Coordination Chemistry Amsterdam
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

ELECTRONIC SPECTRA OF QUADRATE CHROMIUM(III) COMPLEXES

JAYARAMA R. PERUMAREDDI*

Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pa. 15231 (U.S.A.) and Department of Chemistry, Florida Atlantic University, Boca Raton, Fla. 33432 (U.S.A.)

(Received July 5th, 1968)

CONTENTS

ABBREVIATIONS

en = ethylenediamine
phen = *o*-phenanthroline
dipy = dipyridyl
ox = oxalate
das = *o*-phenylenebisdimethylarsine
ζ = spin orbit coupling coefficient

tetren = tetraethylenepentamine
trien = triethylenetetramine
pn = propylenediamine
ibn = isobutylenediamine
DMSO = dimethylsulfoxide

A. INTRODUCTION

Our understanding of the electronic structures of transition metal compounds has rapidly gained momentum in the past decade and a half with the advent of ligand field theory. Various physicochemical observations such as the stereochemistry, magnetism, and spectroscopic behavior of a variety of systems have been satisfactorily interpreted by recent bonding theories[1–5]. This has been particularly true in the case of compounds of cubic symmetry. Even in systems of non-cubic symmetry, some successful interpretations of electronic spectra have been reported[6–35]. In order to make further progress on these non-cubic compounds not only do the theories have to be systematically extended but more precise and exact experimental spectroscopic measurements have to be made. These experimental studies have to be carried out with the aims of locating the exact band positions, of achieving better resolution of the band components, and of uncovering bands

---

[*] Present address Department of Chemistry, Florida Atlantic University, Boca Raton, Florida 33432 (U.S.A.).

Coordin. Chem. Rev., 4 (1969) 73–105

of low intensity. Until recently most of the spectroscopic data available on the known non-cubic transition metal compounds have been obtained only in connection with synthetic, kinetic, and photolytic studies and not with the sole aim of making intensive spectroscopic investigations. As a result, much needs to be done in the area of visible and ultraviolet electronic spectroscopy of transition metal compounds.

In this report we will limit our survey and discussion to complexes of chromium(III) belonging mainly to quadrate symmetry. The aim of this review is to summarize briefly the theory of cubic and non-cubic ligand fields with special emphasis on the effect of quadrate fields on d^3 configuration, to survey all the available spectroscopic data, the band positions and the intensities of all the known mono and disubstituted octahedral complexes of chromium(III), and to attempt to systematize and interpret the data as much as possible by the theory developed. The result of such a survey should bring into focus appropriate systems for further studies and provide guidelines to extending both experimental and theoretical investigations on non-cubic compounds of transition metals in general.

B. THEORY

The theory of cubic compounds is well-known. Figure 1 shows the Tanabe–Sugano energy plot for the d^3 configuration in octahedral fields. This energy diagram is plotted somewhat differently in the sense[36] that the ordinate is the absolute energy with the ground state being zero, varied as a function of Dq from 0 to 4000 cm^{-1}. The B and C values are chosen to be suitable to the hexaaquo-chromium(III) complex cation *i.e.*, $B = 700\ cm^{-1}$ and $C/B = 4$. The optical spectrum of the hexaaquo ion fits very well at a Dq value of 1740 cm^{-1}. With a slight variation of B and C/B such energy plots can be used to explain the spectra of a variety of octahedral chromium(III) complexes. Thus the spectra of hexacyano ($Dq = 2650\ cm^{-1}$, $B = 500$ to $550\ cm^{-1}$), trisethylenediamine ($Dq = 2185\ cm^{-1}$, $B = 625\ cm^{-1}$), hexaammine ($Dq = 2155\ cm^{-1}$, $B = 650\ cm^{-1}$), hexaisothiocyanato ($Dq = 1765\ cm^{-1}$, $B = 575\ cm^{-1}$), hexafluoro ($Dq \cong 1600\ cm^{-1}$, $B = 750\ cm^{-1}$) and of many other systems can be interpreted. In both chromium(III) and nickel(II) octahedral complexes the lowest energy spin-allowed band directly gives 10 Dq (or Δ), and the evaluation of B can be made by the use of any of the following formulae[37].

$B = (2\nu_1{}^2+\nu_2{}^2-3\nu_1\nu_2)/(15\nu_2-27\nu_1)$ (fitting the second band)

$B = (2\nu_1{}^2+\nu_3{}^2-3\nu_1\nu_3)/(15\nu_3-27\nu_1)$ (fitting the third band)

$B = (\nu_2+\nu_3-3\nu_1)/15$ (fitting the sum of the second and the third band maxima)

$B = 1/75\{3\nu_1+[25(\nu_3-\nu_2)^2-16\nu_1{}^2]^{\frac{1}{2}}\}$ (fitting the difference of the third and the second band maxima)

In the above equations ν_1, ν_2, and ν_3 are the first, second, and the third spin-allowed transitions in the order of increasing energy, respectively.

Thus in cubic fields only one ligand field parameter, *Dq*, is needed to describe the spectra. On the other hand, in quadrate fields, two more ligand field parameters, *Dt* and *Ds*, are introduced because of the added axial fields. The axial ligand field parameter, *Dt*, is very similar to *Dq* in that both are matrix elements of the fourth order harmonic potential, whereas *Ds* is the matrix element of the second order harmonic potential[21a]. In the limit of crystal field formalism it can be shown that $Dt = -2/7\ (Dq_x-Dq_y)$ for an octahedral complex of the formula MX_5Y and twice this for *trans*-MX_4Y_2. Although more general symmetry arguments require ten electron correlation parameters in cubic fields and twenty three in quadrate fields these can be averaged to three both in quadrate and cubic fields[21a] if the differences among these parameters are assumed small. They are the usual Racah parameters A, B, and C (or the related Slater–Condon–Shortley parameters F_0, F_2, and F_4). Since the parameter A occurs in all energy levels and since our interest is in energy differences, we are concerned with only B and C, which depend upon the positions of the spin-allowed and spin-forbidden bands, respectively. Spin-orbit perturbation is not included in the present report.

In the limit of zero spin–orbit interaction the quadrate theory can be developed on the basis of either of the representations that axial fields being perturbative additions to the cubic fields or that they are large enough being included along with the cubic fields to start with[21a]. The latter scheme would be more appropriate to describe systems of pentacoordinate square pyramidal, tetracoordinate square planar, and highly tetragonally distorted octahedral geometry. On the other hand, mono- and *trans*-disubstituted hexacoordinate octahedral systems which are under present study can be conveniently described by the former scheme, *i.e.* these systems would be treated as slightly deviated from cubic symmetry. The symmetry adapted wave functions in this representation are simply the cubic wave functions but properly decomposed in going to quadrate symmetry. The decomposition of the representations of cubic symmetry relative to quadrate is as follows: $A^C_{1g} \rightarrow A^Q_{1g}$, $A^C_{2g} \rightarrow B^Q_1$, $E^C_{ga} \rightarrow A^Q_1$, $E^C_{gb} \rightarrow B^Q_1$, $T^C_{1ga} \rightarrow A^Q_2$, $T^C_{1gb,c} \rightarrow E^Q_{a,b}$, $T^C_{2ga} \rightarrow B^Q_2$, and $T^C_{2gb,c} \rightarrow E^Q_{a,b}$. These symmetry adapted strong-field d^3 quadrate wave functions are listed in Appendix A. Using the same decomposition it is, of course, possible to carry out the perturbation of axial fields over the octahedral weak-field representation. Since it is the strong-field functions that more aptly describe the real systems we chose to carry out our calculations in strong-field formalism. The structure of the energy matrices is obvious from the decomposition of representations described above. The matrix elements in cubic fields, *i.e.*, cubic ligand field and electron correlation terms, would stand as they are. Now in addition to the added axial field parameters in the diagonal elements, the A_{1g}^{C} and E_{ga}^{C} representations both being transformed to A_{1}^{Q} representation in quadrate would be connected by axial ligand field off-diagonal elements. Similarly the A_{2g}^{C} and E_{gb}^{C}, the $T_{1gb,c}^{C}$ and $T_{2gb,c}^{C}$ representations will have non zero off-diagonal elements in axial ligand field parameters, *Dt* and *Ds*. The energy matrices of d^3 configuration in quadrate fields are listed in Appendix B*.

The splitting of the octahedral energy levels in quadrate fields is shown in Figure 2 which has been constructed with the parametric values $B = 650$ cm^{-1}, $C/B = 4$, $Dt = +300$ cm^{-1} and $\kappa \equiv Ds/Dt = 2$. Such a plot is applicable to systems where an octahedral complex is either monosubstituted or *trans*-disubstituted by a ligand whose *Dq* value is larger than the *Dq* value of the parent complex. Note that this diagram is also appropriate to describe the energy levels of an elongated tetrahedral complex of d^7 configuration. In this diagram *Dq* is varied from 0 to 4000 cm^{-1}. At zero *Dq* value, we have linear symmetry with $Dt = +300$ cm^{-1} and $\kappa = 2$. The energy levels on this line correspond to those of cylindrical labels. At the right hand side of the diagram are given the strong-field labels for the quadrate representation. Each of the orbitally doubly and triply degenerate octahedral levels split into two quadrate levels as expected. Considering only the diagonal elements the doublets of (t_{2g}^{3}) configuration do not split but they do so when configuration interaction is included. Our primary interest in this energy plot is the splittings of the three excited spin quartet levels. In the first approximation it can be seen from the diagonal elements of the energy matrices that these are given by $+35/4\ Dt$ ($^4E-{}^4B_2$), $+6Ds-5/4\ Dt$ ($^4A_2-{}^4E$), and $+3Ds-5Dt$ ($^4E-{}^4A_2$). For the parameters chosen here the splitting of the third quartet cannot be observed in this diagram. If configuration interaction is included the ^4E levels repel each other so that the splittings of the first two quartets would be actually lower than given by these formulae. For negative values of *Dt* the quartet levels will be reversed so that configuration interaction actually enhances the splitting of these quartets. The effects of configuration interaction can be seen very nicely in the energy diagrams displayed in Figures 3 and 4. The $^4B_2$ component of the first excited quartet is placed at an energy of 10 *Dq* from the $^4B_1$ ground state even when configuration interaction is included. The value of 10 *Dq* is fixed in these energy plots and *Dt* is varied so that such plots will be applicable for a series of mono and *trans*-disubstituted derivatives of given parent octahedral complex[21b]. The *Dq* value chosen in Figures 3 and 4 is 1740 cm^{-1} which is that of an hexaaquo complex cation. As pointed out above these diagrams reveal that the splitting of the first excited quartet depends not only upon the magnitude of *Dt* but also upon its sign. In fact, in Fig. 3 for positive *Dt* the splitting of the first quartet band becomes smaller as the *Dt* value is increased as a consequence of the non-crossing of the ^4E levels. Another interesting observation that can be made in

---

* Appendices A and B which have been deposited with the ADI as part of ref. 21a are reproduced here by permission from *J. Phys. Chem.*

(text continued p. 84)

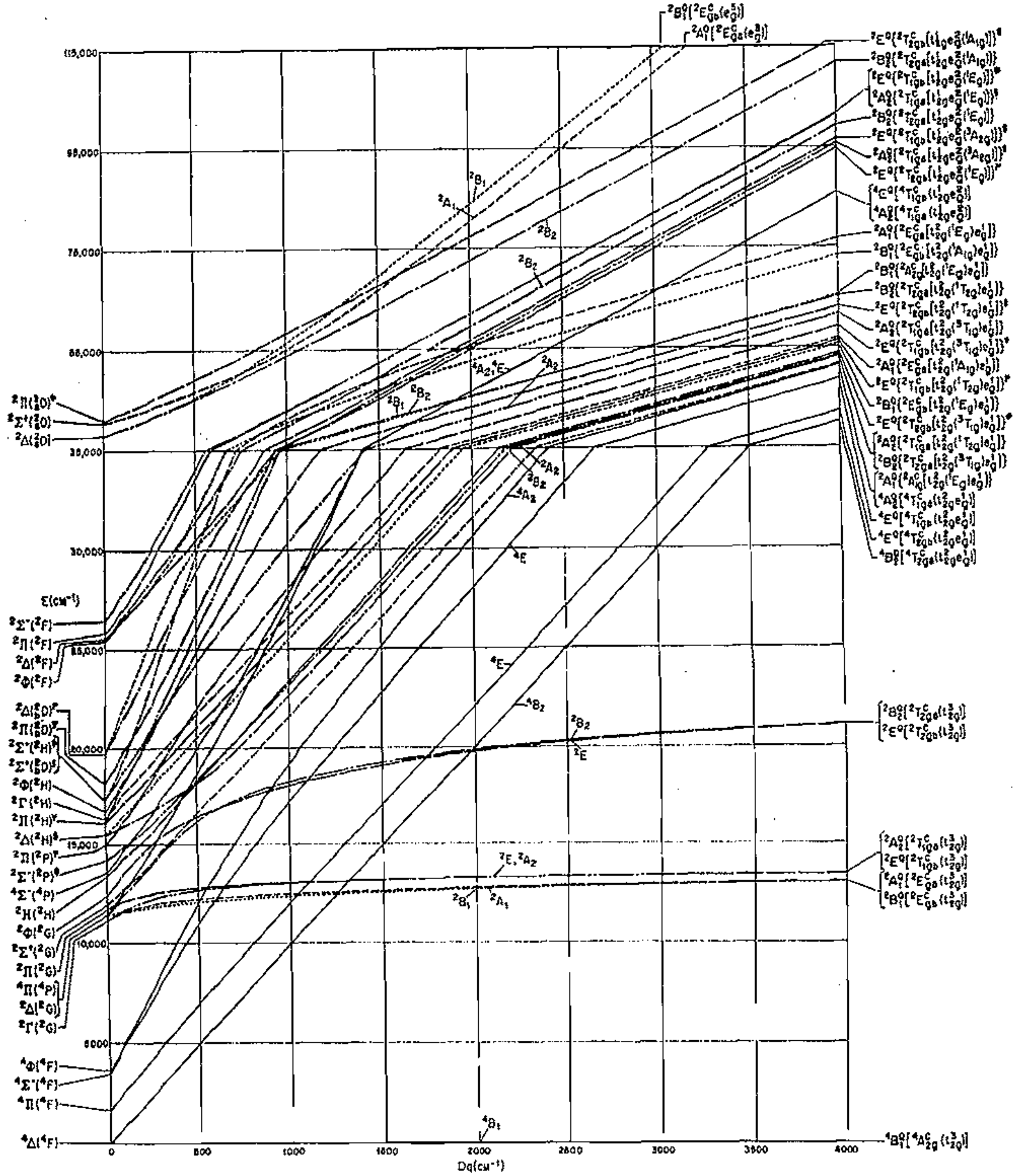

Fig. 2. Energy level diagram for d^3 configuration in quadrate fields (varying Dq): $\zeta = 0$, $B = 650$ cm^{-1}, $C/B = 4$, $Dt = +300$ cm^{-1}, $\kappa = 2$.

