflection at $\sim 0.7\mu$ or $\sim 14,300\text{ cm}^{-1}$. Various solution spectra^{46, 47} and the spectrum of Ni^{2+} in MgO done by Low³⁵ show a relatively strong band in the infra-red at $8,600\text{ cm}^{-1}$ and the transition is predicted to be ${}^3T_{2g} \leftarrow {}^3A_{2g}$ which is magnetic dipole allowed. This assignment is thus clearly confirmed and the second inflection is probably to be associated with the ${}^1E_g \leftarrow {}^3A_{2g}$ transition which

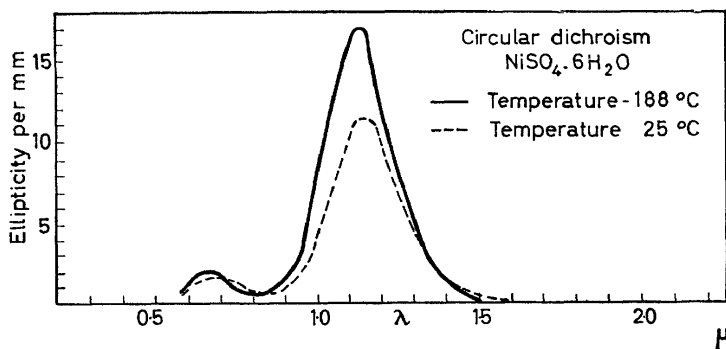


Figure 10. Effect of low temperature on circular dichroism in nickel sulphate

has "stolen" T_{2g} character from the level at $8,600\text{ cm}^{-1}$. Many similar investigations⁵²⁻⁵⁴ are to be found in the literature and may now be interpreted according to the ideas outlined above.

Electron spin resonance, the Zeeman effect and magnetic data

E.s.r. will not be discussed in detail but is nonetheless very important because it is necessary to know the ground state electronic symmetry unambiguously before conclusions can be drawn regarding excited state symmetries, since the spectrum involves them both equally. Much work has been done in these fields⁵⁵⁻⁵⁷ and it is necessary to select only one example—that of the Cr^{3+} ion in an octahedral field³⁴. The assignments rest upon three types of data,

- (a) the bulk magnetic moment
- (b) the magnitude of g (the spectroscopic splitting factor)
- (c) magnetic anisotropy (as determined from the g values in different crystallographic directions).

The results of (a) are so well known as to require almost no comment except to draw attention to the refinements which have been made by inclusion of the effects of spin-orbit coupling and asymmetric ligand fields which mix higher levels with the ground state, together with the utilization of magnetic susceptibilities obtained over a temperature range⁵⁸⁻⁶¹.

The resonance condition of e.s.r. is given by⁵⁵

$$h\nu = \beta gH$$

whence

$$g = \frac{h\nu}{\beta H} \equiv \frac{21.4178}{H\lambda}$$

(λ being the wavelength in cm and H is in kilogauss) *i.e.* g is directly determinable from experiment.

g is not necessarily isotropic since in the general case it varies with the orientation of H with respect to the crystal axes. For orbitally non-degenerate levels, however, g should be isotropic except for small, but important, effects due to higher order interactions with excited degenerate levels. The Cr^{3+} has been investigated under conditions of almost exact cubic symmetry, *viz.* in MgO solution, by Low³⁴, and only a single resonance line is observed if the nuclear hyperfine structure of Cr^{53} is ignored. This suggests that the ion is in an orbitally non-degenerate state and that the site symmetry is rigorously octahedral. The value of g (1.9800 ± 0.0006) implies a small orbital contribution from an upper degenerate level but the isotropic behaviour of g , together with the resonance line "pattern" observed, fits the predicted ${}^4A_{2g}$ ground state symmetry almost exactly.

