

Systematic Interpretation of Experimentally Measured and Theoretically Calculated Spectra of Transition-Metal Compounds by an Optimized, Linearized Crystal Field Fitting Procedure

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Linearized, least-squares fitting of experimental and theoretical spectra of transition-metal clusters by the crystal field (CF) model yields not only the usual systematically optimized CF orbital splitting and Racah parameters but also a convenient and direct measure of the sensitivity of the transition energies to those various quantities. Specifically considered are the transitions observed for Cr^{3+} and Ni^{2+} ions in octahedral fluoride clusters. The quality of the fit is less influenced by the Racah C/B ratio than by the scaling of the metal d orbitals (i.e., the nephelauxetic effect). Consistent fittings of observed and SCF-MO-calculated spectra of NiF_6^{4-} and CrF_6^{3-} show very close agreement in values of, and sensitivities to, the CF parameter $10 Dq$, the nephelauxetic factor, and the effective orbital population, the last being a direct measure of breakdown of the orbital approximation to the wavefunction. In comparing Racah parameters for free and complexed ions it is essential to choose values such that the same degree of electron correlation is encompassed in both cases.

I. Introduction

It is not a new matter to interpret spectra of transition-metal compounds by means of crystal field theory and to obtain effective values of the various parameters of that theoretical model appropriate to each system. The procedure employed may make use of the familiar Orgel or Tanabe-Sugano diagrams (1) (with the fitting done visually) or of analytic expressions for certain of the observed transitions (with the several parameters obtained in some convenient sequence), or occasionally a least-squares-type fitting is made (2, 3) with the cor-

responding expense of considerable numerical calculations of large matrices.

The basic crystal field is long known to be incorrect as fundamental theory—despite its ability to represent observed spectra—and in that regard is now superseded by sophisticated SCF MO calculational procedures culminating even in some incorporation of configuration interaction effects. In attempting to bridge the gap between the complexities of such detailed calculations and the simple crystal field picture, some authors have begun to recast their calculated spectral results for a given compound in terms of theoretical parameters; they are then

compared to the empirical parameters which result from a crystal field fit to the measured spectrum.

Clearly it is important to define fitting procedures which not only accurately, but consistently, portray the essentials of all types of spectra.

In this paper we employ a simplified procedure for the least-squares fitting of the full crystal field matrices to a given set of transition energies. The method operates through a linear representation of the eigenvalues in terms of the crystal field fitting parameters. At the outset, one achieves the stated objectives of optimum fittings. But, furthermore, the terms in these expansions are seen to furnish considerable, immediate and quantitative insight into the factors determining the energy of a given d^n electronic transition: crystal field splitting, interelectronic repulsions, and nephelauxetic effects resulting from the metal-ligand covalency.

Here the methods developed are applied to two transition-metal cluster systems, CrF_6^{3-} and NiF_6^{4-} . In each case we consider the results of fittings both to the experimental and to the theoretical spectra. Furthermore, we also investigate the adequacy of a conceptually simpler basic crystal field reference model, which includes only the first-order perturbation effects upon the strong-field orbital states.

In analytic form, our results will resemble those MacFarlane obtained in studying the spectrum of Cr^{3+} in ruby (3), although the approaches are quite different. He first fit cubic and trigonal crystal field and Racah parameters to the observed spectrum; then, considering this fit to constitute an approximate basis for this system, he refined that fit by determining the sensitivity of each approximate eigenstate to each of those parameters, using first-order perturbation theory. The procedure used here accomplishes both objectives, optimally and simultaneously.

We examine the experimental data on CrF_6^{3-} in K_2NaCrF_6 obtained by Ferguson *et al.* (4) and on NiF_6^{4-} in KNiF_3 obtained by Knox *et al.* (5). We further interpret the parameters obtained by Gladney and Veillard (6) and by Wachters and Nieuwpoort (7) from their accurate Gaussian SCF MO calculations on NiF_6^{4-} . For CrF_6^{3-} we consider the recent SCF MO calculations of Pueyo and Richardson (8), which included effects of external lattice potential in K_2NaCrF_6 (9), spin-orbit and configuration interactions, a further correlation energy correction (10), and variation of total energy along the totally symmetric vibrational coordinate. Since the calculated transition energies, equilibrium distances, and force constants are in close agreement with the experimental, we take this system as especially useful in comparing fits to theoretical and experimental data.