The superscripts on the energy labels refer to the percent of that eigenvector component of the eigenfunction. The various symbols have the following meaning:

₦ 100% ± 2½%,	₵ 95% ± 2½%,	‖ 90% ± 2½%,
₰ 85% ± 2½%,	⟊ 80% ± 2½%,	§ 75% ± 2½%,
ǂ 70% ± 2½%,	ǂ 65% ± 2½%,	$ 60% ± 2½%,
₵ 55% ± 2½%,	₱ 50% ± 2½%,	¥ 45% ± 2½%,
# 40% ± 2½%,	¥ 35% ± 2½%,	Đ 30% ± 2½%,
∓ 25% ± 2½%,	₦ 20% ± 2½%,	

pp. 77-80

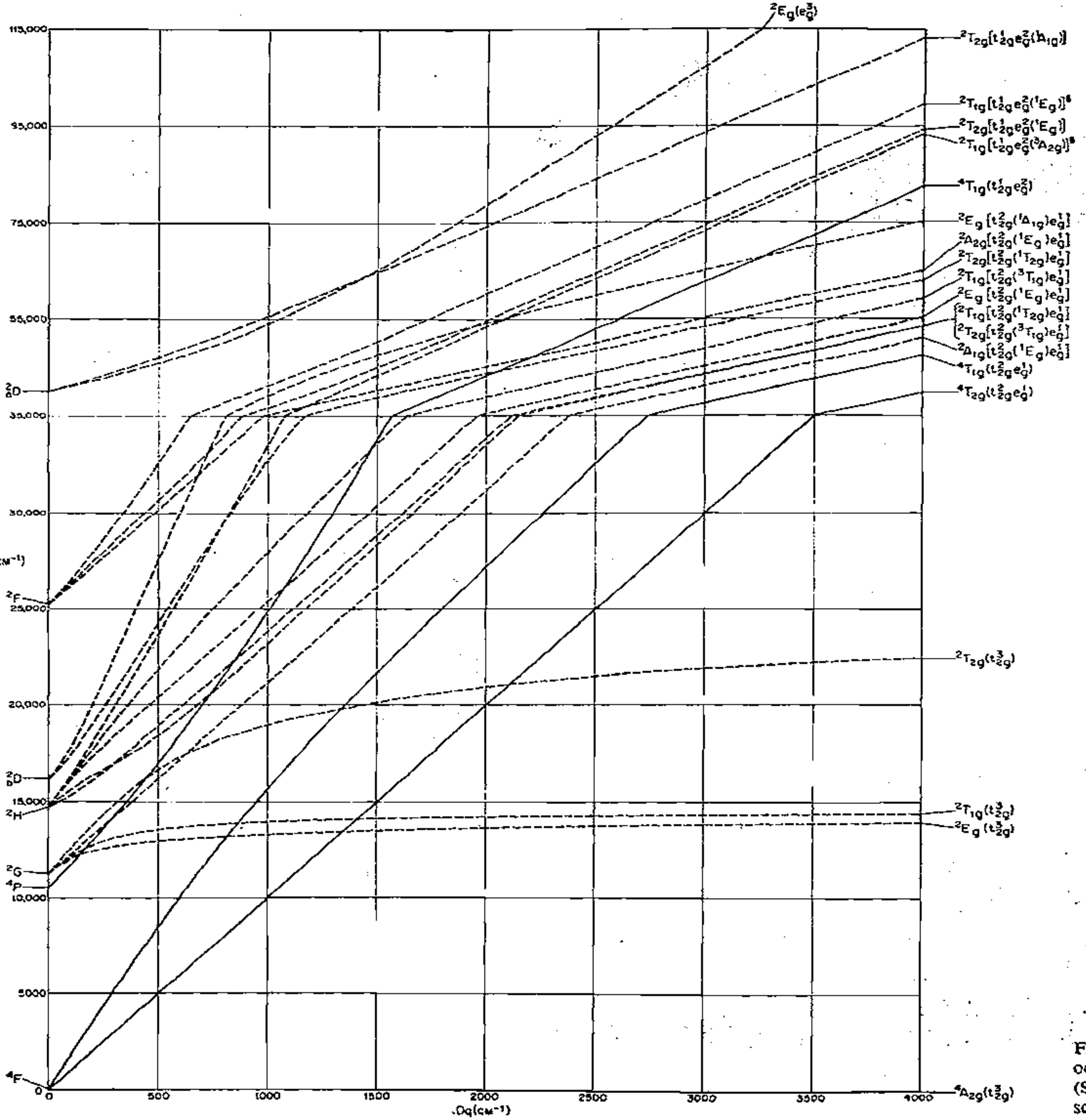

Fig. 1. Energy level diagram for d^3 configuration in octahedral fields: $\zeta = 0$, $B = 700$ cm^{-1}, $C/B = 4$. (See the caption of Fig. 2 for the meaning of the superscript symbols of the energy labels.)

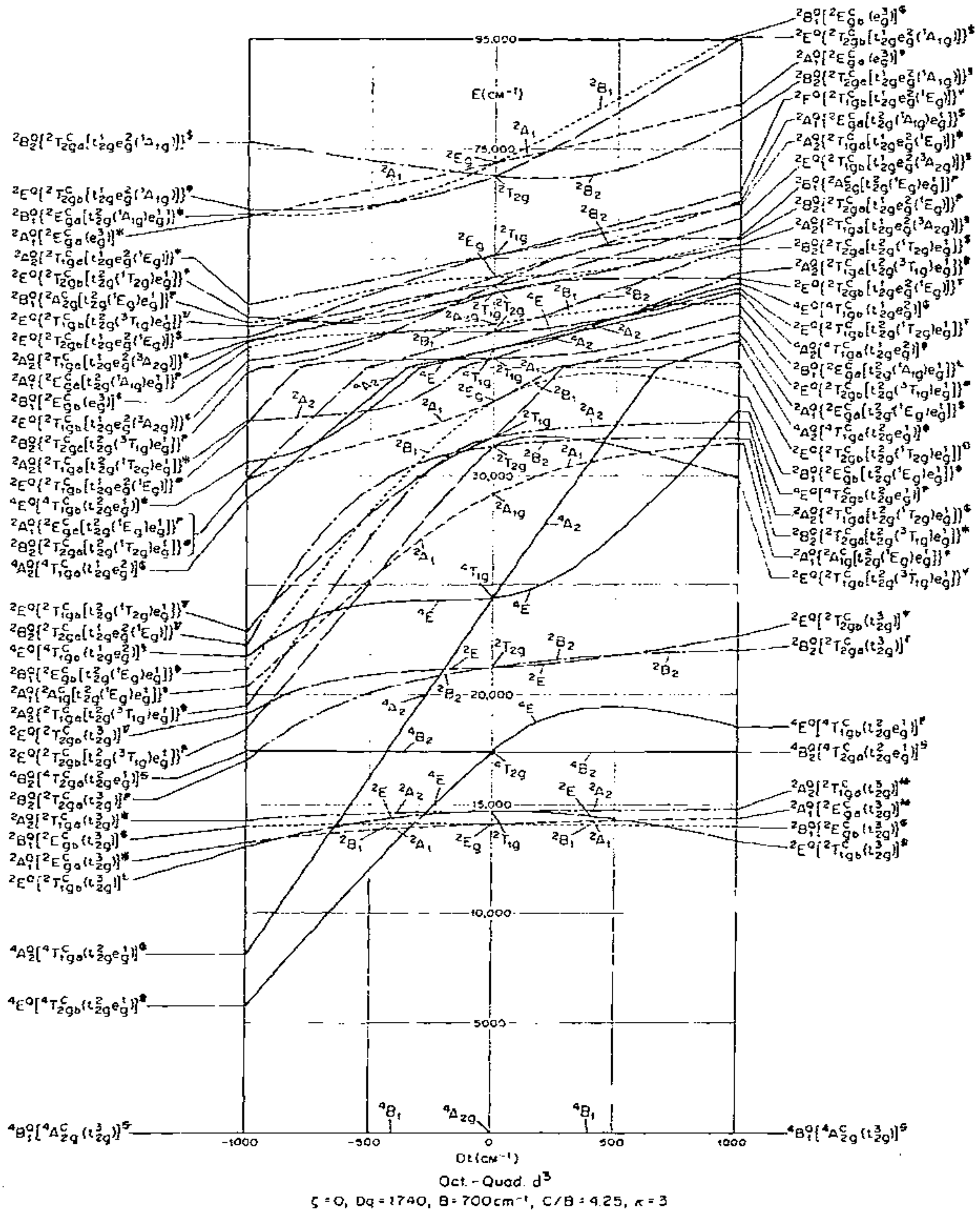

Fig. 3. Energy level diagram for d^3 configuration in quadrate fields (varying Dt) $\zeta = 0$, $Dq = 1740$ cm^{-1}, B = 700 cm^{-1}, $C/B = 4.25$, $\kappa = 3$ (see the caption of Fig. 2 for the meaning of the superscript symbols on the energy labels).

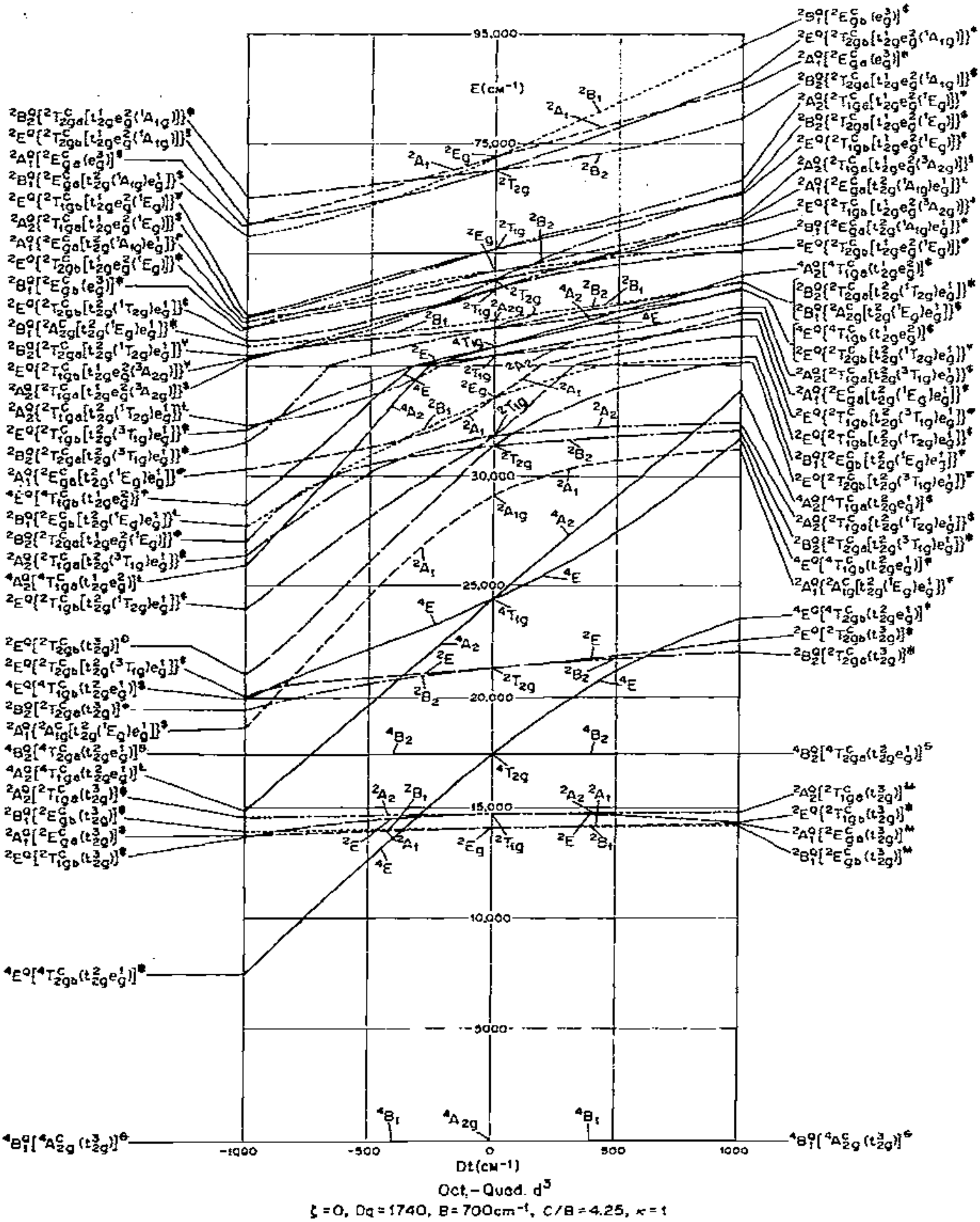

Fig. 4. Same as Fig. 3 but $\kappa = 1$.