Information has recently been obtained⁶⁶ by application of the Zeeman effect to some of the optical transitions, although so far only guest ion in host lattices have been examined (ignoring rare earth spectra). There is nothing different in principle between e.s.r. and the Zeeman effect, (except that the former is applicable only to ground states and some metastable excited states) but its applications are severely limited by the breadth of the majority of transition metal complex spectra. The exceptions are some of the spin forbidden bands such, as the R_1 , R_2 fluorescence lines in ruby³⁰, and in the MgO lattice^{30, 34} where it has proved⁶²⁻⁶⁶ possible to assign the transition as ${}^2E \leftarrow {}^4A_{2g}$ rather than the ${}^2T_{1g} \leftarrow {}^4A_{2g}$ which is predicted^{13, 67} to lie in almost the same region. Assignments have frequently been made^{2, 68} in the rare earth spectra by use of the Zeeman effect but as yet its use is limited in the transition metal series.

From the above discussion it can be seen that not only have the assignments made on the basis of CF theory been confirmed by a single experimental technique, but that methods as difference as direct absorption spectroscopy and circular dichroism agree with each other and with theory regarding these assignments.

ENERGY CALCULATIONS

One other aspect of theory which is capable of rigorous testing is the calculation of the transition energies of the various crystal field bands. Calculations based upon a full molecular orbital basis have, apart from one recent example⁶⁹, so far been disappointing in predicting the order of levels⁷⁰, let alone exact energies, and the only calculations discussed here are essentially crystal field ones using refined parameters.

The calculations fall into two main classes according to whether spin-orbit coupling is included^{67, 71-74} or not⁹⁻¹². In addition, the calculations

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are sometimes made using "strong field" formalism and sometimes "weak field". In the strong field limit the parameters which arise are Δ , the $t_{2g}-e_g$ one electron interval, and B and C the Racah interelectronic repulsion parameters (or the F_k of Slater-Condon theory); while in weak field theory the parameters are Δ and the energy intervals between the free-atom terms arising from the configurations d^n (which may, of course, be expressed in terms of B and C). It is also possible to add further complexities by subdividing the individual free atom Racah parameters into their cubic field analogues^{67, 75}, since the radial wave functions are different in the t_{2g} and e_g sets and so have different electron repulsion parameters. By this further subclassification the number of parameters is increased considerably, e.g., it becomes thirteen in the case of the d^3 configuration⁶⁷ and it has not so far been possible to rigorously test the complete consequences of such a refinement.

The most complete calculations including spin-orbit coupling have been done by Ballhausen and Liehr for the d^3 , d^8 octahedral and tetrahedral cases⁶⁹, by Runciman and Schroeder⁷⁴ and Eisenstein⁶⁷ for d^3 , d^7 , by Liehr⁷² for d^1 , d^9 and by Clogston⁷⁶ for d^5 while the results have been tested most carefully by Low³⁴ and by the Bell Telephone group at Murray Hill³⁶⁻³⁸. The results confirm the essential quantitative accuracy of the simple theory (without spin-orbit coupling) but the amount of fine structure observed at low temperatures is excessive for simple interpretation (see *Figure 11*) and certainly involves considerable interaction of the ion with the surrounding lattice. In some spectra³⁶ there is agreement with the number of levels to be expected but the quantitative aspect is not as reassuring, due in part, it appears, to the sensitivity of the calculations on the second order contributions of spin-orbit coupling. Further analysis will probably depend upon the interpretation of high pressure data and upon Zeeman experiments before unambiguous assignments can be obtained.

The position is a little better in the third transition series where thirteen band systems in the spectra of ReF_6 , OsF_6 , IF_6 and PtF_6 have been assigned⁷⁷ using only two energy parameters (ζ_{5d} and an interelectronic repulsion parameter G). These assignments appear reasonable on statistical grounds but have not as yet been verified by other means. The only authentic examples of spin-orbit structure being positively spectroscopically identified are in the rare earths where Zeeman experiments are possible^{2, 68} and where it has been possible to calculate the energies of the levels to extremely high accuracy⁷⁸⁻⁸⁰ and to confirm the calculations experimentally^{24, 80}.