II. Methodology

Let us consider as given a set of $d-d$ excitation energies for a particular octahedral cluster, obtained either experimentally or by elaborate SCF-MO-based theoretical techniques. Let the i th member of this set be $W_i(\Gamma)$, where Γ is an irreducible representation of the appropriate group. These are associated with (a subset of) the eigenvalues, $E_i(\Gamma)$, of the collection of strong crystal field (CF) matrices $\mathbf{H}(\Gamma)$ (1), defined relative to the ground level, E_0 . The elements of each $\mathbf{H}(\Gamma)$ are well-known functions of the CF orbital splitting parameter, Δ , the Racah parameters, B and C , and possibly even the spin-orbit coupling parameter, ξ (1). Hence, the $E_i(\Gamma)$ are also functions of these same parameters. Our first objective is to minimize the mean-square deviation of the $E_i(\Gamma)$ from the given $W_i(\Gamma)$, with respect to variations of the CF parameters.

In practice we may consider certain simplifications, in particular neglecting ξ and invoking a fixed ratio between the values of C and B . As in the original CF theory, the same

values of these parameters are associated with every state of the entire manifold.

Free-ion values for B and C may be established by fitting theoretical expressions for $d-d$ excitation energies to empirical spectra or by assuming particular forms for the radial wave functions for the $3d$ orbitals, $R_{3d}(r)$, and evaluating the Slater–Condon integrals, F^k , defined (in atomic units) by

$$F^k = \int_0^\infty \int_0^\infty R_{3d}^2(r_1) R_{3d}^2(r_2) (r_<^k / r_>^{k+1}) \cdot r_1^2 r_2^2 dr_1 dr_2.$$

In the simplest case, one may take a Slater-type orbital (STO), with orbital exponent ζ :

$$R_{3d}(r) = [(2\zeta)^7 / 6!]^{1/2} r^2 e^{-\zeta r}.$$

Then, in atomic units, the integrations yield

$$B = \frac{1}{49} F^2 - \frac{5}{441} F^4 = 0.00177331\zeta,$$

$$C = \frac{35}{441} F^4 = 0.00705302\zeta,$$

and

$$C/B = 3.9773.$$

Alternatively, near-Hartree–Fock orbitals may be used; calculated results for free Cr^{3+} and Ni^{2+} are given in Table I, along with values found in fits to the observed spectra.

In Table II we present our fitting, in terms of the simple $3d$ STO orbital exponent, to the observed free-ion terms for Ni^{2+} (11) and Cr^{3+} (12). Note that we include the 1S in the Ni^{2+} case (13), the missing state in Shenstone's compilation (11). With these values of ζ we obtain the B and C parameters collected in Table II. It is interesting that the resulting ζ (free ion) are very close to the orbital exponents of the outer $3d$ STO components in the so-called double- ζ representation of the $3d$ AOs (14): $\zeta(\text{Ni}^{2+}) = 2.40$, $\zeta(\text{Cr}^{3+}) = 2.20$.

In our approach here, the delocalization effect of covalency upon the $3d$ AOs, i.e., the

TABLE I
RACAH PARAMETERS FOR Cr^{3+} AND Ni^{2+} (IN cm^{-1})

	Theoretical		Experimental	
	Watson HFAO ^a	Present basis ^b	Griffith ^c	Better fits ^d
Cr^{3+}				
B	1163	1149	1030	1012
C	4340	4270	3850	3921
C/B	3.73	3.72	3.74	3.87
Ni^{2+}				
B	1330	1334	1084	1135
C	4911	4943	4831	4480
C/B	3.69	3.71	4.46	3.95

^a Reference 19, from $3d^8$ average-of-configuration calculation.

^b Reference 14.

^c Compiled by J. S. Griffith (1; Appendix 6).

^d Cr^{3+} parameters from Watson (19). Ni^{2+} parameters from E. Tondello, G. DeMichelis, L. Oleari, and L. DiSipio, *Coord. Chem. Rev.* 2, 65 (1967); fitting to Ni^{2+} spectrum omitted the 1S state.

