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Semi-Empirical Evaluations of the Racah *B* and *C* Parameters from the Crystal Field Spectra of Chromium(III) Complexes*

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The methods that have been used in the past to derive the electron repulsion parameters, *B* and *C*, from the spectra of octahedral Cr(III) complexes have been reinvestigated. A number of Cr(III) complexes were chosen for which the spin-forbidden transitions to the three lowest doublet states are known. The complete strong field and weak field matrices have been used to derive the parameters *B* and *C* from the known spectral data. A convenient graphical method is given which makes it a simple matter to choose the "best" values of *B* and *C*. The assumption that $C = 4B$ was discarded because it is incompatible with the nephelauxetic effect.

The three parameter (Δ, B, C) crystal field theory reproduces the band positions of the *d–d* transitions of most Cr(III) complexes to within a few hundred wavenumbers. Because the free ion theory of Condon and Shortley involves about the same uncertainty, it is felt that the results obtained here represent the best that can be obtained from the three parameter crystal field theory.

Einige Methoden, die bislang benutzt wurden, um die Elektronenabstoßungsparameter *B* und *C* aus den Spektren der oktaedrischen Cr(III)-Komplexe zu berechnen, wurden nochmals untersucht, und zwar wurden solche Cr(III)-Komplexe ausgewählt, für die die spinverbotenen Übergänge in die drei untersten Doublet-Zustände bekannt sind. Mittels der vollständingen Matrizen für starkes und schwaches Feld wurden dann die Parameter *B* und *C* aus den vorliegenden spektralen Daten berechnet, und eine brauchbare graphische Methode wird angegeben, die das Auffinden der „besten" Werte von *B* und *C* einfach macht. Die Annahme $C = 4B$ wurde verworfen, weil sie mit dem nephelauxetischen Effekt unvereinbar ist.

Die drei-parametrige (Δ, *B*, *C*)-Kristallfeldtheorie gibt die Lagen der Banden der *d–d* Übergänge bei den meisten Cr(III)-Komplexen bis auf einige hundert Wellenzahlen richtig wieder. Weil die Theorie der freien Ionen von Condon und Shortley etwa gleich große Fehler impliziert, kann man annehmen, daß die hier erzielten Resultate das Beste darstellen, was von einer drei-parametrigen Kristallfeldtheorie zu erhalten ist.

On a réétudié les méthodes utilisées dans le passé pour obtenir les paramètres de répulsion électronique, *B* et *C*, à partir des spectres des complexes octaédriques de Cr (III). Le choix s'est porté sur un certain nombre de complexes de Cr (III) pour lesquels les transitions interdites par le spin vers les trois plus bas états doublets sont connues. Les matrices complètes à champ fort et à champ faible ont été utilisées pour obtenir les paramètres *B* et *C* à partir des données spectrales connues. Une méthode graphique convenable permet de choisir simplement les meilleures valeurs de *B* et *C*. L'hypothèse selon laquelle $C = 4B$ a été rejetée parcequ'elle est incompatible avec l'effet nephelauxetique.

La théorie du champ cristallin à trois paramètres (Δ, B, C) reproduit les positions des bandes des transitions $d - d$ de la plupart des complexes de Cr (III) à moins de quelques centaines de nombre d'onde près. La théorie de l'ion libre de Condon et Shortley comportant la même incertitude, il semble que les résultats obtenus ici représentent ce que l'on peut obtenir de mieux dans la théorie du champ cristallin à trois paramètres.

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* Dedicated to the memory of Professor Hans-Ludwig Schläfer.

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Introduction

The crystal field theory as developed by Bethe [1], Van Vleck [2] and others [3], predicts that the energies of the states derived from a d^n configuration in a cubic field can be given in terms of three parameters: Δ (or 10Dq), the ligand field strength, and the Racah electron repulsion parameters, B and C. The theory predicts qualitatively the correct type of splittings of the d orbitals, but is only partially successful in a quantitative manner [4–6]. Molecular orbital theory [7] has overcome some of the shortcomings of the crystal field model, but calculations have been carried out for only a limited number of examples [8–10], simply because the method is too cumbersome and time-consuming for survey-type calculations. The crystal field model, on the other hand, is straightforward and may be modified semi-empirically for covalency effects [11].

The spectra of transition metal complexes may be analyzed by crystal field theory according to either the weak field or the strong field formalism. In the former, the states of the complex are considered to be those of the free ion, perturbed by the crystal field. The matrix elements of the crystal field potential in terms of Dq (defined in Ref. [2]) for d^3 complex ions were first obtained by Finkelstein and Van Vleck [12] for Cr(III) in chrome alum. Orgel [13] has given the solutions for other d^n ions.

In the case of strong fields, the energy levels of the complex ion are determined mainly by the crystal field. In cubic fields, the five degenerate d orbitals of the free ion are split into a three-fold degenerate t_{2g} set and a two-fold degenerate e_g set. This splitting is generally called 10Dq or Δ. The states are then determined from crystal field configurations by assigning electrons to the t_{2g} or e_g orbitals. Tanabe and Sugano [14] have determined the complete solutions for the d^3 configuration in a cubic field by starting with a set of wave-functions diagonal in the crystal field potential term and then applying the electron repulsion term of the Hamiltonian as a perturbation.

Since the only difference between the weak and strong field formalisms is the starting point of the calculation (Finkelstein and Van Vleck started with wave-functions diagonal in the electrostatic interaction term), the strong and weak field matrices must be completely equivalent[1]. This will be shown explicitly for the quartet matrices of d^3 ions in Sect. 1 of the Calculations, and for the doublet matrices in Sect. 2.