Thus, for the transition metal spectra at the present time, it appears possible to fit the experimentally observed energy level scheme theoretically to within a few percent but it is not possible to either predict the magnitude of the "best fit" parameters required or to analyse the finer structure on the basis of spin-orbit effects. (The R_1R_2 lines of ruby being a possible exception^{62, 64, 65}). The parameters used to fit the data are not, in general, the same as found for field-free ions; e.g. both the B and ζ values appear to be reduced considerably by complex formation, while the magnitude of the ratios γ ($\gamma = c/B$) also appears to change in an unpredictable manner. The interpretation of the reasons for the decreased values has resulted in a great deal of information of interest to the chemist, particularly with regard to the

nature of the metal-ligand bond^{81, 82}, but the conclusions are not, on the whole, verifiable by spectroscopic means so will not be discussed here. They are, however, adequately discussed in two recent monographs^{83, 84}.

SOURCE OF THE INTENSITY

Absorption or emission spectra can theoretically be of three main types

- (i) electric dipole ($f \sim 1 - 10^{-1}$)
- (ii) magnetic dipole ($f \sim 10^{-6}$)
- (iii) electric quadrupole ($f \sim 10^{-8}$)

and the intensities which are expected for such spectra are placed in brackets after them. Since CF spectra involve $d \longleftrightarrow d$ transitions then they should not be of type (i) since such transitions are formally forbidden by the Laporte rule ($g, u \leftrightarrow g, u$; $g \leftrightarrow u$ for electric dipole radiation). However, it has been pointed out⁸⁵ that non-totally symmetric vibrations of static asymmetric electric fields can remove the centre of symmetry and make these transitions "slightly" allowed for electric dipole radiation, the f values observed for CF bands ($f \sim 10^{-4}$; $\epsilon_{\max} \sim 10-10^2$) seeming too large to be other than electric dipole in character.

That this is so has been demonstrated and discussed^{47, 86-88} but the species of the actual vibration(s) causing the electronically forbidden transition to become allowed, has not yet been demonstrated in detail (experimentally) for any transition metal complex. The main difficulties are that most of the spectra are broad and diffuse and also that it is not possible to observe fluorescence (phosphorescence) from most of the excited states to the ground state.

The predominant mechanism in the rare earths is the removal of the centre of symmetry by static asymmetric crystal fields together with some contribution from magnetic dipole and electric quadrupole sources^{2, 89}. This is shown clearly by the fact that the emission and absorption frequencies coincide within experimental error⁸⁰ so that vibrations cannot be active in making the transition allowed. The predominance of the electric dipole contribution is proven from experiments on uniaxial crystals⁹⁰ where the spectrum taken along the axis is almost identical with that taken with the direction of propagation and the electric vector of a polarized beam of light both at right angles (σ) to the optic axis. This technique has been applied both by McClure²⁸ and by Piper and Carlin²⁵ to the transition metal CF spectra and the results show that the bulk of the intensity is indeed electric dipole in origin. Both McClure²⁸ and Englman⁹¹ have considered the intensity variation with temperature and have concluded that the "odd" vibration mechanism accounts for the observed rapid decrease with decreasing temperature^{28, 47, 91}, the anharmonicity contribution being large⁹¹. As discussed above, however, there is at least a small magnetic dipole contribution to the lowest frequency spin-allowed CF band, and it has been shown by Sugano, Schawlow and Varsanyi⁶⁶ that the weak spin-forbidden band at $14,319 \text{ cm}^{-1}$ in the spectrum of Cr^{3+} in a magnesium oxide lattice is entirely magnetic dipole in character. This was at least highly likely since, in this cubic lattice with lattice sites rigorously

octahedral, it is known that the fluorescence and absorption frequencies are identical within experimental error and that the intensity of absorption is much lower than in the corundum lattice (where there is no centre of symmetry).