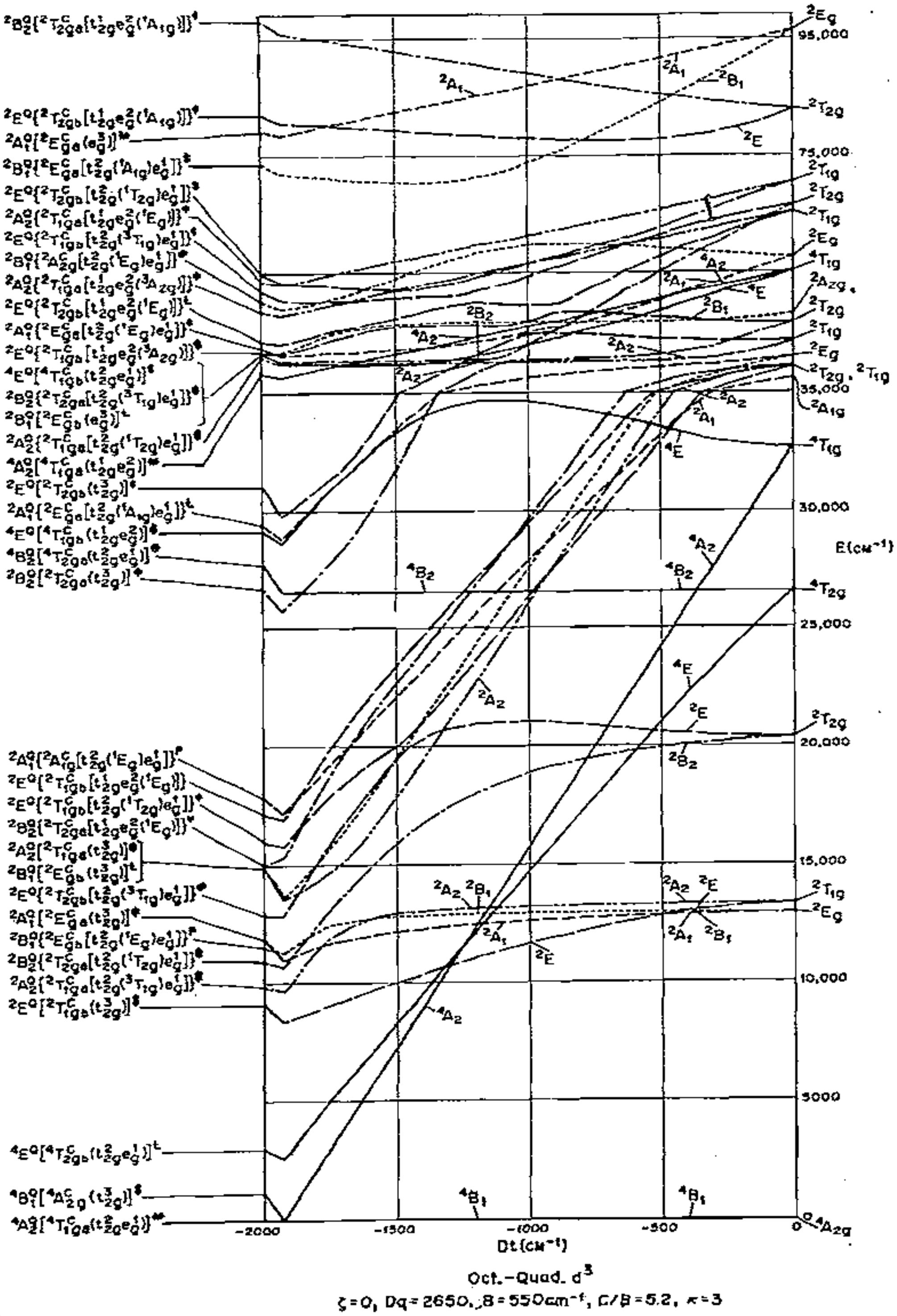

Fig. 5. Same as Fig. 3 but $Dq = 2650\ \mathrm{cm}^{-1}$, $B = 550\ \mathrm{cm}^{-1}$, $C/B = 5.2$.

this same plot is that for negative values of Dt around 400 cm^{-1} the $^4A_2$ and $^4B_2$ levels are so close to each other so that in systems which can be described by this set of parameters, only three transitions may be observed instead of the more general four component structure of the two cubic quartet transitions.

There is no definitive answer at present as to whether κ is a constant or whether it varies from system to system. Further extensive investigations, in particular polarized spectroscopic measurements by which definitive assignments can be given for the observed transitions are required. Until then we use alternate values of κ resulting in alternate assignments for the second cubic quartet components.

Figures 5 and 6 are the quadrate energy diagrams with $Dq = 2650$ cm^{-1} applicable to substituted cyanocomplexes of chromium(III). Since cyanide is at the extreme strong-field end of the spectrochemical series most of the substituted cyano complexes would have negative Dt values, so the energy levels are not derived for positive values of Dt in these diagrams. Energy plots appropriate to substituted ammine and ethylenediamine systems have been constructed earlier by the author[21b].

The theory described above rigorously applies to monosubstituted and *trans* disubstituted derivatives of parent O_h complexes belonging to C_{4v} and D_{4h} symmetries, respectively. Although the *cis*-disubstituted complexes strictly belong to C_{2v} or lower symmetry, they can be treated as approximately belonging to D_{4h} symmetry if each of the *trans* ligand pairs can be averaged in considering the ligand fields[3,22]. The *cis*-disubstituted compound MX_4Y_2 would then become pseudo *trans*-MZ_4X_2 where Z is a ligand intermediate in ligand field strength to X and Y. The Dt for such a *cis*-MX_4Y_2 is then $-4/7\ (Dq_Z - Dq_X)$ and since $Dq_Z = 1/2\ (Dq_X + Dq_Y)$, $Dt = -2/7\ (Dq_Y - Dq_X)$ which is the same as the value for a monosubstituted C_{4v} complex but of opposite sign. This is in harmony with the fact that the *cis* compounds MX_4Y_2 or MX_2Y_4 can be considered as monosubstituted derivatives of 1, 2, 3 or *cis* MX_3Y_3. If $Dq_X > Dq_Y$ then $Dq_Z = 1/2\ (Dq_X + Dq_Y) > Dq_Y$ so that Dt for *cis*-MX_4Y_2 is positive in contrast to the negative Dt for the corresponding *trans* compound. Similarly if $Dq_X < Dq_Y$ then $Dq_Z = 1/2\ (Dq_X + Dq_Y) < Dq_Y$ so that Dt for *cis*-MX_4Y_2 is negative in contrast to the positive Dt for the corresponding *trans* compound.

Neglecting configuration interaction these Dt relations can be substituted in the energy equations for the first quadrate quartet components. Schematic spectral profiles in this region for mono, *cis* and corresponding *trans* disubstituted compounds are displayed in Figure 7 which also includes the above derivations pictorially. Two points are of significance in the spectroscopic relationships between *cis* and *trans* for the cases MX_4Y_2 where $Dq_X > Dq_Y$ and $Dq_X < Dq_Y$. Comparing the two cases for *trans* only, we would expect a larger splitting of the first cubic band for the $Dq_X > Dq_Y$ because of configuration interaction. Similar wider splitting, though not to the same extent, can be expected in the *cis* case for the reverse

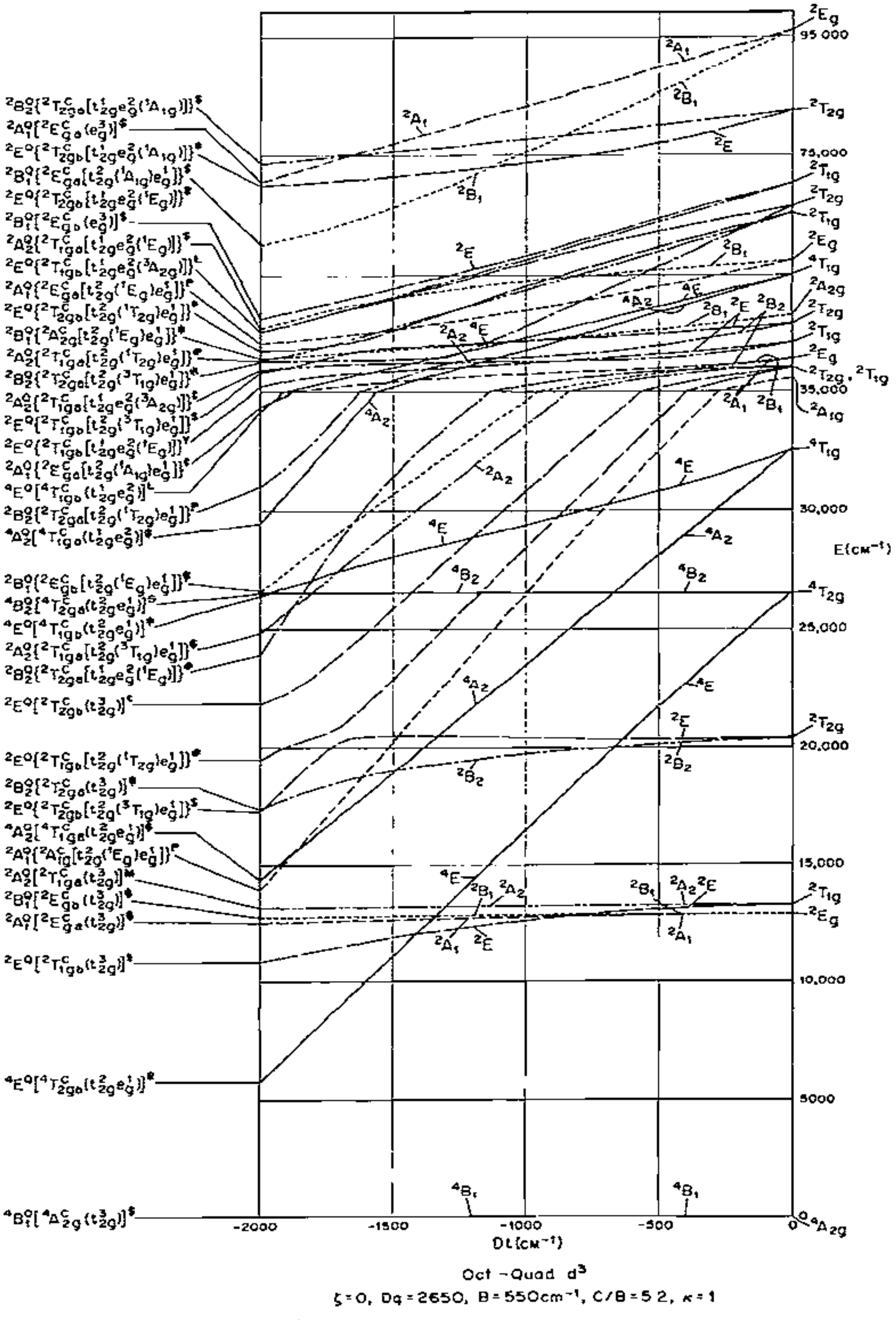

Fig. 6. Same as Fig. 5 but $\kappa = 1$.

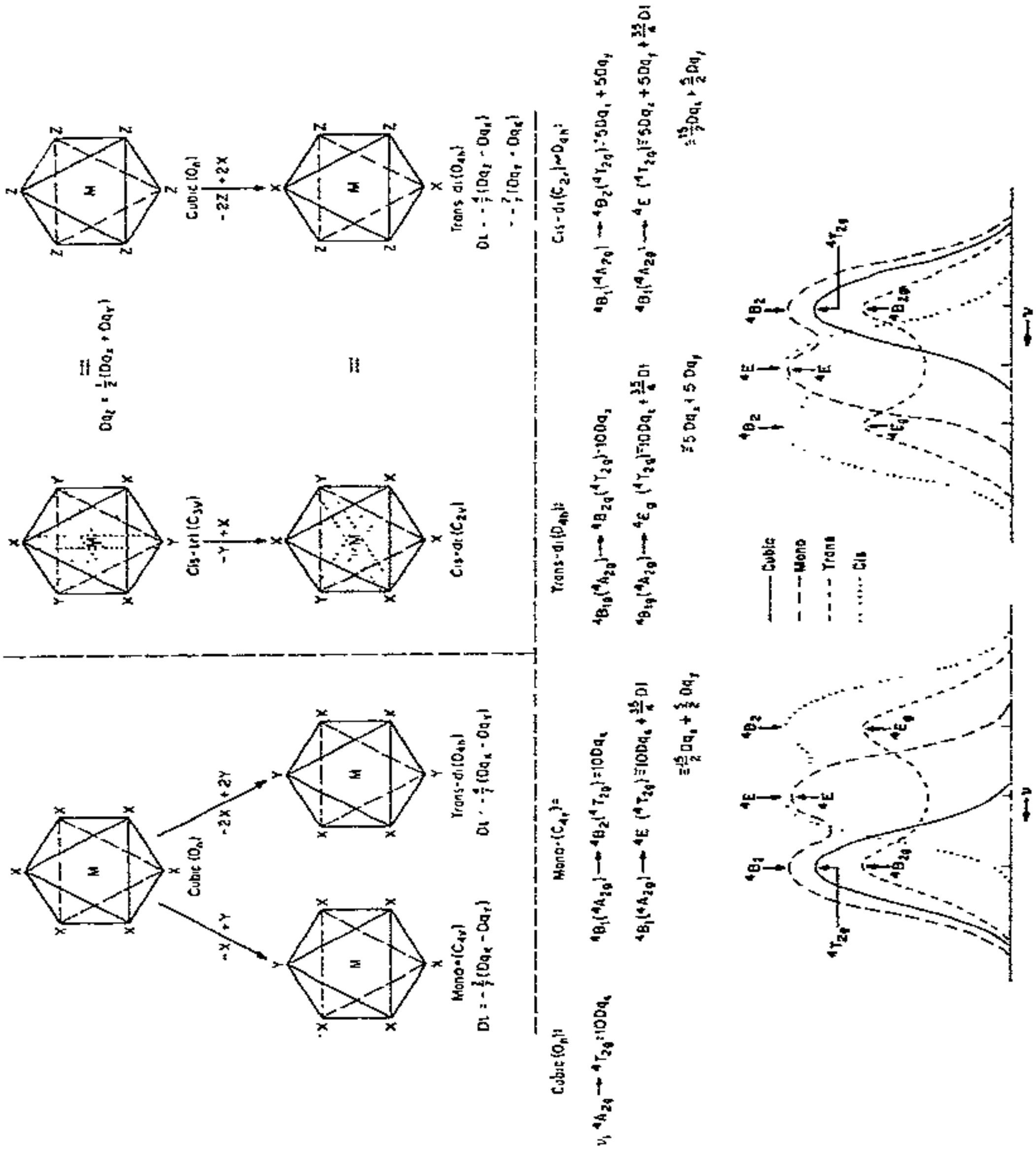

Fig. 7. Schematic spectroscopic relationships between MX_6, MX_5Y; and *cis* and *trans* isomers of MX_4Y_2. (The upper part of this diagram is reproduced from ref. 22 by permission from *Inorg. Chem.*)

systems, *i.e.* $Dq_X < Dq_Y$. Another interesting observation is that the $^4B_2$ level of a *cis* compound is predicted to be positioned roughly at the same energy as the ^4E_g level of the corresponding *trans* compound and the ^4E level of a *cis* compound to be roughly placed in the middle of ^4E_g and $^4B_{2g}$ levels of the corresponding *trans* complex, which is also the approximate frequency maximum of the ^4E component of the monosubstituted complex. Thus the $^4B_2$ levels of *cis* and *mono* derivatives are mirror images to each other with the ^4E level of both forming the mirror plane. These predictions along with the fact that greater intensities are expected in the *cis* compounds because of lower symmetry should aid as spectroscopic criteria in distinguishing the *cis* and *trans* disubstituted derivatives of octahedral complexes[22].