Two points of view may be taken in comparing the predictions of the crystal field theory with observed spectra: [i] to what extent can the observed spectra be described by a consistent set of crystal field parameters, and [ii] what information may be obtained from the empirical parameters about the bonding in transition metal ion complexes? It is clear that [i] must be answered before [ii] should be attempted.

Various methods have been used in the past to derive the electron repulsion parameters B and C from the strong field point of view [15, 16]. Jorgensen [16–22] has by far been the most prolific author in this field. Several approximations are, however, inherent in Jorgensen's approach and it is the validity and consequences of these approximations that inspired the present work.

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[1] Note, however, that for d^4, d^5, d^6 and d^7 in octahedral fields, there is a change in ground state in the extreme weak and strong field cases [4].

Table 1. *Crystal field states of an octahedral* Cr(III) *complex*

Free ion state	Crystal field state (O_h)	Strong field configuration
^4F	$^4A_{2g}$[a]	t_{2g}^3
	$^4T_{2g}$	$t_{2g}^2e_g$
	$^4T_{1g}$	$t_{2g}^2e_g$
^2G	^2E_g	t_{2g}^3
	$^2T_{1g}$	
	$^2T_{2g}$	

[a] Ground state.

Only the spectra of those Cr(III) complexes for which the low-lying spin-forbidden transitions have been observed will be analyzed. Both the strong field and weak field models will be applied rigorously. The effect of including the Racah-Trees correction [23], $\alpha L(L+1)$, first used by Pryce, *et al.* [24] for Ni(II) fluosilicate and recently proposed for octahedral Cr(III) and tetrahedral Co(II) complexes by Ferguson and Wood [25][2] will also be investigated. Spin-orbital coupling, which is known to be relatively unimportant in describing the optical spectra of Cr(III) complexes [25], will be neglected, and only octahedral or nearly octahedral complexes will be considered.

The crystal field states of an octahedral Cr(III) complex which are of interest here are collected in Table 1. The free ion levels and the strong field configurations giving rise to these states are also indicated. (The subscript g, denoting parity, will be omitted for the remainder of the text).

Spectral Data

The observable d–d transitions of Cr(III) complexes lie in the visible and near infra-red region of the spectrum, and the general features of the absorption spectra have been discussed in many places [4, 6, 17, 26, 27]. The broad, structureless spin-allowed transitions to the $^4T_2$ and $^4T_1(F)$ states and the sharp, low-intensity spin-forbidden transition to the lowest doublet state, ^2E, have received the most attention in the literature. The third quartet-quartet transition, $^4T_1(P; t_2e^2) \leftarrow {}^4A_2$, is usually masked by the much more intense charge-transfer transitions beginning at approximately 30 kK[3] [17]. The other low-lying doublets, $^2T_1$ and $^2T_2$, have received very little attention experimentally, and then only in selected cases such as in the spectrum of Cr^{+3} as an impurity in a variety of inorganic host lattices [15].

The pertinent spectral data and assignments are given in Table 2 together with the appropriate literature references. Although the complexes in Table 2 are all essentially octahedral, splittings due to lower symmetry components in the crystal field have been observed for some [29, 34, 35]. Spin-orbital splittings

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[2] The author is indebted to D. L. Wood for kindly supplying a manuscript of this paper prior to publication.

[3] $kK = 1000\,cm^{-1}$.

Table 2. *Frequencies of the observed d–d transitions in* Cr(III) *complexes (in kK)*

Complex[a]	$\bar{\nu}(^4T_2)$	$\bar{\nu}(^4T_1)$	$\bar{\nu}(^2E)$	$\bar{\nu}(^2T_1)$	$\bar{\nu}(^2T_2)$	Refs.
$[CrF_6]^{-3}$	15.06	22.70	(15.67)[b]	(16.56)	—	[28]
Ruby	18.15	25.73	14.43	15.11	21.14	[29]
$[Cr(NH_3)_6]^{+3}$	21.45	28.41	15.12	(15.98)	—	[14]
$[Cr(ur)_6]^{+3}$	16.15	22.60	14.19	(15.04)	20.83	[30, 31]
$[Cr(H_2O)_6]^{+3}$	18.00	24.60	14.90	(15.10)	21.00	[14]
$[Cr(ox)_3]^{-3}$	17.50	23.81	14.44	(15.19)	20.53	[32–34]
$[Cr(CN)_6]^{-3}$	26.70	32.68	12.46	(13.07)	18.37	[18, 35]
$[Cr(CH_3)_6]^{-3}$	20.80	26.50	14.02	—	—	[35, 36]
$CrCl_3$	13.62	18.90	14.33	(14.75)	—	[35]
$CrBr_3$	13.43	17.57	14.00	14.36	18.92	[37]
$Cr(exan)_3$	16.00	20.20	12.73	—	—	[38]

[a] Abbreviations for ligands: ur = urea; ox = oxalate; exan = ethylxanthate.
[b] Figures in brackets are tentative assignments.

can usually be observed only at very low temperatures and under high resolution. Since most of the data refer to room temperature or 77° K, this effect will be neglected.

The $^2E \leftarrow {}^4A_2$ assignments are the most reliable in Table 2, because the transition can be seen in emission as well as in absorption [27]. The $^2T_1 \leftarrow {}^4A_2$ transition must be distinguished from vibrational structure of the $^2E \leftarrow {}^4A_2$ transition and is often quite difficult to identify. Unambiguous assignments of these two transitions are especially difficult to make when the bands lie very near to the maximum of the first spin-allowed transition. The $^2T_2 \leftarrow {}^4A_2$ transition is somewhat easier to locate, since no other doublets are expected in the spectral region where it occurs (usually between the first two spin-allowed bands).