TABLE II
OBSERVED d^n LEVELS OF FREE Ni^{2+} ^a AND Cr^{3+} ^b AND SIMPLE STO FITTING OF RACAH PARAMETERS (ENERGIES IN cm^{-1})

Transition	Observed	Fit	Parameters
$\text{Cr}^{3+} \ ^4F \rightarrow \ ^4P$	13,770	13,396	$B = 893$
$\rightarrow \ ^2G$	14,704	14,228	$C = 3552$
$\rightarrow \ ^2H$	20,660	18,693	$\zeta = 2.295$
$\rightarrow \ ^2P$	13,676	18,693	
$\rightarrow \ ^2D_-$	19,933	20,463	
$\rightarrow \ ^2F$	36,182	32,089	
rms deviation		2,782	
$\text{Ni}^{2+} \ ^3F \rightarrow \ ^1D$	13,038	13,513	$B = 1043$
$\rightarrow \ ^3P$	15,836	15,646	$C = 4149$
$\rightarrow \ ^1G$	20,813	22,115	$\zeta = 2.680$
$\rightarrow \ ^1S$	51,538	51,987	
rms deviation		735	

^a Reference 11, except for the 1S level, which was supplied to us by Dr. Olga Garcia-Riquelme.

^b Reference 12.

nephelauxetic effect, is regarded as a uniform distance scaling, or radial expansion, of whatever basic $3d$ AO function is used: $R_{3d}(r)$ for the free ion is replaced by $R_{3d}(rs)$ in the model for the cluster. Regarding B and C as functions of s , it follows that

$$B(s) = sB(1) \quad \text{and} \quad C(s) = sC(1),$$

where $B(1)$ and $C(1)$ here refer to free-ion values. Clearly, then, s is identified with Jorgensen's nephelauxetic ratio β (15). Note that C/B is independent of s . In the simplest case of $R_{3d}(r)$ being an STO, its orbital exponent ζ may be regarded as the fitting parameter to both free-ion and cluster excitation energies. In this circumstance,

$$\beta = s = \zeta(\text{cluster})/\zeta(\text{free ion}).$$

With these considerations, each element of \mathbf{H} reduces, in general, to a multiple of Δ plus a sum of reference B 's and C 's, $B(1)$ and $C(1)$, which sum is multiplied by the scaling factor s . That is, \mathbf{H}_{ij} has the form

$$\mathbf{H}_{ij} = n\Delta + [kB(1) + lC(1)]s = \mathbf{H}_{ij}(\Delta, s),$$

where n , k , and l are specified numbers. Likewise the eigenvalues of each $\mathbf{H}(\Gamma)$, $E_i(\Gamma)$, are regarded as functions of Δ and s .

To find optimum values of Δ and s for the given set of $W_i(\Gamma)$, we perform an iterative least-squares procedure. It begins with some trial values (Δ_0 and s_0) and increments ($\delta\Delta_0$ and δs_0). For each Γ , the matrices $\mathbf{H}(\Delta_0, s_0)$, $\mathbf{H}(\Delta_0 + \delta\Delta_0, s_0)$, and $\mathbf{H}(\Delta_0, s_0 + \delta s_0)$ are diagonalized. Next are formed the quantities

$$\begin{aligned} n_i^{(0)} &= [E_i(\Delta_0 + \delta\Delta_0, s_0) - E_i(\Delta_0, s_0)]/\delta\Delta_0 \\ &\approx (\partial E_i/\partial \Delta)_{\Delta_0, s_0}, \end{aligned}$$

$$\begin{aligned} b_i^{(0)} &= [E_i(\Delta_0, s_0 + \delta s_0) - E_i(\Delta_0, s_0)]/\delta s_0 \\ &\approx (\partial E_i/\partial s)_{\Delta_0, s_0}. \end{aligned}$$

(Note that the n_i are dimensionless, but that the b_i have units of energy.)

Then a linearized form for all eigenvalues, $E_i(\Gamma)$, being considered is written

$$\tilde{E}_i(\Gamma) = n_i^{(0)}(\Gamma)\Delta + b_i^{(0)}(\Gamma)s.$$

Finally, Δ and s are varied so as to least-squares fit these $\tilde{E}_i(\Gamma)$ to the $W_i(\Gamma)$. The optimum values found at this point, Δ_1 and s_1 , become input to the next iteration. In the cases studied here, only three or four iterations were required to converge all n_i and b_i (and \tilde{E}_i) to $\pm 10^{-8}$ starting with a reasonable guess for Δ , $s = 1$, and $\delta\Delta/\Delta = \delta s/s = 0.01$. We now also have realized the second objective, since the converged quantities n_i and b_i indicate in a simple way the rates at which the transition energies of the given cluster would change if Δ and s , respectively, were changed—properties having significant chemical and physical interest.