C. APPLICATIONS

While it is not our intention here to calculate and compare the transition energies with the observed bands, we intend to give quadrate assignments where definitive, remark on the derived values of the parameters, in particular *Dt* and finally predict the band positions of some hitherto uncharacterized substituted complexes.

Table 1 collects the data of all the known monosubstituted complexes of chromium(III). Among the acidopentaammines only the halopentaammines show splitting of the $^4T_{2g}$ band. Resolution has not been achieved in the others which are expected to show a splitting of about 1000 cm^{-1}. Among the pentaaquo systems definite splitting has been observed in the iodo and chloro systems whilst an asymmetric appearance of the $^4T_{2g}$ band suggests the presence of a second component in the bromo and other complexes. Precise measurements should certainly resolve this band; a definite component should appear at about 17,400 cm^{-1} corresponding to the $^4B_2$ transition. There are only two complexes of positive *Dt* in this list. Resolution has not been achieved in the aquopentaammine itself so that the pentaaquoammine with the corresponding positive *Dt* does not show any splitting of the $^4T_{2g}$ band. The cyanopentaaquo system displays a second component upon gaussian analysis. The splitting of the second cubic quartet band $^4T_{1g}$ into two components has only been observed in two or three systems and the third cubic spin-allowed band which has been uncovered in only two systems, the fluoropentaaquo and the aquopentafluoro, does not split at all.

Most of the *trans* disubstituted systems show splitting of the $^4T_{2g}$ band as can be seen from Table 2. This is because *Dt* in these systems is twice that of the corresponding monosubstituted derivatives resulting in a larger splitting of the $^4T_{2g}$ level. In contrast to the C_{4v} systems splitting of the second band has been observed in many D_{4h} compounds. Once again the third cubic quartet was uncovered in only two systems, the *trans*-difluoro and the dichlorotetraaquo, and in both cases does not show any splitting. For the reasons already noted only a few

(text continued p. 93)

TABLE I

SPECTROSCOPIC DATA OF MONOSUBSTITUTED COMPLEXES (C_{4v})

(Absorption maxima in cm^{-1} followed by extinction coefficients in l mole^{-1} cm^{-1} in parentheses are given in this and following Tables. The maxima in parentheses are from diffuse reflectance spectroscopic studies.)

Complex	$^2A_1, ^2B_1(^2E_g)$;	$^2A_2, ^2E(^2T_{1g})$	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$	$^4A_2(^4T_{1g})$;	$^4E(^4T_{1g})$	$^4A_2(^4T_{1g})$; $^4E(^4T_{1g})$	References
$[Cr(NH_3)_5I]^{2+}$			18,500 (53.7)	21,250 (38.9)	~26,000 (50.0)			38
$[Cr(NH_3)_5Br]^{2+}$			19,050 (38.0)	21,770 (27.5)	26,490 (45.7)			38
		(14,800)	(18,800)	(21,300)	(26,000)			21b
$[Cr(NH_3)_5Cl]^{2+}$		14,858 (0.7)	19,400 (38.0)	22,100 (27.5)	26,600 (43.6)			38
	(14,800)	(15,500)	(19,200)	(21,400)	(26,400)			21b
$[Cr(NH_3)_5(OH)]^{2+}$			19,700 (40.0)		25,500 (36.7)	29,800 (13.3)		39, 40, 41
$[Cr(NH_3)_5F]^{2+}$			20,000 (42.6)		27,030 (22.0)			42, 43, 44
$[Cr(NH_3)_5(N_3)]^{2+}$			20,070 (145.0)		26,180 (93.4)			42, 45
$[Cr(NH_3)_5(NCS)]^{2+}$	14,600 (0.15)	~15,385	20,533 (82.8)		27,548 (51.8)			46, 47, 48, 49, 42, 45
$[Cr(NH_3)_5(H_2O)]^{3+a}$		15,267 (0.25)	20,661 (35.0)		27,777 (29.0)			39, 40, 50, 41, 42, 48, 51, 44
$[Cr(NH_3)_5(ONO)]^{2+}$			20,746 (42.7)		28,089 (79.4)			48, 42, 45
α-[Cr(tetren)Cl]$^{2+}$			20,202 (118.0)		26,666 (82.0)			52
α-[Cr(tetren) (NCS)]$^{2+}$			19,417 (125.0)	22,988 (33.7)	25,773 (63.2)			53
$[Cr(H_2O)_5I]^{2+}$			15,408 (36.5)	17,250 (16.5)	21,097 (32.6)			54, 55, 56
$[Cr(H_2O)_5Br]^{2+}$		~14,814 (~12.0)	16,077 (21.3)		~21,277 (~15.0)	23,148(23.7)		55, 56
$[Cr(H_2O)_5Cl]^{2+}$		~14,836 (7.5)	16,447 (17.4)	17,025 (16.0)	23,364 (21.9)			55, 57, 58, 56, 54
$[Cr(H_2O)_5F]^{2+}$		14,992 (~5.1)	16,835 (12.9)		23,980 (12.4)		37,313 (5.0)	55, 54, 59
		(14,930)	(16,080)		(22,940)		(38,000)	60
$[Cr(H_2O)_5(SO_4)]^+$		~14,903 (5.3)	17,035 (19.0)		23,980 (18.8)			61
$[Cr(H_2O)_5(NO_3)]^{2+}$			17,211 (16.1)		24,271 (18.9)			62, 63
$[Cr(H_2O)_5(NCS)]^{2+}$		15,598	17,544 (31.1)		24,390 (32.8)			46
$[Cr(H_2O)_5(NH_3)]^{3+}$		15,152 (2.0)	18,115 (18.0)		25,000 (17.3)			50, 51, 64
$[Cr(H_2O)_5(CN)]^{2+}$		~14,700	~19,200 (26.0)	~17,500 (~12.5)	25,500 (20.5)			22
$[Cr(CN)_5(H_2O)]^{2-}$			23,500 (89.0)	26,400 (106.0)	29,000 (45.0)	32,100 (50.0)		22
$[CrF_5(H_2O)]^{2-}$		(15,130)		(15,850)	(23,310)		(35,490)	60

[a] The extinction coefficients reported in reference 42 for this complex are incorrect.

TABLE 2

SPECTROSCOPIC DATA OF *trans*-DISUBSTITUTED COMPLEXES (D_{4h})

Complex	$^2A_{1g}, ^2B_{1g}(^2E_g); ^2A_{2g}, ^2E_g(^2T_{1g})$	$^4E_g(^4T_{2g})$	$^4B_{2g}(^4T_{2g})$	$^4A_{2g}(^4T_{1g})$;	$^4E_g(^4T_{1g})$	$^4A_{2g}(^4T_{1g}); ^4E_g(^4T_{1g})$	*References*
$[Cr(en)_2(I)_2]^+$		16,350	21,000				27
$[Cr(en)_2(Br)_2]^+$		16,474 (34.7)	~21,739 (24.0)	24,630 (30.9)			65
$[Cr(en)_2(Cl)_2]^+$		17,300 (24.5)	22,075 (22,9)	25,252 (33.9)	27,250 (22,9)		66, 67, 68, 69a, 69b
$[Cr(en)_2(OH)_2]^+$	14,598 (1.4)	19,900 (31.8)		25,250 (28.9)	29,000 (11.0)?		70, 71
$[Cr(en)_2(F)_2]^+$		19,047 (19.0)	21,459 (24.0)	25,000 (16.1)	28,571 (18.0)		72
$[Cr(en)_2(H_2O)_2]^{3+}$		19,700 (22.4)	22,600 (29.5)	27,700 (38.9)			73, 74, 65, 67, 70
$[Cr(en)_2(ONO)_2]^+$	~15,000	20,964		30,487			75
$[Cr(en)_2(NCS)_2]^+$		20,700 (93.0)		27,470 (67.0)			27, 76
$[Cr(en)_2(H_2O)Br]^{2+}$		17,825 (23.4)	21,978 (25.1)	26,041 (44.6)			65
$[Cr(en)_2(H_2O)Cl]^{2+}$		18,315 (20.4)	22,321 (24.5)	26,315 (47.9)			67
$[Cr(en)_2(H_2O)(OH)]^{2+}$	14,706 (2.1)	20,200 (38.0)		25,125 (49.0)	29,000 (24.0)?		71
$[Cr(en)_2(H_2O)F]^{2+}$		19,267 (24.2)	22,026 (25.6)	26,954 (31.2)			72
$[Cr(en)_2(H_2O)(NCS)]^{2+}$		~19,000 (72.0)		~25,500 (45.0)			77
$[Cr(en)_2(OH)Cl]^+$		18,796 (35.0)		25,125 (39.0)			78
$[Cr(H_2O)_4(Cl)_2]^+$	15,000	15,750		22,200		36,800	57, 58
$[Cr(H_2O)_4(F)_2]^+$	14,800	16,300		22,700	25,500	37,000	59
$[Cr(H_2O)_4(NCS)_2]^+$		17,540 (31.6)		23,810 (31.6)			82
$[Cr(H_2O)_4(NH_3)_2]^{3+}$		~19,230 (~21.0)		~25,500 (~24.5)			51
$[Cr(NCS)_4(NH_3)_2]^-$	13,400; 13,800; 14,250; 14,550	19,230 (105.0)	~17,600 (60.2)	~25,640 (77.6)			83, 84
	(13,800)						21b
$[Cr(ox)_2(H_2O)_2]^-$		18,520 (20.5)		24,635 (24.2)			79, 80, 81
$[Cr(dipy)_2(Cl)_2]^+$		18,020 (46.0)	22,470	24,100	25,510		27
$[Cr(dipy)_2(OH)_2]^+$		~19,000 (43.0)					85
$[Cr(dipy)_2(H_2O)_2]^{3+}$		20,410 (42.8)					85
$[Cr(phen)_2(OH)_2]^+$		~19,000 (40.0)					85
$[Cr(phen)_2(H_2O)_2]^{3+}$		20,200 (40.7)					85
$[Cr(das)_2(I)_2]^+$	(13,300)	15,400 (100.0)					86
$[Cr(das)_2(Br)_2]^+$	(13,300)	16,300 (140.0)	~20,000 (180.0)	22,600 (1150)	~24,500 (680)		86
$[Cr(das)_2(Cl)_2]^+$	(13,300)	17,000 (80.0)	~20,800 (270.0)	23,600 (1300)	~25,500 (900)		86

TABLE 3

SPECTROSCOPIC DATA OF *cis*-DISUBSTITUTED COMPLEXES (C_{2v})

Complex	${}^2A_1, {}^2B_1({}^2E_g); {}^2A_2, {}^2E({}^2T_{1g})$	${}^4E({}^4T_{2g})$	${}^4B_1({}^4T_{2g})$	${}^4A_2({}^4T_{1g})$	${}^4E({}^4T_{1g})$	${}^4A_2({}^4T_{1g}); {}^4E({}^4T_{1g})$	*References*
$[Cr(en)_2(Br)_2]^+$		18,382 (89.4)			24,096 (83.0)		65
$[Cr(en)_2(Cl)_2]^+$		18,939 (70.6)			24,875 (68.5)		68, 66, 69a
		19.400	18,100	25,200	24,500		69b
$[Cr(en)_2(OH)_2]^+$	14,450 (1.4)		18,939 (65.0)		26,525 (69.0)		71, 70
$[Cr(en)_2(F)_2]^+$			~19,380 (75.0)		26,670 (37.0)		87, 88
$[Cr(en)_2(N_3)_2]^+$			19,417 (224.0)		25,125 (148.0)		89, 27
$[Cr(en)_2(H_2O)_2]^{3+}$	15,037 (0.5); 15,503 (0.35); 15,748 (0.4)	20,608 (67.6)			27,322 (43.6)		71, 70, 90, 74
$[Cr(en)_2(ox)]^+$		20,202 (97.0)			27,027 (87.0)		91
$[Cr(en)_2(ONO)_2]^+$	~15,000 (split)	20,790 (90.0)			28,011 (152.0)		75
$[Cr(en)_2(NCS)_2]^+$		20,408 (148.0)			27,027 (91.0)		27, 92
$[Cr(en)_2(H_2O)Br]^{2+}$		19,267 (72.2)			25,839 (60.5)		65
$[Cr(en)_2(H_2O)Cl]^{2+}$		19,608 (71.4)			25,974 (55.7)		68
$[Cr(en)_2(H_2O)(OH)]^{2+}$	14,684 (1.4)		19,417 (72.0)	28,550 (30.0)	25,510 (47.0)		71
$[Cr(en)_2(OH)Cl]^+$			18,484 (74.0)		26,455 (51.0)		78
$[Cr(en)_2(F)Br]^+$		19,531 (61.2)			26,246 (37.6)		72
$[Cr(en)_2(F)Cl]^+$		19,305 (62.4)			25,839 (42.8)		72
$[Cr(en)_2(F)(NCS)]^+$		20,000 (85.1)			26,667 (52.0)		72
$[Cr(Pn)_2(F)_2]^+$			19,157 (55.1)		26,316 (31.5)		88
$[Cr(NH_3)_4(H_2O)_2]^{3+}$		~20,400 (~36.0)	18,870 (25)?		27,200 (~24.5)		51
$[Cr(NH_3)_4(ox)]^+$			20,000 (57.5)		26,670 (70.8)		42, 93
$[Cr(NH_3)_4(ONO)_2]^+$			20,240 (79.4)		27,680 (126.0)		42
$[Cr(NH_3)_4(NCS)_2]^+$			20,160 (83.2)		26,880 (55.0)		42

TABLE 3 (continued)