Ruby was included in these calculations, because it is the only Cr(III) compound for which the assignment of all three spin-forbidden transitions has been confirmed by optical pumping experiments [29]. It should be noted, however, that the data for ruby in Table 2 were obtained from Ref. [29] by ignoring the splitting due to the combined effect of spin-orbital coupling and the trigonal field.

Because the spin-allowed transitions are rather broad, the $^4T_2$ frequencies are accurate to only 100 cm^{-1}, while the $^4T_1(F)$ frequencies are uncertain to 200 cm^{-1}. The spin-forbidden transition energies are known to at least 50 cm^{-1}, and in most cases to $\pm 10\ cm^{-1}$.

Calculations

The three parameters, Δ, B and C, are treated as empirical. Both the weak and strong field models equate the energy difference between the $^4A_2$ ground state and the lowest quartet state of an octahedral Cr(III) complex to Δ or 10Dq. The position of the $^4T_2 \leftarrow {}^4A_2$ transition thus gives Δ directly, and this value will be used throughout all the calculations. With different ligands, a particular metal ion shows a range of Δ values, and in this way the spectrochemical series for ligands is found [39]. Upper limits for B and C can be obtained from an analysis of the free ion spectrum according to the theory of Condon and Shortley [40]. When spin-orbital coupling is neglected, the five lowest free ion states of Cr^{+3} can be reproduced to within about 0.20 kK with the following parameters[4] [25, 35]: $B = 0.980$ kK; $C = 3.41$ kK, and $\alpha = 0.0782$ kK.

1. Derivation of B from the Spin-Allowed Transitions of Cr(III) *Complexes*

If only the diagonal elements of the strong field quartet matrix given by Tanabe and Sugano [14] are considered, the separation between the two lowest spin-allowed transitions is approximately $12\,B$. If configuration interaction is included, i. e., the off-diagonal elements of the ${}^4T_1$ matrix are included, this separation is given by Eq. (1):

$$\bar{\nu}({}^4T_1(F)) - \bar{\nu}({}^4T_2) = \tfrac{1}{2}(\Delta + 15B - \sqrt{\Delta^2 - 18\Delta B + 225\,B^2}) \tag{1}$$

where $\bar{\nu}$ are the transition frequencies.

In order to use the weak field matrices of Finkelstein and Van Vleck [12], the Russell-Saunders energies [40] of the free ion states must be added to the diagonal terms. The ${}^4T_1$ secular equation, including the Racah-Trees correction [23], is given in determinantal form as:

$$\begin{vmatrix} E({}^4F) + 0.6\,\Delta - E & 0.4\,\Delta \\ 0.4\,\Delta & E({}^4P) - E \end{vmatrix} = 0 \tag{2}$$

where E denotes the eigenvalues of the ${}^4T_1$ states.

Since
$$\begin{aligned} E({}^4T_1) &= E({}^4A_2) + \bar{\nu}({}^4T_1) \\ &= -1.2\Delta + \bar{\nu}({}^4T_1), \\ E({}^4F) &= 0, \\ E({}^4P) &= 15B - 10\alpha\,; \end{aligned}$$

Eq. (2) becomes:
$$\begin{vmatrix} 1.8\Delta - \bar{\nu} & 0.4\Delta \\ 0.4\Delta & 15B - 10\alpha + 1.2\Delta - \bar{\nu} \end{vmatrix} = 0 \tag{3}$$

where $\bar{\nu}$ is written for $\bar{\nu}({}^4T_1)$.

Upon solving Eq. (3), B has the form:

$$B({}^4T_1) = \frac{(2\Delta - \bar{\nu})(\bar{\nu} - \Delta)}{(27\Delta - 15\bar{\nu})} + \frac{2}{3}\alpha\,. \tag{4}$$

Only the first term of Eq. (4) is obtained from Eq. (1), demonstrating the equivalence of the strong and weak field equations if the Racah-Trees correction is neglected. Since $\alpha = 78.2\ \mathrm{cm}^{-1}$ for the free Cr^{+3} ion [35], the inclusion of the Racah-Trees correction increases the B value determined from the quartet states by $52\ \mathrm{cm}^{-1}$.

The B values derived from Eq. (4) are given in column two of Table 3. The complexes have been arranged in order of decreasing B, demonstrating the well-known nephelauxetic effect [19]. The uncertainty in $B({}^4T_1)$ is $\pm 45\ \mathrm{cm}^{-1}$.

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[4] The parameters given in Ref. [25] differ slightly, but not significantly from those given here.

Table 3. *The Racah C parameters*[a] *for the doublet states at* $B(^4T_1)$

Complex	$B(^4T_1)$	C		
		^2E	$^2T_1$	$^2T_2$
$[CrF_6]^{-3}$	0.910	2.92	2.89	—
Ruby	0.822	2.66	2.59	2.60
$[Cr(NH_3)_6]^{+3}$	0.711	3.08	3.15	—
$[Cr(ur)_6]^{+3}$	0.697	2.86	2.91	2.85
$[Cr(H_2O)_6]^{+3}$	0.695	3.07	2.92	2.82
$[Cr(ox)_3]^{-3}$	0.664	2.99	3.03	2.79
$[Cr(CN)_6]^{-3}$	0.589	2.45	2.49	2.26
$[Cr(CH_3)_6]^{-3}$	0.577	3.02	—	—
$CrCl_3$	0.575	3.18	3.15	—
$CrBr_3$	0.440	3.37	3.37	3.02
$Cr(exan)_3$	0.436	2.94	—	—

[a] In kK, derived from the weak field matrices with $\alpha = 0.0782$ kK. The corresponding parameters from the strong field matrices, or the weak field matrices with $\alpha = 0$, are obtained by subtracting 0.052 kK from $B(^4T_1)$ and adding 0.29, 0.33, and 0.18 kK to the C values for the ^2E, $^2T_1$ and $^2T_2$, respectively.