It also appears likely that some electric quadrupole contribution is also present in the CF spectra of transition metal ions but it will be difficult to detect since it will be masked by other, possibly stronger, effects such as the presence of "stolen intensity" caused by vibrational interaction²⁸. There are, however, certain cases where a decision may be possible.³⁹

THE JAHN-TELLER EFFECT

The Jahn-Teller theorem is by now familiar to most chemists even if its manifestations are neither numerous nor obvious. The theorem, based as it was originally⁹² upon group theoretical arguments, states quite unambiguously that electronically degenerate states of non-linear polyatomic molecules always confer instability on the symmetrical nuclear configuration (upon which the electronic degeneracy depends) so that the molecule must always "distort" from high symmetry in attaining equilibrium. The effect was recognized at a relatively early stage⁹³ as being divisible into two main parts—the static and the dynamic. This separation can be thought of as arising because the energy difference between the two components of the previously degenerate electronic state may either be large compared with the zero point energy of the vibration which brings about the splitting, or it may be of the same order. In the former case it is possible to describe the electronic and vibrational wavefunctions almost in the usual way and the molecule merely suffers a "static" distortion from its previous symmetry, whereas in the latter the nuclei are not "bound" to one electronic hypersurface and so the description is much more complex⁹⁴⁻⁹⁶, involving as it does interaction between "vibrational" and "electronic" wavefunctions.

CF and LF theories frequently predict electronically degenerate states and so it is interesting to see whether any phenomena occur which can be traced to Jahn-Teller origins and hence to the predicted degeneracies. In general, exactly the same spectroscopic techniques can be used as are necessary to clarify the questions of assignments, *i.e.*

- (i) e.s.r. (and magnetic susceptibility)
- (ii) infra-red, Raman and microwave spectra
- (iii) optical spectra.

Since some excellent summaries of this topic have recently appeared⁹⁷⁻⁹⁹ it will not be necessary to deal with the evidence in detail but simply to relate the results.

E.s.r. (and magnetic susceptibility)

In octahedral complexes the e_g vibration, which is one of the Jahn-Teller "active" species, clearly has three possible equivalent absolute structures depending upon which of the three *trans* pairs of ligands are stretched or contracted while the other four are contracted or stretched respectively.

The resulting energy surface of an electronically degenerate state will have three minima and three saddle points and, if the latter are not too high, the nuclei in thermally occupied vibrational levels are able to either tunnel through or pass over the barriers. Thus, the e.s.r. spectrum will yield an isotropic g value at high temperatures and this will become anisotropic at low temperatures when interconversion becomes impossible.

Such effects have indeed been observed, in octahedral copper (II) complexes^{100, 101} and in Pt(II) and Ni(II) complexes¹⁰² in the corundum lattice. Such phenomena do not occur with electronically non-degenerate ions in the same lattices and the evidence must be looked upon as at least permissive if not quite compulsive.

Infra-red, Raman and microwave spectra

The theoretical expectations are nowhere as well documented as in the infra-red Raman and microwave spectra⁹⁷⁻¹⁰³. Briefly, these expectations are¹⁰³

(a) if a tetrahedral molecule is in an E state all its vibrations are Raman active;

(b) if an octahedral molecule is in an E_g or E_u state, all its g vibrations are Raman active;

(c) a tetrahedral molecule in a T_1 or T_2 state should have an apparent dipole moment and exhibit a pure rotation microwave spectrum.

(a) The infra-red and Raman spectra of VCl_4 have been reported recently^{104, 105} and comparison with the $TiCl_4$ results¹⁰⁴ does not clarify the issue, since all the fundamentals of $TiCl_4$ appear in the Raman spectrum, while in VCl_4 only three are seen, one being broad and possibly double. This does not appear to be an example where the intensity has flowed into the overtones¹⁰³, since the assignment of the other bands seen are supported by infra-red studies.

(b) No example is known to the author where a complete analysis as is required, has been carried out.

(c) The microwave spectrum has not yet been reported for VCl_4 or any other suitable molecule.

The second line of approach has been that of Claassen and Weinstock¹⁰⁶⁻¹⁰⁸ who have attempted to interpret the Raman intensities found for the e_g vibration (σ_2) in octahedral hexafluorides—this being the most probable Jahn-Teller active vibration. Confirmation is as yet lacking but the method seems promising. Caution must be exercised, however, as there are very many possible causes for splittings, decreases or increases in intensity or other "anomalous" occurrences in infra-red and Raman spectra¹⁰⁹ and these should be borne in mind when considering such phenomena.