The procedure just described, in which the complete CF matrices $\mathbf{H}(\Gamma)$ are employed and diagonalized, will be termed the full matrix fit (FMF). To aid in interpreting results found thereby, it is useful also to consider fits obtained in exactly the same way, *except* that all off-diagonal elements of the $\mathbf{H}(\Gamma)$ are set to zero, so that the $\mathbf{H}_{ii}(\Gamma)$ become the set of eigenvalues directly. This diagonal only fit (DOF) encompasses just the first-order perturbative effects of interelectronic repulsion and crystal fields upon the " $3d$ " orbitals of the cluster. Thus, in a DOF fitting to the given set of $W_i(\Gamma)$, clearly one should obtain each n_i as the integral number of $t_2 \rightarrow e$ promotions presumed to be involved in the i th excitation and obtain each b_i as the particular combination of Racah B and C which occurs in $\mathbf{H}_{ii}(\Gamma)$. On the other hand, the FMF procedure allows for configurational mixing in the resulting eigenstates; hence a given $d-d$ excitation yields (following a reoptimization of the fitting parameters) new values of n_i , which correspond to weighted averages of promotion numbers for the pure configuration states mixed into each eigenstate and thus are not necessarily integers. Likewise, the configurational mixing modulates the amount of B and C incorporated into the new values of b_i .

It must be emphasized that the differences between the FMF and the DOF sets of n_i , b_i are not solely the result of configurational mixing. Rather, they reflect also the changes produced initially in the $H_{ij}(\Gamma)$ by the use of reoptimized values of Δ and s .

Apart from the mathematical simplification of the least-squares procedure, linearization permits a more quantitative assessment to be made of the relative influences of orbital splitting and nephelauxicity on transition energies. As well it permits an easy comparison of the DOF form $\tilde{E}_i(\Gamma) = H_{ii}(\Gamma) = n\Delta + [kB + lC]s$ with the FMF form $\tilde{E}_i(\Gamma) = n_i\Delta + b_i s$, since both results have the same analytic form.

Clearly, this linearization procedure can be generalized to systems with other choices of parameters, certainly including spin-orbit interaction and perturbations of lower-symmetry crystal fields (3). Later in this paper, for instance, we consider fittings with B and C varied independently.

III. Results and Discussion

Applying the DOF and FMF procedures to experimental spectra of NiF_6^{4-} in $KNiF_3$ and CrF_6^{3-} in K_2NaCrF_6 yields the numerical results presented in Tables III and IV, respectively. Coefficients in the linearized $\tilde{E}_i = \tilde{E}_i(\Delta, s)$ equations can be seen for both clusters in Table V. For these results the simple STO form of the $3d$ AOs was used.

From the tables, the differences between the full matrix and diagonal element only fits can be readily appreciated. Root mean square deviations are reduced by a factor of 7 in NiF_6^{4-} and 5 in CrF_6^{3-} . In NiF_6^{4-} the rms deviation of our fit (with a fixed ratio of C/B) is somewhat smaller than that obtained by Knox *et al.* (5), who fit Δ to the transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and then independently evaluated B and C to fit the transitions to 1E and b^3T_{1g} . It is interesting that their C/B ratio obtained thereby (4.43) is larger than any

TABLE III
EXPERIMENTAL SPECTRUM OF NiF_6^{4-} IN $KNiF_3$
AND CRYSTAL FIELD FITTINGS (ENERGIES IN
 cm^{-1})

Transition	Observed ^a	KSS fit ^a	\tilde{E}_i from CF fitting ^b	
			DOF	FMF
${}^3A_{2g} \rightarrow {}^3T_{2g}$	7,250	7,250	5,840	7,152
$\rightarrow a^3T_{1g}$	12,530	12,270	14,875	12,133
$\rightarrow {}^1E_g$	15,440	15,430	16,992	14,826
$\rightarrow {}^1T_{2g}$	20,920	22,190	22,831	21,471
$\rightarrow b^3T_{1g}$	23,810	23,810	18,620	23,930
rms deviation		579	2,846	415
Free Ni^{2+} ion ^c				
Δ	7,250	5,840	7,152
B	1,043	955	1,065	974
C	4,149	4,234	4,236	3,873
Single STO ζ	2,680		2,736	2,502
s	1,000	d	1,021	0,934

^a Knox *et al.* (5).