2. *Derivation of B and C from the Spin-Forbidden Transitions of* Cr(III) *Complexes*

a) Approximate Methods

In the lowest approximation of the crystal field model, only the diagonal elements of the Tanabe-Sugano matrices are used [28, 41]. This, however, implies that the ^2E and $^2T_1$ states are degenerate, which is clearly not the case. In the next higher approximation, configuration interaction between states of the same multiplicity and symmetry, but arising from different strong field configurations is included and $C = 4B$ is assumed [18, 20]. The latter approximation has its origin in the free ion analysis where the ratio between C and B is approximately four. Jorgensen [20] has given equations for the frequencies of the lowest three doublets, assuming $C = 4B$, in terms of the diagonal strong field elements plus a term of the type $-k\,B^2/\Delta$. The latter was derived from the off-diagonal elements of the Tanabe-Sugano matrices. These equations are given below:

$$\bar{\nu}(^2E) = 21B - 90B^2/\Delta\,, \tag{5}$$

$$\bar{\nu}(^2T_1) = 21B - 24B^2/\Delta\,, \tag{6}$$

$$\bar{\nu}(^2T_2) = 35B - 176B^2/\Delta\,. \tag{7}$$

Previous investigations [20] focused mainly on the ^2E transition, and were thus attempts to fit three observed transitions ($^4T_2$, $^4T_1(F)$, and ^2E) with only two parameters, Δ and B. However, different B values were found for the spin-allowed and spin-forbidden transitions. The difference between the two parameters was rationalized by noting that the spin-allowed transitions are interconfigurational, while the $^2E \leftarrow {}^4A_2$ transition is intraconfigurational. To denote this difference, the parameter found from Eq. (1) was labelled B_{35}, while that found from the diagonal element of the ^2E matrix or Jorgensen's equations was called B_{55} [20]. The subscripts arise from Bethe's notation, where the t_2 and e orbitals are labelled γ_5 and γ_3, respectively.

The data available in this study make possible a test of the above treatment. Since all of the three lowest spin-forbidden transitions are intraconfigurational, $t_2^3 \leftarrow t_2^3$, the B_{55} parameter determined from these three transitions should be identical for a particular complex.

The B_{55} parameters derived from Jorgensen's equations need not be reproduced here, but are, in fact, not identical for the three doublet states of the complexes of this investigation. For $CrBr_3$, they differ by as much as 200 cm^{-1}. These equations only approximate the effect of configuration interaction and generally overestimate the B calculated from the complete strong field equations, assuming $C = 4B$, by 0.140, 0.012 and 0.050 kK for the ^2E, $^2T_1$ and $^2T_2$ states, respectively.

The approximation $C = 4B$ is suspect since it is inconsistent with the nephelauxetic series (see Discussion) and will be discarded in the calculations reported below.

b) Derivation of B and C from the Complete Strong and Weak Field Matrices

The usual approach in this type of calculation [15, 26] is to solve for the eigenvalues directly, varying the parameters until a "best fit" is obtained. In this investigation a different mode of attack is used.

The secular equations for the three doublet states were obtained from the Tanabe-Sugano matrices [14], and the eigenvalue equated to the energy of the ground state $(-1.2\Delta - 15B)$ plus the energy of the observed transition (analogous to Eqs. (2) to (3)). As an example, the rewritten secular equation for the lowest ^2E state is given in Eq. (8) in determinantal form. For the sake of clarity, $\bar{\nu}$ is written for $\bar{\nu}(^2E)$. The strong field configurations giving rise to the four ^2E states are also indicated.

$$\begin{array}{c}
\begin{array}{cccc} t_2^3 & t_2^2e & t_2^2e & e^3 \end{array} \\
\begin{vmatrix}
9B+3C-\bar{\nu} & -6\sqrt{2}B & -3\sqrt{2}B & 0 \\
-6\sqrt{2}B & \Delta+23B+6C-\bar{\nu} & 10B & \sqrt{3}(2B+C) \\
-3\sqrt{2}B & 10B & \Delta+14B+3C-\bar{\nu} & 2\sqrt{3}B \\
0 & \sqrt{3}(2B+C) & 2\sqrt{3}B & 3\Delta+7B+4C-\bar{\nu}
\end{vmatrix}
\end{array} = 0. \quad (8)$$

The weak field secular equations [12] were treated in the same manner as the strong field equations, except that the Racah-Trees correction was included in the analysis. For illustrative purpose, the weak field secular equation for the lowest ^2E state is given in Eq. (9) in determinantal form. Again $\bar{\nu}$ is written for $\bar{\nu}(^2E)$, and the free ion states from which the four ^2E states arise are also indicated.