Complex	$^2A_1, {}^2B_1(^2E_g); {}^2A_2, {}^2E(^2T_{1g})$	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$	$^4A_2(^4T_{1g})$	$^4E(^4T_{1g})$	$^4A_2(^4T_{1g}); {}^4E(^4T_{1g})$	*References*
$[Cr(trien)(Cl)_2]^+$	~14,388 (5.5)	19,011 (95.5)	17,544 (77.6)	25,380 (87.1)			94, 95, 96
$[Cr(trien)(N_3)_2]^+$		19,305 (185.0)		24,875 (106.0)			95
$[Cr(trien)(ox)]^+$		20,000 (139.0)		26,881 (96.5)			95
$[Cr(trien)(NCS)_2]^+$		20,491 (15.70)		26,881 (86.7)			95
$[Cr(H_2O)_4(Cl)_2]^+$	(14,493)	15,750 (24.0)		22,220 (28.2)			57
		(15,385)					
$[Cr(H_2O)_4(OX)]^+$		18,018 (34.2)		23,980 (39.6)			97
$[Cr(H_2O)_4(NCS)_2]^+$		18,180 (35.5)		23,810 (39.8)			82
$[Cr(H_2O)_4(en)]^{3+}$			19,342 (32.0)	25,839 (22.0)			98, 90, 99
$[Cr(H_2O)_4(pn)]^{3+}$			19,417 (36.0)	26,109 (24.4)			100
$[Cr(H_2O)_4(ibn)_2]^{3+}$			19,305 (29.0)	25,641 (11.9)			100
$[Cr(H_2O)_4(CN)_2]^+$		18,518 (18.0)	21,433 (45.0)	26,455 (20.0)			22
$[Cr(ox)_2(H_2O)_2]^-$	14,534 (3.3)	17,730 (52.0)		24,096 (69.0)			79, 80, 81
$[Cr(ox)_2(NH_3)_2]^-$		18,690 (77.6)		26,670 (70.8)			42
$[Cr(ox)_2(en)]^-$	14,493 (2.1)	18,868 (88.0)		25,316 (94.4)			91, 101
$[Cr(ox)_2(dipy)]^-$		18,865 (100.0)		~25,320 (~205.0)			102 107
$[Cr(ox)_2(phen)]^-$		18,520 (~80.0)		~25,000 (~140.0)			102 107
$[Cr(DMSO)_4(Cl)_2]^{+a}$		14,814 (50.1)	14,184 (45.7)	20,618 (38.0)			103, 104
$[Cr(F)_4(en)]^-$	15,050	17,450 (34.0)		24,390 (18.5)		37,310	105
	(14,970)	(17,270)		(23,870)		(37,580)	60
$[Cr(CN)_4(H_2O)_2]^-$		23,420 (110.0)		30,120 (50.0)			22
$[Cr(phen)_2(H_2O)_2]^{3+}$			19,600 (60.0)				85
$[Cr(phen)_2(ox)]^+$		23,810(126)	19,920(62)	28,490(1810)?	28,810(126)		108
$[Cr(dipy)_2(ox)]^+$		22,380(90)	19,610(60)	25,510(364)	23,980(220)		108

[a] $Dq = 1587\ cm^{-1}$.

TABLE 4

Dt VALUES IN cm^{-1} FOR COMPLEXES OF THE FORMULA $[Cr(X)_5Y]^a$

(The *Dt* values for *trans*-$[Cr(X)_4(Y)_2]$ are twice and for *cis*-$[Cr(X)_4(Y)_2]$ are the same but of opposite sign.)

Y\X	CN^-	NH_3	NCS^-	H_2O	N_3^-	F^-	OH^-	Cl^-	Br^-	I^-
CN^-	—	+141	+253	+260	+291	+297	+339	+380	+416	+466
NH_3	−141	—	+111	+119	+150	+156	+197	+239	+275	+325
NCS^-	−253	−111	—	+ 7	+ 39	+ 44	+ 86	+127	+163	+213
H_2O	−260	−119	− 7	—	+ 31	+ 37	+ 79	+120	+156	+206
N_3^-	−291	−150	− 39	− 31	—	+ 6	+ 47	+ 89	+125	+175
F^-	−297	−156	− 44	− 37	− 6	—	+ 41	+ 83	+119	+169
OH^-	−339	−197	− 86	− 79	− 47	− 41	—	+ 41	+ 78	+128
Cl^-	−380	−239	−127	−120	− 89	− 83	− 41	—	+ 36	+ 86
Br^-	−416	−275	−163	−156	−125	−119	− 78	− 36	—	+ 50
I^-	−466	−325	−213	−206	−175	−169	−128	− 86	− 50	—

[a] *Dq* values: $CN^- = 2650$, $NH_3 = 2155$, $NCS^- = 1765$, $H_2O = 1740$, $N_3^- = 1630$, $F^- = 1610$, $OH^- = 1465$, $Cl^- = 1320$, $Br^- = 1193$, $I^- = 1018\ cm^{-1}$.

---

[*] Thus the observed $^4T_{1g}$ components can best be fitted by the following κ values (with slightly varying B values):

$[Cr(NH_3)_5(OH)]^{2+}$ $\kappa = 7/2$; $[Cr(H_2O)_5Br]^{2+}$, $[Cr(CN)_5(H_2O)]^{2-}$ $\kappa = 2$.

trans-$[Cr(en)_2(OH)_2]^+$, $[Cr(en)_2F_2]^+$, $[Cr(en)_2(H_2O)(OH)]^{2+}$ $\kappa = 2$;

$[Cr(en)_2Cl_2]^+$ $\kappa = 1$; $[Cr(H_2O)_4F_2]^+$ $\kappa = 5$;

$[Cr(dipy)_2Cl_2]^+$, $[Cr(das)_2Cl_2]^+$, $[Cr(das)_2Br_2]^+$ $\kappa = 3/4$.

cis-$[Cr(en)_2(H_2O)(OH)]^{2+}$ $\kappa = 7/2$, $[Cr(dipy)_2(ox)]^+$ $\kappa = 2$. Note that the corresponding negative κ values would also predict the observed splittings but reverse quadrate assignments. Definitive assignments may probably be arrived at by further polarized spectroscopic studies.

It should be added that the negative κ value not only reverses the quadrate assignments (for the modulus $\kappa > 5/3$) but gives rise to the prediction of a much enhanced splitting (for all values of κ) of the third spin-allowed cubic band, $^4T_{1g}$, compared with the corresponding positive κ for both positive and negative *Dt*. This enhanced splitting which increases with the increasing value of *Dt* is due to the energy difference of the two quadrate components, ($3Ds$–$5Dt$). The configuration interaction effects are expected to be similar on both the quadrate components since both $^4A_2$ and ^4E, respectively, being the second and third energy levels (both being highest) of the same symmetry designations in the order of increasing energy will be raised in energy although may not be to the same extent. Thus the magnitude of splitting of the third band in conjunction with a knowledge of the *Dt* value can be used indirectly to derive the sign of the κ parameter. Unfortunately, the third band which is usually buried under intense charge transfer absorption itself has been uncovered only in very few systems and in no case has been found to be split.

Based on the possibility that the *Dt*, *Ds* parameters can be regarded as symmetry parameters in ligand field and molecular orbital theories, it has been suggested earlier (ref. 21b) that κ may also assume negative values. However, the corresponding assignments have not been given either in ref. 21b or here only to restrict the alternative choices of assignments until further studies, particularly polarized spectral measurements, are carried out. Using an empirical molecular orbital approach[23,24] with certain assumptions on the σ and π bonding characteristics of ligands, references 27, 30, and 106 discuss and give the reverse assignments for the quadrate components of the second quartet (and the third) in the spectra of some of the trans complexes listed in Table 2. It is interesting to note that the recent polarized spectral measurements of Yamada (ref. 69b) on *trans*-$[Cr(en)_2Cl_2]^+$, the only such study to date on any chromium(III) complex, confirms our earlier and present assignment, but not the reverse assignments based on negative κ.

of the *cis* disubstituted systems listed in Table 3, show splitting of the $^4T_{2g}$ band. The second band has not been found to split in any of these except the hydroxyaquo(bisethylenediamine) and the oxalato(bisdipyridyl) systems; the third band which has been revealed only in the tetrafluoro ethylenediamine system does not show any splitting.

The Dt values calculated from the simple crystal field assumptions seem to agree with the observations and are noted for some of the systems in Table 4. Using appropriate Dt values from this Table, the predicted positions of the quadrate components in the spectra of the mono- and disubstituted ammine, aquo and cyano complexes of chromium(III) are calculated and listed in Tables 5, 6 and 7. In these Tables the quadrate components of the $^4T_{2g}$ and $^4T_{1g}$ cubic bands are given for the mono and *trans*-disubstituted derivatives whereas only the $^4T_{2g}$ components are listed for the *cis*-disubstituted compounds. Although the predicted maxima of the $^4T_{2g}$ components in these systems are expected to be accurate the $^4T_{1g}$ components may be found to be somewhat different from the values given here, since these are obtained with constant B and κ values. The B and κ values may be different for different derivatives of a parent octahedral complex[8]. The transition energies for C_{4v} and D_{4h} systems are derived exactly from the energy matrices for the same set of parameters as in the appropriate energy diagrams of $\kappa = 1$. [It may be pointed out here that the author had directly read the transition energies from the energy diagrams and found that they are within about ± 50 cm^{-1} of the actual computed values and the discrepancy is usually very close to ± 10 cm^{-1} and in no case exceeded 100 cm^{-1}]. Those of the *cis* disubstituted are obtained by the use of the formulae of Figure 7 and do not include configuration interaction. Although the $^4B_2$ values are exact, including configuration interaction, the ^4E values will probably be reduced by about 100 to 500 cm^{-1} for these *cis* systems. The spectroscopic predictions of these Tables agree well with those bands observed in systems which are well characterized, if it is assumed that whenever the expected splitting is of the order of 2000 cm^{-1} or less, only one band is observed at either of the predicted positions or some mean value of them (see also the footnote on p. 92). It appears that the resolution of the quadrate components depends not only on the extent of splitting but also on the widths of the bands and their intensities. Another factor is their position relative to the electronically allowed transitions. It is rather difficult to achieve resolution if they appear as humps on the intense charge transfer bands.

D. CONCLUSIONS

Definitive quadrate assignments have been given only for those systems where resolutions of the cubic quartets has been observed. Such resolution in most of these systems has only been found for the components of the $^4T_{2g}$ band. Alternate

TABLE 5

PREDICTED SPECTRA OF SUBSTITUTED AMMINE COMPLEXES (B = 600 cm^{-1}, κ = 1)[a]

X	$[Cr(NH_3)_5X]$				trans-$[Cr(NH_3)_4X_2]$				cis-$[Cr(NH_3)_4X_2]$	
	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$	$^4A_2(^4T_{1g})$	$^4E(^4T_{1g})$	$^4E_g(^4T_{2g})$	$^4B_{2g}(^4T_{2g})$	$^4A_{2g}(^4T_{1g})$	$^4E_g(^4T_{1g})$	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$
CN^-	22,734	21,550	29,277	28,672	23,802	21,550	30,568	29,471	22,788	24,025
NCS^-	20,553	21,550	26,965	27,504	19,511	21,550	25,945	27,065	20,575	19,600
H_2O	20,479	21,550	26,892	27,471	19,357	21,550	25,798	27,004	20,513	19,475
N_3^-	20,191	21,550	26,607	27,346	18,757	21,550	25,228	26,775	20,238	18,925
F^-	20,135	21,550	26,552	27,322	18,640	21,550	25,118	26,731	20,188	18,825
OH^-	19,749	21,550	26,175	27,161	17,831	21,550	24,363	26,441	19,825	18,100
Cl^-	19,348	21,550	25,789	27,001	16,989	21,550	23,590	26,153	19,463	17,375
Br^-	19,000	21,550	25,458	26,866	16,258	21,550	22,926	25,912	19,145	16,740
I^-	18,513	21,550	24,998	26,685	15,232	21,550	22,003	25,583	18,208	15,865
NH_3	21,550		27,966		21,550		27,966		21,550	

[a] Spectra of the *trans*- and *cis*-$[Cr(en)_2X_2]$ will be expected to be similar to the corresponding *trans* and *cis*-$[Cr(NH_3)_4X_2]$ since the 10 *Dq* of the ethylenediamine complex (21,850 cm^{-1}) is very close to that of the ammine complex (21,550 cm^{-1}).

TABLE 6

PREDICTED SPECTRA OF SUBSTITUTED AQUO COMPLEXES (B = 700 cm^{-1}, κ = 1)[a]

X	$[Cr(H_2O)_5X]$				trans-$[Cr(H_2O)_4X_2]$				cis-$[Cr(H_2O)_4X_2]$	
	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$	$^4A_2(^4T_{1g})$	$^4E(^4T_{1g})$	$^4E_g(^4T_{2g})$	$^4B_{2g}(^4T_{2g})$	$^4A_{2g}(^4T_{1g})$	$^4E_g(^4T_{1g})$	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$
CN^-	19,517	17,400	26,829	25,808	21,257	17,400	29,255	27,569	19,675	21,950
NH_3	18,411	17,400	25,507	25,003	19,351	17,400	26,623	25,676	18,438	19,475
NCS^-	17,461	17,400	24,456	24,425	17,522	17,400	24,522	24,459	17,464	17,525
N_3^-	17,127	17,400	24,098	24,239	16,850	17,400	23,806	24,090	17,125	16,850
F^-	17,074	17,400	24,042	24,210	16,742	17,400	23,693	24,033	17,075	16,750
OH^-	16,697	17,400	23,646	24,010	15,971	17,400	22,901	23,646	16,713	16,025
Cl^-	16,323	17,400	23,260	23,819	15,199	17,400	22,126	23,283	16,350	15,300
Br^-	15,990	17,400	22,920	23,655	14,506	17,400	21,445	22,972	16,033	14,665
I^-	15,522	17,400	22,448	23,432	13,526	17,400	20,495	22,547	15,095	13,790
H_2O	17,400		24,345		17,400		24,345		17,400	

[a] Spectra of the corresponding isothiocyanato complexes will be expected to be similar since the *Dq* of the isothiocyanato complex is very close to that of the aquo complex (*cf.* Table 4).