^b Recall that C/B is fixed at the STO-calculated value.

^c Our least-squares fit to observed spectrum, including the 1S (see text and Table VI), simple STO $3d$ AO.

^d The independent fittings of B and C by KSS yield $s \sim 0.93$ for B and $s \sim 0.87$ for C (5).

other cited here, especially the value 3.98 assumed in our better fit.

In our DOF results for NiF_6 , all states are rather poorly fit. The FMF procedure, however, corrects all the problems. As a consequence, the n_i and b_i parameters obtained with FMF differ markedly from the DOF ones. Our best Δ and B , but not C , on the other hand, are very close to those of Knox *et al.* (5).

In the case of CrF_6^{3-} we observe a similar functioning of FMF. Again, very remarkable are its good fittings of the low-spin states 1E and ${}^1T_{1g}$ compared to DOF results. We recall that these states were obtained consistently too high in the HF SCF MO calculation even after limited CI was included (8); the additional correlation energy correction was essential to locate them properly.

TABLE IV
EXPERIMENTAL SPECTRUM OF CrF_6^{3-} IN
 K_2NaCrF_6 AND CRYSTAL FIELD FITTINGS
(ENERGIES IN cm^{-1})

Transition	Observed ^a	\bar{E}_i from CF fitting ^{b,c}	
		DOF	FMF
${}^4A_{2g} \rightarrow {}^2E_g$	15,200	14,094	15,090
$\rightarrow {}^2T_{1g}$	15,600	14,094	15,829
$\rightarrow {}^4T_{2g}$	16,400	17,040	16,336
$\rightarrow {}^2T_{2g}$	22,450	23,490	22,441
$\rightarrow a^4T_{1g}$	23,260	25,120	23,752
$\rightarrow b^4T_{1g}$	37,350	36,100	37,083
rms deviation		1,291	252
	Free Cr^{3+} ion ^d		
Δ	17,040	16,336
B	893	673	788
C	3,552	2,677	3,136
Single STO ζ	2.295	1.730	2.026
s	1.000	0.754	0.883

^a Reference 4.

^b For comparison, Liehr (2) obtained $B = 760$, $C = 3020$, and $\Delta = 16,100$.

^c In the fitting here, C/B is the STO-calculated value.

^d Our least-squares fit to observed spectrum (see text and Table II), simple STO $3d$ AO.

Here, however, the FMF locates them in the right place, presumably by optimizing the Racah parameters artificially to compensate for this correlation effect. We conclude, furthermore, that the "third-band problem" (16) (i.e., the early difficulty in simultaneously fitting the ${}^4T_{2g}$ and two ${}^4T_{1g}$ states with only Δ and B), even extended to include the higher spin-forbidden transitions, is simply solved if fixed-ratio, but scaled Racah parameters are used in the FMF procedure.

Liehr, in his early fitting to this same spectrum (2), included spin-orbit coupling. It considerably splits most of the levels reported here and renders difficult any direct comparison with our results. The parameters he obtained ($\Delta = 16,100$, $B = 760$, $C = 3020$, in cm^{-1}) are very close to our FMF results, however. Thus his spectrum, recal-

culated with $\xi = 0$, would be very similar to our FMF spectrum.

Other aspects of the fittings are seen in Table V, where the linear coefficients for the transition energies analyzed are collected. Noticeable differences are observed between the DOF and FMF sets of coefficients. Of course, the transitions to ${}^3T_{2g}$ of NiF_6^{4-} and to ${}^4T_{2g}$ of CrF_6^{3-} , which depend only upon Δ in CF theory, give the same results in the two cases and appear independent of s .