$$\begin{array}{c}
\begin{array}{cccc} ^2H & ^2G & ^2D_a & ^2D_b \end{array} \\
\begin{vmatrix}
9B+3C+18\alpha+1.4\Delta-\bar{\nu} & 0.964\Delta & 0.548\Delta & -0.1195\Delta \\
0.964\Delta & 4B+3C+8\alpha+1.1715\Delta-\bar{\nu} & 0.586\Delta & -0.766\Delta \\
0.548\Delta & 0.586\Delta & 22B+7C-6\alpha+1.5\Delta-\bar{\nu} & 3\sqrt{21}B-0.327\Delta \\
-0.1195\Delta & -0.766\Delta & 3\sqrt{21}B-0.327\Delta & 18B+3C-6\alpha+0.9285\Delta-\bar{\nu}
\end{vmatrix}
\end{array} = 0. \, (9)$$

In order to solve Eqs. (8) and (9), the observed Δ and spin-forbidden transition frequency from Table 2 for a particular complex were substituted into the

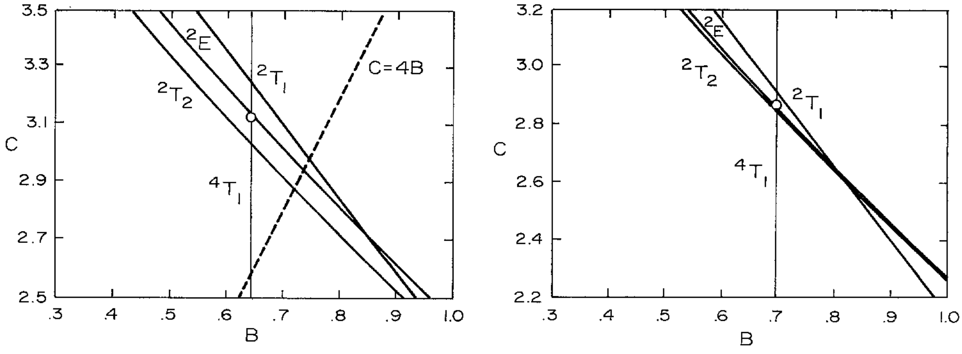

Fig. 1a Fig. 1b

Fig. 1a and b. C as a function of B (in kK) for $[Cr(ur)_6]^{+3}$; a) from strong or weak field matrices with $\alpha = 0$, b) from weak field matrices with $\alpha = 0.0782$ kK

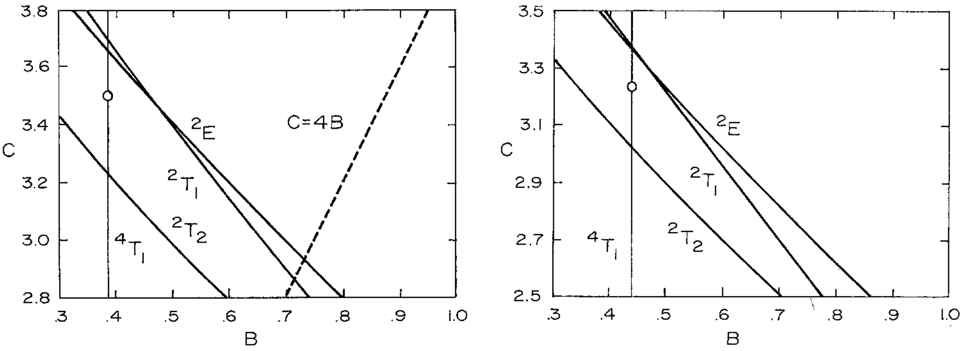

Fig. 2a Fig. 2b

Fig. 2a and b. C as a function of B (in kK) for $CrBr_3$; a) from strong or weak field matrices with $\alpha = 0$, b) from weak field matrices with $\alpha = 0.0782$ kK

modified secular equations. B was then given arbitrary values from 0.30 to 1.00 kK and the roots of the resulting polynomials in C found numerically[5], giving a family of solutions for each observed doublet state of the complex. At any particular B, only one of the four roots of the ^2E secular equation, and only one of the five roots of the $^2T_1$ and $^2T_2$ secular equations, were physically meaningful. The others were negative, imaginary, or at least an order of magnitude larger than the free ion C.

The families of solutions for the observed doublet transitions of each complex were displayed graphically, examples of which are given in Figs. 1 and 2, for $[Cr(ur)_6]^{+3}$ and $CrBr_3$, respectively. If the Racah-Trees correction is neglected (i.e. $\alpha = 0$ in Eq. (9)), the resulting families of solutions (Figs. 1a and 2a) from the strong and weak field secular equations are identical to three significant figures. Figs. 1b and 2b show the resulting curves if α is given the free ion value. The B values found from Eq. (4) are also indicated on the graphs.

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[5] A program employing Bairstow's method [42] for finding the zeros of polynomials was used on the IBM 360 computer of the University of British Columbia Computing Centre. The assistance of Mr. M. Thomas is gratefully acknowledged.

If the crystal field model worked perfectly, then all four curves for a particular complex would intersect in one point, defining a unique B and C for the complex. That this is not so, is not surprising if the free ion analysis [25, 35] is kept in mind. If Jorgensen's proposal that different parameters are required for the doublet and quartet states is accepted, then one would expect that the three doublet solution curves should intersect in one point (or nearly so) which may be at a different B value than that found from the ${}^4T_1(F)$ state. This appears to be the case for the $[\mathrm{Cr(ur)_6}]^{+3}$ complex if the Racah-Trees correction is included (Fig. 1(b)). However, this particular intersection is probably fortuitous. The curves for $[\mathrm{Cr(ur)_6}]^{+3}$ and $\mathrm{CrBr_3}$ demonstrate the best and worst cases of this analysis.