TABLE 7

PREDICTED SPECTRA OF SUBSTITUTED CYANO COMPLEXES ($B = 550\ cm^{-1}$, $\kappa = 1$)

X	$[Cr(CN)_5X]$				*trans*-$[Cr(CN)_4X_2]$				*cis*-$[Cr(CN)_4X_2]$	
	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$	$^4A_2(^4T_{1g})$	$^4E(^4T_{1g})$	$^4E_g(^4T_{2g})$	$^4B_{2g}(^4T_{2g})$	$^4A_{2g}(^4T_{1g})$	$^4E_g(^4T_{1g})$	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$
NH_3	25,222	26,500	31,324	32,029	23,874	26,500	30,042	31,519	25,263	24,025
NCS^-	24,156	26,500	30,306	31,619	21,636	26,500	28,003	30,799	24,288	22,075
H_2O	24,088	26,500	30,242	31,595	21,494	26,500	27,876	30,757	24,425	21,950
N_3^-	23,786	26,500	29,960	31,488	20,859	26,500	27,311	30,572	23,950	21,400
F^-	23,728	26,500	29,906	31,468	20,735	26,500	27,202	30,536	23,900	21,300
OH^-	23,314	26,500	29,523	31,327	19,866	26,500	26,437	30,292	23,538	20,575
Cl^-	22,907	26,500	29,150	31,194	19,011	26,500	25,689	30,058	23,175	19,850
Br^-	22,547	26,500	28,823	31,079	18,256	26,500	25,033	29,856	22,858	19,215
I^-	22,043	26,500	28,368	30,922	17,202	26,500	24,121	29,579	21,920	18,340
CN^-	26,500		32,560		26,500		32,560		26,500	

assignments based on alternate choices of B and κ values are possible for the observed transitions in the higher energy region because of lack of resolution of the ${}^4T_{1g}$ cubic quartets. In most of the systems surveyed, spin-forbidden bands have not been uncovered let alone the observation of their splitting. Thus more and precise experimental data are needed in the area of the spectra of quadrate chromium(III) complexes. Of particular interest would be polarized spectra of single crystals at low temperatures in the hope of achieving better resolution and definitive assignments. The detection of low intensity spin-forbidden bands will aid in evaluating more definitive values for the electron correlation parameters B and C and thus in understanding the covalency effects in these compounds. The energy diagrams presented in this report and earlier[21b] would be valuable in the interpretation of the spectra of a variety of substituted ammine, aquo, and cyano compounds. Similar energy diagrams can be constructed for appropriate sets of parameters from the energy matrices of Appendix B. Finally, when more precise and abundant data become available on the band positions and intensities spin-orbit perturbation can be included in these calculations.

ACKNOWLEDGMENTS

The author wishes to thank Mr. R. L. Anderson and his associate, Mr. J. Beasley, of the Mellon Institute for computer programming and Mr. J. F. Benes and Mr. E. L. Helgerman, also of the Mellon Institute Research Drafting Department, for their expert aid in the preparation of the figures.

REFERENCES

1 W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, 7 (1956) 107.
2 J. S. Griffith, *The Theory of Transition Metal Ions*, The University Press, Cambridge, England, 1961.
3 C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill Book Company, Inc., New York, N.Y. 1962.
4 C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1962.
5 B. N. Figgis and J. Lewis, in: *Progress in Inorganic Chemistry*, Ed. F. A. Cotton, Interscience Publishers, Vol. 6, pp. 37–239 (1964).
6 A. D. Liehr, *J. Phys. Chem.*, 64 (1960) 43.
7 R. F. Fenske, D. S. Martin, Jr. and K. Ruedenberg, *Inorg. Chem.*, 1 (1962) 441.
8 H. Hartmann, C. Furlani and A. Bürger, *Z. Phys. Chem. N.F.*, 9 (1956) 62.
9 M. H. L. Pryce and W. A. Runciman, *Disc. Faraday Soc.*, 26 (1958) 34.
10 S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan*, 13 (1958) 880.
11 (a) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 33 (1960) 1208; (b) *Ibid.*, 35 (1961) 1809; (c) *Ibid.*, 36 (1962) 3330.
12 (a) R. M. MacFarlane, *J. Chem. Phys.*, 40 (1964) 373; (b) *Ibid.*, 39 (1963) 3118.
13 D. H. Goode, *J. Chem. Phys.*, 43 (1965) 2830.
14 J. R. Perumareddi and A. D. Liehr, *Abstracts, 150th National Meeting of the American Chemical Society*, Atlantic City, New Jersey, Sept. 1965, and to be published.

15 S. Sugano and I. Tsujikawa, *J. Phys. Soc. Japan*, 13 (1958) 899.
16 W. Low, *J. Chem. Phys.*, 33 (1960) 1162.
17 D. S. McClure, *Ibid.*, 36 (1962) 2757.
18 D. L. Wood, J. Ferguson, K. Knox and J. F. Dillon Jr., *Ibid.*, 39 (1963) 890.
19 D. L. Wood, *Ibid.*, 42 (1965) 3404.
20 S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 33 (1960) 98.
21 (a) J. R. Perumareddi, *J. Phys. Chem.*, 71 (1967) 3144; (b) *Ibid.*, 71 (1967) 3155.
22 R. Krishnamurthy, W. B. Schaap and J. R. Perumareddi, *Inorg. Chem.*, 6 (1967) 1338.
23 H. Yamatera, *Bull. Chem. Soc. Japan*, 31 (1958) 95.
24 D. S. McClure, in *Advances in the Chemistry of Coordination Compounds*, Ed. S. Kirschner, The Macmillan Co., New York, N.Y., 1961.
25 C. E. Schäffer and C. K. Jørgensen. *Mat. Fys. Medd. Dan. Ved. Seslk.*, 34 (1965) No. 13.
26 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4 (1965) 709.
27 W. A. Baker, Jr., and M. G. Phillips, *Ibid.*, 5 (1966) 1042.
28 D. A. Rowley and R. S. Drago, *Ibid.*, 6 (1967) 1092.
29 (a) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, 40 (1964) 788; (b) *Ibid.*, (1964) 792.
30 (a) A. B. P. Lever, *Coordin. Chem. Rev.*, 3 (1968) 119; (b) *Idem.*, *ACS. Adv. Chem. Ser.*, 62 (1967) 430.
31 K. E. Lawson, *J. Chem. Phys.*, 47 (1967) 3627.
32 D. R. Scott and F. A. Matsen, *J. Phys. Chem.*, 72 (1968) 16.
33 (a) C. W. DeKock and D. M. Gruen, *J. Chem. Phys.*, 44 (1966) 4387. (b) *Ibid.*, 46 (1967) 1096.
34 J. T. Hougen, G. E. Leroi and T. C. James, *J. Chem. Phys.*, 34 (1961) 1670.
35 M. Ciampolini, N. Nardi and G. P. Speroni, *Coordin. Chem. Rev.*, 1 (1966) 222.
36 C. R. Hare in *Spectroscopy and Structure of Metal Chelate Compounds*, Ed. K. Nakamoto and P. J. McCarthy, S. J., John Wiley and Sons, Inc., New York, N.Y. (1968).
37 J. R. Perumareddi, *Z. Naturforschung*, 22 (1967) 908.
38 M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 266 (1951) 49.
39 M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, 63 (1959) 327.
40 C. E. Schäffer, *J. Inorg. Nucl. Chem.*, 8 (1958) 149.
41 M. A. Levine, T. P. Jones, W. E. Harris and W. J. Wallace, *J. Am. Chem. Soc.*, 83 (1961) 2453.
42 E. Kyuno, M. Kamada and N. Tanaka, *Bull. Chem. Soc. Japan*, 40 (1967) 1848.
43 M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 278 (1955) 24.
44 R. Lowry and J. R. Perumareddi, unpublished data.
45 R. Tsuchida and M. Kobayashi, *Bull. Chem. Soc. Japan*, 13 (1938) 471.
46 A. W. Adamson, *J. Inorg. Nucl. Chem.*, 13 (1960) 275.
47 R. D. Lindholm, E. Zinato and A. W. Adamson, *J. Phys. Chem.*, 71 (1967) 3713.
48 M. Linhard, H. Siebert and M. Weigel, *Z. Anorg. Allg. Chem.*, 278 (1955) 287.
49 R. Tsuchida, *Bull. Chem. Soc. Japan*, 13 (1938) 388.
50 M. R. Edelson and R. A. Plane, *Inorg. Chem.*, 3 (1964) 231.
51 E. Jørgensen and J. Bjerrum, *Acta Chem. Acand.*, 12 (1958) 1047.
52 D. A. House and C. S. Garner, *Inorg. Chem.*, 5 (1966) 2097.
53 M. Linhard and M. Weigel, *Z. Physik. Chem.*, 11 (1957) 308.
54 T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4 (1965) 532.
55 P. Moore and F. Basolo, *Ibid.*, 4 (1965) 1670.
56 H. Taube and H. Myers, *J. Am. Chem. Soc.*, 76 (1954) 2103.
57 P. J. Elving and B. Zemel, *Ibid.*, 79 (1957) 1281.
58 E. L. King, Sr., M. J. M. Woods and H. J. S. Gates, *Ibid.*, 80 (1958) 5015.
59 Y. T. Chia and E. L. King, *Disc. Faraday Soc.*, 29 (1960) 109.
60 H. L. Schläfer, H. Gausmann and H. Zander, *Inorg. Chem.*, 6 (1967) 1528.
61 J. E. Finholt, R. W. Anderson, J. A. Fyfe and K. G. Kaulton, *Ibid.*, 4 (1965) 43.
62 M. Ardon and N. Sutin, *Ibid.*, 6 (1967) 2268.
63 T. W. Swaddle, *J. Am. Chem. Soc.*, 89 (1967) 4338.
64 J. Bjerrum and E. Jørgensen, *J. Inorg. Nucl. Chem.*, 8 (1958) 313.
65 L. P. Quinn and C. S. Garner, *Inorg. Chem.*, 3 (1964) 1348.
66 M. Linhard and M. Weigel, *Z. Physik. Chem.* (Frankfurt) 5 (1955) 20.

67 C. S. Garner and D. J. MacDonald, in: *Advances in the Chemistry of Coordination Compounds*, Ed. S. Kirschner, The Macmillan Co., New York, N.Y., 1961, pp. 266–275.
68 D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, 83 (1961) 4152.
69 (a) C. E. Slaten and C. S. Garner, *J. Phys. Chem.*, 63 (1959) 1214; (b) S. Yamada, *Coordin. Chem. Rev.*, 2 (1967) 83.
70 F. Woldbye, *Acta Chem. Scand.*, 12 (1958) 1079.
71 A. W. Adamson, in: *Mechanisms of Inorganic Reactions*, Advances in Chemistry Series, No. 49, ACS, Washington, D.C. 1965, p. 237.
72 J. W. Vaughn, O. J. Stvan, Jr. and V. E. Magnuson, *Inorg. Chem.*, 7 (1968) 736.
73 H. L. Schlafer, *Z. Physik. Chem. (Frankfurt)* (2) 11 (1957) 65.
74 H. L. Schlafer and O. Kling, *Z. Anorg. Allg. Chem.*, 287 (1956) 296.
75 W. W. Fee, C. S. Garner and J. N. M. Harrowfield, *Inorg. Chem.*, 6 (1967) 87.
76 J. M. Veigel, Ph.D. Dissertation, U.C.L.A., Jan. 1965, p. 59.
77 J. M. Veigel and C. S. Garner, *Inorg. Chem.*, 4 (1965) 1569.
78 D. C. Olson and C. S. Garner, *Ibid.*, 2 (1963) 558.
79 H. L. Schlafer, O. Kling, L. Mähler and H. P. Opitz, *Z. Physik. Chem. (N.F.)*, 24 (1960) 307.
80 G. E. Cunningham, R. W. Burley and M. T. Friend, *Nature*, 169 (1952) 1103.
81 R. E. Hamm, *J. Am. Chem. Soc.*, 75 (1953) 609.
82 J. T. Hougen, K. Schug and E. L. King, *Ibid.*, 79 (1957) 519.
83 E. E. Wegner and A. W. Adamson, *Ibid.*, 88 (1966) 394.
84 A. W. Adamson, *Ibid.*, 80 (1958) 3183.
85 R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, 15 (1961) 62.
86 R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 7 (1968) 1154.
87 K. R. A. Fehrmann and C. S. Garner, *J. Am. Chem. Soc.*, 88 (1960) 6294.
88 J. W. Vaughn and B. J. Kranic, *Inorg. Chem.*, 4 (1965) 1077.
89 M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 271 (1953) 131.
90 H. L. Schläfer and R. Kollrack, *Z. Physik. Chem. N.F.*, 18 (1958) 348.
91 A. Mead, *Trans. Faraday Soc.*, 30 (1934) 1052.
92 K. G. Poulsen and C. S. Garner, unpublished data (quoted in 95).
93 R. Lowry, M. P. Corsmeier and J. R. Perumareddi, unpublished data.
94 O. Kling and H. L. Schläfer, *Z. Anorg. Allg. Chem.*, 313 (1961) 187.
95 D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, 88 (1966) 2156.
96 H. Hartmann and H. H. Kruse, *Z. Physik. Chem. (Frankfurt*, (2) 5 (1955) 9.
97 H. L. Schlafer and W. Tausch, *Essays in Coord. Chem.*, Exper. Suppl. IX, pp. 179–200.
98 D. A. House and C. S. Garner, *Inorg. Chem.*, 5 (1966) 840.
99 M. Ohta, H. Matsukawa and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 37 (1964) 692.
100 D. A. House, R. G. Hughes and C. S. Garner, *Inorg. Chem.*, 6 (1967) 1077.
101 C. H. Johnson and A. Mead, *Nature*, 131 (1933) 399.
102 T. Bürer, *Helv. Chem. Acta*, 46 (1963) 242.
103 H. L. Schlafer and H. P. Opitz, *Z. Chem.*, 6/7 2 (1962) 216.
104 H. L. Schlafer and H. P. Opitz, *Z. Anorg. Allg. Chem.*, 313 (1961/62) 178.
105 J. W. Vaughn, L. C. Coward and B. K. Winter, *Inorg. Chem.*, 5 (1966) 2061.
106 L. Dubicki and R. L. Martin, private communication (1968).
107 J. A. Broomhead, *Austral. J. Chem.*, 15 (1962) 228.
108 J. A. Broomhead, M. Dwyer, and N. Kane-Maguire, *Inorg. Chem.*, 7 (1968) 1388.