It is instructive to look at the pairs of high-spin T_{1g} levels in the two clusters. No other such $3d^n$ states can occur in either case. Thus, in CrF_6^{3-} , for example, only the two ${}^4T_{1g}$ arising from $t_2^3e^1$ and $t_2^1e^3$ can be configurationally mixed. Summing the DOF n_i and b_{is} obtained for a^4T_{1g} and b^4T_{1g} gives exactly 3 and 15 B , respectively, as it should. The same summing of the FMF n_i and b_{is} yields the same totals. Clearly indicated, however, is the extent of the mixings of the pure configuration $t_2^2e^1$ and $t_2^1e^2$ states which yield the a^4T_{1g} and b^4T_{1g} levels. Since each FMF n_i measures the weighted average of the number of t_2 -to- e promotions involved in a configurationally mixed state, we may use the FMF n_i to estimate (directly from this linearized fit to the experimental spectrum) that the a^4T_{1g} state, for example, is 85% $t_2^2e^1$ and 15% $t_2^1e^1$ in character.

The mixing in the ${}^3T_{1g}$ states of NiF_6^{4-} is even greater by this analysis: The lower a^3T_{1g} state, for example, is estimated to be 57% $t_2^4e^4$ and 43% $t_2^5e^3$ in character. From an earlier theoretical SCF MO treatment of NiF_6^{4-} which included CI (17), the best calculated values of those percentages are 64 and 36%, respectively.

While such deductions could also have been made following previous CF fittings to experimental spectra, we point out that the present linearized procedures makes such interesting conclusions immediately obvious and available.

Returning to Table V, similar considerations indicate the extent to which the low-

TABLE V
COEFFICIENTS IN THE LINEARIZED FITTINGS TO THE EXPERIMENTAL SPECTRA OF NiF_6^{4-} AND CrF_6^{3-} , $\tilde{E}_i = n_i\Delta + b_i s^a$

Transition	DOF		FMF	
	n_i	b_i/B_0	n_i	b_i/B_0
$\text{NiF}_6^{4-}: {}^3A_{2g}$				
$\rightarrow {}^3T_{2g}$	1.0	0.0	1.0	0.0
$\rightarrow a {}^3T_{1g}$	2.0	3.0000	1.56689	0.9304
$\rightarrow {}^1E_g$	0.0	15.9532	0.08455	15.5942
$\rightarrow {}^1T_{2g}$	1.0	15.9532	1.11464	13.8498
$\rightarrow b {}^3T_{1g}$	1.0	12.0000	1.43311	14.0696
$(\Delta, s) =$	(5840, 1.0209)		(7152, 0.9340)	
$\text{CrF}_6^{3-}: {}^4A_{2g}$				
$\rightarrow {}^2E_g$	0.0	20.9326	0.03722	18.3668
$\rightarrow {}^2T_{1g}$	0.0	20.9326	0.03045	19.4439
$\rightarrow {}^4T_{2g}$	1.0	0.0	1.0	0.0
$\rightarrow {}^2T_{2g}$	0.0	34.8839	0.20031	24.3105
$\rightarrow a {}^4T_{1g}$	1.0	12.0000	1.14915	6.3159
$\rightarrow b {}^4T_{1g}$	2.0	3.0000	1.85087	8.6841
$(\Delta, s) =$	(17,040, 0.7538)		(16,336, 0.8828)	

^a Recall that the s and the n_i are dimensionless; Δ is given in cm^{-1} . For convenience in comparing with other tables, the b_i are given as multiples of the appropriate value of B_0 , given in Tables III and IV, for each of the four cases.

spin states of the ground configurations of the two systems appear to have gained modest Δ dependences through CI mixing (8% in 1E_g of NiF_6^{4-} and 3% in ${}^2E_g, {}^2T_{1g}$ of CrF_6^{3-}) along with a moderate reduction in dependence on interelectronic repulsion.

Essentially the same numerical results could be expected if HF free-ion wavefunctions had been used in these calculations. Indeed, they provide C/B ratios (see Table I) which differ only slightly from the 3.98 value used in the calculations of Tables III, IV, and V.

In Table VI we present the fitting of transition energies theoretically calculated for CrF_6^{3-} in K_2NaCrF_6 . For the sake of comparison with fits to experimental spectra, we select here only those corresponding to the observed transitions. Since these values differ so slightly from the experimental, little

new is to be gained from following exactly the same procedure. Instead, we present some further insights by allowing the values of both B and C to be varied independently during the fitting.