In general, the inclusion of the Racah-Trees correction lowers the ${}^2E$ solution curve by a constant 0.17 kK, the ${}^2T_1$ curve by 0.17 to 0.21 kK, and the ${}^2T_2$ curve by 0.96 to 0.60 kK, as B varies from 0.30 to 1.00 kK. The relative sensitivities of the three states to the Racah-Trees correction can be understood by noting the free ion states from which the four ${}^2E$ states and the five ${}^2T_1$ and ${}^2T_2$ states arise. The net effect of the Racah-Trees correction is to reduce the spread between the ${}^2E$ and ${}^2T_2$ curves at $B({}^4T_1)$ by 0.10 kK.

Table 3 summarizes the results of the analysis including the Racah-Trees correction, by giving the value of the parameter C for the doublet states at the B value found from the ${}^4T_1$ state. The corresponding parameters from the strong field matrices, or the weak field matrices with $\alpha = 0$, are higher by 0.29 kK, 0.33 kK and 0.18 kK, for the ${}^2E$, ${}^2T_1$ and ${}^2T_2$, respectively. Generally, the C values for the ${}^2E$ and ${}^2T_1$ are not too different, while the C value for the ${}^2T_2$ is up to 0.40 kK smaller.

An uncertainty of ± 0.03 kK in the ${}^2E$ and ${}^2T_1$ positions and ± 0.04 kK in the ${}^2T_2$ position results in an uncertainty of ± 0.01 kK in C for any particular Δ and B.

3. *Choosing the Best Parameters*

The great advantage of the graphical method of analysis introduced in this investigation is that it is now a simple, although somewhat arbitrary, matter to choose the "best" parameters for any one complex. It is apparent from Figs. 1 and 2 that there is no justification in assigning different B values to the doublet and quartet states. In order to obtain reproducible results it is therefore suggested that Δ and B be determined from the ${}^4T_2$ and ${}^4T_1(F)$, respectively, and that a C, appropriately weighted (see last paragraph of Sect. 2), be chosen for the three doublet states.

These parameters, derived from the analysis including the Racah-Trees correction, are collected in Table 4 and indicated by the open circles in Figs. 1b and 2b. The corresponding B and C values from the analysis without the Racah-Trees correction are 0.052 kK smaller and approximately 0.30 kK larger, respectively (Figs. 1a and 2a). As B decreases through the series of complexes, the ratio C/B tends to increase and is by no means constant, nor equal to 4.0. To what accuracy these parameters reproduce the observed transitions will be shown below.

Table 4. *Best empirical crystal field parameters for* Cr(III) *complexes*[a]

Complex	Δ	B	C	C/B
$[CrF_6]^{-3}$	15.06	0.910	2.91	3.2
Ruby	18.15	0.822	2.62	3.2
$[Cr(NH_3)_6]^{+3}$	21.45	0.711	3.12	4.4
$[Cr(ur)_6]^{+3}$	16.15	0.697	2.87	4.1
$[Cr(H_2O)_6]^{+3}$	18.00	0.695	2.93	4.2
$[Cr(ox)_3]^{-3}$	17.50	0.664	2.92	4.4
$[Cr(CN)_6]^{-3}$	26.70	0.589	2.39	4.1
$[Cr(CH_3)_6]^{-3}$	20.80	0.577	3.02	5.2
$CrCl_3$	13.62	0.575	3.17	5.5
$CrBr_3$	13.43	0.440	3.23	7.3
$Cr(exan)_3$	16.00	0.436	2.94	6.7

[a] In kK, derived from the weak field analysis including the Racah-Trees correction ($\alpha = 0.0782$ kK). The B and C values from the analysis without the Racah-Trees correction are 0.052 kK smaller and approximately 0.30 kK larger, respectively.

4. *Comparison of Observed and Calculated Frequencies*

One of the uses of the crystal field model is to predict the frequencies of observable *d–d* transitions; the classic paper by Finkelstein and Van Vleck [12] is the first such example. They used the free ion Cr^{+3} energies to predict the levels of chrome alum, but were successful in a qualitative manner only. Since then it has been realized that the electron repulsion parameters (or the term distances) must be reduced from the free ion values in order to approach semi-quantitative agreement between calculated and observed transitions. Consequently a semi-empirical approach is necessary. The foregoing analysis demonstrates that even if the frequencies of the quartet transitions are known, it is not possible to predict quantitatively where the spin-forbidden transitions will lie. If $B(^4T_1)$ from Eq. (4) is used with Jorgensen's equations or with the complete secular equations (assuming $C = 4B$, say), the calculated doublet frequencies are in error by at least some 2.0 kK, and by as much as 7.0 kK for complexes with low B values. A useful question to ask, however, is to what accuracy the $^2T_1$ and $^2T_2$ may be predicted if the frequencies of the two spin-allowed and the ^2E transition are known.

a) Calculated $^2T_1$ and $^2T_2$ Frequencies with the Parameters Derived from the $^2E \leftarrow {}^4A_2$ Transition

If Jorgensen's equation are assumed and $B_{55}(^2E)$ is used to calculate $\bar{\nu}(^2T_1)$ and $\bar{\nu}(^2T_2)$, the resulting frequencies are in error by ± 2.0 kK.