APPENDIX A

SYMMETRY ADAPTED STRONG FIELD WAVE FUNCTIONS: QUADRATE FIELDS

(Q = quadrate, C = cubic)

Spin quartets:

$^4B_1{}^Q[^4A_{2g}{}^C(t_{2g}{}^3)] : |(xy)\,(zx)\,(yz)|$

$^4B_2{}^Q[^4T_{2ga}{}^C(t_{2g}{}^2e_g)] : |(zx)\,(yz)\,(x^2-y^2)|$

$^4A_2{}^Q$:

$[^4T_{1ga}{}^C(t_{2g}{}^2e_g)] : |(zx)\,(yz)\,(z^2)|$

$[^4T_{1ga}{}^C(t_{2g}e_g{}^2)] : |(xy)\,(z^2)\,(x^2-y^2)|$

$^4E_a{}^Q$:

$[^4T_{2gb}{}^C(t_{2g}{}^2e_g)] : [-\frac{1}{2}\,|(yz)\,(xy)\,(x^2-y^2)| + \frac{\sqrt{3}}{2}\,|(yz)\,(xy)\,(z^2)|]$

$[^4T_{1gb}{}^C(t_{2g}{}^2e_g)] : [-\frac{1}{2}\,|(yz)\,(xy)\,(z^2)| - \frac{\sqrt{3}}{2}\,|(yz)\,(xy)\,(x^2-y^2)|]$

$[^4T_{1gb}{}^C(t_{2g}e_g{}^2)] : |(zx)\,(z^2)\,(x^2-y^2)|$

$^4E_b{}^Q$:

$[^4T_{2gc}{}^C(t_{2g}{}^2e_g)] : [-\frac{1}{2}\,|(xy)\,(zx)\,(x^2-y^2)| - \frac{\sqrt{3}}{2}\,|(xy)\,(zx)\,(z^2)|]$

$[^4T_{1gc}{}^C(t_{2g}{}^2e_g)] : [-\frac{1}{2}\,|(xy)\,(zx)\,(z^2)| + \frac{\sqrt{3}}{2}\,|(xy)\,(zx)\,(x^2-y^2)|]$

$[^4T_{1gc}{}^C(t_{2g}e_g{}^2)] : |(yz)\,(z^2)\,(x^2-y^2)|$

Spin Doublets: (Bar indicates negative spin)

$^2A_1{}^Q$:

$^2A_{1g}{}^C[t_{2g}{}^2(^1E_g)e_g] : \sqrt{\frac{1}{2}}\,\{\sqrt{\frac{1}{6}}[-2\,|(xy)\,\overline{(xy)}\,(z^2)| + |(yz)\,\overline{(yz)}\,(z^2)| + (zx)\,\overline{(zx)}\,(z^2)|\,] +$
$+ \sqrt{\frac{1}{2}}[\,|(zx)\,\overline{(zx)}\,(x^2-y^2)| - |(yz)\,\overline{(yz)}\,(x^2-y^2)|\,]\}$

$^2E_{ga}{}^C(t_{2g}{}^3) : \sqrt{\frac{1}{2}}[\,|(xy)\,(zx)\,\overline{(yz)}| - |(xy)\,\overline{(zx)}\,(yz)|\,]$

$^2E_{ga}{}^C[t_{2g}{}^2(^1A_{1g})e_g] : \sqrt{\frac{1}{3}}[\,|(xy)\,\overline{(xy)}\,(z^2)| + |(zx)\,\overline{(zx)}\,(z^2)| + (yz)\,\overline{(yz)}\,(z^2)|\,]$

$^2E_{ga}{}^C[t_{2g}{}^2(^1E_g)e_g] : \sqrt{\frac{1}{2}}\{\sqrt{\frac{1}{6}}[-2\,|(xy)\,\overline{(xy)}\,(z^2)| + |(zx)\,\overline{(zx)}\,(z^2)| + |(yz)\,\overline{(yz)}\,(z^2)|\,] -$
$- \sqrt{\frac{1}{2}}[\,|(zx)\,\overline{(zx)}\,(x^2-y^2)| - |(yz)\,\overline{(yz)}\,(x^2-y^2)|\,]\}$

$^2E_{ga}{}^C(e_g{}^3) : |(z^2)\,(x^2-y^2)\,\overline{(x^2-y^2)}|$

$^2A_2{}^Q$:

$^2T_{1ga}{}^C(t_{2g}{}^3) : \sqrt{\frac{1}{2}}[\,|(zx)\,\overline{(zx)}\,(xy)| - |(yz)\,\overline{(yz)}\,(xy)|\,]$

$^2T_{1ga}{}^C[t_{2g}{}^2(^3T_{1g})e_g] : \sqrt{\frac{1}{6}}[-2\,|(zx)\,(yz)\,\overline{(z^2)}| + |(zx)\,\overline{(yz)}\,(z^2)| + |\overline{(zx)}\,(yz)\,(z^2)|\,]$

$^2T_{1ga}{}^C[t_{2g}{}^2(^1T_{2g})e_g] : \sqrt{\frac{1}{2}}[\,|(zx)\,\overline{(yz)}\,(x^2-y^2)| - |\overline{(zx)}\,(yz)\,(x^2-y^2)|\,]$

$^2T_{1ga}{}^C[t_{2g}e_g{}^2(^3A_{2g})] : \sqrt{\frac{1}{6}}[-2\,|\overline{(xy)}\,(z^2)\,(x^2-y^2)| + |(xy)\,(z^2)\,\overline{(x^2-y^2)}| + |(xy)\,\overline{(z^2)}\,(x^2-y^2)|\,]$

$^2T_{1ga}{}^C[t_{2g}e_g{}^2(^1E_g)] : \sqrt{\frac{1}{2}}[-|(xy)\,(z^2)\,\overline{(x^2-y^2)}| + |(xy)\,\overline{(z^2)}\,(x^2-y^2)]$

$^2B_1{}^Q$:

$^2A_{2g}{}^C[t_{2g}{}^2(^1E_g)e_g] : \sqrt{\frac{1}{2}}\{\sqrt{\frac{1}{6}}[-2\,|(xy)\,\overline{(xy)}\,(x^2-y^2)| + |(zx)\,\overline{(zx)}\,(x^2-y^2)|$
$+ |(yz)\,\overline{(yz)}\,(x^2-y^2)|\,] + \sqrt{\frac{1}{2}}[\,|(zx)\,\overline{(zx)}\,(x^2-y^2)|$
$- |(yz)\,\overline{(yz)}\,(x^2-y^2)|\,]\}$

$^2E_{gb}{}^C(t_{2g}{}^3) : \sqrt{\frac{1}{6}}[-2\,|\overline{(xy)}\,(zx)\,(yz)| + |(xy)\,\overline{(zx)}\,(yz)| + |(xy)\,(zx)\,\overline{(yz)}|\,]$

$^2E_{gb}{}^C[t_{2g}{}^2(^1A_{1g})e_g] : \sqrt{\frac{1}{3}}[\,|(xy)\,\overline{(xy)}\,(x^2-y^2)| + |(zx)\,\overline{(zx)}\,(x^2-y^2)| + |(yz)\,\overline{(yz)}\,(x^2-y^2)|\,]$

$^2E_{gb}{}^{C}[t_{2g}{}^2(^1E_g)e_g]$: $\sqrt{\tfrac{1}{2}}\{\sqrt{\tfrac{1}{6}}[-2\,|(xy)\,\overline{(xy)}\,(x^2-y^2)|+|(zx)\,\overline{(zx)}\,(x^2-y^2)|$

$+|(yz)\,\overline{(yz)}\,(x^2-y^2)|]+\sqrt{\tfrac{1}{2}}[|(zx)\,\overline{(zx)}\,(z^2)|-|(yz)\,\overline{(yz)}\,(z^2)|]\}$

$^2E_{gb}{}^{C}(e_g{}^3)$: $|(z^2)\,\overline{(z^2)}\,(x^2-y^2)|$

$^2B_2{}^{Q}$:

$^2T_{2ga}{}^{C}(t_{2g}{}^3)$: $\sqrt{\tfrac{1}{2}}[|(zx)\,\overline{(zx)}\,(xy)|+|(yz)\,\overline{(yz)}\,(xy)|]$

$^2T_{2ga}{}^{C}[t_{2g}{}^2(^3T_{1g})e_g]$: $\sqrt{\tfrac{1}{6}}[-2\,|(zx)\,(yz)\,\overline{(x^2-y^2)}|+|(zx)\,\overline{(yz)}\,(x^2-y^2)|$

$+|\overline{(zx)}\,(yz)\,(x^2-y^2)|]$

$^2T_{2ga}{}^{C}[t_{2g}{}^2(^1T_{2g})e_g]$: $\sqrt{\tfrac{1}{2}}[|(zx)\,\overline{(yz)}\,(z^2)|-|\overline{(zx)}\,(yz)\,(z^2)|]$

$^2T_{2ga}{}^{C}[t_{2g}e_g{}^2(^1A_{1g})]$: $\sqrt{\tfrac{1}{2}}[|(xy)\,(z^2)\,\overline{(z^2)}|+|(xy)\,(x^2-y^2)\,\overline{(x^2-y^2)}|]$

$^2T_{2ga}{}^{C}[t_{2g}e_g{}^2(^1E_g)]$: $\sqrt{\tfrac{1}{2}}[|(xy)\,(z^2)\,\overline{(z^2)}|-|(xy)\,(x^2-y^2)\,\overline{(x^2-y^2)}|]$

$^2E_a{}^{Q}$:

$^2T_{1gb}{}^{C}(t_{2g}{}^3)$: $\sqrt{\tfrac{1}{2}}[|(yz)\,\overline{(yz)}\,(zx)|-|(xy)\,\overline{(xy)}\,(zx)|]$

$^2T_{1gb}{}^{C}[t_{2g}{}^2(^3T_{1g})e_g]$: $\sqrt{\tfrac{1}{6}}\{\tfrac{1}{2}[2\,|(yz)\,(xy)\,\overline{(z^2)}|-|(yz)\,\overline{(xy)}\,(z^2)|-|\overline{(yz)}\,(xy)\,(z^2)|]$

$+\dfrac{\sqrt{3}}{2}[2\,|(yz)\,(xy)\,\underline{(x^2-y^2)}|-|(yz)\,\underline{(xy)}\,(x^2-y^2)|$

$-|\overline{(yz)}\,(xy)\,(x^2-y^2)|]\}$

$^2T_{1gb}{}^{C}[t_{2g}{}^2(^1T_{2g})e_g]$: $\sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[-|(yz)\,\overline{(xy)}\,(x^2-y^2)|+|\overline{(yz)}\,(xy)\,(x^2-y^2)|]$

$+\dfrac{\sqrt{3}}{2}[|(yz)\,\overline{(xy)}\,(z^2)|-|\overline{(yz)}\,(xy)\,(z^2)|]\}$

$^2T_{1gb}{}^{C}[t_{2g}e_g{}^2(^3A_{2g})]$: $\sqrt{\tfrac{1}{6}}[-2\,|\overline{(zx)}\,(z^2)\,(x^2-y^2)|+|(zx)\,(z^2)\,\overline{(x^2-y^2)}|+|(zx)\,\overline{(z^2)}\,(x^2-y^2)|]$

$^2T_{1gb}{}^{C}[t_{2g}e_g{}^2(^1E_g)]$: $\sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[|(zx)\,(z^2)\,\overline{(x^2-y^2)}|-|(zx)\,\overline{(z^2)}\,(x^2-y^2)|]$

$+\dfrac{\sqrt{3}}{2}[|(zx)\,(z^2)\,\overline{(z^2)}|-|(zx)\,(x^2-y^2)\,\overline{(x^2-y^2)}|]\}$

$^2T_{2gb}{}^{C}(t_{2g}{}^3)$: $\sqrt{\tfrac{1}{2}}[|(yz)\,\overline{(yz)}\,(zx)|+|(xy)\,\overline{(xy)}\,(zx)|]$

$^2T_{2gb}{}^{C}[t_{2g}{}^2(^3T_{1g})e_g]$: $\sqrt{\tfrac{1}{6}}\{\tfrac{1}{2}[2\,|(yz)\,(xy)\,\overline{(x^2-y^2)}|-|(yz)\,\overline{(xy)}\,(x^2-y^2)|$

$-|\overline{(yz)}\,(xy)\,(x^2-y^2)|]+\dfrac{\sqrt{3}}{2}[-2\,|(yz)\,(xy)\,\overline{(z^2)}|$

$+|(yz)\,\overline{(xy)}\,(z^2)|+|\overline{(yz)}\,(xy)\,(z^2)|]\}$

$^2T_{2gb}{}^{C}[t_{2g}{}^2(^1T_{2g})e_g]$: $\sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[-|(yz)\,\overline{(xy)}\,(z^2)|+|\overline{(yz)}\,(xy)\,(z^2)|]$

$+\dfrac{\sqrt{3}}{2}[-|(yz)\,\overline{(xy)}\,(x^2-y^2)|+|\overline{(yz)}\,(xy)\,(x^2-y^2)|]\}$

$^2T_{2gb}{}^{C}[t_{2g}e_g{}^2(^1A_{1g})]$: $\sqrt{\tfrac{1}{2}}[|(zx)\,(z^2)\,\overline{(z^2)}|+|(zx)\,(x^2-y^2)\,\overline{(x^2-y^2)}|]$

$^2T_{2gb}{}^{C}[t_{2g}e_g{}^2(^1E_g)]$: $\sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[-|(zx)\,(z^2)\,\overline{(z^2)}|+|(zx)\,(x^2-y^2)\,\overline{(x^2-y^2)}|]$

$+\dfrac{\sqrt{3}}{2}[|(zx)\,(z^2)\,\overline{(x^2-y^2)}|-|(zx)\,\overline{(z^2)}\,(x^2-y^2)]\}$

$^2E_b{}^{Q}$:

$^2T_{1gc}{}^{C}(t_{2g}{}^3)$: $\sqrt{\tfrac{1}{2}}[|(xy)\,\overline{(xy)}\,(yz)|-|(zx)\,\overline{(zx)}\,(yz)|]$

$^2T_{1gc}{}^{C}[t_{2g}{}^2(^3T_{1g})e_g]$: $\sqrt{\tfrac{1}{6}}\{\tfrac{1}{2}[2\,|(xy)\,(zx)\,\overline{(z^2)}|-|(xy)\,\overline{(zx)}\,(z^2)|$

$-|\overline{(xy)}\,(zx)\,(z^2)|]+\dfrac{\sqrt{3}}{2}[-2\,|(xy)\,(zx)\,\overline{(x^2-y^2)}|$