In common with the \tilde{E}_i in Table IV, those in Table VI present a noticeable reduction in rms deviation when passing to the FMF results. We note that the positions of the calculated low-spin t^3 states, ${}^2E, {}^2T_1$, are slightly below experimental observation, mainly due to the action of the correlation energy correction (CEC) which was incorporated in the theory. With the ratio C/B here freed from having a preset value, B decreases more to fit those doublets, while C increases to compensate elsewhere, for reasons discussed in connection with the experimental spectrum. This is especially pronounced in the DOF results. While the

TABLE VI
 THEORETICAL SPECTRUM OF CrF_6^{3-} ^a AND CRYSTAL FIELD FITTINGS^b (ENERGIES IN cm^{-1})

Transition	Theoretical	DOF	FMF					
			Diagonal ^c	E_i^d	\tilde{E}_i	n_i	b_i	c_i
${}^4A_{2g} \rightarrow {}^2E_g$	14,758	14,070	16,052	14,888	14,786	0.0315	6.356	3.051
$\rightarrow {}^2T_{1g}$	14,850	14,070	16,052	15,515	15,416	0.0244	7.648	3.000
$\rightarrow {}^4T_{2g}$	16,713	17,533	16,826	16,826	16,826	1.0000	0.0	0.0
$\rightarrow {}^2T_{2g}$	22,571	23,451	26,754	22,292	22,131	0.1825	8.382	4.104
$\rightarrow a^4T_{1g}$	24,017	24,134	25,293	23,796	23,759	1.1099	7.202	0.0
$\rightarrow b^4T_{1g}$	37,185	36,716	35,769	37,266	37,308	1.8901	7.798	0.0
rms deviation		678			318			
Δ		17,533			16,826			
B		550			706			
C		3,040			3,202			
C/B		5.53			4.54			

^a Reference 8. Spectrum calculated from SCF on ${}^4T_{av}$ state, including external potential of K_2NaCrF_6 , at the experimental geometry and CEC.

^b Racah B and C independently fit; here, $\tilde{E}_i = n_i\Delta + b_iB + c_iC$, where Δ , B , and C have the values given in the FMF column of this table.

^c Diagonal elements of the full CF matrices, at the last iteration of the fitting procedure.

^d Eigenvalues of the full CF matrices, at the last iteration. The difference between this and the previous column indicates the effect of CI upon the observed states.

FMF parameters are quite similar to those of Table IV, C/B has noticeably increased. Likewise the n_i of Tables IV and VI are very close and stand as another index of the degree to which the theoretical and experimental transition energies coincide.

Incidentally, the n_i for the two ${}^4T_{1g}$ states of Table V indicate 11% $t_2^1e^2$ configurational mixing with $t_2^2e^1$ in a^4T_{1g} , for example, compared with the 15% figure arising from the fit to the experimental spectrum. On the other hand, from the original SCF MO theoretical calculation, we obtain 12%, so that the basic SCF MO calculations and their CF fitting encompass the same effects.

The FMF nephelauxetic ratios given in the bottom lines of Tables III and IV compare well with those reported by Jorgensen (15): 0.92 in NiF_6^{4-} and 0.89 in CrF_6^{3-} . On the other hand, very different values are generated with the parameters from the theoretical spectrum in Table VI and the theoretical B and C (1149 and 4270 cm^{-1} ,

respectively, from Table I). These yield DOF s 's of 0.479 and 0.712 and FMF s 's of 0.614 and 0.750, respectively, for B and C . More striking is the related increase to 4.54 in the C/B ratio, which is surely due, as discussed earlier, to the fact that the t_2^3 doublets are appreciably lowered by electron correlation effects which extend substantially beyond the $3d$ shell.

We now suggest that in calculating s , the values taken for the free-ion B and C should be chosen according to whether the cluster calculation being studied did, or did not, encompass these extra correlation effects. Hence, the values of B and C obtained here from fitting both the experimental and the theoretical spectra calculated *with* CEC should be compared to our free-ion values obtained by least-squares fitting to the *experimental* Cr^{3+} spectrum (Table II), which, by definition, includes CEC. In this way the FMF s for B is 0.793 and that for C is 0.901. While the s for B is still somewhat

small, that for C is very close to the values from fits to experimental spectra.