If $B(^4T_1)$ and $C(^2E)$ from columns two and three of Table 3 are used in the complete $^2T_1$ and $^2T_2$ secular equations (with $\alpha = 0.0782$ kK), the calculated frequencies differ from the observed by ± 0.16 kK for the $^2T_1$ and $+0.76$ kK for the $^2T_2$. (The corresponding errors for the calculation using the $\alpha = 0$ parameters are ± 0.19 and $+1.2$ kK, respectively.) The average deviations for this method simply reflect the general appearance of the families of solutions shown in Figs. 1 and 2. The ^2E and $^2T_1$ curves are generally quite close together, while the $^2T_2$ curve lies below them.

Table 5. *Calculated*[a] *doublet frequencies with the best crystal field parameters*

Complex	$\bar{\nu}(^2E)$		$\bar{\nu}(^2T_1)$		$\bar{\nu}(^2T_2)$		m.a.d.
	obs.	calc.	obs.	calc.	obs.	calc.	
Ruby	14.43	14.32	15.11	15.19	21.14	21.24	0.10
$[Cr(ur)_6]^{+3}$	14.19	14.24	15.04	14.93	20.83	20.92	0.08
$[Cr(CN)_6]^{-3}$	12.46	12.27	13.07	12.78	18.37	18.98	0.36
$CrBr_3$	14.00	13.58	14.36	13.92	18.92	19.76	0.57
m.a.d.[b]		0.15		0.17		0.44	

[a] In kK, from the complete weak field matrices with Δ, B and C from Table 4 and $\alpha = 0.0782$ kK, m.a.d. = mean absolute deviation.

[b] For all the complexes of Table 2.

b) Calculated Frequencies with the Best Crystal Field Parameters

Table 5 gives, for four representative complexes, the frequencies of the doublet states calculated from the complete weak field matrices with the parameters listed in Table 4 and $\alpha = 0.0782$ kK. The mean absolute deviations (m.a.d.) for the three doublet states (for all the complexes of Table 2), as well as the mean deviation for the four exemplary complexes are given. If the parameters derived from the analysis without the Racah-Trees correction are used, the corresponding errors are about 30% higher.

Discussion

Jorgensen [19] has proposed two explanations for the nephelauxetic effect. These have been termed central field covalency and symmetry restricted covalency, respectively. The former describes the screening of the nuclear charge by coordinating σ-electrons or by polarizable π-electrons of the ligands, with a resultant "expansion" of the *d*-orbitals, while the latter refers to delocalization of the metal *d*-electrons onto ligand orbitals due to σ- or π-bonding. Both effects may be operative in a particular complex, and make plausible the reduction of the *d*-electron repulsion integrals, and hence the Racah parameters, when a free transition metal ion is incorporated into a complex. Various attempts have been made to relate the experimentally determined B_{35} and B_{55} parameters to the importance of σ- and π-bonding in transition metal complexes. Simple molecular orbital theory [43] predicts that the e and t_2 orbitals will be involved exclusively in σ and π interactions, respectively, with the ligand orbitals. Since the empirical B_{55} value (determined from the ^2E usually), describing the repulsion of two electrons in the t_2 orbitals, is generally greater than the B_{35} parameter for the same complex, it has been concluded that σ-bonding is the more important in most transition metal complexes of the type considered in the present investigation. This approach therefore implies that the t_2 and e orbitals are expanded to different degrees for any particular complex. Using a similar approach, Koide and Pryce [11] introduced a covalency parameter, ε, which would give a measure of the difference in expansion of the t_2 and e orbitals. De Armond and Forster

[41] suggested a phenomenological π-bonding parameter, γ, arbitrarily setting it equal to one for $[\mathrm{Cr(en)_3}]^{+3}$, where no π-bonding would be expected. The rather low B_{55} values for $[\mathrm{Cr(CN)_6}]^{-3}$ and Cr(exan)$_3$, in which π-bonding should be important, were thus rationalized.

The B_{55} parameters obtained from Eqs. (5) to (7) do not follow the nephelauxetic series and in some cases are greater than the free ion B value. Furthermore, even though all three of the lowest spin-forbidden transitions are intra-configurational ($t_2^3 \rightarrow t_2^3$), the B_{55} parameters for the doublet states of any one complex are not identical. Eqs. (5) to (7) considerably overestimate the value of B which is obtained from the complete strong field secular equations when $C = 4B$ is assumed.

Two inconsistencies are contained in the above treatment:

1. The assumption $C/B = 4$, or even that this ratio should remain constant for a series of complexes, is not compatible with the interpretation of the nephelauxetic effect. The Racah parameters [44] are linear combinations of the Condon-Shortley parameters F_2 and F_4, which are integrals containing the radial functions describing the d-electrons [40]. If the ratio is set equal to four (the approximate free ion value), it is implied that the d-orbital radial functions within the complex are identical to those of the free ion. Indeed, a constant ratio for a series of complexes should be expected only if the radial functions are assumed not to vary from complex to complex. However, as discussed above, the nephelauxetic effect has been proposed to arise from "expansion" of the d-orbitals, i.e. variation of the radial functions.

2. A necessary consequence of the introduction of two parameters, B_{35} and B_{55}, for states arising from $t_2^2 e$ and t_2^3, respectively (implying differential expansion of the t_2 and e orbitals), is that the energy of the lowest spin-allowed transition no longer corresponds to Δ directly. This may be seen from Eq. (10):

$$\begin{aligned}\bar{\nu}(^4T_2) &= E(^4T_2) - \mathrm{E}(^4A_2)\\ &= -0.2\Delta - 15B_{35} - (-1.2\Delta - 15B_{55})\\ &= \Delta - 15(B_{35} - B_{55})\,.\end{aligned} \tag{10}$$

Thus to equate Δ to $\bar{\nu}(^4T_2)$ requires that B_{35} and B_{55} be equal. Although the effect on the evaluation of B_{55} will be negligible since the energies of the three lowest doublet states are independent of Δ in first order (cf. Eqs. (5) to (7)), the B_{35} value may change markedly if the "correct" Δ is used in Eq. (1).