$+|(xy)\,\overline{(zx)}\,(x^2-y^2)|+|\overline{(xy)}\,(zx)\,(x^2-y^2)|]\}$

$$\begin{aligned}
{}^2T_{1gc}{}^{C}[t_{2g}{}^2({}^1T_{2g})e_g] :\ & \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[-|(xy)\overline{(zx)}(x^2-y^2)|+|\overline{(xy)}(zx)(x^2-y^2)|] \\
& +\frac{\sqrt{3}}{2}[|\overline{(xy)}(zx)(z^2)|-|(xy)\overline{(zx)}(z^2)|]\}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1gc}{}^{C}[t_{2g}e_g{}^2({}^3A_{2g})] :\ & \sqrt{\tfrac{1}{6}}[-2|\overline{(yz)}(z^2)(x^2-y^2)|+|(yz)(z^2)\overline{(x^2-y^2)}| \\
& +|(yz)\overline{(z^2)}(x^2-y^2)|]
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1gc}{}^{C}[t_{2g}e_g{}^2({}^1E_g)] :\ & \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[|(yz)(z^2)\overline{(x^2-y^2)}|-|(yz)\overline{(z^2)}(x^2-y^2)|] \\
& +\sqrt{\tfrac{3}{2}}[|(yz)(x^2-y^2)\overline{(x^2-y^2)}|-|(yz)(z^2)\overline{(z^2)}|]\}
\end{aligned}$$

$${}^2T_{2gc}{}^{C}(t_{2g}{}^3) :\ \sqrt{\tfrac{1}{2}}[|(xy)\overline{(xy)}(yz)|+|(zx)\overline{(zx)}(yz)|]$$

$$\begin{aligned}
{}^2T_{2gc}{}^{C}[t_{2g}{}^2({}^3T_{1g})e_g] :\ & \sqrt{\tfrac{1}{6}}\{\tfrac{1}{2}[2|(xy)(zx)\overline{(x^2-y^2)}|-|(xy)\overline{(zx)}(x^2-y^2)| \\
& -|\overline{(xy)}(zx)(x^2-y^2)|]+\frac{\sqrt{3}}{2}[2|(xy)(zx)\overline{(z^2)}| \\
& -|(xy)\overline{(zx)}(z^2)|-|\overline{(xy)}(zx)(z^2)|]\}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{2gc}{}^{C}[t_{2g}{}^2({}^1T_{2g})e_g] :\ & \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[-|(xy)\overline{(zx)}(z^2)|+|\overline{(xy)}(zx)(z^2)|] \\
& +\frac{\sqrt{3}}{2}[|(xy)\overline{(zx)}(x^2-y^2)|-|\overline{(xy)}(zx)(x^2-y^2)|]\}
\end{aligned}$$

$${}^2T_{2gc}{}^{C}[t_{2g}e_g{}^2({}^1A_{1g})] :\ \sqrt{\tfrac{1}{2}}[|(yz)(z^2)\overline{(z^2)}|+|(yz)(x^2-y^2)\overline{(x^2-y^2)}|]$$

$$\begin{aligned}
{}^2T_{2gc}{}^{C}[t_{2g}e_g{}^2({}^1E_g)] :\ & \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}[|(yz)(x^2-y^2)\overline{(x^2-y^2)}|-|(yz)(z^2)\overline{(z^2)}|] \\
& +\frac{\sqrt{3}}{2}[-|(yz)(z^2)\overline{(x^2-y^2)}|+|(yz)\overline{(z^2)}(x^2-y^2)|]\}
\end{aligned}$$

APPENDIX B

ENERGY MATRICES OF THE d^3 CONFIGURATION: QUADRATE FIELDS

(All matrices are symmetric.)

${}^4B_1{}^Q$	${}^4A_{2g}{}^C(t_{2g}{}^3)$	${}^4B_2{}^Q$	${}^4T_{2ga}{}^C(t_{2g}{}^2e_g)$
${}^4A_2{}^C(t_{2g}{}^3)$	$-12Dq-7Dt$ $+3A-15B-E$	${}^4T_{2ga}{}^C(t_{2g}{}^2e_g)$	$-2Dq-7Dt$ $+3A-15B-E$

${}^4A_2{}^Q$	${}^4T_{1ga}{}^C(t_{2g}{}^2e_g)$	${}^4T_{1ga}{}^C(t_{2g}e_g{}^2)$
${}^4T_{1ga}{}^C(t_{2g}{}^2e_g)$	$-2Dq+4Ds-2Dt$ $+3A-3B-E$	$+6B$
${}^4T_{1ga}{}^C(t_{2g}e_g{}^2)$		$8Dq-2Ds+8Dt$ $+3A-12B-E$

${}^4E^Q$	${}^4T_{2gb}{}^C(t_{2g}{}^2e_g)$	${}^4T_{1gb}{}^C(t_{2g}{}^2e_g)$	${}^4T_{1gb}{}^C(t_{2g}e_g{}^2)$
${}^4T_{2gb}{}^C(t_{2g}{}^2e_g)$	$-2Dq+\frac{7}{4}Dt$ $+3A-15B-E$	$-\frac{\sqrt{3}}{4}(4Ds+5Dt)$	0
${}^4T_{1gb}{}^C(t_{2g}{}^2e_g)$		$-2Dq-2Ds-\frac{3}{4}Dt$ $+3A-3B-E$	$+6B$
${}^4T_{1gb}{}^C(t_{2g}e_g{}^2)$			$8Dq+Ds+3Dt$ $+3A-12B-E$

$^2A_1{}^Q$	$^2A_{1g}{}^C[t_{2g}{}^2(^1E_g)e_g]$	$^2E_{ga}{}^C(t_{2g}{}^3)$	$^2E_{ga}{}^C[t_{2g}{}^2(^1A_{1g})e_g]$	$^2E_{ga}{}^C[t_{2g}{}^2(^1E_g)e_g]$	$^2E_{ga}{}^C(e_g{}^3)$
$^2A_{1g}{}^C[t_{2g}{}^2(^1E_g)e_g]$	$-\frac{1}{6}(12Dq+7Dt)$ $+3A-11B+3C$ $-E$	0	$\frac{2}{3}(3Ds-5Dt)$	$5\frac{5}{6}\,Dt$	0
$^2E_{ga}{}^C(t_{2g}{}^3)$		$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$-6\sqrt{2}B$	$-3\sqrt{2}\,B$	0
$^2E_{ga}{}^C[t_{2g}{}^2(^1A_{1g})e_g]$			$\frac{2}{3}(-3Dq+3Ds+2Dt)$ $+3A+8B+6C$ $-E$	$\frac{2}{3}(3Ds-5Dt)$ $+10B$	$\sqrt{3}\,(2B+C)$
$^2E_{ga}{}^C[t_{2g}{}^2(^1E_g)e_g]$				$-\frac{1}{6}(12Dq+7Dt)$ $+3A-B+3C$ $-E$	$2\sqrt{3}\,B$
$^2E_{ga}{}^C(e_g{}^3)$					$18Dq-2Ds+8Dt$ $+3A-8B+4C$ $-E$

$^2A_2{}^Q$	$^2T_{1ga}{}^C(t_{2g}{}^3)$	$^2T_{1ga}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$	$^2T_{1ga}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$	$^2T_{1ga}{}^C[t_{2g}e_g{}^2(^3A_{2g})]$	$^2T_{1ga}{}^C[t_{2g}e_g{}^2(^1E_g)]$
$^2T_{1ga}{}^C(t_{2g}{}^3)$	$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$3B$	$-3B$	0	$-2\sqrt{3}\,B$
$^2T_{1ga}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$		$-2Dq+4Ds-2Dt$ $+3A+3C$ $-E$	$-3B$	$-3B$	$-3\sqrt{3}\,B$
$^2T_{1ga}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$			$-2Dq-7Dt$ $+3A-6B+3C$ $-E$	$+3B$	$\sqrt{3}\,B$
$^2T_{1ga}{}^C[t_{2g}e_g{}^2(^3A_{2g})]$				$8Dq-2Ds+8Dt$ $+3A-6B+3C$ $-E$	$2\sqrt{3}\,B$
$^2T_{1ga}{}^C[t_{2g}e_g{}^2(^1E_g)]$					$8Dq-2Ds+8Dt$ $+3A-2B+3C$ $-E$

$^2B_1{}^Q$	$^2A_{2g}{}^C[t_{2g}{}^2(^1E_g)e_g]$	$^2E_{gb}{}^C(t_{2g}{}^3)$	$^2E_{gb}{}^C[t_{2g}{}^2(^1A_{1g})e_g]$	$^2E_{gb}{}^C[t_{2g}{}^2(^1E_g)e_g]$	$^2E_{gb}{}^C(e_g{}^3)$
$^2A_{2g}{}^C[t_{2g}{}^2(^1E_g)e_g]$	$-\frac{1}{6}(12Dq+7Dt)$ $+3A+9B+3C$ $-E$	0	$\frac{2}{3}(3Ds-5Dt)$	$-\frac{1}{3}(-24Ds+5Dt)$	0
$^2E_{gb}{}^C(t_{2g}{}^3)$		$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$-6\sqrt{2}\,B$	$-3\sqrt{2}\,B$	0
$^2E_{gb}{}^C[t_{2g}{}^2(^1A_{1g})e_g]$			$-\frac{1}{3}(6Dq+6Ds+11Dt)$ $+3A+8B+6C$ $-E$	$-\frac{2}{3}(3Ds-5Dt)$ $+10B$	$\sqrt{3}\,(2B+C)$
$^4E_{gb}{}^C[t_{2g}{}^2(^1E_g)e_g]$				$-\frac{1}{6}(12Dq+7Dt)$ $+3A-B+3C$ $-E$	$2\sqrt{3}\,B$
$^2E_{gb}{}^C(e_g{}^3)$					$18Dq+2Ds+13Dt$ $+3A-8B+4C$ $-E$

$^2B_2{}^Q$	$^2T_{2ga}{}^C(t_{2g}{}^3)$	$^2T_{2ga}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$	$^2T_{2ga}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$	$^2T_{2ga}{}^C[t_{2g}e_g{}^2(^1A_{1g})]$	$^2T_{2ga}{}^C[t_{2g}e_g{}^2(^1E_g)]$
$^2T_{2ga}{}^C(t_{2g}{}^3)$	$-12Dq-7Dt$ $+3A+5C$ $-E$	$3\sqrt{3}\,B$	$-5\sqrt{3}\,B$	$4B+2C$	$-2B$
$^2T_{2ga}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$		$-2Dq-7Dt$ $+3A-6B+3C$ $-E$	$-3B$	$3\sqrt{3}\,B$	$-3\sqrt{3}\,B$
$^2T_{2ga}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$			$-2Dq+4Ds-2Dt$ $+3A+4B+3C$ $-E$	$-\sqrt{3}\,B$	$-\sqrt{3}\,B$
$^2T_{2ga}{}^C[t_{2g}e_g{}^2(^1A_{1g})]$				$8Dq-2Ds+8Dt$ $+3A+6B+5C$ $-E$	$4Ds+5Dt$ $-10B$
$^2T_{2ga}{}^C[t_{2g}e_g{}^2(^1E_g)]$					$8Dq-2Ds+8Dt$ $+3A-2B+3C$ $-E$

$^2E^Q$	$^2T_{1gb}{}^C(t_{2g}{}^3)$	$^2T_{1gb}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$	$^2T_{1gb}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$	$^2T_{1gb}{}^C[t_{2g}e_g{}^2(^3A_{2g})]$
$^2T_{1gb}{}^C(t_{2g}{}^3)$	$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$3B$	$-3B$	0
$^2T_{1gb}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$		$-\frac{1}{4}(8Dq+8Ds+3Dt)$ $+3A+3C$ $-E$	$-3B$	$-3B$
$^2T_{1gb}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$			$\frac{1}{4}(-8Dq+7Dt)$ $+3A-6B+3C$ $-E$	$3B$
$^2T_{1gb}{}^C[t_{2g}e_g{}^2(^3A_{2g})]$				$8Dq+Ds+3Dt$ $+3A-6B+3C$ $-E$
$^2T_{1gb}{}^C[t_{2g}e_g{}^2(^1E_g)]$				
$^2T_{2gb}{}^C(t_{2g}{}^3)$				
$^2T_{2gb}{}^C[t_{2g}{}^2(^3T_{1g})e_g]$				
$^2T_{2gb}{}^C[t_{2g}{}^2(^1T_{2g})e_g]$				
$^2T_{2gb}{}^C[t_{2g}e_g{}^2(^1A_{1g})]$				
$^2T_{2gb}{}^C[t_{2g}e_g{}^2(^1E_g)]$				

${}^2T_{1gb}{}^C[t_{2g}e_g{}^2({}^1E_g)]$	${}^2T_{2gb}{}^C(t_{2g}{}^3)$	${}^2T_{2gb}{}^C[t_{2g}{}^2({}^3T_{1g})e_g]$	${}^2T_{2gb}{}^C[t_{2g}{}^2({}^1T_{2g})e_g]$	${}^2T_{2gb}{}^C[t_{2g}e_g{}^2({}^1A_{1g})]$	${}^2T_{2gb}{}^C[t_{2g}e_g{}^2({}^1E_g)]$
$-2\sqrt{3}\,B$	$3Ds-5Dt$	0	0	0	0
$-3\sqrt{3}\,B$	0	$-\frac{\sqrt{3}}{4}(4Ds+5Dt)$	0	0	0
$\sqrt{3}\,B$	0	0	$-\frac{\sqrt{3}}{4}(4Ds+5Dt)$	0	0
$2\sqrt{3}\,B$	0	0	0	0	0
$8Dq+Ds+3Dt$ $+3A-2B+3C$ $-E$	0	0	0	$\frac{\sqrt{3}}{2}(4Ds+5Dt)$	0
	$-12Dq-7Dt$ $+3A+5C$ $-E$	$3\sqrt{3}\,B$	$-5\sqrt{3}\,B$	$4B+2C$	$-2B$
		$\frac{1}{4}(-8Dq+7Dt)$ $+3A-6B+3C$ $-E$	$-3B$	$3\sqrt{3}\,B$	$-3\sqrt{3}\,B$
			$-\frac{1}{4}(8Dq+8Ds+3Dt)$ $+3A+4B+3C$ $-E$	$-\sqrt{3}\,B$	$-\sqrt{3}\,B$
				$8Dq+Ds+3Dt$ $+3A+6B+5C$ $-E$	$-\frac{1}{2}(4Ds+5Dt)$ $-10B$
					$8Dq+Ds+3Dt$ $+3A-2B+3C$ $-E$