By parallel reasoning, we examine the values of B and C obtained by Gladney and Veillard (6) (1280 and 4910 cm^{-1} , respectively) and by Wachters and Nieuwpoort (7) (1280 and 4810 cm^{-1} , respectively) from their *ab initio* theoretical SCF MO calculations on NiF_6^{4-} , which did not include the CEC type of correction to excitation energies. The nephelauxetic ratios calculated from them using free-ion B and C fit to the experimental Ni^{2+} spectrum are unreasonably greater than unity. The B and C theoretically calculated from the free-ion $3d$ AOs, however, yield values of s a few percent less than 1, closer to the estimates from fits to *experimental* cluster spectra.

It is most interesting to compare the CrF_6^{3-} results in Table VI to the previously mentioned results MacFarlane obtained for the Cr-O system in ruby (3). For CrF_6^{3-} we set each

$$\begin{aligned}\tilde{E}_i &\doteq (\partial E/\partial \Delta)\Delta + (\partial E/\partial B)B + (\partial E/\partial C)C \\ &\doteq n_i\Delta + b_iB + c_iC.\end{aligned}$$

MacFarlane, considering small changes in the parameters $\delta\Delta$, δB , and δC to be perturbations upon an approximately fit set of cluster states, evaluates the first-order expression

$$\delta E_i \doteq E_{i,\Delta}^{(1)} \delta\Delta + E_{i,B}^{(1)} \delta B + E_{i,C}^{(1)} \delta C.$$

Clearly

$$n_i \sim E_{i,\Delta}^{(1)}; \quad b_i \sim E_{i,B}^{(1)}; \quad \text{and} \quad c_i \sim E_{i,C}^{(1)}.$$

The separation among the ruby quartet levels shown in his Fig. 1 to one significant figure agrees with our corresponding n_i values. Coefficients for the doublets, shown in his Table V, are very close to ours, the major difference being that our n_i for ${}^2T_{1g}$ and ${}^2T_{2g}$ are 20% larger. These agreements between fluoride and oxide data show again the extent to which the t_2^3 states are insulated from their ligand environment.

In line with the comments by König (16) about the relevance of sample temperature to the quality of the crystal field fitting, it is noted that the spectrum of CrF_6^{3-} suggests that the minimum of the $t_2^2e-{}^4T_{2g}$ total energy surface is near to that of the ground state $t_2^3-{}^4A_{2g}$. This is consistent with our calculated displacement of only 0.02 Å. This circumstance permits a more accurate location of the $10Dq$ (and other $t_2^3 \rightarrow t_2^2e^1$) transition energies and, consequently, a better crystal field fitting. If this argument is true, then having obtained a larger rms deviation in the fit to NiF_6^{4-} suggests a greater displacement in its excited configurations. Obviously, however, such a conclusion requires further confirmation.

IV. Conclusions

With the assistance of sufficient computer capacity to diagonalize at most 10×10 matrices, the linearization procedure permits easy and systematic CF parametrization of a given set of spectral energies for *any* cubic d^n transition-metal system, neglecting spin-orbit interaction. The full matrix fitting is hardly more complicated to effect than the diagonal only fitting and gives much better results.

The procedure automatically resolves every given transition energy into independent linear contributions from effective orbital populations, crystal field splitting parameter, interelectronic repulsion energies, and nephelauxetic ratios. The significant new advantage obtained here, then, is the enhanced capacity to interpret directly the fitting parameters and to compare theoretical and experimental results for the same and for different compounds.

The prior fixing of the C/B ratio is seen here not to alter significantly the statistical quality of the fit; but it is seen how independent variation of B and C permits subtle alterations which reveal specific features of

states in which electron correlation is particularly extensive. In that regard also, the importance of correct choice of free-ion values of B and C —so as to be consistent with the extent to which electron correlation is encompassed in the cluster states being fit—is emphasized.

We also suggest that, when CF fitting theoretically calculated states for comparison to experimental, only that set of states should be taken which corresponds to the experimentally observed set.

The work here has been limited to the two octahedral fluoride clusters. Application to other ligand systems and extensions to cases of lower symmetry (in which other CF parameters enter) are mathematically straightforward and will, of course, be considered later. With more parameters required for such more general systems, the necessity for more accurate and extensive input spectral data increases, in order to avoid possible complications with the numerical aspects of the method.

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