(iii) If the Jahn-Teller effect is large then it is clear that there must be a progression of some non-totally symmetric vibration. It now seems clear that such progressions have been observed in host-guest ion lattices in the cases V^{3+}/Al_2O_3 ^{28, 110} and Cr^{3+}/Al_2O_3 ^{28, 111} (as well as in a few organic examples). These spectra are particularly impressive in that the "hot" bands are seen weakly $\sim 200\text{ cm}^{-1}$ to low frequencies, of the first temperature-independent band. This is good evidence that the upper state progression of 194 cm^{-1} seen is, in fact, the e_u vibration of the corundum lattice

(e in C_3), and that the first sharp band seen is the 0, 0. The intensity maximum occurs in the 8th or 9th quantum for vanadium and in the 7th for the chromium compound²⁸ yielding a rough value for the oxygen displacement of $0.3-0.4 \text{ \AA}^{28}$. This seems too large, however, and many have to be modified in the light of more refined work.

There would thus seem to be many cases where it is convenient to invoke the Jahn-Teller effect to explain apparently anomalous spectra and it is possible to see its insidious influence behind every unusual spectroscopic feature. It is probably not a phenomenon which will be proven or disproven on the basis of a single experiment but rather it will most likely depend upon a large number of experimental findings allied to rigorous theoretical prediction or correlation. The evidence at the present time seems to be in favour of relatively small magnitudes for its manifestations rather than the very large values expected in the early days of its investigation.

STEREOCHEMISTRY

CF and LF theories purported to say much about stereochemistry of the transition metal complexes. However, it is as well to bear in mind that predictions about stereochemistry are likely to fail, since it is clear that relatively small energetic differences may lead to completely different stereochemistry. The rôle of CF and LF theories in predicting stability and stereochemistry is not a particularly happy one and can perhaps be best illustrated by reference to the tetrahalogeno metalates—cobalt and nickel.

Originally it was thought that $[\text{NiCl}_4]^{2-}$ would be unstable because of its small CF stabilization energy *vis-à-vis* the octahedral complex and, even if it could be made, it was expected to be strongly distorted by the Jahn-Teller mechanism, its ground electronic state being ${}^3T_{1g}$. It has recently been demonstrated by X-ray crystallography¹¹², that the NiCl_4 nucleus is a perfect tetrahedron, within experimental error, and this has been explained by pointing out⁷² that the effect of spin-orbit coupling is to place a non-degenerate spin-orbit component Γ_5 lowest and so become Jahn-Teller resistant. By itself this seems a reasonable explanation until it is realized that the same argument applies to $[\text{CuCl}_4]^{2-}$ which is distorted from a tetrahedron despite a Γ_7 ground state⁷², and that $[\text{CoCl}_4]^{2-}$ which has a Γ_8 level lowest, and so should be Jahn-Teller inactive under almost any circumstances, is itself just as distorted as $[\text{CuCl}_4]^{2-}$, the angles being about 106 and 118° for both of them (flattened tetragonally). The argument becomes even more tenuous when it is realized that the vibration responsible for converting a tetrahedron into a square planar form (e) is not Jahn-Teller active, so that such distortions cannot be attributed to Jahn-Teller sources.

This in itself should perhaps suggest caution with regard to similar stereochemical arguments based upon CF and LF theories allied to the Jahn-Teller theorem.

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**“APPRAISAL OF EXPERIMENT AND THEORY IN THE
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by

T. M. Dunn

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ERRATA

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Figure 6: both dotted curves should be labelled σ and solid curves π .

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For “ $\Gamma_{(A_{2g})x} \Gamma_{(T_{2g})} \supset \Gamma_{(T_{1g})}$ ” and “ $\Gamma_{(A_{1g})x} \Gamma_{(T_{1g})} \supset \Gamma_{(T_{1g})}$ ” on line 14 from the bottom and for “ $\Gamma_{(A_{2g})x} \Gamma_{(T_{1g})} \supset \Gamma_{(T_{2g})}$ ” on line 12 from the bottom read “ $\Gamma_{(A_{2g})} \times \Gamma_{(T_{2g})}$ ” *etc.*

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Reference 101: for “Blearey” read “Bleaney”.