These two inconsistencies have been removed in the present rigorous application of the crystal field model. Quantitative agreement between theory and experiment is of course not possible with this model. This is demonstrated by Table 3. In order to reproduce exactly the five transitions under consideration, five parameters need to be specified: Δ, B and three Racah C parameters. If the free ion analysis [25, 35] is kept in mind, however, one should expect to be able to reproduce the crystal field transitions to at best $\pm 200\,\mathrm{cm}^{-1}$ with the three parameter theory. This upper limit is almost reached for most of the complexes of this investigation if the parameters given in Table 4 are used. The Racah-Trees correction which improves the free ion analysis considerably [25, 35], does not seem to be of great importance in crystal field spectra. This, no doubt, is because there are more serious discrepancies between the crystal field theory and reality than the neglect of core-outer shell exchange in the free ion theory.

The most important conclusion to draw from the foregoing analysis is that the crystal field model, if applied rigorously, does not offer any evidence of differential expansion of the t_2 and e orbitals. The two lowest spin-allowed and the three lowest spin-forbidden transitions can be described to within a few hundred wavenumbers (at worst to within 600 cm^{-1}) within the three parameter crystal field theory. Whether or not the t_2 and e orbitals are modified to different degrees in actuality is not disputed here, but the crystal field model theory does not offer any evidence for this. The difference between B_{35} and B_{55} must be ascribed mainly to the assumption $C = 4B$, and partly to the approximate nature of Eqs. (5) to (7).

This conclusion was reached independently by Wood and Ferguson [25], who derived empirical "effective" (i.e. reduced) free ion term energies from the spectra of a number of octahedral Cr(III) and tetrahedral Co(II) compounds. They then attempted to reproduce these with a unique set of F_2, F_4 and α, and where a comparison can be made, their results generally agree with those of the present study. They ascribe the success of their treatment to their use of the weak field matrices, the Condon-Shortley parameters (instead of B and C) and the Racah-Trees correction term. This study, however, has shown that the strong and weak field analyses for octahedral Cr(III) complexes are completely equivalent. The only advantage of the weak field matrices is the ease with which the theoretical free ion energies along the diagonal may be modified (e.g. the Racah-Trees correction). The use of the Racah parameters, instead of F_2 and F_4, allows one to order the ligands into the qualitatively appealing nephelauxetic series [19].

The B and C values derived in this investigation are smaller than the free ion values for all the complexes studied, but are reduced by different amounts. The ratio C/B tends to increase as B decreases through the series of complexes (the well established nephelauxetic series), because the values of C vary much less than the B values. The reason for the smaller variation in C can be anticipated from Wood and Ferguson's study [25] of the sensitivity of F_2 and F_4 to the outer region of the d radial function.

It has already been pointed out above that the crystal field theory cannot be used to predict the spin-forbidden transition frequencies if only the quartet-quartet transitions are known. If the ^2E has been observed, the $^2T_1$ and $^2T_2$ may be predicted to within 0.16 and 0.76 kK, respectively, if the complete secular equations are solved. A purely empirical observation should also be mentioned here. To within a few hundred wavenumbers, the difference in energy between the $^4T_2$ and ^2E transitions is equal to the separation between the $^4T_1(F)$ and $^2T_2$ transitions (see Table 2).

Concluding Remarks

The shortcomings of the crystal field theory, when applied to finer details of the observed spectra of transition metal complexes, are not surprising in view of the inherent assumptions of the model. However, the author considers the method of deriving the best crystal field parameters presented here to be a clearer and certainly a more consistent way of comparing the crystal field spectra with the predictions of the theory, than those presented previously. As pointed out so eloquently by Liehr [26], the crystal filed model must be used with great caution, and attempts to draw even semi-quantitative conclusions from the deviations of experiments from the theory by the introduction of arbitrary parameters are not really warranted.

The present investigation has neglected spin-orbital coupling and deviations from octahedral micro-symmetry. The former should undoubtedly be considered for those complexes where the two lowest spin-forbidden transitions (^2E and $^2T_1$) are quite close to the $^4T_2$ transition (as for $[CrF_6]^{-3}$), since the question arises to what extent the doublet states are contaminated by mixing with the quartet state and *vice versa*. A treatment similar to Jorgensen's [45] for a number of Ni(II) complexes should be attempted here, but not enough spectral data are available for cases where the ^2E lies higher than the maximum of the $^4T_2$ transition. Wood and Ferguson [25] have suggested that the three parameter theory is very bad for $CrBr_3$ because of interaction between the low-energy charge transfer states (near 21 kK) of this compound with the crystal field states. This may be the reason why the $^2T_2$ family of solutions for this compound (see Fig. 2) lies so far below the ^2E and $^2T_1$ curves (implying that the $^2T_2$ lies at lower energy than would be expected from the positions of the other two doublet states).

The crystal field theory, when applied semi-empirically, can be used with reasonable success to interpret the optical absorption spectra of most octahedral Cr(III) complexes. The developments presented here should apply to other transition metal complexes as well if the theory is applied in a rigorous fashion. Only very limited conclusions, however, should be drawn about the bonding in these compounds from these analyses; that aspect must be left to the more sophisticated molecular orbital treatments [7–10].

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